

# CATALYTIC WET PEROXIDE OXIDATION OF WATER DISSOLVED ORGANIC POLLUTANTS UNDER MILD CONDITIONS

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**Doctoral Dissertation**  
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**Doctoral dissertation**

KATALITSKA MOKRA PEROKSIDNA OKSIDACIJA V  
VODI TOPNIH ORGANSKIH ONESNAŽIL PRI BLAGIH  
POGOJIH

**Doktorska disertacija**

**Supervisor:** Prof. Dr. Goran Dražić

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Ljubljana, Slovenia, November 2018







# Acknowledgments

Firstly, I would like to express my most sincere gratitude towards my supervisor, Prof. Dr. Goran Dražić, whose support, guidance and encouragement led to the creation of this work.

I would also like to express my gratitude to my working supervisor, Prof. Dr. Albin Pintar, for all the help provided during my work at his department.

A big thank you also goes to my “silent” supervisors, Dr. Boštjan Erjavec and Dr. Petar Djinović, for all the ideas, constructive criticism and help that they provided during my PhD.

I would also like to express my gratitude to everyone whose help enabled the creation of this work.

Firstly, I would like to thank Ing. Jelka Grdadolnik for the IC analysis and Ing. Špela Božić for the help and guidance provided during the conduction of the CHNS analysis.

To Prof. Dr. Jože Grdadolnik I am grateful for the *in-situ* Raman analysis, his help with the interpretation of data, constructive advice and the shared knowledge.

To Asst. Prof. Janez Cerkovnik I am grateful for providing the synthesized  $\text{H}_2^{17}\text{O}_2$ , as well as for the guidance and help given in the short time that we met during my PhD work.

To Dr. Primož Šket I am grateful for the conducted NMR analysis and his help with the interpretation of data.

To Janvit Teržan I am grateful for all the help, constructive brainstorming and his support.

To Dr. Tatjana Tišler and Dr. Magda Cotman I am grateful for all the given advice.

To all my co-workers, which eventually became my dear friends, Renata, Andraž, Jelka and Janvit, I am thankful for all those special moments which made every day better.

The biggest gratitude and love is expressed towards my mother Snježana whose love and support are given unconditionally; to my husband Tomy who stood by me even in the hardest moments; and to my friend Lara for all the advice, support and motivation.

Last but not least, to my little furry family, Fifi, Kora and Jack – those who understand and love without any spoken word. You will always be the most important part of my life.

The author of this dissertation gratefully acknowledges the financial support from the Slovenian Research Agency through Research core funding No. P2-0150.



# Abstract

Peroxo species decorated amorphous  $\text{TiO}_2$ -based materials, namely nanosheets, nanotubes, nanorods and rice-like morphology, have been obtained through alkaline hydrothermal restructuring of different Ti-based precursors. Obtained materials were tested in catalytic wet peroxide oxidation (CWPO) of methyl orange (MO) under mild conditions, where prevalent catalytic activity has been attributed to  $\text{TiO}_2$ -based nanotubes characterized with high specific surface area and high amount of surface peroxo species.

Low-temperature thermal treatment of the  $\text{TiO}_2$  based nanotubes has revealed loss in the amount of ion-exchangeable -OH groups, and consequently in the amount of peroxo species, which causes lowering of the catalytic activity. In contrast, by applying optimal acid treatment catalytic activity increased and with the usage of 2 g/L of peroxide-treated  $\text{TN/ClO}_4$  0.01 material, and double stoichiometric amount of  $\text{H}_2\text{O}_2$ , 50 ppm MO solution was purified up to ~93 % during 90 min at 40 °C with adsorption of only ~1 %. Catalytic performance remained constant during 5 consecutive runs using the same batch of the material.

With detailed  $\text{O}_2$  TPD/MS, temperature-dependent UV/Vis DR, *in-situ* Raman,  $^1\text{H}$  MAS and  $^{17}\text{O}$  NMR analyses it has been proposed that peroxide treatment induces complete changes in the material, although high catalytic activity can directly be ascribed to end-on  $\eta^2$  peroxo species whose amount remains almost constant during 5 consecutive runs, namely  $5.9 \cdot 10^{-7}$  mol  $\text{O}_2/\text{m}^2$  and  $5.2 \cdot 10^{-7}$  mol  $\text{O}_2/\text{m}^2$  prior and after usage. Remaining thermally labile two-coordinated oxygen species, detected with  $\text{O}_2$  TPD/MS and  $^{17}\text{O}$  NMR and used during CWPO of MO without affecting high catalytic activity, is proposed to serve as a place for novel peroxo species formation through creation of terminal  $\text{Ti-O}\bullet$  radicals and -OH groups.



# Povzetek

S perokso skupinami okrašeni amorfni material na osnovi  $\text{TiO}_2$ , in sicer nanoplasti, nanocevke, nanopalčke in z morfologijo riža, smo pridobili z alkalno hidrotermalnim prestrukturiranjem različnih predhodnih sestavin na osnovi Ti. Dobljene materiale smo testirali v katalitski mokri peroksidni oksidaciji (CWPO) metil oranža (MO) pri blagih pogojih, kjer je bila prevalentna katalitska aktivnost pripisana nanocevkam na osnovi  $\text{TiO}_2$  z visoko specifično površino in veliko količino površinskih peroksidnih vrst.

Nizkotemperaturna toplotna obdelava nanocevk na osnovi  $\text{TiO}_2$  je pokazala izgubo v količini ionsko izmenljivih -OH skupin in posledično količino peroksidnih vrst, kar je povzročilo znižanje katalitske aktivnosti. V nasprotju s tem smo z uporabo optimalne kislinske obdelave povečali katalitsko aktivnost. Tako smo z uporabo 2 g/L TN/ $\text{ClO}_4$  0.01 materiala, obdelanega s peroksidom, in dvojne stehiometrične količine  $\text{H}_2\text{O}_2$  raztopino 50 ppm MO očistili do ~93 % v času 90 min pri 40 °C, pri čemer je adsorpcija MO znašala le ~1 %. Katalitična učinkovitost je ostala nespremenjena med 5 zaporednimi poizkusi z uporabo iste serije materiala.

S podrobnimi  $\text{O}_2$  TPD/MS, temperaturno odvisnimi UV/Vis DR, *in-situ* Raman,  $^1\text{H}$  MAS in  $^{17}\text{O}$  NMR analizami je bilo ugotovljeno, da obdelava s peroksidom povzroči znatne spremembe v materialu, čeprav se lahko visoka katalitska aktivnost neposredno pripisuje končnim  $\eta$  perokso skupinam, katerih količina ostane skoraj konstantna med 5 zaporednimi poizkusi, in sicer  $5,9 \cdot 10^{-7}$  mol  $\text{O}_2/\text{m}^2$  in  $5,2 \cdot 10^{-7}$  mol  $\text{O}_2/\text{m}^2$  pred in po uporabi. Predvidevamo, da preostale termalno labilne dvo-vezne kisikove specije, ki so bile identificirane z  $\text{O}_2$  TPD/MS in  $^{17}\text{O}$  NMR tehnikama in se porabljajo med CWPO MO, ne da bi to vplivalo na visoko katalitsko aktivnost, sodelujejo pri nastanku novih zvrsti peroksidov preko tvorbe terminalnih  $\text{Ti-O} \cdot^-$  radikalov in -OH skupin.



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# Abbreviations

|                 |                                                                   |
|-----------------|-------------------------------------------------------------------|
| AC              | ... Activated carbon                                              |
| AOPs            | ... Advanced oxidation processes                                  |
| ATR             | ... Attenuated total reflectance                                  |
| BAS             | ... Brønsted acid sites                                           |
| BET             | ... Brunauer-Emmett-Teller                                        |
| CHNS            | ... Carbon-hydrogen-nitrogen-sulphur                              |
| CPMD            | ... Carr Parrinello molecular dynamics                            |
| CWAO            | ... Catalytic wet air oxidation                                   |
| CWPO            | ... Catalytic wet peroxide oxidation                              |
| DFT             | ... Density functional theory calculations                        |
| DFTB            | ... Density-functional based tight binding                        |
| DMPO            | ... 5,5-dimethyl-1-pyrroline N-oxide                              |
| DR              | ... Diffuse reflectance                                           |
| DRIFT           | ... Diffuse reflectance Fourier transform infrared (spectroscopy) |
| EDS             | ... Energy dispersive X-ray spectrometry                          |
| EELS            | ... Electron energy loss spectroscopy                             |
| EPR             | ... Electron paramagnetic resonance                               |
| EXAFS           | ... Extended X-ray absorption fine structure                      |
| FE SEM          | ... Field emission scanning electron microscopy                   |
| FTIR            | ... Fourier transform infrared spectroscopy                       |
| FWHM            | ... Full width at half maximum                                    |
| IA              | ... Inorganic anions                                              |
| ICDD            | ... International Centre for Diffraction Data                     |
| IPS             | ... International Postgraduate School                             |
| JSI             | ... Jožef Stefan Institute                                        |
| LAS             | ... Lewis acid sites                                              |
| LMCT            | ... Ligand to metal charge transfer                               |
| LMP             | ... Low molecular products                                        |
| LN <sub>2</sub> | ... Liquid nitrogen                                               |
| MAS             | ... Magic angle spinning                                          |
| MCT             | ... Mercury-cadmium-telluride                                     |
| MD              | ... Molecular dynamics                                            |
| MO              | ... Methyl orange                                                 |
| NMR             | ... Nuclear magnetic resonance                                    |

|                |                                                         |
|----------------|---------------------------------------------------------|
| PSE            | ... Periodic system of elements                         |
| Pzc            | ... Point of zero charge                                |
| RMC            | ... Reverse Monte Carlo                                 |
| ROS            | ... Reactive oxygen species                             |
| SEM            | ... Scanning electron microscopy                        |
| Ssb            | ... Spinning side band                                  |
| TEM            | ... Transmission electron microscopy                    |
| TPD/MS         | ... Temperature-programmed desorption/mass spectrometry |
| TGA            | ... Thermogravimetric analysis                          |
| TS-1           | ... Titanium silicalite                                 |
| US             | ... Ultrasound                                          |
| UV             | ... Ultraviolet                                         |
| UV/Vis         | ... Ultraviolet/Visible                                 |
| UV/Vis DR      | ... Ultraviolet/Visible Diffuse Reflectance             |
| V <sub>o</sub> | ... Oxygen vacancy                                      |
| WAXS           | ... Wide angle X-ray scattering                         |
| WO             | ... Wet oxidation                                       |
| XAFS           | ... X-ray absorption fine structure                     |
| XRD            | ... X-ray diffraction                                   |
| 0D             | ... Zero-dimensional                                    |
| 1D             | ... One-dimensional                                     |
| 2D             | ... Two-dimensional                                     |
| 3D             | ... Three-dimensional                                   |

# Symbols

|              |     |                                                 |
|--------------|-----|-------------------------------------------------|
| $\text{\AA}$ | ... | Angström                                        |
| $A$          | ... | Area ( $\text{m}^2$ )                           |
| $Abs$        | ... | Absorbance (/)                                  |
| $a, b, c$    | ... | Side length ( $\text{\AA}$ )                    |
| $c$          | ... | Molar concentration ( $\text{mol/L}$ )          |
| $d_p$        | ... | Pore diameter ( $\text{nm}$ )                   |
| $E_0$        | ... | Oxidation potential ( $\text{eV}$ )             |
| $k$          | ... | Rate constant ( $\text{M}^{-1}\text{s}^{-1}$ )  |
| $K\alpha_1$  | ... | K alpha1; i.e. XRD wavelength ( $\text{\AA}$ )  |
| $m$          | ... | Mass ( $\text{g}$ )                             |
| $n$          | ... | Amount of substance ( $\text{mol}$ )            |
| $p$          | ... | Pressure ( $\text{Pa}$ )                        |
| $R$          | ... | Ideal gas constant ( $R=8.314\text{J/molK}$ )   |
| $S_{BET}$    | ... | Specific surface are ( $\text{m}^2/\text{g}$ )  |
| $t$          | ... | Time ( $\text{s}$ )                             |
| $T$          | ... | Temperature ( $^{\circ}\text{C}$ )              |
| $V$          | ... | Volume ( $\text{L}$ )                           |
| $V_p$        | ... | Pore volume ( $\text{m}^3/\text{g}$ )           |
| $w$          | ... | Mass fraction ( $\%$ or $\text{wt}\%$ )         |
| $X_{MO}$     | ... | Methyl orange conversion ( $\%$ )               |
| $\gamma$     | ... | Gamma; i.e. mass concentration ( $\text{g/L}$ ) |
| $\delta$     | ... | Delta; i.e. NMR chemical shift ( $\text{ppm}$ ) |
| $\lambda$    | ... | Lambda; i.e. wavelength ( $\text{nm}$ )         |



# Glossary

**Fitting vs. Deconvolution-** In this thesis term fitting is used rather than deconvolution since deconvolution is a process of the signal filtering in order to recreate original signal before convolution occurred, while fitting is finding an adequate peaks to fulfil the area under the original curve.

**Larmor frequency-** can be defined as a tendency of the electron to align itself under the influence of the magnetic field.

**Leaching-** removal of a solute from a porous solid using liquid solvent.

**m/z fragmentation-** elemental fragmentation based on the mass to charge ratio.

**Oxygen vacancy-** is a type of point defect which is created when oxygen atoms are missing from the crystal lattice.

**Pollutants-** in this thesis it concerns organic substances introduced into the environment causing negative impact (undesired effect) on the water resources.

**Pseudo-persistent pollutant-** pollutant that shows negative effect due to continuous introduction into the environment although their half-life and toxicity can be rather low.

**Pollution-** negative effect caused with the introduction and/or presence of pollutant.

**ROS-** highly reactive free radical species containing reactive oxygen or peroxides.

**Scavenger-** an organic or inorganic substance that covalently bond with free radicals and form stable adducts that does not participate in oxidation reaction.

**Spin-trap-** organic compound used for “trapping” of created ROS by means of covalent bonding. It is used for creation of stable ROS adduct which can be easily detected using EPR or fluorescence measurements.

**Structural defects-** in this thesis it refers to interruptions of the periodic crystal structure.

**Quinoid structure-** structure similar to quinine meaning that one aromatic ring contains double bond.



# Chapter 1

## Introduction

In the era of industrial and technological growth, deterioration of water quality has become one of the most pronounced environmental problems nowadays. The presence of persistent and highly toxic organic and inorganic substances (i.e. pollutants) is causing negative impact on the aquatic environment and human health, so a lot of effort has been made in order to minimize their influence. List of the priority pollutants is defined by the upgraded European directive (Directive 2013/39/EU)[1] and includes pesticides, dyes and solvents, pharmaceuticals, dioxine and dioxine-like compounds, heavy metals etc., which can cause severe negative impact even in the small concentrations ranging from  $\text{ng L}^{-1}$ – $\mu\text{g L}^{-1}$  [1]. Due to their high chemical and photolytic stability, application of conventional treatment methods (e.g. physico-chemical and biological) does not yield satisfactory results, so over the last twenty-five years political and social pressure has forced environmental scientists to find novel and alternative ways of water purification.

### 1.1 Advanced Oxidation Processes

Treatment methods based on application of superior oxidation have shown astonishing results in the removal of persistent and pseudo-persistent pollutants. These processes, defined as advanced oxidation processes (AOPs), are a set of catalytically driven reactions whose primary purpose is generation of highly reactive and non-selective reactive oxygen species (ROS) accounted for complete degradation of even the most persistent pollutants [2]. In all AOPs, ideal scenario for complete degradation of organic pollutants is their mineralization to small molecules of carbon dioxide ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ), but realistic picture for more complex systems is conversion of each molecular species into belonging ionic or molecular product, namely conversion of carbon into  $\text{CO}_2$ , hydrogen to  $\text{H}_2\text{O}$ , phosphorus to phosphates ( $\text{PO}_4^{3-}$ ), sulphur to sulphate ( $\text{SO}_4^{2-}$ ), nitrogen to nitrates ( $\text{NO}_3^-$ ), and halogens to halogen acids (HX). In most cases, an ideal scenario cannot be achieved, therefore a partial conversion of pollutants to non-harmful products, which can be easily degraded by simple biological treatment, is highly desirable [1].

Production of ROS can be achieved in many ways and over the years a wide variety of different AOPs has been developed. Depending on the number of phases that are in contact during reaction, they can be easily divided into two basic groups, namely homogeneous and heterogeneous advanced oxidation processes [1]. In homogeneous systems, the formation of wanted ROS strongly depends on the interaction between the oxidant, such as ozone ( $\text{O}_3$ ) or hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and the targeted pollutant [1]. Usually these reactions occur in the presence of oxidative reagents (for example, ferric ion salts) or energy (ultraviolet (UV) and visible (Vis) light, ultrasound (US), thermal or electrical energy) [1]. In contrast, in heterogeneous systems solid catalytic materials, such as metal catalysts supported on a metal oxide surface, metal oxides on their own or organometal catalysts,

are used for the formation of ROS [1], [3], [4]. They can also be activated by energy (UV and Vis radiation, US etc.), with or without the presence of a strong oxidant [3], [5]. The main difference between heterogeneous and homogenous AOPs is the dependence of the former ones on the adsorption and desorption of reactants on the surface of the solid catalytic material. In addition, in the systems where reactants and oxidative reagent are simultaneously present, competitive adsorption on the catalyst surface determines overall removal, i.e. degradation of pollutants [6]–[8]. Flowchart in Fig. 1.1 consolidates some of the AOPs comprehended into two major groups.

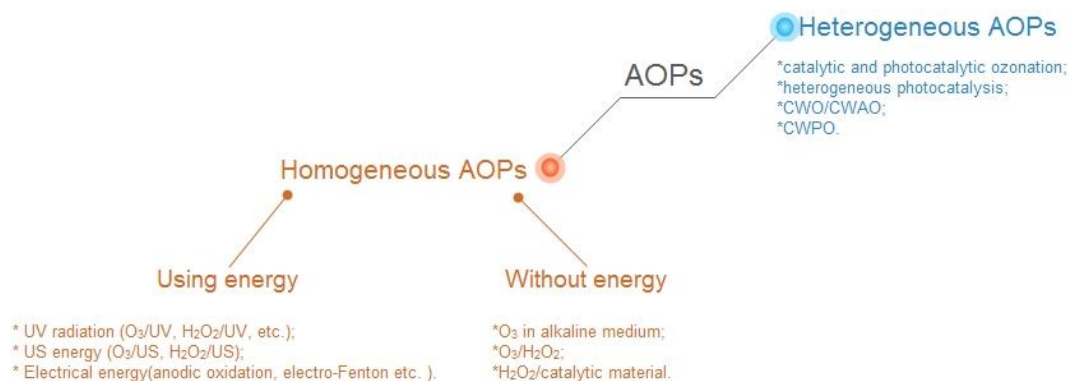


Figure 1.1: Consolidated flowchart showing simplified classification of AOPs. Figure taken from Poyatos et al. [3].

Based on the methodology applied for the ROS production AOPs from both major groups can further be divided into chemical, electro-chemical, sono-chemical and photo-chemical heterogeneous and homogeneous processes [1].

Although all AOPs have many distinctive benefits (i.e. ROS formation, complete or partial degradation of pollutants, high stability in the presence of toxic chemicals etc.), it is necessary to understand that they can be very cost demanding and hard to apply on a larger scale. For example, one of the drawbacks that occur during the implementation of AOPs for the removal of pollutants from the wastewater systems is the presence of organic and inorganic species which behave as ROS scavengers which terminate radical reactions and disable efficient degradation of pollutants. Some of the well-known organic and inorganic ROS scavengers are humic and fulvic acid, amino acids, proteins, carbohydrates, dissolved sulphides, carbonate ( $\text{CO}_3^{2-}$ ), bicarbonate ( $\text{HCO}_3^-$ ), bromide ( $\text{Br}^-$ ),  $\text{NO}_3^-$  etc. [1]. Another drawback that can occur during the implementation of AOPs (for example catalytic wet peroxide oxidation or Fenton process) is secondary contamination due to leaching of active metal species into the reaction suspension. This happens only when solid catalytic materials contain copper, aluminium, iron, silver etc., as catalytically active species [3]. In addition, usage of oxidants or increased consumption of energy (for heating of reaction suspension or charging of UV lamps) drastically influences the overall cost factor, and in most cases a more economically feasible process should be used [1], [3]. Nevertheless, AOPs can offer an acceptable solution for the removal of specific pollutants, but only if we conduct proper selection and optimization of the best AOPs and therefore we can conclude that favorization of specific “unique” AOPs is nothing but redundant [1]–[3]. The most commonly used AOPs processes are:

- 1) **Heterogeneous photocatalysis** – Heterogeneous process where pure or coupled semiconductor material (ex. titanium dioxide  $\text{TiO}_2$ , zirconium dioxide  $\text{ZrO}_2$ , cadmium sulphide titania  $\text{CdS-TiO}_2$ , etc.) is irradiated with UV or Vis radiation in order to create ROS on the surface of the catalytic material [1], [9].

- 2) **Ozonation** – Usually refers to a homogeneous chemical process in which  $O_3$  is activated in the presence of catalytically active metal ions. Nevertheless, heterogeneous ozonation has also been widely accepted, so novel materials, such as metal oxides ( $TiO_2$ , cerium dioxide  $CeO_2$ , manganese dioxide  $MnO_2$ , aluminium oxide  $Al_2O_3$  and iron oxide  $FeOOH$ ), metals (copper, Cu, cobalt, Co, ruthenium, Ru and platinum, Pt) on supports ( $TiO_2$ ,  $CeO_2$ , silicon dioxide  $SiO_2$  and activated carbon), metal modified zeolites and activated carbon, serve as carriers of ROS production [1], [10].
- 3) **Catalytic wet air oxidation (CWAO)** – Heterogeneous process in which usage of solid catalytic material (metal oxides or metals deposited on different supports) enables efficient removal of pollutants under milder operating conditions (in comparison with parental wet oxidation process, WO). Source for ROS creation is usually oxygen ( $O_2$ ) or air, which is introduced into fixed-bed column reactor operating in the temperature (T) range of 125°C to 250°C and pressure (p) of 5-50\*10<sup>5</sup> Pa [3], [7].
- 4) **Fenton process** – Usually refers to homogeneous iron catalyzed decomposition of  $H_2O_2$  under ambient conditions in the narrow acidic pH range (pH≈2.5–3.5). Although Fenton process is directly connected with the exploitation of fast changing oxidation state of  $Fe^{2+}/Fe^{3+}$ , some novel approaches have been adapted over the time so metal salts of metals that have different oxidation states (such as cobalt ( $Co^{2+}/Co^{3+}$ ), copper ( $Cu^+/Cu^{2+}$ ), aluminium ( $Al^0/Al^{3+}$ ) etc.) have been employed for  $H_2O_2$  decomposition [1], [4]. Lately, application of heterogeneous Fenton process and combination of electro-Fenton or photo-Fenton have been exploited in order to ameliorate the process efficiency and minimize the influence of the secondary pollution [1], [11].
- 5) **Catalytic wet peroxide oxidation (CWPO)** – Similar to the Fenton process CWPO is an additional heterogeneous process in which  $H_2O_2$  and suitable solid catalytic materials are used for the creation of ROS [1]. In contrast to the original Fenton process CWPO is usually conducted under more severe operational conditions ( $p_{atm}=101325$  Pa,  $T<100^\circ C$ ), although some research has been conducted under atmospheric conditions ( $p_{atm}$ ;  $T=25^\circ C$ ) [11], [12].

## 1.2 Catalytic Wet Peroxide Oxidation

Catalytic wet peroxide oxidation (CWPO; alternative names are also wet peroxidation, wet hydrogen peroxide oxidation and wet oxidation by hydrogen peroxide [11]) is one of the heterogeneous AOPs process in which the production of reactive oxygen species, primary hydroxyl radicals  $\bullet OH$ , occurs through homolytic decomposition of  $H_2O_2$  in the presence of a suitable catalyst [5]. It has been recognized as an environmentally friendly process which is able to operate with a very simple technology under the mild conditions ( $p_{atm}$ ,  $T<100^\circ C$ ), but it did not gain a lot of attention in comparison with other processes, such as the Fenton process, CWAO or photocatalysis [1], [11]. This occurs mostly because of drawbacks connected with the high price of industrial grade  $H_2O_2$ , specific operating conditions and problems that occur during the development and application of solid catalytic material.

The main environmental benefit and economical drawback of the CWPO, is the usage of  $H_2O_2$ . Industrial grade  $H_2O_2$  is versatile, colourless, bitter tasting liquid oxidant whose remaining oxidation products, namely  $H_2O$  and  $O_2$ , do not produce a negative impact on the environment [1], [11], [13], [14]. Nevertheless, commercial industrial grade  $H_2O_2$

(concentrated up to 30 % or 70 %) is produced through the anthrahydroquinone oxidation process and costs up to 390–500 \$ per ton, so its successive usage leads to a drastic increase of the CWPO operative costs [1], [11], [13], [14]. Although new catalytic materials and innovative processes for the production of  $\text{H}_2\text{O}_2$  have been applied, further optimization is essential in order to financially justify the usage of excessive amounts of  $\text{H}_2\text{O}_2$  for the degradation of pollutants. To promote economic viability of the CWPO process, some researchers have been oriented towards *in-situ* production of  $\text{H}_2\text{O}_2$ , but additional methodological and operational optimization needs to be done for this principle to be successfully implemented in the industrial scale [15].

Additional negative operational and financial facet of the CWPO process is observed through standardized implementation of the main classes of catalytic materials. Since CWPO is based on Fenton chemistry, these materials rely on the usage of different catalytically active metal species for  $\text{H}_2\text{O}_2$  decomposition [1]. Although they are deposited on different supports (mixed oxides, zeolites, activated carbon etc.), leaching into the reaction solution is usually inevitable, so secondary contamination with metal ions occurs [1], [11], [14]. Besides that, in order to ensure sufficient reaction rates, operational conditions, such as low pH and elevated temperature ( $T < 100^\circ\text{C}$ ), need to be properly adjusted [1], [3], [11]. This, however, requires a considerable energy input (84 MJ for heating of  $1 \text{ m}^3$  of water by  $20^\circ\text{C}$ ) and consumption of chemicals for pH adjustment, which are both highly undesirable.

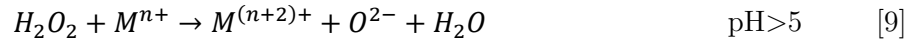
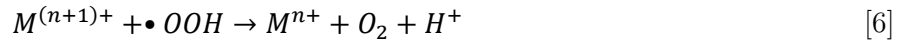
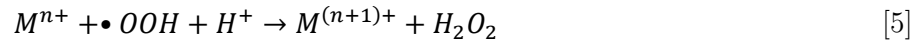
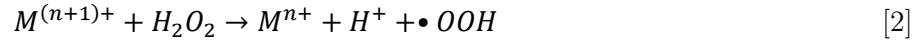
Based on the observed facts it is noticeable that CWPO is a preferred process only in those situations in which capital costs of each process (developed purification technologies that can be applied for degradation of pollutants in the wastewaters) is much higher than the operational cost of CWPO itself. This is based on the simple fact that although CWPO requires a lot of operational, and consequently financial optimization, it is still able to operate with a very “primitive” technology and achieve efficient degradation of pollutants [11]. So CWPO is usually used as a [7], [11]:

1. pre-treatment for the partial degradation of highly toxic pollutants before the implementation of a more cost-effective biological degradation, and
2. cost-effective treatment for wastewaters with medium or low organic content ( $\gamma = 1\text{--}30 \text{ g/L}$  of carbon originating from the organic matter).

### 1.2.1 CWPO chemistry, operating conditions and reactor systems

As already mentioned, CWPO has been developed based on the chemistry of the Fenton process (Fenton, 1984; [1], [11]), meaning that metals with different oxidation states, deposited on the adequate support, have been employed for decomposition of  $\text{H}_2\text{O}_2$  into primary ROS hydroxyl radicals ( $\bullet\text{OH}$ ) [11]. The main benefit of  $\bullet\text{OH}$  radicals is their high oxidation capacity ( $E_0 = 2.8 \text{ eV}$ ), fast reactivity and non-selectivity which enables efficient degradation of even the most persistent pollutants [11]. Nevertheless, although  $\bullet\text{OH}$  are primary radicals due to the complexity of the systems, it is hard to exclude the formation of other ROS such as hydroperoxyl radicals ( $\bullet\text{OOH}$ ,  $E_0 = 1.7 \text{ eV}$ ), and in some cases superoxide anion ( $\text{O}_2\bullet^-$ ) and peroxide dianion ( $\text{O}_2^{2-\bullet}$ ) radicals [11], [16]–[18]. It has been shown that the creation of specific ROS highly depends on the pH of the reaction solution so the creation of  $\bullet\text{OH}$  and  $\bullet\text{OOH}$  radical usually occurs in the acidic medium, while  $\text{O}_2\bullet^-$  and  $\text{O}_2^{2-\bullet}$  prefer the neutral pH range ( $\text{pH} \approx 5\text{--}7$ ) [1], [3], [18]. Nevertheless, there are many factors that will influence the creation of ROS and affectivity of the process, namely temperature, presence and concentration of pollutant and  $\text{H}_2\text{O}_2$ , type of pollution, presence of scavengers etc. [11].

If we take into consideration that CWPO is based on the Fenton-type chemistry, the proposed mechanism for radical creation can rely on Haber-Weiss equations which include the creation of  $\bullet\text{OH}$  and  $\bullet\text{OOH}$  species in the presence of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  [11]. Nevertheless, it would be more correct not to exclude the presence of  $\text{O}_2\bullet^-$  radicals since it has been proposed by Haber and Weiss that oxidation of  $\text{O}_2$  in the presence of ferrous ions leads to the creation of  $\text{H}_2\text{O}_2$  and  $\text{O}_2\bullet^-$  radicals [18]. Simplified reaction mechanism based on the Haber-Weiss equations can be explained with the following equations [1], [11], [18], [19]:



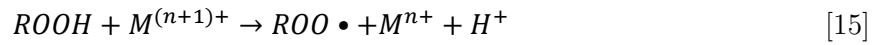
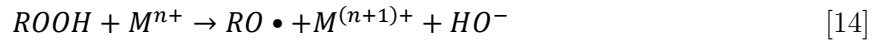
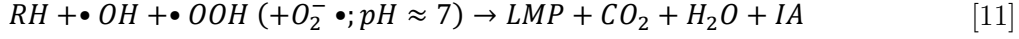
where  $M^{n+}$ ,  $M^{(n+1)+}$  and  $M^{(n+2)+}$  represent metal ions with different oxidation states. With given equations only the main reaction steps that occur under acidic conditions are taken into consideration, namely the reaction of initiation (Eqs. 1–2), propagation (Eqs. 3–4) and termination (Eqs. 5–8).

The first two equations represent reactions of initiation in which hydroxyl radicals are produced. The third and fourth equation are scavenger reactions in which metal ions serve as traps for produced  $\bullet\text{OH}$  radicals causing its conversion into  $\bullet\text{OOH}$  or unavailing hydroxide ions ( $\text{HO}^-$ ). Equations 5–8 represent reactions of termination, i.e. disappearance of created ROS. The last two equations represent a possible formation of  $\text{O}_2\bullet^-$ , but as already stated, this occurs above  $\text{pH} \approx 5$ . In addition, it is assumed that  $\text{O}_2\bullet^-$  radicals have very little activity in the aqueous solution due to their expressed nucleophilicity, which leads towards pronounced reactivity towards  $\text{H}^+$  and  $\text{H}_2\text{O}$  and the formation of  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$  and hydroxide ions [7], [18].

Although scavenger and termination reactions are unveiling reactions which cause disappearance of wanted  $\bullet\text{OH}$  radicals, it is expected that the reaction described by equation 1 is the rate limiting step since calculated rate constant,  $k$ , of  $55 \text{ M}^{-1} \text{ s}^{-1}$  is much lower in comparison with rate constants of  $3.3 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$  and  $7.8 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}$  given for equation 3 and 6, respectively [19]. As described, values are given as an example for the

system in which  $\text{Fe}^{2+}/\text{Fe}^{3+}$  metal ions represent catalytically active species and reaction occurs under atmospheric conditions in acidic media.

If an organic pollutant is present in the system, partial or complete degradation can occur as presented with the following equation:



where *LMP* represents low molecular products, such as remaining partially oxidized aromatics or organic acids, and *IA* represent inorganic anions (ex.  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ). In equations 12–15 we can see that organic pollutants can also participate in the reaction through trapping of ROS and the formation of organic radical ( $R \bullet$ ), organic oxide radical ( $RO \bullet$ ), organic peroxide radical ( $ROO \bullet$ ) and organic hydroperoxide ( $ROOH$ ). As the described phenomena enables higher process efficiency and in order to achieve it,  $\text{H}_2\text{O}_2$  concentration should be kept at minimum [14]. As described, observations are usually connected with the measurement made on the laboratory scale, but the same principle can be applied on the industrial scale since it affects the overall cost of the process. It is worth mentioning that as-written equations for the oxidation of organic pollutant are rather simplified since complex mixture of pollutants in the real wastewaters can also be oxidized through non-chain hydroxyl radical oxidation by  $\bullet X$  radicals ( $X=\text{Cl}$  or  $\text{F}$ ), which can be found as a by-product of chlorination and fluorination pre-treatment, as well as by direct  $\text{H}_2\text{O}_2$  oxidation [20].

Most of the CWPO connected research has been made on the laboratory scale by using a simple batch reactor system [1], [11], although it has been proven that CWPO can be implemented for the treatment of low concentration wastewaters on the industrial scale [7], [11]. For the majority of laboratory scale processes, simple thermostated stirred batch reactors are in use. They are easy to handle and provide an easy way to keep operational conditions (such as *T* and *p*) constant, which is of great importance for kinetic studies. Here, a suspension of solid catalytic material, chosen model pollutant and  $\text{H}_2\text{O}_2$  is simultaneously introduced into the heated jacketed reaction vessel in order to ensure temperature uniformity. Suspension is continuously stirred which enables uniform distribution of solid catalytic material in the reactor. When the reaction is carried out at higher temperatures reflux condenser is used in order to avoid evaporation of water from reaction suspension.

Fixed-bed reactors, for continuous catalytic reactions, are also in use although not to such an extent [21], [22]. In this case uniformly mixed thermostated solution of a chosen pollutant and  $\text{H}_2\text{O}_2$  is constantly introduced at the bottom of a thermally isolated cylindrical tube filled with solid catalytic material. As solution passes through the layer of catalytic materials, it is converted into degradation products and they are collected at the top of the tube.

### 1.2.2 CWPO – materials in usage and future perspectives

As already mentioned, the main classes of catalytically active materials used in the CWPO rely on the exploitation of catalytically active metal species (metals that have different oxidation states) for successful homolytic decomposition of  $\text{H}_2\text{O}_2$ . In such a manner, production of ROS effectively follows the proposed Haber-Weiss mechanism. Pillared clays, metal-ion exchanged zeolites, doped metal oxides and metal catalysts (metals supported on metal oxides, carbon-based materials and polymers) have been one of the most used catalytic materials in the CWPO [3], [4], [11], [12], [23]–[26].

Al/Fe-, Al/Cu- and Al/(Fe-Cu)-pillared clays are one of the most used clay-based materials in the CWPO. Due to a relatively low price, good catalytic activity and high natural abundance of clays (most used clays are montmorillonites, bentonites and saponites), implementation of these materials as a catalyst in the CWPO seems like a good solution [11], [12]. Nevertheless, although they possess a lot of benefits, it is hard to optimize their preparation conditions in order to achieve necessary chemical stability (i.e. minimal or no leaching) for long-term usage [11], [12]. pH value, T, time of aging, concentration of metal ions etc. will influence the final composition and structure of the pillars, as well as the location of active metal species [11], so it is very hard to obtain uniform and repeatable material. In addition, for each material containing different metal species optimal CWPO operational conditions should be set prior to every usage and that makes catalysis even more complicated [12]. Similar implementation problems occur during the usage of metal ion-exchanged zeolites [25], although in some cases it has been reported that their chemical stability is much higher in comparison to the above-mentioned pillared clays [25]. Metal ions, such as Fe, Cu, Mn etc., are more efficiently fixed to the rigid zeolite framework, which decreases leaching and precipitation into the reaction solution [25].

In doped metal oxides and metal catalysts, still the most frequently used catalytically active centres are Fe, Cu and Al, mostly due to their low price and high efficiency in the creation of ROS [11]. Nevertheless, the same problems occur during their implementation. Metal leaching, special operation conditions and demand for optimal catalyst preparation procedure (simple preparation method, choosing of optimal catalytic support etc.) still remains unresolved and a lot of research needs to be focused on their improvement in order to be successfully applied in the industrial scale CWPO [11]. For now, implementation of solid catalytic materials is still focused on the research done on the laboratory scale [11].

Leaching of metals can be avoided with the implementation of noble metal catalysts. Current trends in the CWPO are addressed towards implementation of supported gold (Au) nanoparticles, in which most commonly used supports are hydroxyapatite, diamond, activated carbon and  $\text{TiO}_2$  [21], [27]–[29]. Creation of ROS follows the well-described Haber-Weiss mechanism, while efficiency to overcome rate limiting step (equation 1) is governed with the size of gold nanoparticles and proper assortment of the support [29]. Optimal size of deposited gold nanoparticles is ranging between 5-10 nm [29]. Although it has been reported that particles below 5 nm have the highest activity, bigger size of gold nanoparticles prevents agglomeration and deactivation of the catalytic material during long-term usage, therefore it is preferable that larger Au nanoparticles are used in the CWPO [21].

Selection of the optimal support is another crucial factor for achieving high catalytic activity. For example, usage of activated carbon, in comparison with  $\text{TiO}_2$  or hydroxyapatite, is highly preferable since its surface chemistry attributes to higher consumption and decomposition of  $\text{H}_2\text{O}_2$  [28]. Nevertheless, although noble metal catalysts have shown high catalytic activity and chemical stability, conducted research was mostly focused on the removal on low concentrations (molar concentration,  $c=0.1$  M) of small

molecular compounds (such as phenol) [21], [28]. So, if we take into consideration the conducted research and price of the gold necessary to synthesize the catalytic material, it is clearly obvious that the request for novel and more cost-effective materials is of great importance.

### 1.2.3 New-age materials for the $\text{H}_2\text{O}_2$ activation

Environmental and economic problems occurring during the implementation of above-described catalytic materials have led to the development and implementation of novel carbon and mixed oxide-based materials. Obtained results have shown high potential for their application in the CWPO of model organic pollutants, and opened a new path for the utilization of stable, novel and, in some cases, metal-free catalytic materials.

First report about the usage of stable carbon-based catalytic materials was published by Lücking et al. in 1998 [19], so since then catalytic materials such as activated carbons (AC), carbon nanotubes, graphite, nanofibers and xerogels have been implemented in the CWPO [19], [22], [30]–[33]. The most investigated carbon materials are AC whose electron rich surface owns strong electron donor-acceptor properties allowing them to generate radical species through Haber-Weiss mechanism [34]. In addition, their high specific surface area, adequate porosity and structural defects improve adsorptive interactions between the catalytic material, chosen pollutant and  $\text{H}_2\text{O}_2$  [19], [22], [30], [32]. Adsorptive interactions are rather important since in that manner pollutants are held with electrostatic or dispersive interactions and easily degraded in the vicinity of the surface where ROS creation occurs [19]. It is worth mentioning that electrostatic interactions are prevalent when the pollutant is in the ionic form (pH dependant), while dispersive interactions occur when the pollutant is in the molecular form [19]. Adsorptive interactions are also important for  $\text{H}_2\text{O}_2$  decomposition. It has been shown that the presence of acidic sulphate groups accelerates the decomposition of  $\text{H}_2\text{O}_2$  on AC surface, while the presence of basic sites is crucial for ROS creation [19], [30], [31]. Except important morphological, textural properties and distinctive surface chemistry, the presence of metal impurities is one major parameter which influences the overall performance of AC and other carbon-based materials. The presence of a small amount of Fe and Al (max 10 wt. %) may result from the synthesis procedure, or their origin, and it is expected to increase the overall catalytic activity of the these materials [19], [22]. In comparison with pillared clays, doped metal oxides or metal catalyst chemical stability of carbon-based materials is much higher, so minimal or no leaching occurs during their usage [19].

In contrast to carbon-based materials, usage of cerium-based materials mostly relies on the exploitation of cerium oxide ( $\text{CeO}_2$ ) surface redox properties. The presence of a high amount of surface oxygen vacancies ( $\text{V}_\text{O}$ ) in the  $\text{CeO}_2$  enhances the availability of reduced  $\text{Ce}^{3+}$  sites and enables successful homolytic decomposition of  $\text{H}_2\text{O}_2$  through the Haber-Weiss mechanism [4]. The formation and elimination of these oxygen vacancies is almost constant during catalytic experiments, which allows  $\text{CeO}_2$  to continuously create ROS [4]. Nevertheless, application of  $\text{CeO}_2$  in the CWPO demands surface modifications in order to avoid formation of what they thought to be inactive, surface peroxo species ( $\text{Ce}^{3+}\text{-O}_2^{2-}(\text{H}^+)$ ) [4], [8]. It was assumed that surface peroxo species cannot participate in the ROS creation, so sulfonation pre-treatment of the  $\text{CeO}_2$  surface was usually applied [4], [8]. Despite the opinion that surface peroxo species do not participate in the creation of ROS, Chen et al. [35] have proven that they play an important role in the oxidation of organic pollutants [35]. In the presence of  $\text{H}_2\text{O}_2$  as-formed peroxide species oxidize model organic pollutant, in this case azo dye acid orange 7 (AO7), through ROS formation and mechanism of molecular rearrangement [35]. A small amount of  $\bullet\text{OH}$  radicals was detected during the reaction meaning that ROS are created in the presence of surface peroxo species [35].

Conducted experiments have opened a possibility for usage of metal-free catalytic materials in the CWPO, although a lot of research still needs to be done in order to efficiently use these catalytic materials for the degradation of a wide range of pollutants. Considering the acute cytotoxicity of  $\text{CeO}_2$ , it is still under debate if this catalytic material needs to be applied in the CWPO [4], therefore we should strive to develop metal-free materials which will not have a negative impact on the environment and human health.

### 1.3 Azo dyes

First synthetic azo dye, namely Aniline yellow, was produced in 1861 by Mene, and until today they are the most commonly produced type of dyes [36]. More than 50 % of dye production belongs to azo dyes, whose versatility of products offers more than 2000 different azo dyes with a total production of  $7 \cdot 10^5$  tons per year [37]. Widespread production and usage of synthetic azo dyes in medicine, food, textile, pharmaceutical and chemical industry relies on the fact that the production of azo dyes requires simple synthesis procedures for yielding highly chemical and photolytic stable products [36].

In comparison with pigments, one of the two classified organic colorants, dyes are characterized with high solubility in water, and organic solvents, and even the smallest concentrations, i.e.  $1 \mu\text{g/L}$ , can drastically influence the “quality” of wastewaters [36], [38], [39]. In addition, each azo dye is used for a specific application and therefore a wide variety of different types of dyes is currently present [38], and each of them demands a unique way of removal [40]. Due to their specific chemical features the development of the unique method and operating conditions for the removal of mixture of dyes is rather difficult [15], [40].

Characteristic chemical feature of all azo dyes is the presence of one or more conjugated bonds between two nitrogen atoms. This characteristic azo bond ( $-\text{N}=\text{N}-$ ) represents chromophore part of the molecule which is responsible for light absorption in the visible spectrum ( $\lambda=400\text{-}700 \text{ nm}$ ) [38]. Prerequisite for the formation of coloured substances, i.e. azo dyes, is that the azo bond needs to be located between two aromatic rings, meaning that a chromophore needs to be a part of the conjugated system [38]. In addition to chromophore, auxochrome part of the molecule also contributes to the light adsorption and solubility of the synthesized azo dye. That are usually groups such as carboxylic ( $-\text{COOH}$ ) and sulfonic ( $-\text{SO}_3\text{H}$ ) acid groups, or their sodium salts ( $-\text{COONa}$ ,  $-\text{SO}_3\text{Na}$ ), which intensify the ability of chromophore to absorb light [38]. This means that they are not responsible for the light absorption but their presence can shift the light absorption of the colorant, so they are usually called “colour helpers” [38]. For example, if  $-\text{OH}$  groups located on 1,4-position on the aromatic ring are replaced with amine ( $-\text{NH}_2$ ) groups light adsorption shifts from 347 nm to 386 nm [38]. Adding  $-\text{NH}_2$  groups increases the electro donating ability of azo-benzene (azo bond located between two benzene rings) and enhances light adsorption [38]. In addition to characteristic features that define colour and light absorption, azo dyes also have to exhibit highly chemical, microbial and photolytic stability in order to be used for specific application [36]. Therefore, simple biological degradation, as well as photolysis, usually cannot be implemented for their degradation [36], [40]. Physical and chemical methods usually produce secondary waste, as well as the frequently used Fenton process [36], [40], [41]. Nevertheless,  $\text{H}_2\text{O}_2$  is still the most frequently used oxidant for the degradation of azo dyes and therefore the implementation of CWPO for their removal experiences constant growth [8], [12], [23], [33], [35], [40]–[42].

### 1.3.1 Methyl orange

Methyl orange (MO, IUPAC: p-Dimethylamino-Azobenzenesulfonic Acid) is one type of azo dyes with excellent chemical and microbial stability which can be easily synthesized from sulfanilic acid and N,N-dimethylaniline through diazo coupling [43], [44]. It has been most frequently used as a water soluble acid/base indicator, although it has attracted the researchers' attention for the usage as a model organic pollutant in a wide variety of AOPs, as well as for potential usage for the fabrication of different electronic devices [44], [45].

Structural formula of the MO molecule is given in Fig. 1.2. Azo bond merges two aromatic rings on which dimethylamine ( $-(\text{CH}_3)_2\text{NH}$ ) and sulfonic group ( $-\text{S}(=\text{O})_2\text{OH}$ ) are coordinated in 1,4-position on each aromatic ring. Azo bond represents the chromophoric part of the molecule, while dimethylamine and sulfonic group are auxochromes [38]. Its auxochrome is responsible for the characteristic orange colour of MO which allows it to absorb light in the visible region with the absorption peak at 464 nm and 507 nm at neutral and acidic conditions, respectively [39],[46]. Red shift from 464 nm to 507 nm occurs due to protonation of azo bond and the formation of a quinoid structure.

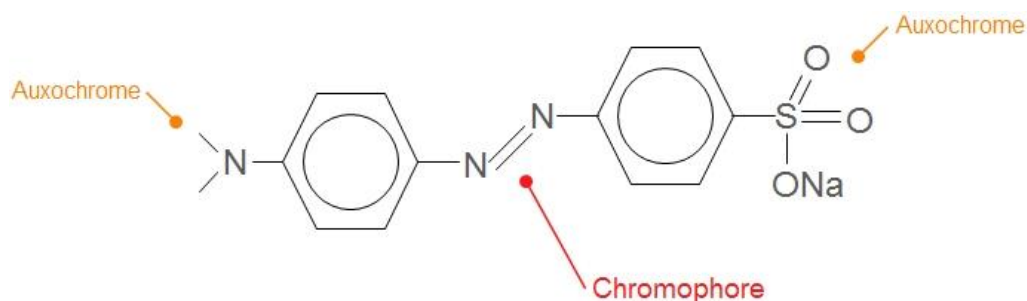


Figure 1.2: Structural formula of methyl orange molecule. Figure taken from Farag et al. [44].

Both, azo-bond and sulphate group of acid sodium salts are considered as xenobiotics, meaning that they interfere with natural organisms and bacterial strains (such as *Pseudomonas*), which can usually easily degrade azo dyes but cannot degrade MO [36]. Therefore, usually photocatalysis or CWPO are used for the removal of MO molecules [12], [23], [39], [47].

Methyl orange degradation can be easily followed by using a simple UV/Vis technique by dividing its UV/Vis spectrum into three parts [12], [23], [47]. Firstly, cleavage of azo bond results in the decrease of the absorption peak in the region 350-600 nm, which is followed with the breakdown of the benzene ring and the formation of small inorganic molecules. Their formation can be observed with an increase and decrease of absorption peaks found in the region between 265-350 nm and 200-265 nm, respectively [47]. MO spectrum with marked degradation regions is given in Fig. 1.3.

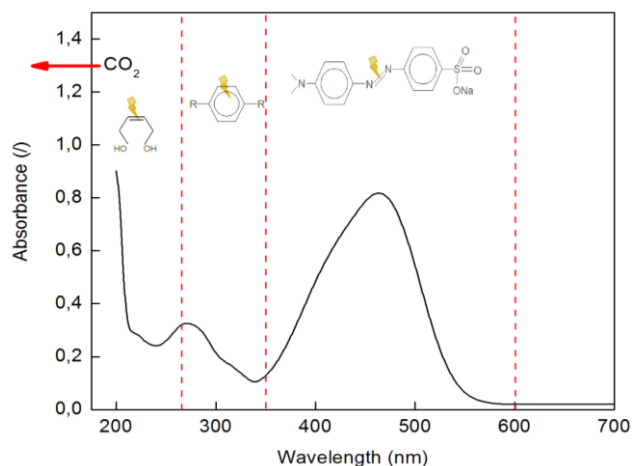


Figure 1.3: Methyl orange UV/Vis spectra with marked oxidation steps. Figure taken from Nie et al. [47].

Due to its low price, simple preparation, high stability and possibility to monitor its degradation products without usage of sophisticated techniques, MO is frequently used as a model organic pollutant in the CWPO.

### 1.3.2 CWPO for the removal of azo dyes

As already mentioned, implementation of CWPO for the removal of azo dyes becomes more interesting every day. Neamtu et al. [42] have achieved effective removal of more than 95 % of the azo dyes Procion marine H-XLE with using only 1 g/L of catalytic material and stoichiometric amount of  $\text{H}_2\text{O}_2$  in 30 min of the process. However, this is only accomplished with the use of Fe modified Y-zeolite at pH=3 and a temperature between 50–90°C. Galeano et al. [12] have used Colombian bentonite treated with Al/Fe-, Al/Cu- and Al/Fe/Cu- solutions for the degradation of 0.1 M methyl orange solution under atmospheric pressure and a temperature of  $18 \pm 2^\circ\text{C}$ . Under optimal pH for specific pillared clay (PILC), namely pH=3.7, 5.5 and 4.6 for Al/Fe-, Al/Cu- and Al/Fe/Cu-PILS, they have removed ~95, ~65 and 70 % of MO during 4 h. Nevertheless, high adsorption rate and leaching of metal species has not been avoided. Al/Fe-, Al/Cu- and Al/Fe/Cu-PILS have adsorbed ~80, ~50 and ~35 % of MO during the first 30 min. Better results were obtained by using Mg modified Colombian bentonite [23]. With the use of 5 g/L of Mg-PILS they have successfully removed ~80 % of MO ( $c=0.1$  M) under atmospheric conditions and pH=7.5. Nevertheless, fresh material (bentonite) contains a significant amount of Fe ions in the structure and around 20 mg/L of  $\text{Fe}^{2+}$  was found in the reaction mixture [23], therefore metal leaching and contamination have not been avoided. In addition, ~70 % of MO is degraded only in the presence of solid Mg-PILS, meaning that Mg modification did not provide high improvement.

In order to avoid leaching of metals Gomes et al. [33] have used activated carbons treated with sulphuric acid for the removal of azo dye Chromotrope 2R. Intense operational conditions ( $T=50^\circ\text{C}$ , pH=3) were applied in order to reach high catalytic activity of a novel catalyst such as activated carbon (AC). Although leaching of metals is avoided with the use of this catalyst, high adsorption on AC reduces real removal of azo dye Chromotrope 2R for one third. Wang et al. [8] have used sulphated ceria for the degradation of azo dye A07 under atmospheric conditions. During 8 h they have successfully degraded ~90 % of 0.035 M solution of A07. Chen et al. [35] have concluded that A07 is oxidized on the surface of sulphated  $\text{CeO}_2$  with the help of surface peroxo species created during the reaction. By using DMPO (5,5-dimethyl-1-pyrroline N-oxide) spin trap they have

successfully detected a small amount of  $\bullet\text{OH}$  radicals, although they have proposed that it is more likely that A07 is oxidized through molecular rearrangement on the reduced  $\text{Ce}^{3+}$ , while  $\text{H}_2\text{O}_2$  is oxidized to  $\bullet\text{OH}$  by means of surface peroxo species, as described above.

From all the experiments it can be observed that metal-based catalysts still have a high application potential, although working under special operating conditions and metal leaching still cannot be avoided. On the other side, usage of novel metal-free materials is still accompanied with the adsorption problems, as well as with a long duration of the process. Therefore, it is necessary to focus on the development of a novel metal-free catalyst that is going to be able to operate under atmospheric conditions and achieve satisfactory removal of azo dyes in a short period of time. In addition, as already mentioned, it is good to be aware that each azo dye has specific characteristics and that all developed materials cannot be used for the removal of a wide range of dyes.

## 1.4 Titanium Dioxide

Titanium dioxide ( $\text{TiO}_2$ ) is a chemically stable, inexpensive ( $<5$  US \$/kg) [48] and harmless naturally occurring material, so over the last two decades it was one of the most investigated systems in surface science of metal oxides. Its “metallic” part, lustrous transition metal titanium (Ti), is one of the ten most ubiquitous metals found in Earth crust and in combination with oxygen it forms three distinctive polymorphs, namely rutile (R), anatase (A) and brookite (B) (detailed description can be found in Section 1.4.1.) [48].

Most common applications of  $\text{TiO}_2$  polymorphs are in the field of catalysis (usually photocatalysis), in solar cells for the production of hydrogen ( $\text{H}_2$ ) and electrical energy, as a white pigment often used in paints, textile, cosmetic and food industry, in corrosion protective and optical coatings, in bone implants etc. [48]–[52], therefore it is not surprising that the production of  $\text{TiO}_2$  has been estimated to  $5 \times 10^6$  tons per year [48]. Around 95 % of mined titanium ores is used for the production of micro and nano-scale  $\text{TiO}_2$  through the so-called sulphate and chloride process [48], [52], while the remaining Ti ores are used for the production of titanium metal foams [53].

Since the focus is given on the Ti oxides, the sulphate and chloride process will be briefly described. In the sulphate process titanium ores are pre-treated with concentrated sulphuric acid ( $\text{H}_2\text{SO}_4$ ) and subsequently oxidized to  $\text{TiO}_2$  and  $\text{H}_2\text{O}$ . Obtained product is annealed at the temperatures between  $800\text{--}1000^\circ\text{C}$  in order to obtain granulated anatase or rutile [48]. In the chloride process, titanium ores are exposed to high temperature ( $T=1000^\circ\text{C}$ ), treated with chlorine gas ( $\text{Cl}_2$ ) and co-fed with coke (C) in order to obtain titanium tetrachloride ( $\text{TiCl}_4$ ) vapour which is further distilled/purified to rutile [48]. From the environmental point of view chloride process is favoured since remaining  $\text{Cl}_2$  can easily be recovered, which is not the case with diluted  $\text{H}_2\text{SO}_4$  remained after the sulphate process.

As-obtained  $\text{TiO}_2$  particles are usually 200-300 nm large, so additional synthesis methods are applied in order to produce nano-scale  $\text{TiO}_2$  ranging from 20 nm to 100 nm [48], [52]. Usage of nano-scale  $\text{TiO}_2$  enables efficient exploitation of size- and structure-related properties, which is rather important in the field of catalysis.

### 1.4.1 $\text{TiO}_2$ polymorphs and amorphous $\text{TiO}_2$

Primitive unit cells of all three polymorphs (Fig. 1.4) are constituted of Ti and O atoms connected to form  $\text{TiO}_6$  octahedra with a different arrangement of unit atoms in unit cell [52]. Tetragonal symmetry is characteristic for both rutile (space group  $P4_2/m\bar{m}$  with  $a=4.587 \text{ \AA}$  and  $c=2.954 \text{ \AA}$ ) and anatase (space group  $I4_1/am\bar{d}$  with  $a=3.782 \text{ \AA}$  and  $c=9.502$

Å), but anatase is characterized with longer Ti-O bonds (compared to horizontal plane) due to a slightly higher distortion of  $\text{TiO}_2$  octahedra [52]. In contrast to anatase and rutile, brookite is characterized with orthorhombic symmetry and it has the largest primitive unit cell with 8  $\text{TiO}_2$  groups per unit cell (space group  $Pcab$  with  $a=9.174$  Å,  $b=5.447$  Å and  $c=5.145$  Å), compared with 4 for anatase and 2 for rutile [52]. Due to their unique unit cell formation, and consequently symmetry, all three polymorphs of  $\text{TiO}_2$  have a characteristic appearance, as well as physical properties such as electrical and optical conductivity, refractive index etc. [48], so all of them are usually designed for specific applications. For example, in comparison to brookite, rutile and anatase are excellent photoactive materials so they are most commonly studied in the field of photocatalysis [48], [50], [52], [54].

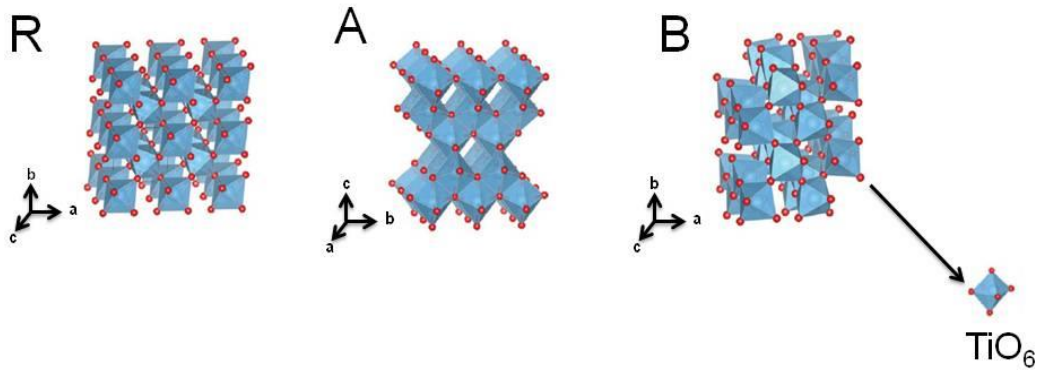


Figure 1.4: Structure of naturally occurring  $\text{TiO}_2$  polymorphs: rutile (R), anatase (A) and brookite (B). Red and blue spheres represent O and Ti atoms, respectively. Figure taken from Choi et al. [55].

Although a lot of research has been devoted to synthesis, characterization and application of above-mentioned polymorphs, naturally occurring and as-synthesized nano-scale  $\text{TiO}_2$ -based oxides usually contain a certain amount of amorphous phase [56]. In order to enhance the applicability of cheaper and less processed  $\text{TiO}_2$  material, scientists have started to investigate properties of amorphous phase and compare it with generally used anatase, rutile and brookite.

Köhler et al. [57] have used computational simulations in order to define structural and electronic properties of amorphous  $\text{TiO}_2$  and compare it with those of anatase and rutile. From the obtained data it can be seen that characteristic octahedral  $\text{TiO}_6$  units are closely stacked and frequently replaced with a large number of under- and over-coordinated Ti atoms as it can be seen in Fig. 1.5 [57]. Under-coordinated  $\text{TiO}_5$  and  $\text{TiO}_4$  ( $\text{TiO}_x$ ;  $x=4.5$ ) units can sometimes be present as surface defects in low pressure  $\text{TiO}_2$  polymorphs, while  $\text{TiO}_7$ ,  $\text{TiO}_8$  and  $\text{TiO}_9$  are characteristic for high pressure polymorphs [57]. For example,  $\text{TiO}_7$  is known from baddeleyite monoclinic polymorph (space group  $P2_1/c$ ), while  $\text{TiO}_8$  can be found in the fluorite type cubic polymorphs (space group  $Fm\bar{3}m$ ) [57]. Nevertheless, average coordination number ( $k_{\text{Ti-O}}$  or  $k_{\text{O-Ti}}$ ) for O and Ti atom is still comparable with those of in anatase, rutile and brookite, giving the  $k_{\text{Ti-O}}$  and  $k_{\text{O-Ti}}$  of 6 and 3, respectively [56], [57]. This means that the fraction of  $\text{TiO}_8$  and  $\text{TiO}_9$  is rather small in comparison with the above-mentioned polymorphs. Electronic properties are more similar to those of anatase than rutile, and that was also confirmed by Prasai et al. [56].

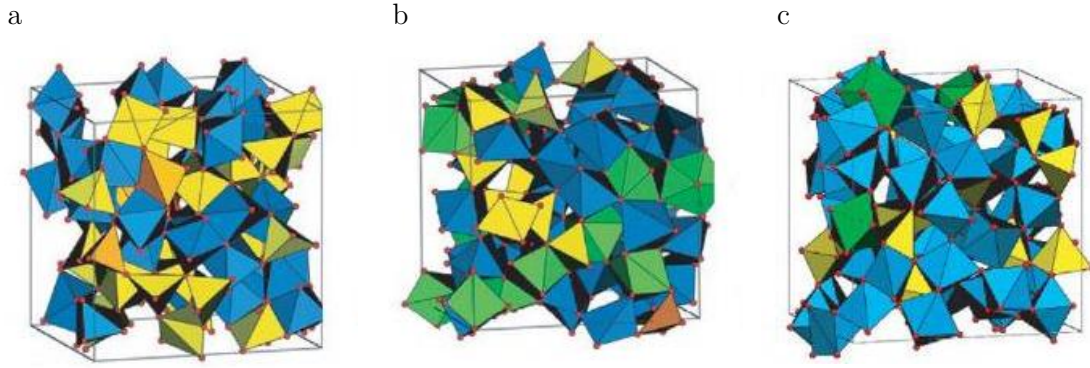


Figure 1.5: Structure of amorphous  $\text{TiO}_2$  obtained from a) CPMD, b) DFTB and c) MD models. Green, yellow and blue coloured unit cells represent over, under and six coordinated  $\text{TiO}_x$  units, while red spheres represent oxygen atoms. Figure taken from Köhler et al. [57].

Chen et al. have used XAFS (X-ray absorption fine structure) [58] and EXAFS (extended X-ray absorption fine structure) [59] analysis in order to experimentally define the local structure of Ti atoms in amorphous nano-scale  $\text{TiO}_2$  particles. From the obtained data it is visible that distortion is mostly localized on the surface and it is directly connected with surface Ti atoms, which are characterized with square pyramidal geometry. Observed distortion increases as the size of nano-scale  $\text{TiO}_2$  particles decreases from  $\sim 3$  nm to  $\sim 2$  nm. Enlarged surface distortion is resulting from shorter Ti-O distance and it has been proposed that these distorted Ti sites are likely to be responsible for the binding with small molecules such as water. In comparison to surface, bulk  $\text{TiO}_6$  octahedral configuration is well preserved and no distortion has been observed. Coordination number for particles with  $\sim 2$  nm and  $\sim 3$  nm in size is  $k_{\text{Ti-O}}=3.9-5.8$  and  $k_{\text{Ti-O}}=4.8$ , respectively. Obtained experimental data is in good correspondence with the values obtained by Zhang et al. [60]. Applying WAXS (wide-angle X-ray scattering) measurements they were able to probe atomic correlations between Ti and O atoms, and used the obtained data in RMC (reverse Monte Carlo) simulation in order to define the atomic structure of nano-sized amorphous  $\text{TiO}_2$  particles with approximate size of  $\sim 2$  nm. The highest distortion is observed on the surface of  $\text{TiO}_2$  particles, while anatase-like core is well preserved. Average coordination number of Ti is around 5.3 ( $k_{\text{Ti-O}}=5.3$ ) and under coordination is mostly attributed to the truncation of surface  $\text{TiO}_6$  octahedra.

Experimental determination of nano-scale amorphous  $\text{TiO}_2$  electrical properties was done by Fukuhara et al. [61]. By testing titanium-nickel-silica (Ti-Ni-Si) amorphous alloy capacitor sandwiched with amorphous  $\text{TiO}_2$  nanoribbons they have proven that amorphous  $\text{TiO}_2$  is characterized with a higher work function, namely 5.5 eV, in comparison to anatase with around 4.0 eV. Above-mentioned truncation of surface  $\text{TiO}_6$  octahedra in amorphous  $\text{TiO}_2$  causes reduction of coordination number from  $k_{\text{Ti-O}}=6$  to  $k_{\text{Ti-O}}=5.3$ , and induces creations of surface oxygen vacancies ( $V_{\text{O}}$ ) which serve as electron trapping sites and accelerate working performance. On the other hand, Hu et al. have used amorphous  $\text{TiO}_2$  coating on the silicon (Si), gallium arsenide (GaAs) and gallium phosphide (GaP) photoanodes in cells for solar fuel production. 2-143 nm thick transparent layer of amorphous  $\text{TiO}_2$  deposited on the surface of the anodes has improved the stability and prevented corrosion of anodes, as well as increased surface conductivity due to the presence of  $V_{\text{O}}$ . Pham et al. [62] have calculated that 1 % of  $V_{\text{O}}$  present on the surface of amorphous  $\text{TiO}_2$  coating improves the conductivity of the water splitting anodes mostly due to the presence of neutral oxygen vacancies ( $V_{\text{O}}^0$ ). As-obtained vacancies are creating “leaky” channels in the middle of the band gap (photoemission peak is around 1-1.5 eV above the

edge of the valence band), so hole mobility is 10 times lower than hole polaron mobility in bulk rutile.

Obtained data clearly suggest that there is room for possible application of amorphous  $\text{TiO}_2$ , although a lot of research still needs to be done in order to completely understand its beneficial properties and spread its use onto different areas. In addition, properties of nano-scale  $\text{TiO}_2$  materials are not correlated only with the size and atomic structure, but also with the morphology and surface properties of nano-scale  $\text{TiO}_2$  materials.

### 1.4.2 Morphological classification of nano-scale $\text{TiO}_2$

It is well known that morphology of nano-scale  $\text{TiO}_2$ , as well as other materials, is of great importance for achieving high activity in various catalytic reactions. Each of them is characterized with specific morphologically induced properties, such as high surface area, enhanced electrical conductivity, mechanical strength etc., and therefore it is of great importance during the planning of the synthesis of materials. Morphology of nano-scale  $\text{TiO}_2$  can be briefly divided into nanosheets, nanotubes, nanorods, nanofibers and nanospheres etc. [50], [51]. That can further be used in the form of powders and extrudates (usually powder  $\text{TiO}_2$  shaped into pellets), thin films and crystallites [50]. Schematic representation of distinctive nano-scale  $\text{TiO}_2$  morphologies is given in Fig. 1.6.

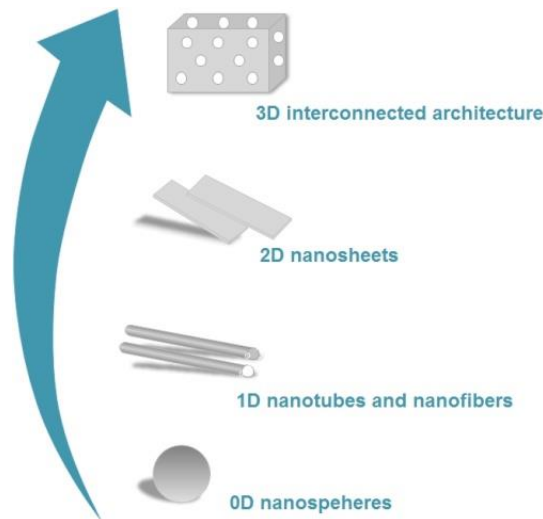


Figure 1.6: Schematic illustration of distinctive nano-scale  $\text{TiO}_2$  morphologies. Figure taken from Shaheed et al. [63].

Two-dimensional (2D) multilayered nanosheets are conjugated 001 facets of titanium oxides (i.e. titanates) usually found in planar or curved shape [51][63]. Typical thickness is below 10 nm, while height and width are larger than 100 nm [51]. Isolated (single layer) nanosheets are usually primary morphology that is formed during hydrothermal synthesis of nanotubes, so their morphology and structure is not uniform [64] and structure directing agents (such as highly corrosive and poisonous hydrofluoric acid, HF) are often used in order to enhance the formation of 001 facets. Nevertheless, due to their high specific surface area ( $S_{\text{BET}} > 400 \text{ m}^2/\text{g}$ ), flat surface and enhanced surface conductivity, they are often used in solar cells or lithium ion-batteries [63]–[65].

Oblong hollow profile of one-dimensional (1D) nanotubes, nanorods and nanofibers makes a shorter distance for charge carrier diffusion so they are often applied in light activated catalytic reactions, such as photocatalysis [63].  $\text{TiO}_2$ -based nanotubes are most commonly obtained by folding nanosheets into a multilayered hollow cylinder with the

aspect ratio (i.e. length divided by diameter) ranging from 10 to several thousand [51][66]. Each hollow tube is surrounded with 2-10 layers whose thickness is around 2-6 nm with the distance between the layers of 0.72-0.78 nm [51], [66]. Inner diameter of 2-20 nm has a tendency to remain constant, although a small amount of  $\text{TiO}_2$ -based nanotubes with a variable inner diameter has been synthesized [51]. The majority of  $\text{TiO}_2$ -based nanotubes are characterized with an open end structure with the exception of nanotubes synthesized by anodic oxidation, which always have one closed end [51]. Due to high specific surface area ( $S_{\text{BET}}=250\text{-}450\text{ m}^2/\text{g}$ ) and characteristic mesoporosity they are one of the most beneficial morphologies used for liquid phase catalytic reactions [67]. In comparison with nanotubes,  $\text{TiO}_2$ -based nanorods do not possess an internal layered structure but only rigid cylindrical structure with a closed circular base [51]. Nevertheless, aspect ratio of nanorods is similar to those of nanotubes. On the other hand, nanofibers are characterized with a hollow multiwall structure, length of several tens of microns and width of about 10-100 nm. [51]. In comparison with nanotubes, nanorods and nanosheets are characterized with good crystallinity. Usually the length of the edges of 001 plane defines the length of nanofibers, while the width is defined with the length of the edges of 001 or 010 plane [51].

Except above-mentioned elongated structures, zero-dimensional (0D) nanospheres are commonly in use due to excellent porosity which is favourable in the liquid-phase reactions. Nevertheless, synthesis of “perfectly” formed spheres usually relies on the application of costly and troublesome structure-directing agents and template synthesis methods [68]. Depending on the wanted properties and potential application, nano and micro-scale spheres can be obtained with a solid, core-shell and hollow structure [68].

Obtained morphologies and forms of nano-scale  $\text{TiO}_2$  greatly depend on the synthesis method and accompanied operational parameters, type of Ti precursor, concentration, pH and type of the solvent etc. [50], [51], so the use of a proper method is of great importance. Precipitation, solvothermal, hydrothermal, sol-gel, microemulsion, combustion and electrochemical synthesis are the most commonly applied solution route-based methods, but among them hydrothermal synthesis was one of the most extensively used methods for the synthesis of nano-scale  $\text{TiO}_2$ -based materials.

#### 1.4.2.1 Hydrothermal synthesis of distinctive nano-scale $\text{TiO}_2$ morphologies

The first application of hydrothermal synthesis method dates back to 1845 when Robert Bunsen successfully synthesized barium ( $\text{BaCO}_3$ ) and strontium ( $\text{SrCO}_3$ ) carbonate in thick silver-lined vessel under “high-temperature-high-pressure” conditions [69]. Since then the apparatus used for hydrothermal synthesis has improved, and now the synthesis is normally conducted in a Teflon-lined stainless steel pressure vessel (i.e. autoclave), under controlled temperature and pressure in the aqueous solution [50], [51], [70]. With increasing the temperature above the boiling point of the solvent we alter the properties of the chosen solvent (such as ionic strength, thermal conductivity, viscosity, heat capacity and dielectric constant), which strongly influences the formation of wanted nano-scale  $\text{TiO}_2$  material [50], [70]. Internal pressure in the vessel is exclusively determined with temperature and the amount of the solvent used, and it is always higher than 1 bar [70]. Some authors state that the hydrothermal synthesis method is only one type of a solvothermal method in which exclusively water is accepted as a solvent [70], but conventionally the term hydrothermal refers also to the aqueous environment of different inorganic compounds, while the term solvothermal is used for organic media (e.g. methanol, butanol, toluene etc.) [50], [51].

Benefits of the hydrothermal synthesis method are the synthesis of nano-scale materials with uniform morphology, size, homogeneity in composition and high degree of crystallinity at relatively mild synthesis conditions [51], [52], [54], [66]. In addition, the hydrothermal

synthesis method favours a decrease in agglomeration between the particles and allows the synthesis of monodispersed particles with narrow size distribution [54], [66]. All these features are beneficial for its application in the synthesis of a variety of nano-scale  $\text{TiO}_2$ -based materials.

In 1998, Kasuga and co-workers [51] have applied this method for the synthesis of  $\text{TiO}_2$ -based nanotubes, and since then it is widely used for their production. In comparison with other methods used for the synthesis of  $\text{TiO}_2$ -based nanotubes, namely chemical template-assisted method and anodic oxidation, hydrothermal synthesis is rather simple and cost-effective [50], [51], [71]. Several grams of powder  $\text{TiO}_2$  precursor can be easily converted into  $\text{TiO}_2$ -based nanotubes with the efficiency of almost 100 % [51], [67]. The process of their formation is usually divided into two directions: formation of  $\text{TiO}_2$ -based nanotubes during hydrothermal treatment in alkaline sodium hydroxide ( $\text{NaOH}$ ,  $c=10$  M) solution and subsequent washing usually in the solution of hydrochloric acid ( $\text{HCl}$ ,  $c=0.1$  M). This step is called protonation or ion-exchange step [51], [70], [72]. Although it was stated that the formation of tubular structure occurs during the protonation step, it has been proven that scrolling occurs during hydrothermal treatment, while the protonation step influences only the crystallinity and surface area of  $\text{TiO}_2$ -based nanotubes [66]. A detailed description of  $\text{TiO}_2$ -based nanotubes properties obtained by hydrothermal synthesis method is given in the upcoming section.

Because of the large interest for the revealing nanotube formation process, partial lamellar fragments formed during hydrothermal synthesis were isolated and examined. It was observed that these fragments have a sheet-like structure, which is highly unstable, and have a tendency to fold into nanotubes in order to minimize their surface energy [51]. As already mentioned, different surface stabilizing agents have been used in order to preserve their formation, but those agents were influencing the final properties of the material. Nevertheless, by tuning the hydrothermal synthesis parameters Pavasupree et al. [73] have successfully synthesized  $\text{TiO}_2$ -based nanosheets with the  $S_{\text{BET}}=648$   $\text{m}^2/\text{g}$ , from titanium (IV) butoxide during short hydrothermal treatment (duration was only 12 h) under mild conditions ( $T=130^\circ\text{C}$ ). Since using non-crystalline  $\text{TiO}_2$  precursor is more cost-effective, Wu et al. [65] have used commercial  $\text{TiO}_2$  powder, P25. By varying the concentration of  $\text{NaOH}$  solution they were able to obtain  $\text{TiO}_2$ -based nanosheets with the structure that resembles the partially opened nanotubes.

Nanosheets/nanotubes can adhere together in order to form a 3D flower-like morphology, although as-obtained nanoflowers cannot be compared with well-defined hierarchical nanoflower structures usually obtained in the presence of surface stabilizing agents (ex.  $\text{HF}$ ). Nevertheless, Liu Min et al. [74] have successfully synthesized  $\text{TiO}_2$ -based nanoflowers during a short low-temperature hydrothermal synthesis ( $T=150^\circ\text{C}$ ; duration  $t=3$  h) with  $\text{NaOH}$  solution. Prior to treatment, commercial  $\text{TiO}_2$  powder was dissolved in the solution mixture of  $\text{H}_2\text{O}_2$  and nitric acid ( $\text{HNO}_3$ ) by heating the solution to  $80^\circ\text{C}$ .

$\text{TiO}_2$ -based nanospheres were also successfully synthesized without the use of structurally directing agents. Zhu et al. [75] have obtained nanospheres through prolonged hydrothermal synthesis ( $T=150^\circ\text{C}$ ; duration 48 h) of P25 in 10 M  $\text{NaOH}$  solution. Results were  $\text{TiO}_2$ -based nanospheres with a rather high specific surface area for this type of the structure ( $S_{\text{BET}}=113$   $\text{m}^2/\text{g}$ ) and enriched with hydroxy groups ( $-\text{OH}$ ). In another example  $\text{TiO}_2$ -based nanoparticles/nanospheres were obtained from the mixture of titanium isopropoxide and acidic ethanol-water solution [76]. By adjusting the concentration of titanium isopropoxide, and molar ratio of solvents, the size of the final product was successfully varied between 7-25 nm without visible agglomeration.

Nevertheless, of all above-mentioned morphologies special attention has always been devoted to  $\text{TiO}_2$ -based nanotubes due to their unique structural and physicochemical properties that ameliorate its catalytic performance in comparison with other morphologies.

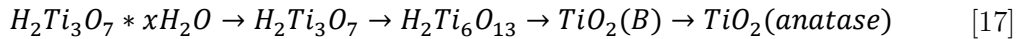
#### 1.4.2.2 Properties of $\text{TiO}_2$ -based nanotubes obtained through hydrothermal synthesis method

When first synthesized by Kasuga and co-workers [51],  $\text{TiO}_2$ -based nanotubes were characterized as anatase polymorph, but till now it was proven that they have a more sophisticated structure which is composed of distinctively coordinated  $\text{TiO}_x$  units, substantial amount of crystallographic/physisorbed water and ion-exchangeable -OH groups which can be presented as hydrated form of polytitanic acid with general formula [51], [77]:

$$H_2Ti_nO_{2n-m+1}(OH)_{2m} * xH_2O \quad [16]$$

where  $n$ ,  $m$  and  $x$  depend on the type and source of starting Ti precursor, conditions of hydrothermal synthesis and concentration and type of acid used in the protonation step [66], [77]. By interpreting obtained crystallographic data several structures were suggested, namely a) monoclinic trititanate ( $H_2Ti_3O_7 * xH_2O$ ), b) orthorhombic dititanate ( $H_2Ti_2O_4(OH)_2 * xH_2O$  and c) lepidocrocite type ( $H_xTi_{2-x/4}\square_{x/4}O_4 * xH_2O$ ;  $\square$  represents  $V_O$ ) [66], [77]. Monoclinic structure has become widely accepted by most researchers, but we have to admit that it is rather hard to distinguish between proposed structures due to problems occurring during collection and interpretation of the data [66]. For example, all of them have rather similar properties and uneven distribution of small crystallites which causes broadening of the XRD (X-ray diffraction) peaks (reflections), consequently making interpretation of data rather difficult [66], [77]. Additionally, it is hard to define the exact location of hydrogen atoms in the structure, so a combination of sophisticated techniques needs to be used in order to propose the best corresponding structure for as-synthesized  $\text{TiO}_2$ -based nanotubes. Commonly used techniques are MAS NMR (magic angle spinning nuclear paramagnetic resonance), XRD, TGA (thermogravimetric analysis) and TEM (transmission electron microscopy) analysis [51], [66], [67], [71], [77].

By using the above-mentioned analysis for determination of thermal stability and atomic structure of  $\text{TiO}_2$ -based nanotubes, it has been observed that calcination treatment up to  $T=500^\circ\text{C}$  induces loss of water, ion-exchangeable -OH groups and topotactic transformation into final anatase or rutile polymorphs [51], [66], [71], [77] by following the simplified equation:



where  $H_2Ti_3O_7$ ,  $H_2Ti_6O_{13}$  and  $TiO_2(B)$  represent intermediate phases of  $H_2Ti_3O_7$  topotactic transformation [51], [66], [77]. With  $^1\text{H}$  MAS NMR analysis Bavykin et al. [77] have successfully identified temperature regions in which loss of protons and above-described transformation occurs (Fig. 1.7). Up to  $T=300^\circ\text{C}$  desorption of intralayered -OH groups occurs, and that is additionally divided into desorption of physical adsorbed water and -OH up to  $T=140^\circ\text{C}$  and loss of crystallographic water up to  $250^\circ\text{C}$ . Above that temperature region topotactic transformations occur and intermediate structures follow above-mentioned  $H_2Ti_3O_7$  and  $H_2Ti_6O_{13}$  [51], [77]. Between  $T=300-400^\circ\text{C}$  disintegration of interlayered -OH groups and formation of  $TiO_2(B)$  is observed, followed by the formation of anatase which usually induces the loss of tubular morphology [51], [67], [77]. Bavykin et al. have also observed that in the low-temperature region one more type of protons, namely ion-exchangeable protons of structural -OH groups are present [77]. These protons are

incorporated into the structure of  $\text{TiO}_2$ -based nanotubes and are mainly responsible for the ion-exchange capacity. In addition, abundance with  $-\text{OH}$  groups affects complete surface chemistry of  $\text{TiO}_2$ -based nanotubes and enables application of different surface functionalization treatments in order to ameliorate its performance in catalytic reactions.

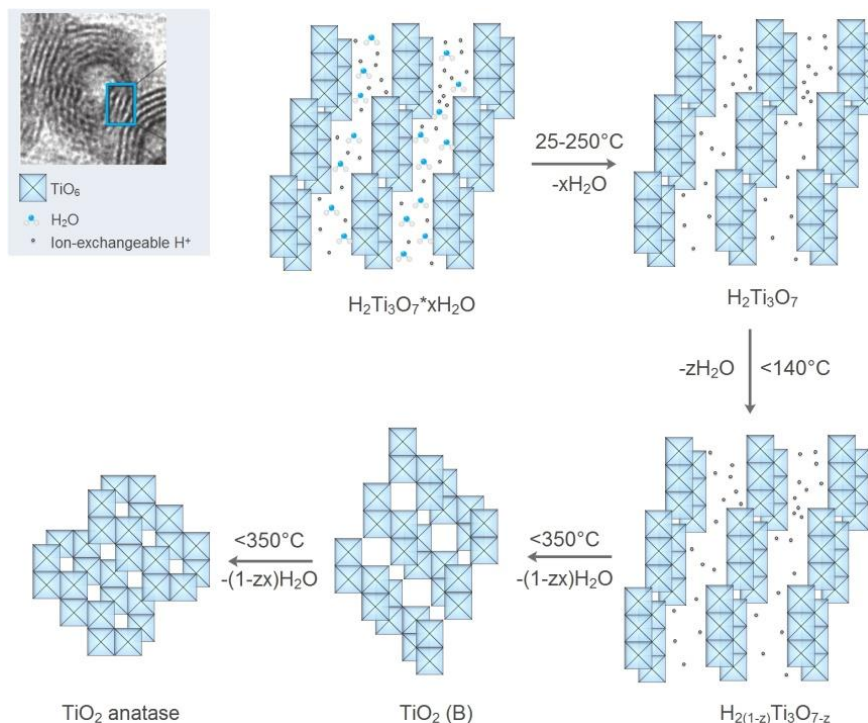


Figure 1.7: Graphical illustration of the changes occurring during mild thermal treatment. Figure taken from Bavykin et al. [77].

$-\text{OH}$  groups are characterized with weak Brønsted acidity and they are evenly distributed on the surface of  $\text{TiO}_2$ , namely in the terminal and bridging mode as shown in Fig. 1.8. Due to the nanometre size of  $\text{TiO}_2$ -based nanotubes the ration between bulk and surface atoms is almost evenly distributed, meaning that abundance with surface  $-\text{OH}$  groups is rather high. It is suggested that area ( $A$ ) of  $1 \text{ nm}^2$  contains approximately 5.8  $-\text{OH}$  groups per se [51]. Crystal polymorphs of  $\text{TiO}_2$  usually do not contain  $-\text{OH}$  groups, which means that it is rather a characteristic of amorphous  $\text{TiO}_2$  obtained through hydrothermal treatment of commercial  $\text{TiO}_2$  powders [51], [71].

One of the specific surface modifications that can be induced only in the presence of surface  $-\text{OH}$  groups is chemical treatment with  $\text{H}_2\text{O}_2$  and formation of surface peroxo species [51], [71], [78]–[80]. In comparison with, for example, sulphate treatment, this is a rather simple and cost-effective way to ameliorate surface redox properties [78], [79]. Due to the ability to absorb in visible light region as-formed surface peroxo species enhance the performance of  $\text{TiO}_2$ -based materials in the photocatalytic reactions [71], [78]–[80]. Nevertheless, they have a rather low thermal stability and completely decompose till  $90^\circ\text{C}$  [51], [71].

One more property of  $\text{TiO}_2$ -based nanotubes is essential for their high catalytic activity. As already mentioned, in  $\text{TiO}_2$ -based nanotubes the ratio between surface and bulk atoms is rather high, meaning that only several bulk atoms can be found in the cross-section of the nanotube wall. Such distribution greatly affects the porosity and specific surface area ( $S_{\text{BET}}=250\text{--}450 \text{ m}^2/\text{g}$ ) of the material. According to the IUPAC classification they are mesoporous materials with predominant interparticle porosity whose hysteresis loop of

nitrogen ( $N_2$ ) isotherms is between H1 (at relative pressure of  $N_2$  between  $0.5 < p/p_0 < 0.8$ ) and H3 ( $p/p_0 > 0.8$ ) [51], [67]. Obtained hysteresis loop is usually very broad, confirming that small and large pores, with the diameter  $d_p$  between 4-20 nm, are present [51]. Smaller pores present pores inside an individual nanotube (internal pores), while larger ones correspond to the external pores resulting from cavities formed between bundles of  $TiO_2$ -based nanotubes [51].

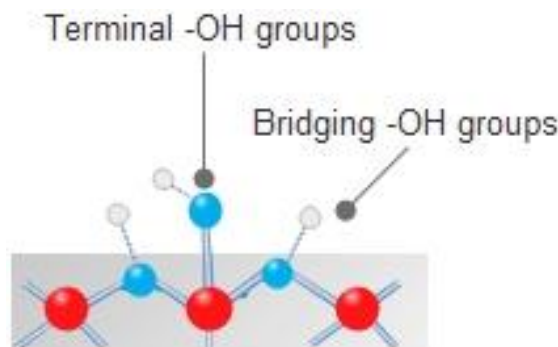


Figure 1.8: Graphical illustration of terminal and bridging -OH groups on the surface of  $TiO_2$  materials. Red, blue and grey spheres represent Ti, O and H atoms, respectively.

All of the above-mentioned properties are strongly dependent on how the hydrothermal synthesis and acid washing, i.e. protonation are performed. By changing the source of Ti precursor, the source of aqueous solution and operational parameters, we can completely differ from the wanted morphology. As mentioned in the previous section, prolonged hydrothermal treatment or change in the type of Ti precursor can induce the formation of nanospheres (without structural stabilizing) agents, rather than nanotubes. Equal importance can be given to the protonation step. As-prepared  $TiO_2$ -based nanotubes (obtained through hydrothermal treatment with 10 M NaOH) contain a large amount of structurally and surface bonded sodium ions ( $Na^+$ ). During washing with HCl,  $Na^+$  are replaced with  $H^+$  (therefore, the process is called protonation or ion exchange) which causes the formation of surface bonded -OH and replacement of  $Na^+$  ions from the structure. The latter influences the surface porosity since it drastically increases due to partial “resentment” of the structure [72]. Therefore, structural and surface properties of  $TiO_2$ -based nanotubes are dependent on the numerous factors and it is of great importance to optimize them in order to obtain a highly active catalytic material.

### 1.4.3 Ti-peroxo species

By adding  $O_2$  into the acidic solution of titanium precursor Schoon et al. (1870) have, for first time in history, observed the creation of intense orange titanium peroxo complex [81]. Since then, liquid-phase peroxo complexes were used for detection of residual  $H_2O_2$  by applying UV/Vis analysis technique, for studying the chemistry of the complex (which is rather important for the application of titanium bone implants) or for the fabrication of titanium coatings [81]. Interaction of  $Ti^{4+}$  with  $H_2O_2$  was also observed in titanium silicalites (TS-1), as well as in  $TiO_2$ -based materials like nanosheets, nanotubes or nanoparticles [17], [71], [78]–[80], [82]–[86]. These peroxo complexes, i.e. “immobilized” titanium peroxo species, enhance the activity and selectivity of  $TiO_2$ -based materials in different catalytic and selective oxidation reactions [71], [78]–[80], [83]–[85].

In the well-known selective oxidation (epoxidation) system peroxo species are generated through activation of  $H_2O_2$  in the presence of TS-1 material [17], [83]. In contrast to TS-1,  $TiO_2$ -based materials used in non-selective catalytic reactions are usually decorated with

surface peroxo species prior to usage, mostly in order to enhance visible light absorption in the liquid-phase photocatalytic reaction [78]–[80]. Except excellent light absorption properties, as-formed species can be used in the liquid-phase catalytic reactions, such as CWPO, in which they can easily activate hydrogen peroxide by increasing electrophilic or nucleophilic character of modified  $\text{TiO}_2$ -based material with respect to the original oxidant  $\text{H}_2\text{O}_2$  [87]. However, in the TS-1 systems these species are formed on  $\text{Ti}^{4+}$  grafted on Si, but  $\text{Ti}^{4+}$  present in  $\text{TiO}_2$  crystal polymorphs does not show any tendency towards the formation of peroxo species [51], [71], [83]. As already mentioned, in order to obtain desired results, it is necessary to use surface -OH rich material (such as amorphous  $\text{TiO}_2$  usually obtained through hydrothermal synthesis method of commercial  $\text{TiO}_2$  powder), where these groups serve as bonding sites for peroxo species formation [51], [71]. Moreover, bonding strength and geometry of surface peroxo species will largely influence the catalytic performance, so a lot of research has been devoted to studying their geometry, bonding strength and catalytic performance.

#### 1.4.3.1 Binding modes and catalytic activity of titanium peroxo species

Diatomic molecules of  $\text{O}_2$  can bind to metal atoms in several different ways depending on the non-covalent  $\pi$  interactions of metal d orbital with  $\pi^*$  orbital of  $\text{O}_2$  [88]. Ligand to metal charge transfer (LMCT) is dependent on the energy of metal d orbital, meaning that in the periodic system of elements (PSE) it increases from left to right for the periods of transition metal section [88], [89]. As-described interaction of  $\text{Ti}^{4+}$  d orbital with  $\text{O}_2$  ligand is rather strong and as-formed species can easily be activated in order to participate in the reaction [88], [89]. Nevertheless,  $\pi$  interaction with proximal oxygen atom is always slightly weakened due to bent geometry of  $\text{O}_2$  ligand, meaning that as-formed peroxo species are slightly “crooked” at the farthest point of the diatomic  $\text{O}_2$  molecule. Capacity of the binding can be simply divided into unidentate (one oxygen per titanium atom) and bidentate (two oxygens atoms per titanium atom) binding mode which gives rise to unidentate end-on ( $\eta^1$ -X; X=Ti atom) and bidentate side-on ( $\eta^2$ -X) geometry [17], [88], [89]. As formed  $\eta^1$  and  $\eta^2$  peroxo species are presented in Fig. 1.9.

Based on the experimental evidence, Zhang et al. [90] and Ulmann et al. [91] have also reported the possibility that unidentate end-on/end-on ( $\mu$ - $\eta^1$ : $\eta^1$ -X) geometry can be formed on the surface of  $\text{TiO}_2$ -based materials, but it is worth mentioning that as-formed bridging  $\text{O}_2$  species are probably results of bonded molecular oxygen rather than peroxo species [88], [92]. Huybrechts et al. [93] have proposed the presence of titanium-oxo species ( $\text{Ti}=\text{O}$ ), but this kind of formation would require a change in the oxidation state of titania from  $\text{Ti}^{4+}$  into  $\text{Ti}^{5+}$ , which has not been observed so far. In comparison with them, Kong et al. [94] have reported that  $\text{H}_2\text{O}_2$  molecules coordinated between two layers of peroxide-treated titanium oxide crystal are responsible for excellent visible light absorption and yellow colour. Nevertheless, most of the researchers agree that  $\eta^2$  peroxo species are those responsible for visible light absorption and characteristic yellow colour of the material, and therefore it is commonly embraced that  $\eta^1$  and  $\eta^2$  peroxo species are characteristic titanium peroxo geometries [17], [51], [71], [78], [83], [85].

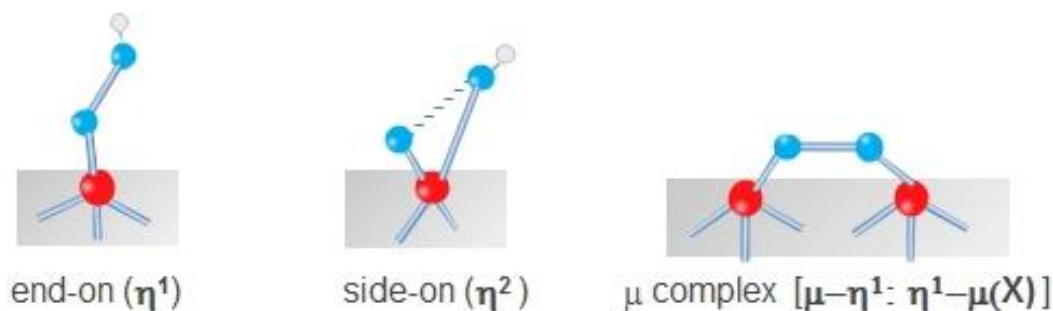


Figure 1.9: Graphical illustration of peroxo species binding modes [88]. Red, blue and grey spheres represent Ti, O and H atoms, respectively.

Both species can be found in the protonated hydroperoxo form, namely  $\text{Ti}(\eta^1\text{-OOH})$ , and protonated peroxy form  $\text{Ti}(\eta^2\text{-OOH})$ , as well as deprotonated  $\text{Ti}(\eta^2\text{-OO-})$  form. The latter ones are those characterized with intense yellow colour and the absorption band at 420 nm [17], [51], [83], [95], so they can be easily detected by using UV/Vis DR (UV/Vis diffuse reflectance) analysis [51], [71], [83], [96]. Nevertheless, Klissuriski et al. [85] have stated that diffuse reflectance spectra of titanium peroxo species in peroxide-treated anatase only reflect ligand to metal charge transfer and can be both due to end-on and side-on configuration. Therefore, we must take into consideration the possible attribution of  $\eta^1$  species to light absorption. In addition, Yoon et al. [17] have observed that the presence of  $\text{H}_2\text{O}$  greatly affects the interconversion between protonated and deprotonated  $\eta^1$  and  $\eta^2$  forms, and that it is far likely that these species are reaching equilibrium in the aqueous conditions. Prestipino et al. [96] have also observed that the presence of  $\text{H}_2\text{O}$  greatly affects the catalytic activity and interconversion between geometries, so we can conclude that the presence of  $\text{H}_2\text{O}$  molecules greatly affects titanium peroxo species geometry and catalytic performance.

It has been proposed that titanium peroxo species are creating  $\bullet\text{OH}$  radicals in the liquid-phase reactions, while in the gas-phase reactions they are only releasing superoxide ( $\text{O}_2^-$ ) [86]. As already mentioned, titanium peroxo species are thermally unstable so it is not surprising that they decompose in order to create  $\text{O}_2$ . In comparison to that, liquid-phase catalytic reactions are far more complicated than the mechanistic point of view. Yoon et al. [17] have used DFT method in order to calculate energetically favourable formation of titanium peroxo species and ROS formation. In comparison to the already known, they have shown that  $\bullet\text{OOH}$  radicals are predominant species formed during aqueous catalytic oxidation of  $\text{H}_2\text{O}_2$  in the presence of peroxo species. In addition, they have concluded that as-formed peroxo species can perform better when the concentration of  $\text{H}_2\text{O}_2$  is rather low in comparison with the concentration of organics [17]. Similar observations were made by Cheng et al. [35] in the cerium-peroxo system. They have attributed such behaviour to competitive adsorption of  $\text{H}_2\text{O}_2$  and organic pollutant on the surface of  $\text{CeO}_2$  nanoparticles. Tengvall et al. [97] have used EPR measurements in order to exclusively detect the formation of different ROS in the presence of titanium peroxo gels. They successfully detected superoxide anion radical ( $\bullet\text{O}_2^-$ ), which was rather “stable under neutral pH, while its detection completely disappeared under acidic conditions.”

From all the conducted studies it can be seen that detection, quantification and performance of titanium peroxo-species in the catalytic reactions is rather complicated and a lot of sophisticated techniques and computation calculations need to be used in order to possibly clarify their behaviour. Nevertheless, it cannot be disproved that these species play an important role in many different catalytic reaction systems.

## Chapter 2

# Hypotheses

Based on the available literature data, the following hypotheses have been made:

1. It is well known that the morphology of the nano-scale  $\text{TiO}_2$ -based materials, especially nanotubes, strongly influences the overall catalytic performance and activity of the material. Therefore, it is worth asking if the morphology of the material influences the catalytic performance of surface peroxo species and why?
2. The presence of peroxo species on the surface of  $\text{CeO}_2$  materials enhances the degradation of the model pollutant due to mutual contribution of  $\text{Ce}^{3+}$  sites and surface peroxo species, so can partial reduction of  $\text{Ti}^{4+}$  into  $\text{Ti}^{3+}$  enhance the degradation of methyl orange in a similar manner?
3. Peroxo species formed on the surface of  $\text{TiO}_2$ -based materials can only be formed in the materials abundant with surface -OH groups. Can the defined type of the -OH groups (intra/interlayered and ion-exchangeable) and their availability enhance the formation of surface peroxo species?
4. Can a protonation (acid washing) step influence the strength of the -OH bonding and the amount of surface peroxo species formed?
5. Binding modes of peroxo species, usually proposed to be found on the surface of  $\text{TiO}_2$ -based materials, are deprotonated end-on  $(\text{Ti}-\text{OO})^-$  and end-on/end-on  $(\text{Ti}-\text{O}-\text{O}-\text{Ti})$  geometry. Are these species only responsible for catalytic activity?
6. It is well known that  $\text{H}_2\text{O}_2$  is a strong mineralizing agent for  $\text{TiO}_2$ -based materials so it causes partial disintegration of the material during the treatment. Therefore, are surface peroxo species only species responsible for catalytic activity of peroxide-treated  $\text{TiO}_2$ -based materials or does peroxide treatment induce complete changes in the materials structure which affects catalytic activity of the materials?

## Chapter 3

# Experimental Part

### 3.1 Materials Synthesis and Modifications

#### 3.1.1 Hydrothermal synthesis of morphologically distinctive nano-scale TiO<sub>2</sub>-based materials

##### 3.1.1.1 Synthesis of TiO<sub>2</sub>-based nanotubes

Amorphous TiO<sub>2</sub>-based nanotubes were obtained following the alkaline hydrothermal synthesis method described by Erjavec et al. [67]. Briefly, 2 g of commercial TiO<sub>2</sub> powder (P25, Sigma Aldrich) was ultrasonically dispersed in 150 mL of 10 M NaOH (Merck) solution and placed in a Teflon-lined autoclave (Berghof, V=200 mL). It is worth mentioning that during all synthesis procedures listed below filling of the autoclave was fixed to same value, namely  $\frac{3}{4}$  of the V was filled up with reaction suspension. Suspension was heated up to 137°C (heating rate 5°C/min) and held at the temperature for 24 h. Obtained fibrous material was separated from the suspension by using Universal 32R (Hettich) centrifuge and thoroughly rinsed with 1 L of ultrapure water (resistivity  $\rho=15.0$  M $\Omega$  cm).

Protonated form of TiO<sub>2</sub>-based nanotubes was obtained by subsequent washing in 0.1 M HCl (Merck) solution and ultrapure H<sub>2</sub>O during 62 h period at 25°C for each. Obtained material was dried in a freeze dryer (Fischer Scientific, model Alpha 1-2 LD<sub>plus</sub>) under cryogenic conditions for 48 h and marked as TN.

##### 3.1.1.2 Synthesis of TiO<sub>2</sub>-based nanosheets

Low temperature hydrothermal synthesis procedure was applied in order to obtain TiO<sub>2</sub>-based nanosheets. 2 g of P25 was hydrothermally treated at 100°C during 24 h (heating rate 5°C/min), followed by subsequent washing, protonation and drying under the conditions described above. Obtained material was marked as NSH.

##### 3.1.1.3 Synthesis of TiO<sub>2</sub>-based nanorods

TiO<sub>2</sub>-based nanorods were synthesized similarly to the procedure described by Žerjav et al. [98]. Namely, 2 g of commercial powder (DT51, Crystal Company) was hydrothermally treated in 10 M NaOH solution at 137°C during 24 h (heating rate 5°C/min). Obtained white precipitate was thoroughly washed with ultrapure water, protonated and dried under the conditions described above. Obtained white powder was marked as NR1.

#### 3.1.1.4 Synthesis of TiO<sub>2</sub>-based nanorice-like material

TiO<sub>2</sub>-based rice-like morphology was obtained by hydrothermal synthesis method in which 2 g of powdered titanium precursor titanium oxysulfate (TiOSO<sub>4</sub>·xH<sub>2</sub>O, Sigma Aldrich) was ultrasonically dispersed in 10 M NaOH solution and hydrothermally treated at 137°C for 24 h (heating rate 5°C/min). Obtained wet granulated material was subsequently washed, protonated and dried under the conditions described above. Obtained material was marked as NR2.

#### 3.1.2 Peroxide treatment of morphologically distinctive nano-scale TiO<sub>2</sub>-based materials

Obtained white powders of TiO<sub>2</sub>-based materials, namely TN, NSH, NR1 and NR2, were chemically functionalized in order to promote formation of distinctive surface peroxo species. Briefly, 1 g of each material was dispersed in 100 mL of concentrated H<sub>2</sub>O<sub>2</sub> solution (30 wt. %, Sigma Aldrich) and held at 25°C for 2 h. Obtained yellow precipitate was separated from the solution, thoroughly washed with ultrapure water and dried under cryogenic conditions. Obtained powders were marked as TNp, NSHp, NR1p and NR2p, respectively.

#### 3.1.3 Thermal and peroxide treatment of TiO<sub>2</sub>-based nanotubes

TiO<sub>2</sub>-based nanotubes were exposed to thermal treatment in order to examine the influence of proton degree on the formation of distinctive peroxo species. Approximately 1 g of as-prepared material was placed in a tubular furnace (Carbolite, model HST/HSZ) furnished with a Eurotherm temperature controller (model 3508) and heated to 140, 250 and 350°C with the heating rate of 10°C/min and held at the targeted temperature for 1 h in air atmosphere. Obtained materials were treated with 30 % H<sub>2</sub>O<sub>2</sub> in the above-described way. As-prepared materials were marked as TN/140, TN/250 and TN/350, while peroxide modified materials were denoted with the extension “p” at the end of the material’s name.

#### 3.1.4 Acid and peroxide treatment of TiO<sub>2</sub>-based nanotubes

Synthesis of amorphous TiO<sub>2</sub>-based nanotubes was carried out by following the procedure described in Section 3.1.1.1. In order to examine the influence of acid type and strength on the protonation degree and formation of surface peroxo species obtained sodium rich materials were subsequently washed in 0.1 M H<sub>2</sub>SO<sub>4</sub> (Merck), H<sub>3</sub>PO<sub>4</sub> (Merck), HClO<sub>4</sub> (Fluka) and HCl acid solution and marked as TN/S, TN/P, TN/ClO<sub>4</sub> 0.1 and TN, respectively. 0.001 M and 0.01 M HCl and HClO<sub>4</sub> protonated materials were made additionally based on the elimination made through materials characterization and catalytic performance. Obtained materials were marked in the previously described manner by changing 0.1 with 0.001 and 0.01 extensions. One material was left in sodium-substituted form and marked as ST.

All the as-prepared materials were submitted to peroxide treatment as described in Section 3.1.2. Peroxide-treated materials were denoted with the extension “p” at the end of the material’s name.

Brief representation of all synthesis and modification procedures is given in Fig. 3.1.

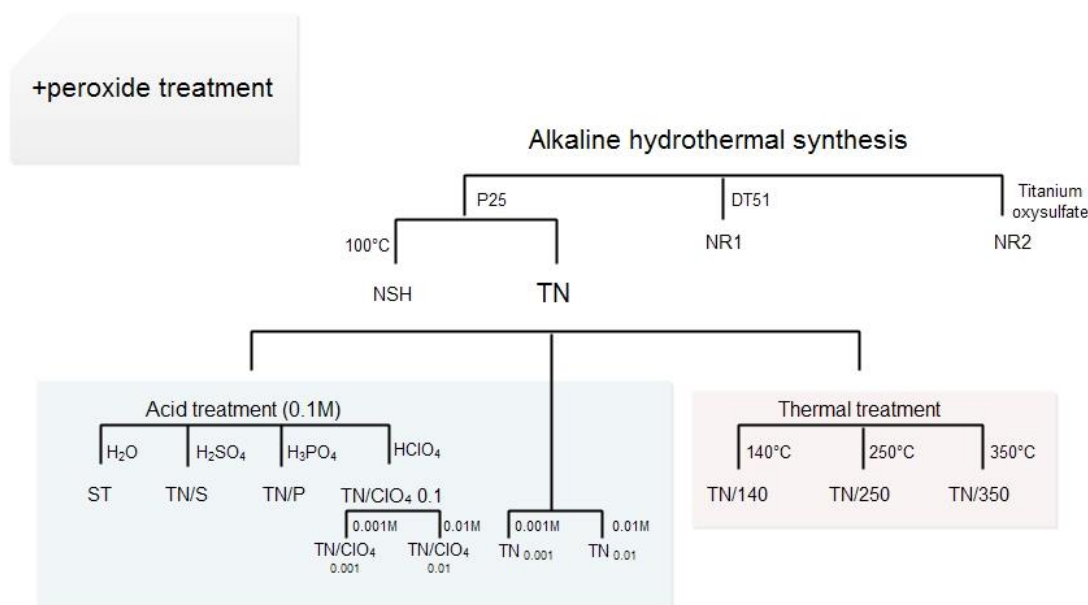


Figure 3.1: Schematic illustration of the synthesis procedures.

## 3.2 Preparation of $^{17}\text{O}$ -labelled Hydrogen Peroxide, $\text{H}_2^{17}\text{O}_2$

Antraquinone oxidation reaction was carried out in order to prepare labelled  $\text{H}_2^{17}\text{O}_2$  from 2-ethylantraquinone,  $\text{NaBH}_4$  and  $^{17}\text{O}$ -labelled oxygen following the patent procedure (Patent No. P-201800006) published by Cerkovnik [99].

Briefly, 12 mmol of 2-ethylantraquinone (Sigma Aldrich) was dissolved in a mixture of toluene (99.8 %, Sigma Aldrich) and methyl acetate (99 %, Sigma Aldrich), and degassed with argon (flow 10 mL/min) in a separatory funnel. At the same time, degassed ethanol (20 ml, Sigma Aldrich) solution of  $\text{NaBH}_4$  (6 mmol, 98 %, Sigma Aldrich) was prepared and introduced to the 2-ethylantraquinone solution. Reaction mixture was stirred for another 20 min and washed with 30 mL of degassed water in order to wash out the reduction by-products and ethanol. Lower phase was separated from the toluene phase and  $^{17}\text{O}$ -labelled oxygen (56.6 at. %  $^{17}\text{O}$ , Isotec) was gradually introduced. After 1 hour of occasional and careful spinning,  $\text{H}_2\text{O}_2$  appears as a separate phase at the bottom of the separatory funnel.  $\text{H}_2\text{O}_2$  phase was cannulated from the funnel and obtained 390 mg of 10 % solution of  $\text{H}_2^{17}\text{O}_2$  (>50 at. %  $^{17}\text{O}$  labelled) was further concentrated under reduced pressure. The concentration of  $\text{H}_2^{17}\text{O}_2$  solution was determined by using standard iodometric titration.

## 3.3 Characterization Techniques

### 3.3.1 Surface area and porosity

Surface porosity of the as-prepared and peroxide-treated nano-scale  $\text{TiO}_2$  materials was measured using surface porosity analyser TriStar II 3020 (Micromeritics) by collecting data of  $\text{N}_2$  adsorption-desorption isotherms acquired at  $-196^\circ\text{C}$ . In order to remove the adsorbed species from the surface and pores of the sample, degassing process was applied as pre-treatment. The sample was gradually heated from  $25^\circ\text{C}$  to  $180^\circ\text{C}$  (heating rate  $10^\circ\text{C}/\text{min}$ ) and degassed in  $\text{N}_2$  stream (purity 6.0) for 5 h. By applying Brunauer-Emmett-Teller (BET) theory on the  $\text{N}_2$  desorption isotherms collected in the region  $p/p_0=0.06-0.3$  specific surface area ( $S_{\text{BET}}$ ), pore volume ( $V_p$ ) and diameter of pores ( $d_p$ ) were calculated.

### 3.3.2 Scanning electron microscopy

Field-emission scanning electron microscopy (Carl Zeiss, model FE-SEM Supra 35VP) was used in order to define the morphology of as-prepared and peroxide-treated materials. A small amount of homogenized powdered sample was stamped into double-stick carbon tape and analyzed using combined SE2 and In-lens detector. Individual EDS (energy dispersive X-ray spectroscopy) analysis was done in order to examine the presence of surface impurities prior and after the peroxide treatment.

### 3.3.3 Transmission electron microscopy

Transmission electron microscope with atomic resolution (JEOL ARM 200 CF, Jeol USA Inc.) equipped with a cold field-emission gun, probe spherical aberration corrector (CESCOR unit from CEOS) and Jeol Centurio EDXS system with 100 mm<sup>2</sup> SDD detector was used in order to examine in detail the morphology of the catalytically best performing materials. Prior to the analysis, powdered samples were dispersed in ethanol (Merck) and deposited on copper lacy-carbon grid.

Gatan Dual electron energy loss spectroscopy (EELS) Quantum ER system was used to determine the possible oxidation state of Ti in the representative catalytic materials.

### 3.3.4 X-ray powdered diffraction

XRD analysis (PANalytical XpertPro) was used in order to identify the crystalline phases present in the as-prepared and peroxide-treated materials. Data were collected using CuK $\alpha$ 1 radiation (wavelength K $\alpha$ 1=1.54056 Å) in reflection geometry in the range of 10-90° and a step of 0.034°. Crystalline phases were identified using the PDF data card obtained from the International Centre for Diffraction Data (ICDD).

### 3.3.5 Fourier transform infrared spectroscopy

FTIR spectroscopy was employed in order to define surface chemistry of as-prepared and peroxide-treated materials. FTIR analyzer (Perkin Elmer Frontier) equipped with Gladi ATR Vision<sup>TM</sup> (Pike Technologies) crystal diamond cell was used to record spectra within the spectral range of 4000-450 cm<sup>-1</sup> with 32 accumulations and spectral resolution of 4 cm<sup>-1</sup>. Spectra were recorded using the MCT (mercury-cadmium-telluride) detector cooled with liquid nitrogen (LN<sub>2</sub>).

### 3.3.6 Diffuse reflectance infrared Fourier transform spectroscopy

DRIFT spectroscopy was used for discrimination between surface Brønsted (BAS) and Lewis (LAS) acid sites. By using pyridine as a probe molecule analysis was carried out in a high-temperature DiffuseIR chamber (Pike Scientific) connected to FTIR analyzer (Perkin Elmer Frontier). Briefly, prior to the analysis the sample was pre-treated, i.e. degassed, for 1 h in N<sub>2</sub> stream (purity 6.0) using HiCube turbomolecular pump (Pfeiffer Vacuum). Later, 10 min saturation with pyridine vapours was performed, followed by degassing in order to remove weakly adsorbed pyridine. Spectra were recorded in the previously described way. LAS and BAS absorption bands were detected at 1445 cm<sup>-1</sup> and 1545 cm<sup>-1</sup>, respectively, and BAS/LAS ratio was calculated following the procedure described by Djinović et al. [100].

### 3.3.7 UV/Vis diffuse reflectance spectroscopy

UV/Vis diffuse reflectance spectroscopy was used in order to qualitatively determine the presence of surface peroxo species by monitoring the presence of the absorption band in the region 400-450 nm. By using UV/Vis spectrophotometer (Perkin Elmer, model Lambda 35) spectral data was collected in the range 200-900 nm, with the scanning speed of 120 nm/min and slit set to 4 nm. White reflectance standard Spectralon® was used in order to perform instrument background correction.

UV/Vis spectrophotometer model Lambda 650 (Perkin Elmer) was also used to monitor the thermal degradation of the surface peroxo species. Until reaching 400°C the sample of the selected peroxide-treated material was heated in steps of 50°C (heating rate 1°C/min) in air (flow rate 25 mL/min) for 50°C. Spectral data was recorded every 30 min in the above described way.

In order to extract additional information regarding the nature of surface peroxo species bonding, as suggested by Klissuriski et al. [85], chosen UV/Vis spectra were fitted using PeakFit program (SPSS Inc.) by applying Voight amplitude.

### 3.3.8 In-situ Raman analysis

*In-situ* Raman analysis was done in order to mimic interactions that occur between surface peroxo species and H<sub>2</sub>O<sub>2</sub> solution during CWPO experiment. FT Ram II Raman spectrometer (Bruker) with the PIN diode detector (TE Siavalanche) was adjusted to laser excitation at 785 nm and 1064 nm (laser power 500 mW) and Raman spectra were recorded on as-prepared and peroxide-treated samples at ambient conditions. Different laser sources were used in order to avoid overwhelming of different peroxo species with the Raman enhancement. Reaction initiation occurred with the addition of 1 mL H<sub>2</sub>O<sub>2</sub> solution (c=0.15 M) onto the catalyst surface and was monitored for 4 h (equivalent to CWPO experiment duration). Raman spectra were recorded in the spectral range of 3000-75 cm<sup>-1</sup> with the nominal resolution of 4 cm<sup>-1</sup>.

### 3.3.9 Thermogravimetric analysis

Surface -OH groups deprotonation and dehydroxylation of as-prepared materials was determined using TGA/TPO analyzer (Perkin Elmer, model Pyris 1). Around 0.8 g of the sample was heated in N<sub>2</sub> flow from 25–800°C with the heating rate of 10°C/min. Obtained weight loss was normalized on the starting value and expressed as a percentage of weight loss (m/m<sub>0</sub>).

### 3.3.10 Temperature-programmed desorption/mass spectrometry

O<sub>2</sub> TPD/MS technique was used to quantitatively determine the amount of desorbed/decomposed surface peroxo species in the peroxide-treated material. Prior to the analysis in Autochem II 2920 O<sub>2</sub> TPD apparatus (Micrometrics), 30 mg of peroxide-treated sample was introduced in the quartz wool filled U-shape reactor tube (quartz glass) and pre-treated with 5 % O<sub>2</sub>/He at 35°C for 1 h. Afterwards, the sample was heated in He up to 800°C (heating rate of 10°C/min) and by following m/z fragments of 18 and 32, O<sub>2</sub> evolution was monitored using ThermoStar GSD320 MS (Pfeiffer Vacuum). Fivefold 5% O<sub>2</sub>/He pulse was injected in the end of each measurement in order to obtain calculation reference. From the obtained MS spectra baseline was extracted and molar amount of O<sub>2</sub> was calculated after applying the general gas equation (ideal gas law):

$$n_{O_2} = \frac{p * V}{R * T} \quad [18]$$

where  $n_{O_2}$  represents the number of oxygen moles,  $p$  represents atmospheric pressure ( $1 \times 10^5$  Pa),  $T$  represents MS detector standardized temperature of  $100^\circ\text{C}$  in Kelvin's ( $383.15$  K),  $R$  represents ideal gas constants ( $R=8.314$  J/ (mol K)).  $V$  is a volume of the loop MS detector loop of approximately  $0.5$  mL. Obtained molar amount of  $O_2$  was normalized on the weighted mass (mol  $O_2$ /g) and specific surface area (mol  $O_2$ /m<sup>2</sup>) of the corresponding material.

Obtained spectra were also fitted using PeakFit program (SPSS inc.) by applying Gauss amplitude in order to accurately associate evolved oxygen to surface peroxo species.

### 3.3.11 Nuclear magnetic resonance

$^1\text{H}$  and  $^{17}\text{O}$  MAS (magic angle spinning) NMR were used in order to identify the nature of bonding and geometry of peroxo species in chosen as-prepared and peroxide-treated materials. Spectra were recorded on the  $600$  MHz NMR spectrometer (Agilent Technologies) equipped with  $1.6$  mm Fast MAS Solid Probe.  $^1\text{H}$  MAS NMR spectra was externally referenced using a diamantine with a chemical shift ( $\delta$ ) of  $1.85$  ppm relative to tetramethylsilane, while  $^{17}\text{O}$  MAS NMR spectra was externally referenced with  $^{17}\text{O}$ -enriched water,  $\text{H}_2^{17}\text{O}$ . Larmor frequencies of  $^1\text{H}$  and  $^{17}\text{O}$  nuclei were  $599.48$  MHz and  $81.27$  MHz. During MAS NMR measurements all samples were spooned at the magic angle with  $40$  kHz and  $40$  kHz or  $26.5$  kHz for  $^1\text{H}$  and  $^{17}\text{O}$  measurements, respectively. The  $^1\text{H}$  spectra were acquired using one pulse sequence with a repetition delay of  $5$  s and  $4$  numbers of scans. The  $^{17}\text{O}$  spectrum was acquired using one pulse sequence with repetition delay of  $0.2$  s and the number of scans  $262000$ .

#### 3.3.11.1 Mass titration

Mass titration was used to determine the materials point of zero charge (pzc), i.e. the pH value at which the surface of the material has no charge.  $0.5$  g of the representative material was gradually introduced into the  $50$  mL of  $0.005$  M NaCl solution thermostated at  $25^\circ\text{C}$ , purged with nitrogen ( $\text{N}_2$  flow  $750$  mL/min) and constantly mixed. pH value of the solution was monitored using the pH meter (Methrohm, model  $827$  pH Lab) until reaching equilibrium which corresponds to the materials'  $\text{pH}_{\text{pzc}}$ .

#### 3.3.11.2 CHNS analysis

Determination of accumulated carbon content was conducted by applying CHNS (carbon-hydrogen-nitrogen-sulphur) analysis.  $1.5$ - $2.5$  mg of fresh and spent (after catalytic experiments) catalytic material was analyzed using the CHNS analyzer (Perkin Elmer, model  $2400$  series II). The amount of accumulated carbon, expressed in weight percent, was obtained by subtracting the amount of carbon contained by the materials prior and after catalytic experiments.

## 3.4 Catalytic Wet Peroxide Oxidation Experiments

Catalytic wet peroxide oxidation experiments were performed in a  $250$  mL glass batch reactor (Lenz Larboglas) furnished with a program-controlled thermostat (Julabo, model F25/ME) and C-MAG HS7 magnetic stirred (IKA) as shown in Fig. 3.2. As a model pollutant  $50$  mg/L of methyl orange (MO, Honeywell Riedel-de Haën) solution was used. First, the MO solution was heated up to the targeted temperature and the adequate amount, namely  $2$  g/L, of catalytic material was introduced into the solution, followed by the stoichiometric amount of the  $\text{H}_2\text{O}_2$  ( $30$  wt.%, Sigma Aldrich) solution ( $V=4$  mL,  $c=0.15$  M) calculated by following the given equation:



CWPO experiments were conducted during 4 h and representative samples were withdrawn from the reaction suspension in the set time intervals, filtered through a Chromafil® RC 20-25 filter (Macherev-Nagel) and instantly analyzed by the UV/Vis technique described in the upcoming section.  $H_2O_2$  conversion was determined through standard iodometric titration described in Section 3.4.2.

Influence of the operational parameters was examined by varying temperature and suspension pH value, as well as influence of the catalyst loading and  $H_2O_2$  amount. For the experiments conducted at higher temperatures, namely 40, 60 and 80°C, a reflux condenser was fitted to avoid water evaporation. pH value of the reaction suspension was adjusted to 3 with 0.1 M HCl (Merck) or NaOH (Merck) solution, respectively, and monitored with a laboratory pH meter (Methrohm, model 827 pH Lab). Influence of the catalyst loading was examined by varying amount of the materials to 1, 2 and 3 g/L. In specific experiments the  $H_2O_2$  amount was adjusted to one and a half and double stoichiometric.

Blank ( $H_2O_2$  + MO) and adsorption (catalytic material + MO) experiments were additionally performed in order to evaluate catalytic CWPO contribution to overall MO removal.

Test consisting of four or five consecutive runs was done under optimized reaction conditions with the adjusted amount of fresh MO and  $H_2O_2$  solution, while added catalytic material was reused from the previous runs. After each consecutive run the remaining catalytic material was washed with ultrapure water and dried at 60°C (Kambič SP-45C) for 24h.

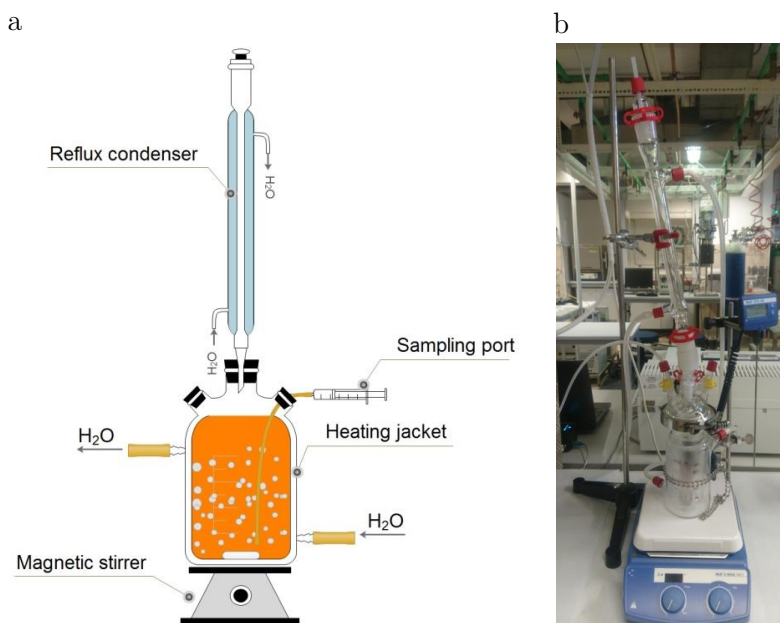


Figure 3.2: a) Graphical illustration and b) photograph of the built-up laboratory scale batch reactor used for CWPO, adsorption and blank MO experiments.

### 3.4.1 UV/Vis analysis

UV/Vis spectrophotometer (Perkin Elmer, model Lambda 35) was used for accurate determination of MO conversion in the CWPO experiments. Spectral data of MO supernatant was collected in the range of 200-800 nm with the scanning speed of 240 nm/min and slit width of 2 nm. Prior to each set of measurements, background correction

was done using ultrapure water. Additional cuvette with ultrapure water was inserted in the second cell holder and used as a reference during measurements. By monitoring the decrease in the absorption peak at 464 nm and 505 nm, for neutral and acidic range, respectively, MO conversion was calculated by following Equation 20:

$$X_{MO} = \frac{Abs_{t=0} - Abs_t}{Abs_{t=0}} * 100 \quad [20]$$

where  $Abs_{t=0}$  and  $Abs_t$  represent the intensity of the absorption peak of MO solution prior and after CWPO experiments, and  $X_{MO}$  is the percentage of MO removal related to cleavage of -N=N- bond that leads to discolouration of the aqueous MO solution.

### 3.4.2 Iodometric redox titration

Automated T50 titrator (Mettler Toledo) equipped with DM 140-SC redox electrode (Mettler Toledo) was used for standard iodometric determination of residual  $H_2O_2$ . Briefly, 2 mL of supernatant and 1.25 mL of 10 wt. %  $H_2SO_4$  solution (Merck) was introduced in the 60 mL of cold ultrapure water and titrated with 0.1 M  $KMnO_4$  solution (Merck) until reaching the equivalence point. Obtained data were used for recalculating  $H_2O_2$  conversion in a similar way as described for MO conversion. Prior to each measurement the amount of  $H_2O_2$  at time zero was determined and used as a reference value for percentile expression of  $H_2O_2$  conversion.

### 3.4.3 Ion chromatography

Ionic composition of the residual liquid-phase samples was determined using DX-120 Dionex apparatus (Thermo Fischer Scientific) equipped with 4x250 mm DionexTM IonPacTM AS19 (Thermo Fischer Scientific) analytical column and IonPacTM AG19 guard precolumn (Thermo Scientific). Gradient analysis was done using a differently concentrated NaOH solution (Merck) as a mobile phase (eluent). All columns were thermostated at 30°C.

Prior to the analysis supernatants were additionally filtered through OnGuard-P\* cartridge (Dionex, Thermo Fischer Scientific) to remove residual MO molecules interfering with the determination of  $NO_3^-$ ,  $NO_2^-$  and  $SO_4^{2-}$  ions. The volume of the injected concentrated or diluted ( $V:V_{H_2O}=1:10$ ) sample was 10  $\mu$ L.

## Chapter 4

# Results and Discussion

### 4.1 Characterization of As-Prepared and Peroxide-Treated Morphologically Distinctive Nano-Scale TiO<sub>2</sub>-Based Materials

#### 4.1.1 Porosity, morphological and structural properties of morphologically distinctive as-prepared and peroxide-treated nano-scale TiO<sub>2</sub>-based materials

$S_{\text{BET}}$ ,  $V_p$  and  $d_p$  of P25 and DT51 precursors, as-well as as-prepared and peroxide-treated materials are listed in Table 4.1. P25 and DT51 precursors exhibit  $S_{\text{BET}}$  of 52.0 m<sup>2</sup>/g and 85.8 m<sup>2</sup>/g, respectively. Larger  $S_{\text{BET}}$  and  $V_p$  of DT51, which is usually around 100 m<sup>2</sup>/g, can be attributed to a different preparation procedure and composition of the material [101]. DT51 is obtained through the sulphate process and contains only well-dispersed anatase in the structure, while P25 contains a mixture of two polymorphs, namely around 75 % of anatase and 25 % of rutile obtained through chloride process.

Table 4.1: Specific surface area ( $S_{\text{BET}}$ ), pore volume ( $V_p$ ) and average pore diameter ( $d_p$ ) of P25, DT51 and as-prepared and peroxide-treated NSH, TN, NR1, NR2 materials.

| Sample | $S_{\text{BET}}$ (m <sup>2</sup> /g) | $V_p$ (cm <sup>3</sup> /g) | $d_p$ (nm) |
|--------|--------------------------------------|----------------------------|------------|
| P25    | 52.0                                 | 0.15                       | 10.2       |
| NSH    | 426                                  | 1.31                       | 11.1       |
| NSHp   | 396                                  | 1.20                       | 11.1       |
| TN     | 383                                  | 1.41                       | 12.6       |
| TNp    | 426                                  | 1.72                       | 14.0       |
| DT51   | 85.8                                 | 0.29                       | 13.7       |
| NR1    | 390                                  | 1.20                       | 10.8       |
| NR1p   | 405                                  | 1.33                       | 11.6       |
| NR2    | 370                                  | 1.03                       | 9.6        |
| NR2p   | 372                                  | 1.06                       | 9.8        |

After hydrothermal synthesis  $S_{\text{BET}}$  of materials increases to 383 m<sup>2</sup>/g, 390 m<sup>2</sup>/g and 426 m<sup>2</sup>/g for TN, NR1 and NSH, respectively.  $S_{\text{BET}}$  of as-prepared TN is in correspondence with the values obtained for well-developed TiO<sub>2</sub>-based nanotubes [71], [102], while NR1 exhibits a similar surface area to the one published by Žerjav et al. for hydrothermally obtained nanorods [98].

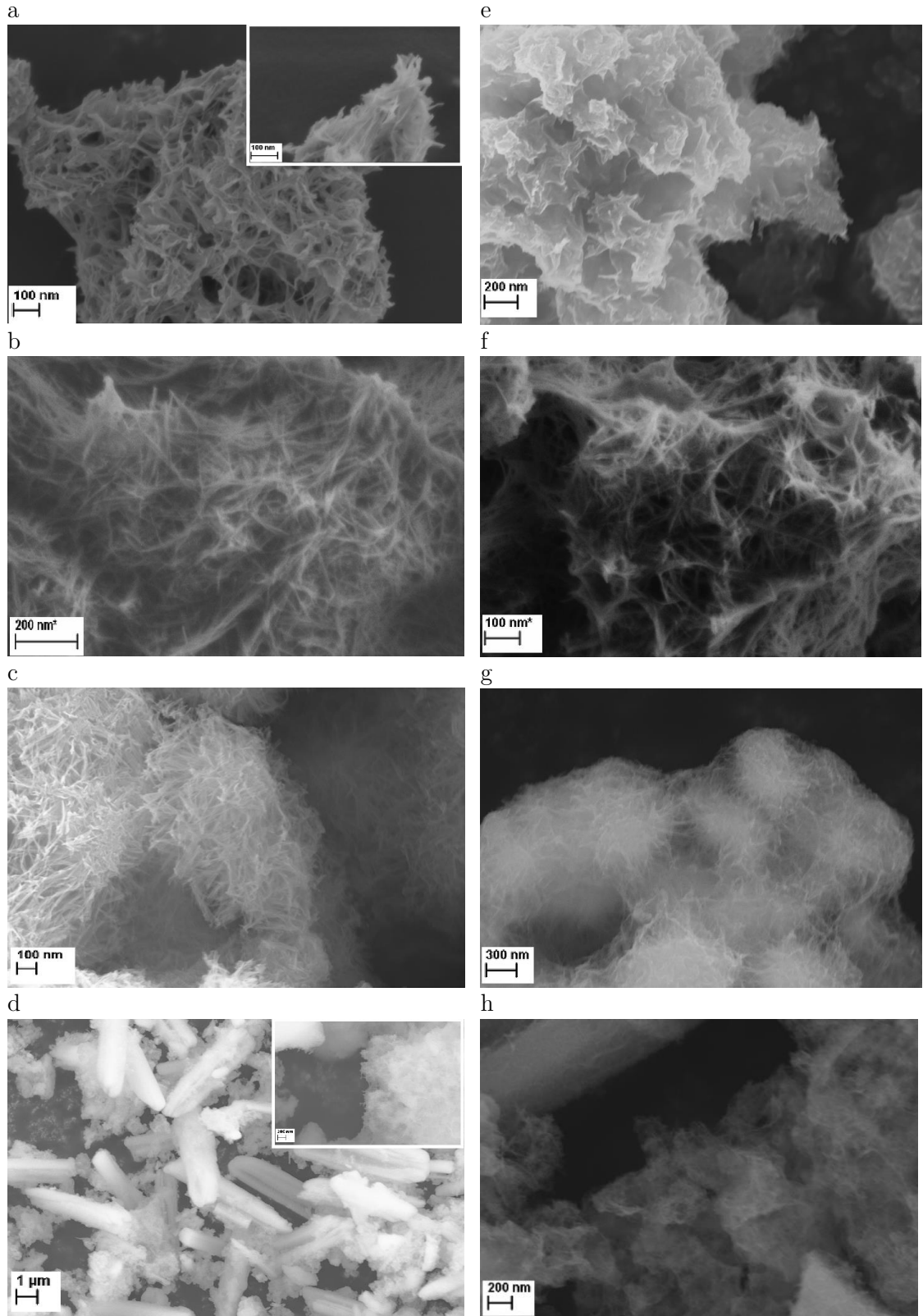


Figure 4.1: SEM images of as-prepared a) NSH, b) TN, c) NR1, d) NR2 and peroxide-treated e) NSHp, f) TNp, g) NR1p and h) NR2p materials.

Nevertheless, from the obtained SEM images (Fig. 4.1c) it can be seen that the obtained morphology of NR1 resembles shorter agglomerated nanotubes rather than nanorods. NSH exhibits the largest  $S_{\text{BET}}$  of 462 m<sup>2</sup>/g, with the slightly smaller  $V_p$  and  $d_p$ , which can be

attributed to the partially developed nanosheet as visible from the SEM images (Fig. 4.1a). In comparison with them NR2 has a well-developed rice-like morphology with the traces of fibrous agglomerates around the surface of the sample (Fig. 4.1d). Due to that we can assume that large  $S_{\text{BET}}$  of NR2, namely  $S_{\text{BET}}=370 \text{ m}^2/\text{g}$ , is partially attributed to these fibrous structures.

After peroxide treatment  $S_{\text{BET}}$  changes differently for each material. The highest increase is observed for TNp whose  $S_{\text{BET}}$  increases for  $43 \text{ m}^2/\text{g}$ , accompanied with an increase in the  $V_p$  and  $d_p$  for  $0.32 \text{ cm}^3/\text{g}$  and  $1.3 \text{ nm}$ , respectively. This occurs due to partial disintegration of the material during peroxide treatment.  $\text{H}_2\text{O}_2$  is a strong mineralizing agent for amorphous  $\text{TiO}_2$  and causes erosion of the structure during prolonged exposure [51], [71], [102]. Nevertheless, the well-developed tubular structure remains preserved as it can be seen in Fig. 4.1f.  $S_{\text{BET}}$  of the NR1 solid slightly increases from  $390 \text{ m}^2/\text{g}$  to  $405 \text{ m}^2/\text{g}$  without drastic changes of the material's morphology (Fig 4.1g). Similar observations are made for NR2, whose  $S_{\text{BET}}$ ,  $V_p$  and  $d_p$  remain intact after peroxide treatment. In comparison with them NSH experiences a decrease of  $S_{\text{BET}}$  and  $V_p$ , which can be attributed to an even stronger influence of  $\text{H}_2\text{O}_2$  during the modification procedure, which causes thickening of the material and coherence of the structure as shown in the SEM image (Fig. 4.1e.) of the NSHp material.

From the above-mentioned we can observe that materials obtained through alkaline hydrothermal restructuring of P25 precursor are more prone to disintegration during peroxide treatment than those obtained from DT51 and titanium oxysulfate. The latter ones both have  $\text{SO}_4^{2-}$  in the structure which is one of the most important impurities used for structural stabilization of the material during hydrothermal synthesis [51], [101]. Nevertheless, in comparison with NSHp, NR1p and NR2p, TNp exhibits the highest catalytic activity in the CWPO of MO (see Section 4.1.3.); therefore, it was subjected to detailed TEM, EELS and XRD examination.

First, the morphological analysis was done by using TEM microscopy. From Fig. 4.2a one can observe that the TN material has a hollow, multiwall open-end tubular morphology. As-obtained nanotubes are several micrometers long with the outer diameter of 3-10 nm and predominantly amorphous structure, which can be observed from the SEAD patterns. Only faint diffraction rings originating from the lapsed, or created, anatase phase are visible, therefore indicating that as-prepared TN is mostly amorphous. In addition to TEM analysis, electron energy loss spectroscopy (EELS) has confirmed that no crystal structure is present in the TN material.

From Fig. 4.2b we can observe that Ti-L edge, with the adsorption energy of around 460 eV, can be divided into two major edges, namely L3 and L2. Both are attributed to the spin orbit splitting of the  $2p$  core hole for a separation by about 6 eV [103]. Additional polymorph (anatase, rutile and brookite) connected branching of L2 and L3 edges due to octahedral crystal field splitting, characteristic for well crystallized form of  $\text{TiO}_2$ , is absent. In addition, hybridization between O  $2p$  and Ti  $3d$  orbitals induces the formation of a small O-K peak at 532 eV [103]. Observed peaks are all characteristic for amorphous Ti-based nanomaterials without a defined crystallographic structure which is also confirmed by means of the XRD analysis.

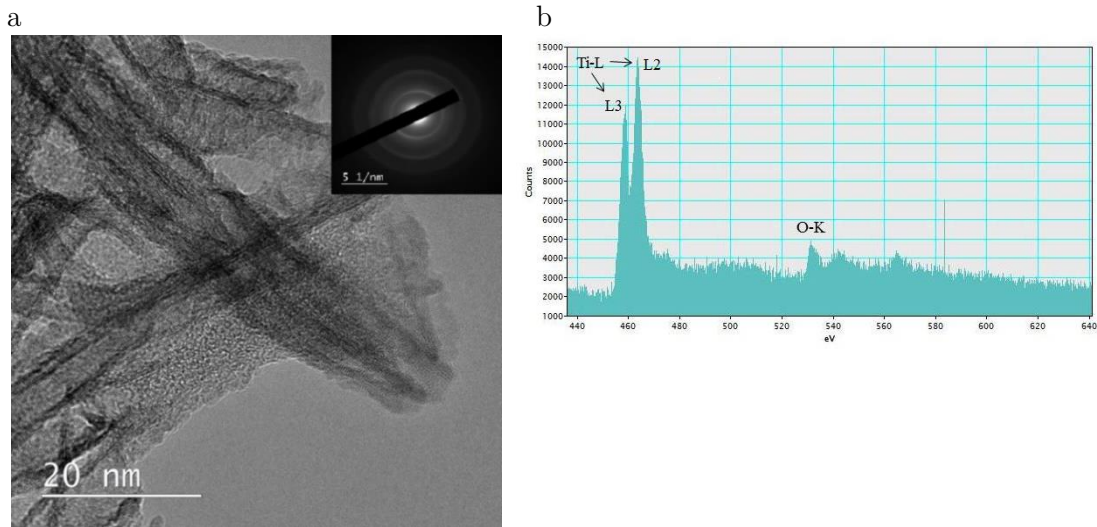


Figure 4.2: a) TEM image with accompanied SAED pattern and b) EELS spectra of as-prepared TN material.

XRD diffraction pattern for as-prepared and peroxide-treated TN material is shown in Fig. 4.3. TN exhibits faint diffraction peaks at 24.5° and 48.2°, which can be attributed to lapsed or created anatase structure (JCPDS, Card 01-0711168). The same spectrum is obtained for TNp, meaning that peroxide treatment did not induce any structural changes of the materials. By combining all the analyses it can be seen that TN and TNp have a well-developed, randomly oriented amorphous nanotubular structure with the admixture of anatase, which can be preserved as a partially unconverted P25 precursor or created during hydrothermal synthesis. According to Erjavec et al. [67],  $\text{Na}_{2x}\text{H}_{2-x}\text{Ti}_2\text{O}_4(\text{OH})_2$  gives the best structural interpretation for the as-prepared TN.

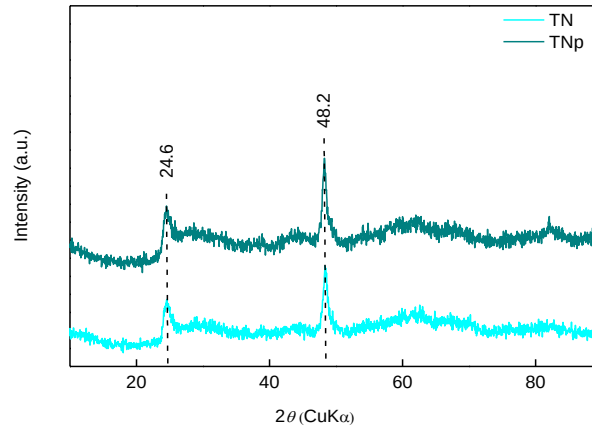


Figure 4.3: XRD diffraction patterns of as-prepared peroxide-treated TN material.

#### 4.1.2 Surface properties of morphologically distinctive as-prepared and peroxide-treated nano-scale TiO<sub>2</sub>-based materials

FTIR/ATR analysis was used in order to extract additional information regarding the surface properties of as-prepared (Fig. 4.4a) and peroxide-treated (Fig. 4.4b) NSH, TN, NR1 and NR2 materials. Acquired spectra are quite similar; therefore, they will be described simultaneously. Lower intensity region in the presented spectra is characterized with a broad asymmetric band located between 2600-4000 cm<sup>-1</sup> attributed to the complex mixture of -OH stretching of H<sub>2</sub>O and Ti-OH molecules. The presence of H<sub>2</sub>O has interfered with the exact determination of the -OH stretching of Ti-OH molecules, but asymmetric

shape of the band implies that a broad variety of hydrogen bonds with different strengths is present. Therefore, the central -OH stretching band located at  $3420\text{ cm}^{-1}$  presents a group of hydrogen bonds of medium strength, while the intensity declination present at  $2600\text{ cm}^{-1}$  is characteristic for strong hydrogen bonding in which oxygen atoms acts as a proton acceptor group. Most likely the former ones arise from the interaction between  $\text{H}_2\text{O}$ -TiOH and TiOH-TiOH molecules. The presence of  $\text{H}_2\text{O}$  molecules is additionally confirmed with the band positions at  $1640\text{ cm}^{-1}$  [51], [67], [80], [102].

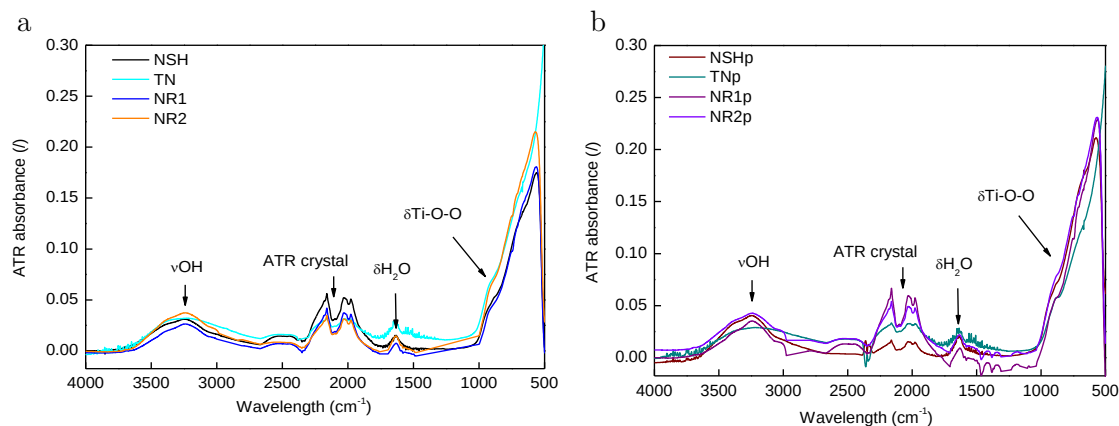


Figure 4.4: FTIR/ATR spectra of a) as-prepared and b) peroxide-treated NSH, TN, NR1 and NR2 materials.

High hydration degree confirmed by means of FTIR/ATR analysis is a prerequisite for the peroxo species formation [51], [71], therefore their quantification was done by means of TGA analysis. Dehydration process was followed in the range of  $25\text{--}750^\circ\text{C}$  and divided into sections as proposed by Bavykin et al. [77]. From Fig. 4.5a we can observe that ion-exchangeable -OH groups, which are believed to be a prerequisite for peroxo species formation, are removed in the region up to  $140^\circ\text{C}$  (range I), followed with dehydration of interlayered -OH groups up to  $300^\circ\text{C}$  (range II). Above  $300^\circ\text{C}$  dehydration of intralayered -OH groups and topotactic transformation of the above-mentioned materials occur. From the obtained TGA profiles it can be observed that weight loss up to  $140^\circ\text{C}$  increases from  $\sim 9 > 10 > 12 > 13\text{ wt. \%}$  for TN, NR2, NSH and NR1, followed with the complete weight loss of  $\sim 16 \sim 16 > 17 > 19\text{ wt. \%}$  for above-mentioned materials, respectively. Therefore, it is expected that peroxide-treated NR1p contains the highest amount of surface peroxo species, which were characterized by applying UV/Vis DR and  $\text{O}_2$  TPD/MS analysis.

Obtained UV/Vis DR spectra, shown in Fig. 4.5b, exhibits a wide absorption band between  $340\text{--}500\text{ nm}$ , with the centre at  $420\text{ nm}$ , which is usually directly correlated with the presence of  $\eta^2$  surface peroxo species [17], [51], [71], [83] (reminder on the peroxo species binding mode and geometry can be found in Section 1.4.3.1.). Nevertheless, Klissurski et al. [85] have shown that the absorption peak can be fitted with two peaks based on the LMCT, therefore it is not possible to exclude that  $\eta^1$  peroxo species do not contribute to absorption. Absorption peak at  $420\text{ nm}$  should only be correlated with the presence of both peroxo species [83], [85], and we can observe that, although all as-prepared materials have a different TGA weight loss, the intensity of the absorption band for peroxide-treated materials is the same. Therefore, UV/Vis DR analysis can only be used for qualitative characterization of surface peroxo species and their LMCT interactions, but quantitative determination has been done by applying a more sophisticated technique, such as  $\text{O}_2$  TPD/MS.

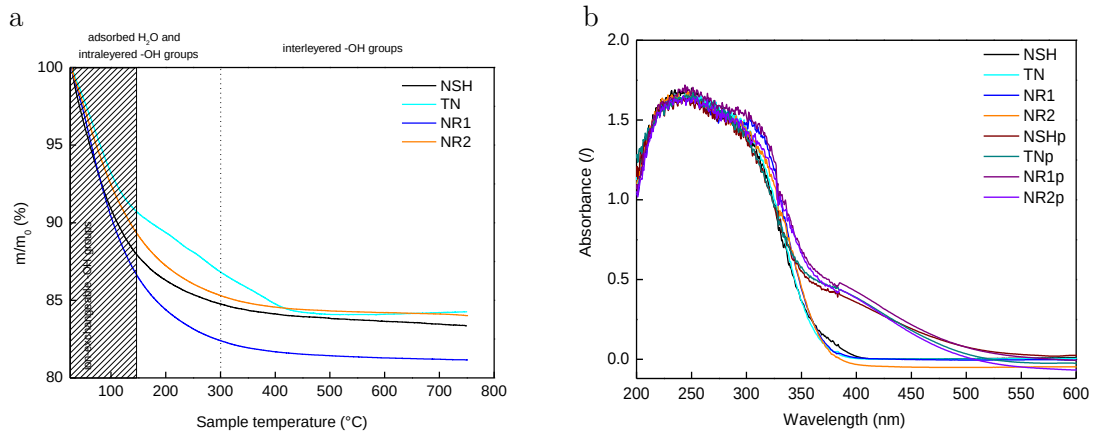


Figure 4.5: a) TGA profiles of as-prepared NSH, TN, NR1 and NR2 materials showing distinctive differences in the amount and type of hydroxy groups. b) UV/Vis DR spectra of as-prepared and peroxide-treated NSH, TN, NR1 and NR2 materials.

O<sub>2</sub> TPD/MS analysis (Table 4.2) has revealed that peroxide-treated TiO<sub>2</sub>-based nanotubes, TNp, possess the highest amount of peroxo species per m<sub>2</sub>. The increase from 0.7 > 0.8 > 1.0 > 1.4 for NR2p, NSHp, NR1p and TNp shows that the expected NR1p material does not possess the prevalent amount of surface peroxo species, although TGA weight loss for as-prepared materials highly deviates from others. In comparison with the TN TGA weight loss up to 140°C for NR1 has 4 wt. % more ion-exchangeable -OH groups and 2.0\*10<sup>-5</sup> mol O<sub>2</sub>/g less desorbed oxygen than TNp. Therefore, we can conclude that the amount of ion-exchangeable -OH groups is not the ultimate prerequisite for peroxo species formation. It is worth mentioning that as-obtained weight loss for TiO<sub>2</sub>-based nanotubes is in good agreement with the values reported by others [51], [67], [77].

Table 4.2: Amount of oxygen obtained by means of O<sub>2</sub> TPD/MS analysis and surface acidity expressed as BAS and LAS for as-prepared and peroxide-treated NSH, TN, NR1 and NR2 materials.

| Sample | LAS<br>(mmol/g) | BAS<br>(mmol/g) | BAS/LAS<br>(/) | O <sub>2</sub><br>(mol/g)*10 <sup>-4</sup> | O <sub>2</sub><br>(mol/m <sup>2</sup> )*10 <sup>-6</sup> |
|--------|-----------------|-----------------|----------------|--------------------------------------------|----------------------------------------------------------|
| NSH    | 0.936           | 0.159           | 0.15           | /                                          | /                                                        |
| NSHp   | 1.982           | 0.354           | 0.18           | 3.3                                        | 0.8                                                      |
| TN     | 0.067           | 0.00(3)         | /              | /                                          | /                                                        |
| TNp    | 1.002           | 0.446           | 0.44           | 6.0                                        | 1.4                                                      |
| NR1    | 0.546           | 0.078           | 0.14           | /                                          | /                                                        |
| NR1p   | 0.015           | 0.015           | 0.28           | 4.0                                        | 1.0                                                      |
| NR2    | 0.588           | 0.038           | 0.06           | /                                          | /                                                        |
| NR2p   | 0.588           | 0.159           | 0.27           | 2.8                                        | 0.7                                                      |

By fitting the obtained O<sub>2</sub> TPD/MS profiles (Fig. 4.6), it has been observed that minimum four different desorption peaks are present and their peak position, amplitude, FWHM (full width at half maximum) are listed in Table 4.3. The first two peaks in NSHp, TNp and NR1p are centred in a very narrow temperature range, namely 107–116°C and 159–175°C, while the last two peaks deviate from this behaviour. The third peak can be centred somewhere between 213–285°C, while the fourth peak has an even wider range from 254–354°C.

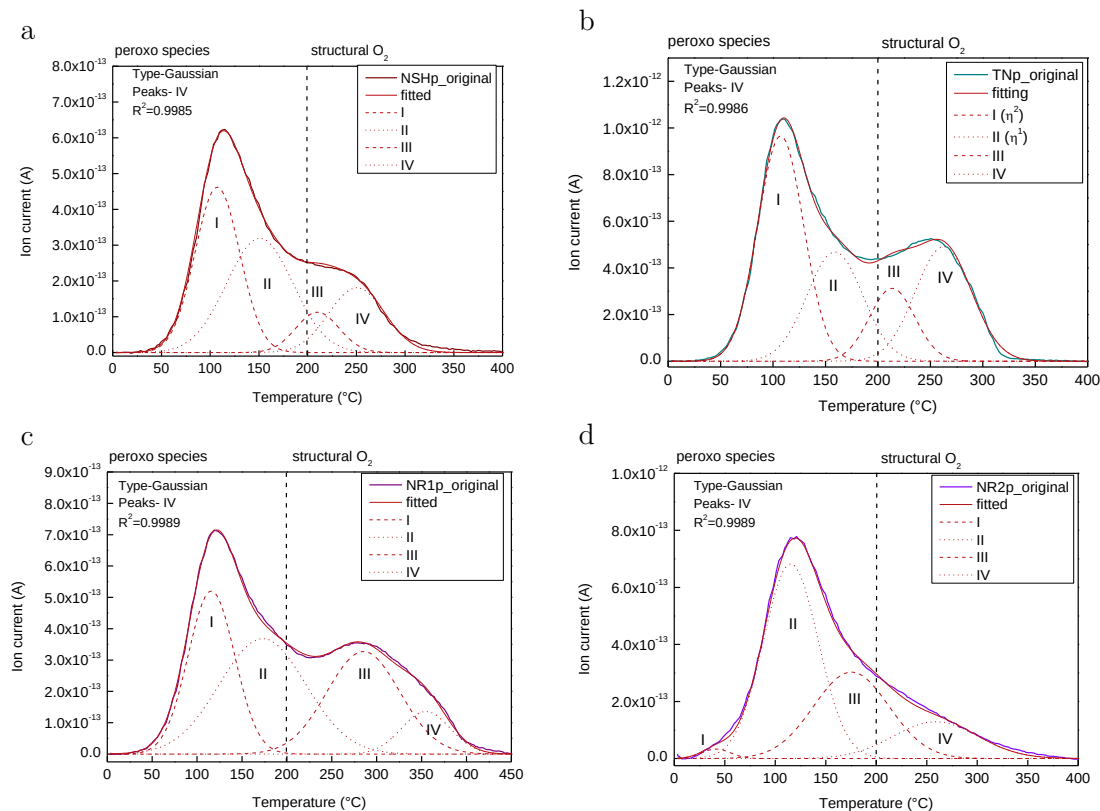


Figure 4.6: Fitted O<sub>2</sub> TPD/MS profiles for peroxide-treated a) NSHp, b) TNp, c) NR1p and d) NR2p materials, and accompanied integrated area. Dashed lines represent Gaussian fits.

Table 4.3: Peak fit parameters for Gaussian fits of peroxide-treated NSHp, TNp, NR1p and NR2p materials and accompanied integrated area.

| Sample | Peak | Position | Amplitude            | FWHM | Area (%) |
|--------|------|----------|----------------------|------|----------|
| NSHp   | I    | 110      | $5.6 \cdot 10^{-13}$ | 55   | 36       |
|        | II   | 160      | $2.8 \cdot 10^{-13}$ | 65   | 37       |
|        | III  | 213      | $1.5 \cdot 10^{-13}$ | 50   | 9        |
|        | IV   | 254      | $1.7 \cdot 10^{-13}$ | 63   | 18       |
| TNp    | I    | 107      | $9.6 \cdot 10^{-13}$ | 51   | 39       |
|        | II   | 159      | $4.7 \cdot 10^{-13}$ | 62   | 23       |
|        | III  | 213      | $3.1 \cdot 10^{-13}$ | 51   | 13       |
|        | IV   | 262      | $4.9 \cdot 10^{-13}$ | 63   | 25       |
| NR1p   | I    | 116      | $5.2 \cdot 10^{-13}$ | 61   | 28       |
|        | II   | 173      | $3.7 \cdot 10^{-13}$ | 113  | 37       |
|        | III  | 285      | $3.3 \cdot 10^{-13}$ | 96   | 27       |
|        | IV   | 354      | $1.4 \cdot 10^{-13}$ | 64   | 8        |
| NR2p   | I    | 41       | $3.3 \cdot 10^{-14}$ | 34   | 1        |
|        | II   | 115      | $6.8 \cdot 10^{-13}$ | 64   | 52       |
|        | III  | 175      | $3.0 \cdot 10^{-13}$ | 88   | 32       |
|        | IV   | 258      | $1.3 \cdot 10^{-13}$ | 99   | 15       |

Deviation from standard behaviour occurs in the case of NR2p, whose peak I is centred at 41°C with the area of 1 %, while peak II is centred at 115°C with the area of 52 %. We

should take into consideration that such low integrated area of the first peak can be neglected, meaning that the second peak includes the first one and as-obtained O<sub>2</sub> TPD/MS profile can be described with only three peaks (Fig. 4.6d). By comparing as-obtained O<sub>2</sub> TPD/MS profile with those from NSHp, TNp and NR1p, we can observe that the amount of desorbed O<sub>2</sub> above 200°C is much lower, and the shape of the curve is completely different. NSHp, TNp and NR1p materials all have an open, more or less tubular structure, while the NR2p sample has a strongly pronounced rice-like morphology without a developed core.

In order to confirm that desorbed O<sub>2</sub> comes exclusively from peroxo species, as-prepared TN material has been subjected to the same analysis. From Fig. 4.7 we can clearly see that desorbed O<sub>2</sub> is a result of peroxo species decomposition, since no O<sub>2</sub> has been desorbed during O<sub>2</sub> TPD/MS analysis of TN material. Their presence only in the peroxide-treated material has also been confirmed with in-situ Raman analysis and UV/Vis DR analysis combined with gradual heating.

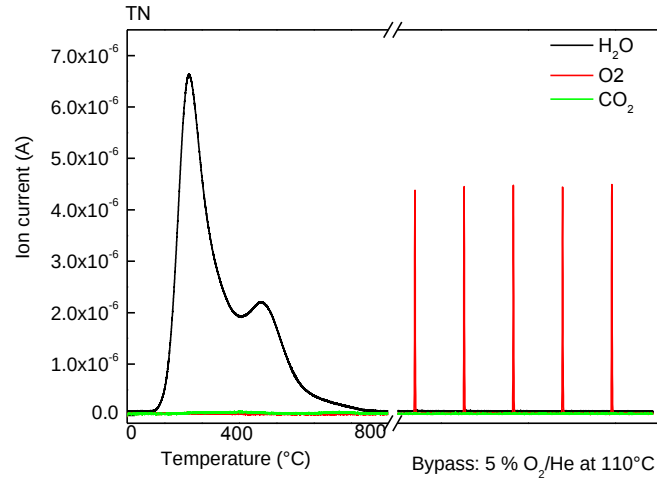


Figure 4.7: MS profile for as-prepared TN material showing H<sub>2</sub>O, O<sub>2</sub> and CO<sub>2</sub> evolution. Red peaks represent the O<sub>2</sub> pulse used for quantification of O<sub>2</sub> desorbed from the surface of the material.

*In-situ* Raman analysis (Fig. 4.8) has shown that TN material exhibits a characteristic band for amorphous TiO<sub>2</sub>, as well as bands that show the presence of anatase at 466 cm<sup>-1</sup>, 277 cm<sup>-1</sup>, 185 cm<sup>-1</sup> and 146 cm<sup>-1</sup> [104]. One additional band at 670 cm<sup>-1</sup> is assigned to stretching and vibration of Ti-O bonds originating from the surface-adsorbed -OH/H<sub>2</sub>O. Raman spectra for the peroxide-treated TNp material slightly differs from the original spectra of the as-prepared material. First, the intensity of the band characteristic for amorphous TiO<sub>2</sub> increases, probably due to disintegration of the material, while the intensity of the band associated with stretching and vibration of Ti-O bonds also increases, probably as a result of side-on bonding between peroxo species and Ti<sup>4+</sup> centres which is confirmed with the appearance of the new band near 890 cm<sup>-1</sup> attributed to O-O vibrations of  $\eta^2$  species [104], [105]. Bands near 1130 cm<sup>-1</sup> and 1070 cm<sup>-1</sup> are attributed to  $\eta^1$  peroxo species [105]. After 4 h interactions with 0.15 M H<sub>2</sub>O<sub>2</sub> solution (simulation of the CWPO experiments), band at 670 cm<sup>-1</sup> reduces and redshifts which confirms the formation of side-on ( $\eta^2$ ) peroxo species at the expense of H<sub>2</sub>O<sub>2</sub> consumption [105]. One additional band occurs at 618 cm<sup>-1</sup> which can be explained as the formation of  $\eta^2$  species that are more prone to degradation during CWPO runs or are more labile bonded to the Ti<sup>4+</sup>.

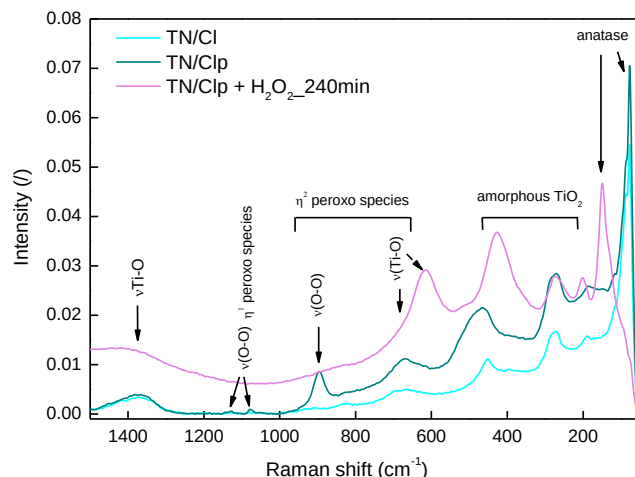


Figure 4.8: *In-situ* Raman spectra of as-prepared and peroxide-treated TN material exposed to 0.15 M  $\text{H}_2\text{O}_2$  during 240 min. Laser excitation was 785 nm.

By subtracting UV/Vis DR spectra of as-prepared and peroxide-treated TN material we can observe that a wide absorption-related curve is located between 300–550 nm (Fig. 4.9a). By applying Voight amplitude the curve can be fitted with two peaks representing the  $\sigma \rightarrow \sigma^*$  and  $\pi \rightarrow \sigma^*$  transition. Peak centred at  $\sim 380$  nm is usually assigned to the  $\sigma \rightarrow \sigma^*$  transition, while the peak centred above 400 nm is usually assigned to the  $\pi \rightarrow \sigma^*$  transition [85]. Although some authors state that only  $\eta^2$  peroxo species contribute to the visible light absorption [17], [83], we cannot exclude the possibility that  $\eta^1$  peroxo species do not, since they are detected by Raman analysis, therefore fitted UV/Vis DR spectra only represent the strength of LTMC that occurs during light absorption. Fitted curves are shifted towards lower wavelengths which can be explained as a stronger interaction with  $\text{Ti}^{4+}$ , and that would be in good correspondence with the effect observed during the in-situ Raman analysis.

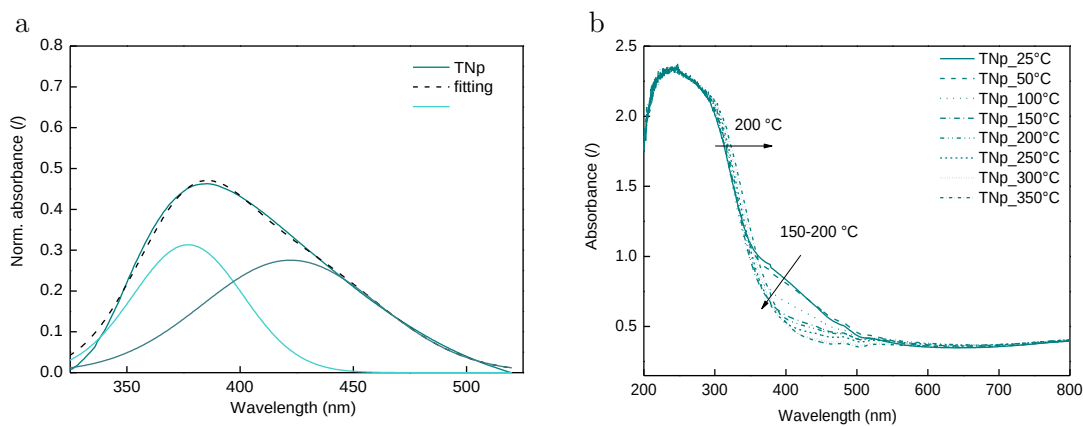


Figure 4.9: a) Fitted UV/Vis DR spectra of peroxide-treated TNp material. Curves represent subtracted values between the peroxide-treated and as-prepared material. b) UV/Vis DR spectra of peroxide-treated TNp material showing thermal instability of the peroxo species in the temperature region up to 350°C.

In addition, by applying UV/Vis DR analysis combined with gradual heating of the material in air flow, we can observe (Fig. 4.9b) that the absorbance peak at 420 nm diminished at temperature of 150°C, while at 200°C it shifts in the region attributed to the structural LMCT of  $\text{O}^{2-} \rightarrow \text{Ti}^{4+}$  [71]. Therefore,  $\text{O}_2$  desorbed at temperatures above 200°C during  $\text{O}_2$  TPD/MS analysis is probably correlated with the structural oxygen incorporated

into the materials during peroxide treatment, while O<sub>2</sub> desorbed in the region up to 200°C can be attributed to the peroxo species. We should not forget that H<sub>2</sub>O<sub>2</sub> is a strong mineralizing agent causing partial disintegration of materials [71], meaning that during peroxide treatment it can be possible to replace the structural O<sub>2</sub> with those coming from H<sub>2</sub>O<sub>2</sub>.

Above-mentioned changes can also influence the exposure of free Ti<sup>4+</sup> which can be easily detected with the measurement of LAS and BAS prior to peroxide treatment. Obtained values are listed in Table 4.2. All the materials, except NR1p, experience an increase in the LAS and BAS. If we take into consideration that unoccupied Ti<sup>4+</sup> sites are responsible for increased Lewis acidity, it can be concluded that during peroxide treatment peroxo species are formed on the places of Ti<sup>4+</sup>, most probably by replacing surface-bonded -OH groups. The formation of surface peroxo species can cause an increase in BAS since peroxo species can be found in protonated form. Additionally, it is also possible that during the formation of peroxo species tearing of -OH groups centred at Ti<sup>4+</sup> occurs, therefore leaving its space deprotonated and causing an increase in LAS [106]. It is already mentioned that peroxide treatment causes disintegration of amorphous structure [71], meaning that it can influence the surface atomic arrangement. In addition, Kitana et al. [107] have reported that acid surface properties are in good correlation with the morphology of the materials with the prevalent LAS and BAS in the case of hydrothermally synthesized TiO<sub>2</sub>-based nanotubes, in comparison with nanosheets and nanorods. Therefore, it has been assumed that high catalytic activity of protonated TiO<sub>2</sub>-based nanotubes relies on the synergistic effect between BAS and LAS, and therefore we cannot exclude that the favourable ratio between BAS and LAS alters the catalytic properties of the TNp material.

#### 4.1.3 Catalytic performance of peroxide-treated morphologically distinctive nano-scale TiO<sub>2</sub>-based materials in the CWPO of MO

Catalytic performance of peroxide-treated NSHp, TNp, NR1p and NR2p materials was tested in the CWPO of model MO solution under mild reaction conditions ( $p_{\text{atm}}$ ,  $T=25^{\circ}\text{C}$ ). From Fig. 4.10a we can observe that MO conversions increased in the following order 25<34<42<72 % for NSHp, NR1p, NR2p and TNp, respectively. NSHp and NR1p, which showed the lowest catalytic activity, contain  $0.8 \cdot 10^{-6}$  mol O<sub>2</sub>/m<sup>2</sup> and  $1.0 \cdot 10^{-6}$  mol O<sub>2</sub>/m<sup>2</sup> of surface peroxo species, and therefore we can attribute higher catalytic performance of NR1p material to an increased amount of surface peroxo species introduced into the reactor. In addition, NR1p experiences increase in the  $S_{\text{BET}}$ ,  $V_p$  and  $d_p$  for ~4 %, ~10 % and ~7 %, respectively. In comparison with the NSHp whose  $S_{\text{BET}}$  and  $V_p$  decrease for ~7 % and ~8 %, respectively, while  $V_p$  remains constant, namely 11.1 nm, which is similar to  $V_p=11.6$  nm of the NR1p sample. Therefore, we can conclude that peroxide treatment influenced the disintegration of the materials and its accessibility to the pores and surface peroxo species making NR1p a bit more efficient in comparison to NSHp. Importance of the high  $S_{\text{BET}}$ ,  $V_p$  and  $d_p$  is a well-known criterion for successful catalytic performance of TiO<sub>2</sub>-based materials in the liquid-phase catalytic reactions [51]. If we look at the H<sub>2</sub>O<sub>2</sub> consumption, we can observe that NR1p material is more efficient in comparison with NSHp. Twice the lower amount of H<sub>2</sub>O<sub>2</sub> was consumed by NR1, which can be a result of the more efficient peroxide treatment and higher stability of the peroxo species in the CWPO of MO. In addition, from the fitted MS spectra (Fig. 4.6c) we can observe that NR1p material contains a higher amount of thermally stable O<sub>2</sub> species (O<sub>2</sub> desorbed above  $T=200^{\circ}\text{C}$ ) in comparison to NSHp. The amount of deposited carbon on both material samples was 0.47 wt. % and 0.54 wt. %, respectively. With the use of NR2p material we can observe that MO removal has increased for 10 % in reference to NR1, while H<sub>2</sub>O<sub>2</sub> consumption was rather high, namely 100 %. The amount of deposited carbon was 0.04 wt. % larger in

comparison with NR1 (Table 4.4). In addition, NR2p has an almost equal amount of surface peroxo species as NSHp, as well as similar  $S_{\text{BET}}$  but slightly smaller  $V_p$  and  $d_p$ , but its fitted MS curve has a completely different curve shape, with a minimal amount of thermally stable  $\text{O}_2$  species. Taking into consideration its morphology, with those of above-mentioned materials and TNp, we can propose that as-liberated thermally stable  $\text{O}_2$  is rather important for activating  $\text{H}_2\text{O}_2$  and achieving higher catalytic activity, and it is obviously connected with the morphology itself.

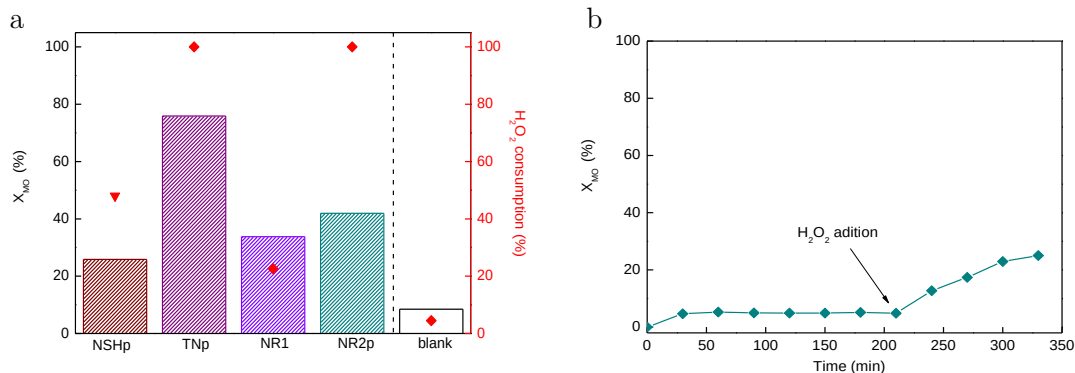


Figure 4.10: MO conversion and accompanied  $\text{H}_2\text{O}_2$  consumption for a) peroxide-treated NSHp, TNp, NR1p and NR2p material at 25°C. b) Graphical presentation of reaction initiation after 210 min of adsorption for peroxide-treated TNp material. Test duration was 240 min and 330 min, respectively.

In contrast to all above-described materials, catalytic activity of the TNp was much higher. 72 % of MO conversion was achieved during a 4 h experiment, with only 0.23 wt. % of carbon deposited on the surface of the material. In addition, only 4 % of adsorption occurs during 4 h of the adsorption experiment. TNp material has the highest  $S_{\text{BET}}$ ,  $V_p$  and  $d_p$ , as well as the amount of surface peroxo species of  $1.4 \times 10^{-6} \text{ mol O}_2/\text{m}^2$ , meaning that as-obtained morphology is far the most active. This can be both due to beneficial morphologically related properties and a sufficient amount of surface peroxo species. As already mentioned,  $\text{TiO}_2$ -based nanotubes are one of the most beneficial morphologies used in catalytic reactions since their high surface area to volume ratio allows uniform dispersion of the material in the reaction systems, while their porosity allows efficient transport of the reactants and products from the surface [51], [67], [71].

In order to verify if surface peroxo species are those responsible for the catalytic activity of the TNp material, an additional adsorption experiment, followed by abrupt addition of  $\text{H}_2\text{O}_2$ , was performed. From Fig. 4.10b it can be observed that during the first 60 min of the process adsorption equilibrium is reached and no reaction occurs during the full 210 min. After adding a stoichiometric amount of  $\text{H}_2\text{O}_2$  at  $t=210$  min, the catalytic reaction starts, therefore confirming that the MO molecule cannot be degraded only in the presence of the peroxide-treated material itself or pure  $\text{H}_2\text{O}_2$  (blank experiment, Fig. 4.10a). pH value of the reaction solution was  $\sim 5.2$  at  $t=0$ , and lowered at  $\sim 4.5$  after CWPO experiments. This can present a confirmation that partial low molecular degradation products are formed during the reaction [47].

Table 4.4: MO conversion and accumulated carbon content for peroxide-treated NSHp, TNp, NR1p and NR2p materials. MO conversion is given as a difference of MO removal occurred during CWPO and adsorption experiments.

| Sample | X <sub>MO</sub> (%) | C <sub>0,TEOR.</sub> (mg/L) | C <sub>ACCUM.</sub> (wt. %) |
|--------|---------------------|-----------------------------|-----------------------------|
| NSHp   | 25                  | 2.75                        | 0.47*                       |
| TNp    | 72                  |                             | 0.23                        |
| NR1p   | 34                  |                             | 0.54                        |
| NR2p   | 42                  |                             | 0.58                        |

\*net carbon content

#### 4.1.4 Influence of the operational parameters on the catalytic activity of the best performing peroxide-treated TNp material

TNp material was tested in the CWPO of MO by varying catalyst loading, pH value and T of the reaction suspension. Firstly, as-prepared TN material was tested in the 4 h CWPO experiments in order to evaluate the contribution of the support to overall performance of TNp. From Fig. 4.11a we can observe that as-prepared TN material achieves 20 % of MO degradation, with only 2 % of adsorption, but TN has not been nearly as active as TNp after peroxide treatment. As already mentioned, TNp achieves 72 % MO conversion, with max 4 % of adsorption at 25°C with the 2 g/L of material.

By varying the initial amount of TNp material to 1 g/L and 3 g/L, we can observe (Fig. 4.11a) that optimum catalytic loading is 2 g/L, while 1 g/L and 3 g/L provide a non-sufficient or negligible difference, respectively. Nominal loadings of the metal-based catalytic materials lie between 0.5-5.0 g/L [21], [27], [28], [30], [42], [108]. In comparison with them, metal-free CeO<sub>2</sub> catalytic material tested in the CWPO of azo dye AO7 had shown excellent results with only 0.5 g/L catalyst loading, but the process was conducted 8 h with the higher initial amount of H<sub>2</sub>O<sub>2</sub> [35]. Therefore, in this case 2 g/L of every catalytic material was used as an optimal catalyst loading in order to alleviate the comparison between the developed catalytic materials.

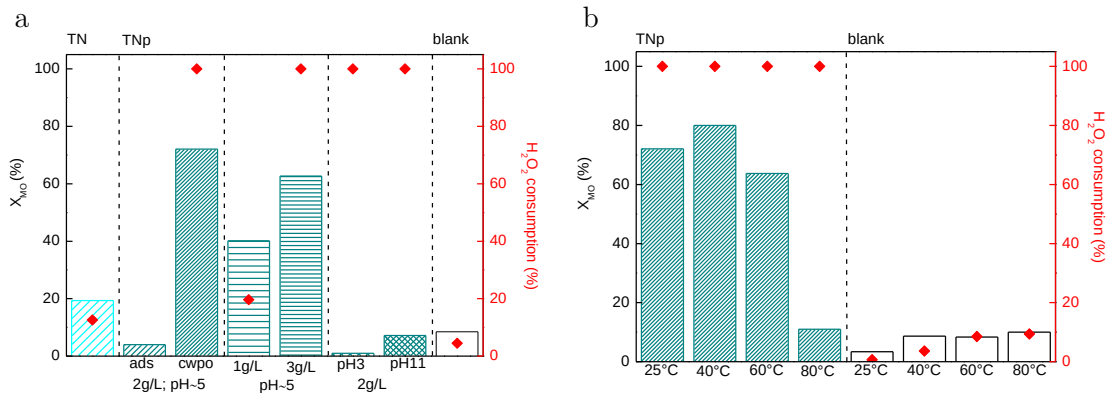


Figure 4.11: MO conversion and H<sub>2</sub>O<sub>2</sub> consumption for as-prepared and peroxide-treated TN material with a) a varied initial amount of catalyst under neutral pH, pH=3 and pH=11 and b) at different reaction temperatures. Test duration was 240 min, stoichiometric amount of H<sub>2</sub>O<sub>2</sub> was used.

Degradation of 50 ppm MO solution was also tested in acidic and basic conditions by adjusting solutions pH to 3 and 11, respectively. Although it is well known that optimal pH for following Haber-Weiss mechanism is ranging from ~2.5-3.5, it has been shown that •OH radical can be obtained under neutral pH (pH=7) by using metal-based and metal-

free catalytic materials [21], [35], [42], [108], [109]. But, as already mentioned, we cannot exclude the possibility of creating other ROS, such as  $O_2^{\bullet-}$  and  $\bullet OOH$ , since it has been proven that they coexist with the  $\bullet OH$  radicals [11], [16]–[18]. Nevertheless, TNp material tested under acidic conditions did not show any catalytic activity and 1 % of MO conversion is solely taken as a difference between the adsorption and CWPO. In addition, in the first 30 min of the process ~69 % of MO was adsorbed on the surface of the TNp material which can be due to the difference between point of zero charge ( $pH_{pzc}$ ) of the material and pH of the reaction solution.  $pH_{pzc}$  of the TNp material is ~4.8, meaning that the surface of the material in the reaction suspension with the  $pH=3$  is positively charged and increasingly attracts negatively charged sulphate group of the quinoid form of the MO molecule [39],[110]. In contrast, at  $pH=11$  only 7 % of the MO molecule was degraded, while the extent of adsorption was below 1 %, although all  $H_2O_2$  was consumed in the first 30 min of the reaction. This can occur due to the instability of  $H_2O_2$  whose acid dissociation constant ( $pK_a$ ) is 11.75, which means that under alkaline conditions it easily decomposes only to  $O_2$  and  $H_2O$  [111]. Therefore, 6 % of MO removal can only be prescribed to the bleaching effect of  $H_2O_2$  during its decomposition and adsorption. The amount of the deposited carbon on the catalyst surface was 0.15 wt.% and 0.28 wt. % for  $pH=3$  and  $pH=11$ , respectively (Table 4.5). From the obtained results it is obvious that TNp sample performs the best without changing the solution starting pH of ~5.

With optimized catalyst loading and suspension pH value, the effect of reaction temperature was tested (Fig. 4.11b). By increasing the temperature from  $25 > 40 > 60 > 80^\circ C$  MO conversion changes in the following order  $72 > 80 > 65 > 11$  %. Abrupt decline in the catalytic activity at  $80^\circ C$  can be ascribed to thermal instability of peroxo species. It is well known that peroxo species are stable up to  $90^\circ C$  when heated in air [72],[89], but apparently its stability and activity in the liquid-phase reactions terminates even at lower temperatures. At  $60^\circ C$ , adsorption is far more pronounced (adsorption ~14 %), while at  $25^\circ C$  and  $40^\circ C$  there is a small difference in the overall activity and adsorption capacity (adsorption ~4 % at  $25^\circ C$  and ~7 % at  $40^\circ C$ ). Therefore, the amount of the deposited carbon is the highest for the TNp material tested at  $60^\circ C$  reaching the value of 0.66 wt. % during 4 h experiments, while at  $40^\circ C$  and  $80^\circ C$  it is around 0.07 wt. % and 0.25 wt. % (Table 4.5.).

Table 4.5: MO conversion and accumulated carbon content for peroxide-treated TNp material tested under different reaction conditions with varied catalyst loading. MO conversion is given as a difference of MO removal occurred during CWPO and adsorption experiments.

| Sample | $\delta_{CAT}$ (g/L) | pH   | T (°C) | X <sub>MO</sub> (%) | C <sub>0,TEOR.</sub> (mg/L) | C <sub>ACCUM.</sub> (wt. %) |
|--------|----------------------|------|--------|---------------------|-----------------------------|-----------------------------|
| TNp    | 1                    | ~5.5 | 25     | 40                  | 2.75                        | 0.10                        |
|        | 2                    |      |        | 72                  |                             | 0.23                        |
|        | 3                    |      |        | 62                  |                             | 0.20                        |
|        | 2                    | 3    | 1      | 0.15                |                             |                             |
|        |                      | 11   | 7      | 0.28                |                             |                             |
|        |                      | ~5.5 | 40     | 75                  |                             | 0.07*                       |
|        | 2                    |      | 60     | 64                  |                             | 0.66                        |
|        |                      |      | 80     | 11                  |                             | 0.25                        |

\*net carbon content

For further applied CWPO and adsorption experiments the temperature of 25°C was taken as the relevant one. In addition, from the performed blank experiment we can observe that the MO molecule is more prone to degradation at elevated temperature even without the presence of the catalytic material. At 25°C ~4 % of MO was degraded in the presence of H<sub>2</sub>O<sub>2</sub>, while at 40–80°C it increased to ~9–10 %. Thermal instability of MO was also tested by Nie et al. [47]. By monitoring the fluorescence spectra of MO at 25, 40, 60 and 80°C they observed that by heating the reaction solution to 40°C internal energy of the structure has been changed. Two possible thermal isomers of the MO molecule can be formed by rotation or inversion of the –N=N– bond angle and they can both be considered as activated form which is more prone to degradation. In order to evaluate the real thermal stability of MO, TGA measurement, in N<sub>2</sub> atmosphere, was performed and the result is shown in Fig. 4.12. Weight loss up to 80°C is connected with the loss of H<sub>2</sub>O occurring from self-humidity and re-crystallization [44], and that does not affect the decomposition of MO. The melting point of MO lies in between 260–310°C, followed by the abrupt decline in mass due to the decomposition of the low molecular mass constituents such as methyl (–CH<sub>3</sub>) and –SO<sub>3</sub>Na group [44]. No visible changes occur after reaching the temperature of 600°C.

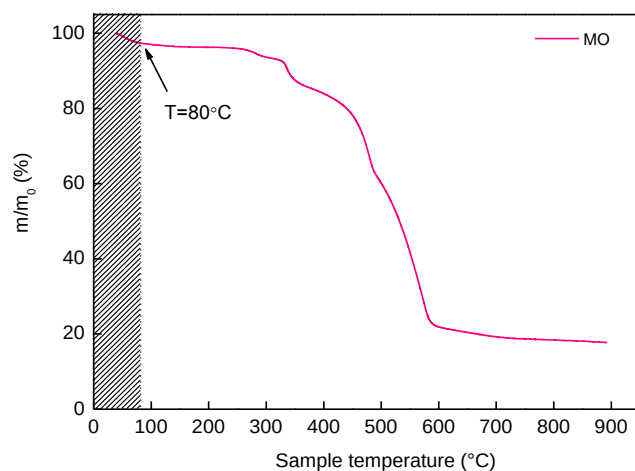


Figure 4.12: TGA profile of powdered methyl orange.

Final inorganic products, namely SO<sub>4</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>, of the MO molecule were quantified by using IC analysis. Obtained values are listed in Table 4.6. The presence of NO<sub>2</sub><sup>-</sup> was not detected in any of the liquid phase samples meaning that the cleavage of the azo bond, or 1,4-positioned dymethylamine groups, will lead to the formation of only NO<sub>3</sub><sup>-</sup>. Even homolytic cleavage of the MO molecule would result in the formation of two aromatic rings substituted with dymethylamine and sulfonic group, but it has been proven that ROS-oriented degradation of the MO molecule does not alter this path. Homolytic bond cleavage is thus competitive with the splintering of the dymethylamine and sulfonic groups [45], meaning that the MO molecule does not decompose evenly. Nevertheless, degradation occurs which can be visible with the formation of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>.

Table 4.6: Amount of  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  obtained after CWPO of MO with peroxide-treated TNp material tested at different operational temperatures.

| Sample    | T (°C) | $\text{NO}_2^-$ (mg/L) | $\text{NO}_3^-$ (mg/L) | $\text{SO}_4^{2-}$ (mg/L) |
|-----------|--------|------------------------|------------------------|---------------------------|
| MO_50 ppm | 25     | /                      | /                      | /                         |
| TNp       | 25     | /                      | 6.2                    | 2.9                       |
|           | 40     | /                      | 3.9                    | 3.7                       |
|           | 60     | /                      | 3.3                    | 3.3                       |
|           | 80     | /                      | /                      | 2.2                       |

\*  $\text{NO}_3^-_{\text{TEOR.}} = 9.5 \text{ mg/L}$ ;  $\text{SO}_4^{2-}_{\text{TEOR.}} = 14.7 \text{ mg/L}$ .

## 4.2 Characterization of Thermal and Peroxide-Treated TN Materials

### 4.2.1 Porosity, morphological, structural and surface properties of thermal and peroxide-treated TN materials

Thermal treatment of  $\text{TiO}_2$ -based nanotubes is usually applied in order to gain a uniform crystal structure, mostly polymorph anatase, but Bavykin et al. [77] have proven that even in the low temperature range, before recrystallization occurs ( $T \sim 350\text{--}400^\circ\text{C}$ ), loss of ion-exchangeable -OH groups and topotactic transformation of the material can be induced [77]. Since the prerequisite for the formation of peroxo species are, as considered, surface-bonded ion-exchangeable -OH groups [51], [71], [102], examination of the proton loss influence on the peroxo species formation and their catalytic activity in the CWPO of MO was tested. TN material was exposed to temperature treatment in the ranges proposed by Bavykin et al., namely  $140$ ,  $250$  and  $350^\circ\text{C}$  [77]. As already mentioned, by applying  $^1\text{H}$  MAS NMR, it has been concluded that ion-exchangeable -OH groups are removed up to  $140^\circ\text{C}$ , interlayered -OH groups up to  $300^\circ\text{C}$  and above that dehydration of intralayered -OH groups occurs [51], [77]. By taking into consideration the XRD analysis published by Erjavec et al. [71], progressive phase transformation of TN material occurs at the temperature of  $400^\circ\text{C}$ , so the TN material has been thermally treated up to this range. In addition, the formation of the surface peroxo species on the TN material thermally treated above  $400^\circ\text{C}$  is not possible due to complete deprivation of surface -OH groups [51], [71].

First, the SEM analysis has confirmed that thermal treatment of TN, shown in Fig. 4.13a, b and c, did not affect the morphology of the material, therefore a well-developed and randomly oriented tubular structure was preserved even after peroxide treatment (Fig. 4.13d, e and f).

Nevertheless, from the photograph shown in Fig. 4.14 we can observe a colour change in the materials thermally treated at  $140^\circ\text{C}$  and  $250^\circ\text{C}$ , which occurs due to partial reduction of  $\text{Ti}^{4+}$  into  $\text{Ti}^{3+}$  [112], [113]. The intensity of colour is directly correlated with the amount of reduced Ti atoms meaning that the completely reduced material should be intensely black [112], [113]. Partial reduction of  $\text{Ti}^{4+}$  atoms near the surface could affect the catalytic activity of the material in a similar manner to  $\text{CeO}_2$  systems ( $\text{Ce}^{3+}/\text{Ce}^{4+}$ ). Namely, peroxo species could be located on the  $\text{Ti}^{4+}$  while MO molecule could be partially degraded, through molecular rearrangement, on the  $\text{Ti}^{3+}$  [35], [112].

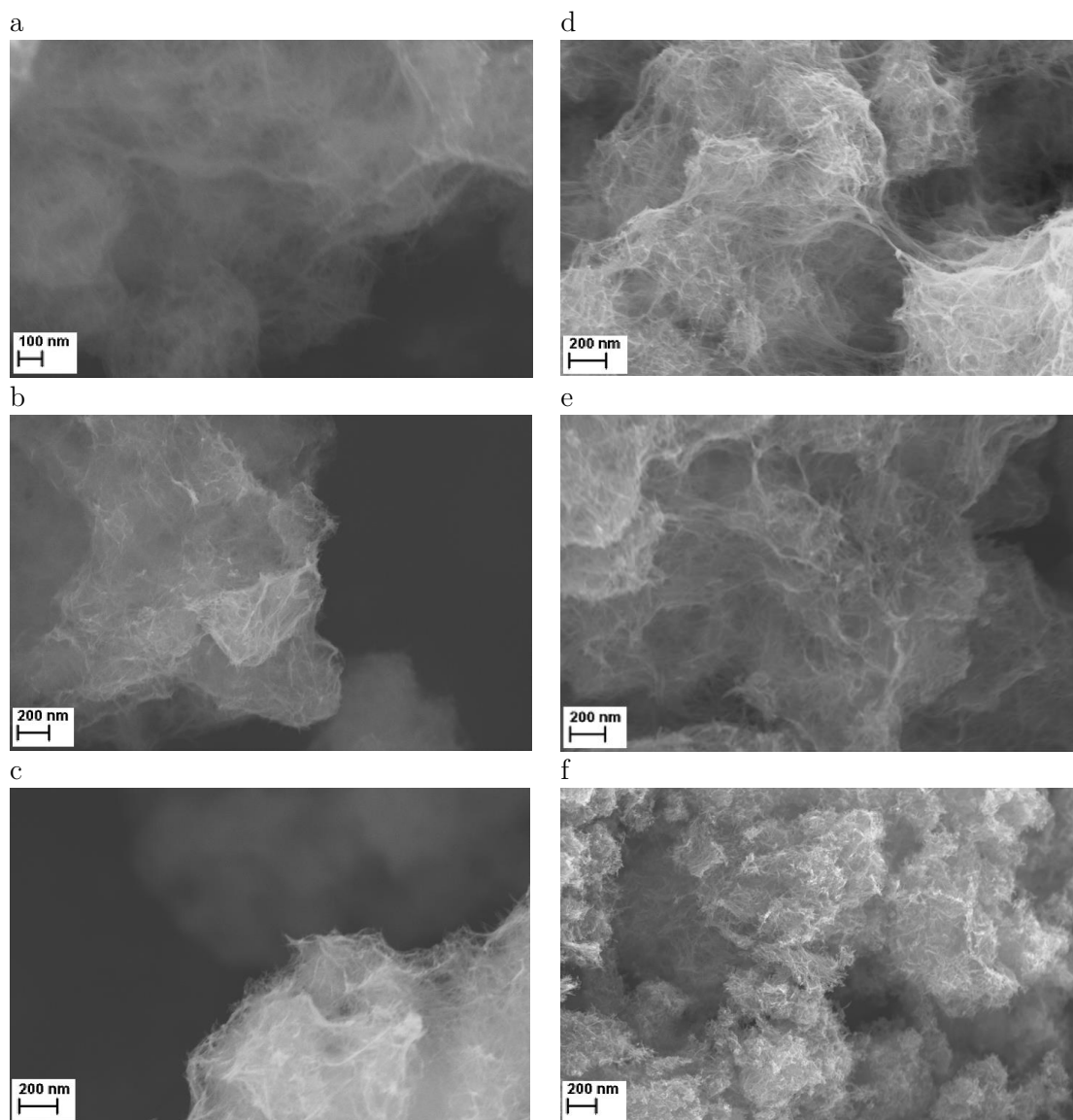


Figure 4.13: SEM images of as-prepared a) TN/140, b) TN/250, c) TN/350 and peroxide-treated d) TN/140p, e) TN/250p and f) TN/350p materials.

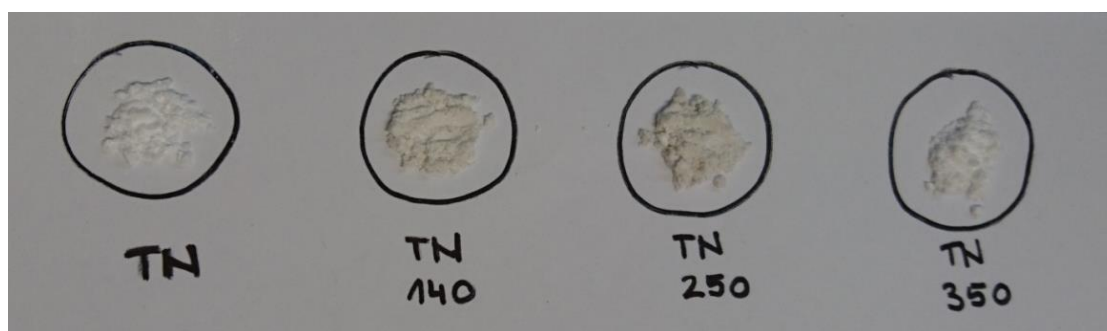


Figure 4.14: Photography of the as-prepared TN and thermally treated TN/140, TN/250 and TN/350 materials.

Although the morphology of the materials was preserved,  $S_{\text{BET}}$  and  $V_p$  drastically decreased from 383 m<sup>2</sup>/g to 281 m<sup>2</sup>/g, while  $d_p$  increases from 11.4 nm to 13.1 nm for the as-prepared TN (Table 4.1) and TN/350 (Table 4.7), respectively. By increasing the temperature of the thermal treatment small pores, attributed to the pore channels inside the TiO<sub>2</sub>-based nanotubes, collapse and only larger pores are preserved [51], [71]. Abatement of the small pores reflects on the N<sub>2</sub> adsorption-desorption isotherms, as well as on the pore size distribution.

Table 4.7: Specific surface area ( $S_{\text{BET}}$ ), pore volume ( $V_p$ ) and average pore diameter ( $d_p$ ) of as-prepared and peroxide-treated TN/140, TN/250 and TN/350 materials.

| Sample  | $S_{\text{BET}}$ (m <sup>2</sup> /g) | $V_p$ (cm <sup>3</sup> /g) | $d_p$ (nm) |
|---------|--------------------------------------|----------------------------|------------|
| TN/140  | 373                                  | 1.19                       | 11.5       |
| TN/140p | 421                                  | 1.30                       | 11.3       |
| TN/250  | 392                                  | 1.27                       | 11.5       |
| TN/250p | 354                                  | 1.15                       | 11.7       |
| TN/350  | 281                                  | 1.03                       | 13.1       |
| TN/350p | 277                                  | 1.00                       | 13.0       |

By following IUPAC classification [114], N<sub>2</sub> adsorption-desorption isotherms (Fig. 4.15a) are classified as type 3, characteristic for mesoporous materials with predominant interparticle porosity [51], [71], [114]. Hysteresis loop of the thermally treated materials slightly deviates from those of as-prepared TN, mostly due to the declination in the pore diameter as shown in Fig. 4.15c.

By increasing the temperature of the thermal treatment up to 350°C, small pores of around 4 nm and 8 nm are replaced with the larger ones of 6 nm and 10–12 nm, respectively. Changes in the pores size distribution, for the TiO<sub>2</sub>-based nanotubes treated in the mild temperature range, are in good correspondence with others [71]. Complete loss of small pores ( $d_p < 10$  nm) is observed only at the temperatures above 400°C, when the interparticle porosity increases and average  $d_p$  is around 20 nm [71]. As already mentioned, at 400°C phase transformation occurs as reported by Erjavec et al. [67]. After peroxide treatment only TN/140p exhibits an increase of the  $S_{\text{BET}}$  and  $V_p$  similar to those observed in the TNp material (Table 4.1), while  $S_{\text{BET}}$  and  $V_p$  of TN/250p and TN/350p slightly decreases. This can occur due to partial disintegration of the material and disintegration of the small pores, which can also be observed by the declination in the hysteresis loop near the  $p/p_0=1$  (Fig. 4.15b) [51], [71]. Nevertheless, declination in the rate of N<sub>2</sub> adsorption-desorption curve is not as expressed as for example in TiO<sub>2</sub>-based nanotubes thermally treated at the temperatures above 500°C [71], therefore we can conclude that there macropores ( $d_p > 50$  nm) are not present, as it can be seen from the values listed in Table 4.7.

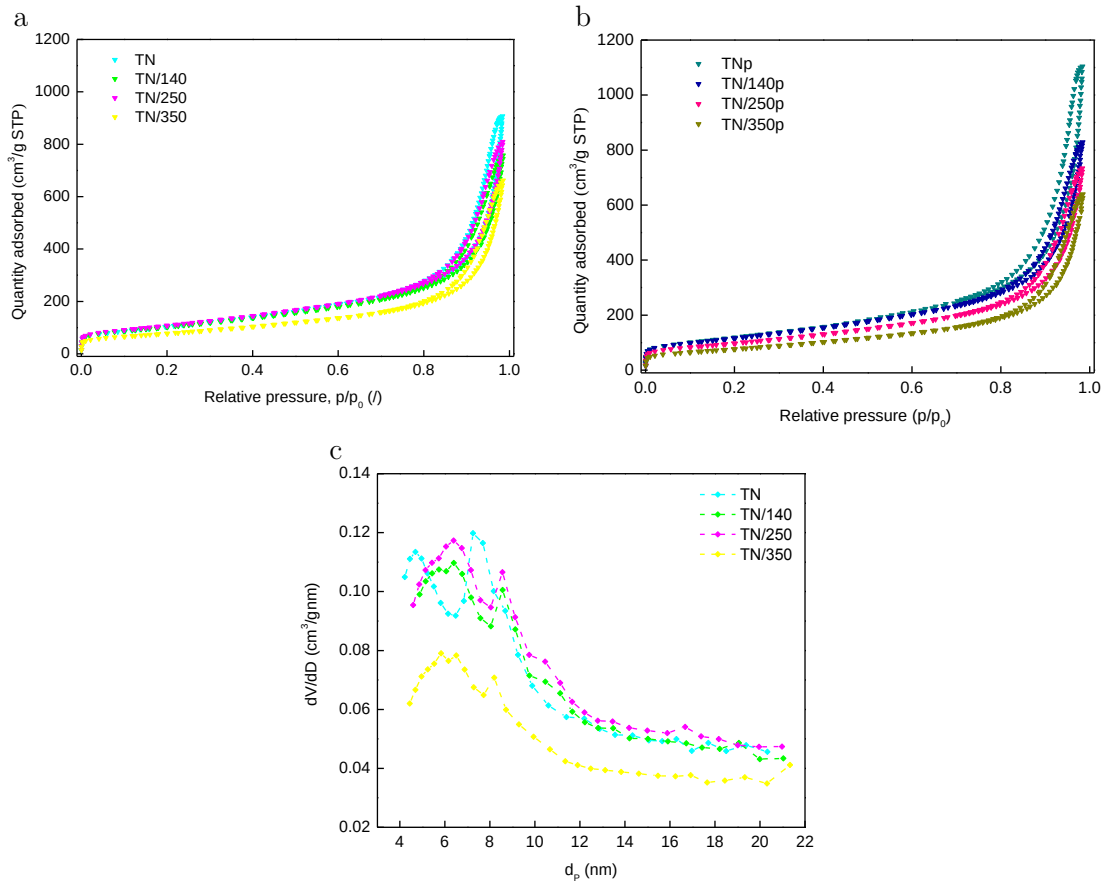


Figure 4.15: N<sub>2</sub> adsorption-desorption isotherms of a) as-prepared and b) peroxide-treated TN, TN/140, TN/250 and TN/350 materials. c) BJH pore size distribution of the as-prepared TN, TN/140, TN250 and TN/350 materials.

By applying FTIR/ATR analysis, surface chemistry of the as-prepared and peroxide-treated materials has been examined. From the obtained spectra we can see that as-prepared (Fig. 4.16a) and peroxide-treated (Fig. 4.16b) TN/140, TN/250 and TN/350 materials have similar surface properties as TN and TNp, respectively (Fig. 4.4a,b). Briefly, a wide asymmetric band attributed to the -OH stretching of Ti-OH and H<sub>2</sub>O molecules is located between 2600-4000 cm<sup>-1</sup>, while the band attributed to stretching of -OH, characterized with medium strength hydrogen bonds, groups is located at 3420 cm<sup>-1</sup> [51], [71], [80]. Although the intensity of the bands is similar, TGA analysis (Fig. 4.17a) has shown that the sample thermally treated at a higher temperature contains a lower amount of adsorbed H<sub>2</sub>O and -OH groups. By increasing the thermal treatment temperature complete weight loss for the individual sample increases in the following order: ~10>13>14>16 wt. % for as-prepared TN/350, TN/250, TN/140 and TN, respectively. A similar trend has been observed in the temperature region up to 140°C where loss of ion-exchangeable -OH groups occurs, as well as up to 300°C where loss on intralayered -OH groups occurs. In the first temperature region weight loss is ~6>9>10<9 wt. %, followed by ~13~13>11>8 wt. % in the second temperature region for the TN, TN/140, TN/250 and TN/350, respectively. Higher weight loss for thermally treated materials is a normal occurrence since thermal treatment, to which they were exposed prior to TGA analysis, results in the irreversible loss of intralayered and interlayered -OH groups and H<sub>2</sub>O [51], [77]. As-applied thermal treatment also influenced the ion-exchange capacity of the above-mentioned materials [77], which influenced the amount of created surface peroxo species.

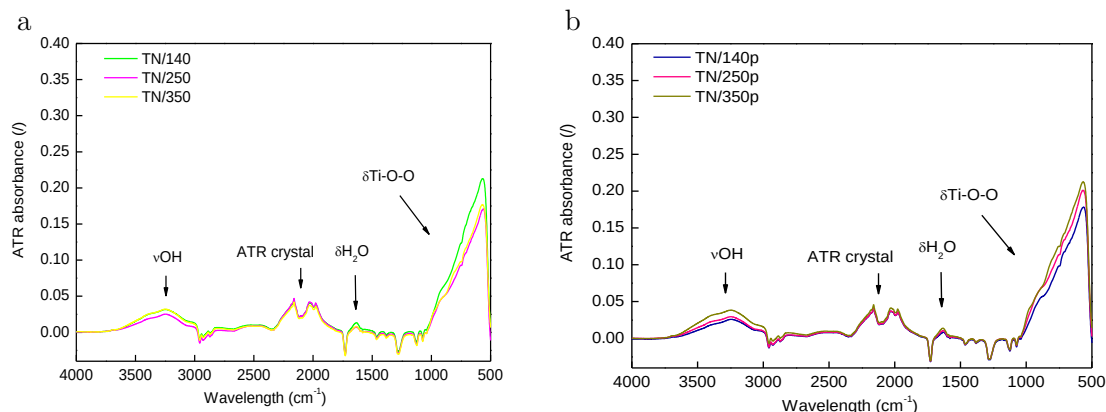


Figure 4.16: FTIR/ATR spectra of a) as-prepared and b) peroxide-treated TN/140, TN/250 and TN/350 materials.

From the UV/Vis DR spectra, Fig. 4.17b, we can observe that materials thermally treated at 250°C and 350°C show a declination in the UV/Vis absorption band in the region characteristic for the visible light peroxo species absorption (absorbance peak at 420 nm) [51], [71], [102]. Among the presented spectra we can also observe that there were no observable changes in the intensity of the band below 380 nm, which is directly correlated with the LMCT of  $O^{2-} \rightarrow Ti^{4+}$  occurring within the material itself [51], [71]. Erjavec et al. [71] have observed that absorption edge of the as-prepared amorphous  $TiO_2$ -based nanotubes and  $TiO_2$ -based nanotubes thermally treated at 300°C and 500°C shows a slight difference in the absorption edge in the UV region. Amorphous  $TiO_2$ -based nanotubes experience a band gap absorption edge shift deeper into UV region, in comparison with the thermally treated material, and such behaviour has been attributed to the changes in the diameter of the nanotubes. Amorphous  $TiO_2$ -based nanotubes possess a slightly larger diameter than those of thermally treated materials and therefore the charge transfer within the material is slightly slower resulting in the wider band gap. Nevertheless, such behaviour has not been observed for the as-prepared and thermally treated TN/350 materials, although, as already mentioned,  $S_{BET}$ ,  $V_p$  and  $d_p$  drastically deviated due to partial destruction of the smaller pores which can also be attributed to the narrowing of the material's diameter [51].

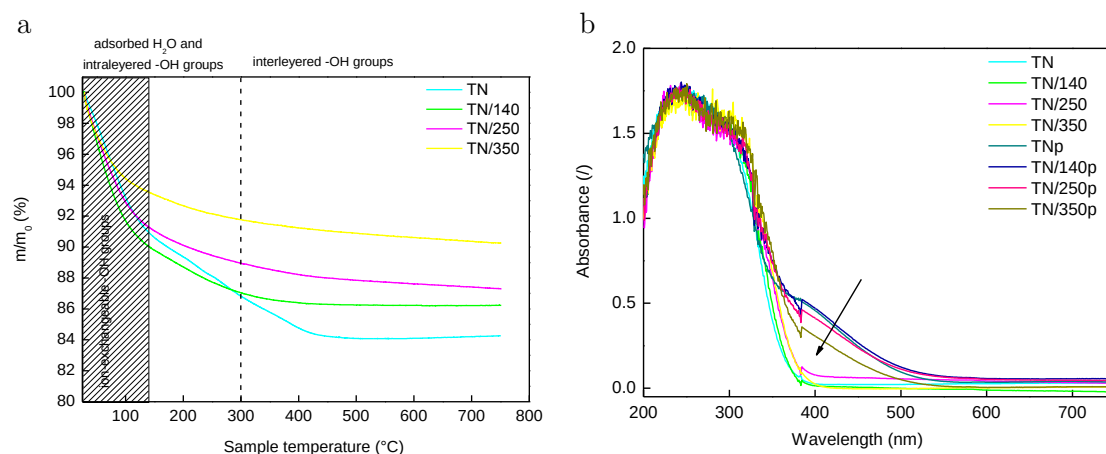


Figure 4.17: a) TGA profiles of as-prepared TN, TN/140, TN/250 and TN/350 materials. b) UV/Vis DR spectra of as-prepared and peroxide-treated TN, TN/140, TN/250 and TN/350 materials.

TN and TN/140 materials exhibit a similar weight loss in the region connected with the ion-exchangeable and intralayered -OH groups, as well as characteristic absorption band in the UV/Vis DR spectra, therefore it would be expected that those materials contain a similar amount of surface peroxo species. Nevertheless, from the obtained TNp O<sub>2</sub> TPD/MS spectra (Fig. 4.18), it is visible that oxygen desorption occurs in the lower and higher temperature region (up to 320°C), while desorption peak for TN/140p material exceeds high evolution around 100°C and completely vanishes already at 130°C. The amount of desorbed O<sub>2</sub> in the case of TN/140p was  $3.5 \cdot 10^{-5}$  mol O<sub>2</sub>/g or  $3.5 \cdot 10^{-8}$  mol O<sub>2</sub>/m<sup>2</sup>, which is much lower in comparison to the TNp sample (Table 4.2). Therefore, ion-exchangeable -OH groups and as-formed peroxo species are not exclusively responsible for the catalytic activity of the material.

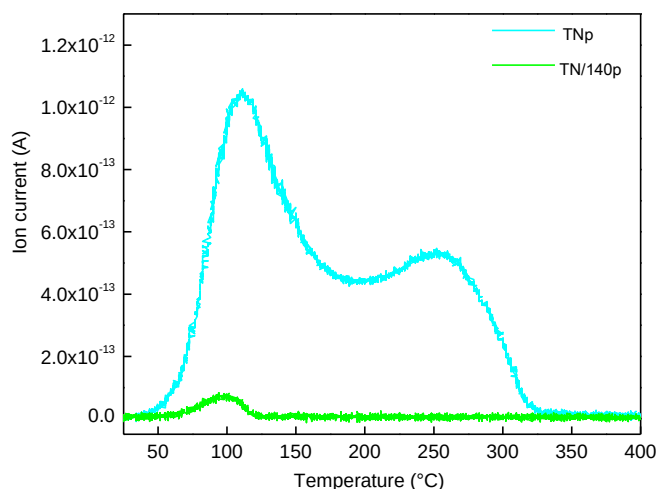


Figure 4.18: MS profile for peroxide-treated TNp and TN/140p materials showing a distinctive difference in temperature-related O<sub>2</sub> evolution.

#### 4.2.2 Catalytic performance of thermal and peroxide-treated TN materials in the CWPO of MO

Among all tested materials TNp still showed prevalent catalytic activity at 25°C with a stoichiometric amount of H<sub>2</sub>O<sub>2</sub> (Fig. 4.19). In comparison with TNp, catalytic activity of TN/140p, TN/250p and TN/350p, as well as MO conversion, decreases in the following order 55>44>23 % for the TN/140p, TN/250p and TN/350p, respectively. Such declination can be attributed to the insufficient amount of surface peroxo species, as confirmed with UV/Vis DR analysis (Fig. 4.17b), as well as a decrease in the S<sub>BET</sub> which influences the desorption/adsorption capacity and availability of the reaction sites in the above-mentioned materials [51], [71]. In addition, apparently thermally induced changes in as-prepared TN/140, TN/250 and TN/350 did not back up the catalytic activity of peroxo species, but rather ameliorate their performance. If we take for comparison just TNp and TN/140p, which show the most similar characteristics in the S<sub>BET</sub> and morphology, we can observe that a small part of thermally labile O<sub>2</sub> species, which has been evolved in the region above 200°C, has a great importance in the H<sub>2</sub>O<sub>2</sub> consumption and MO conversion. By comparing O<sub>2</sub> TPD/MS profile and UV/Vis DR spectra of these two materials, we can propose that O<sub>2</sub> evolved in the region up to 200°C should be attributed to the peroxo species itself, but O<sub>2</sub> evolved in the region above 200°C can be directly correlated with the O<sub>2</sub> desorbed from the material which has been exposed to the mineralizing influence of the H<sub>2</sub>O<sub>2</sub>. Therefore, ion-exchangeable -OH groups could be a prerequisite for peroxo species formation, while the remaining intra- and interlayered -OH groups could enable better

adsorption of  $\text{H}_2\text{O}_2$  on the surface of the material, thus completely changing its surface properties [6].

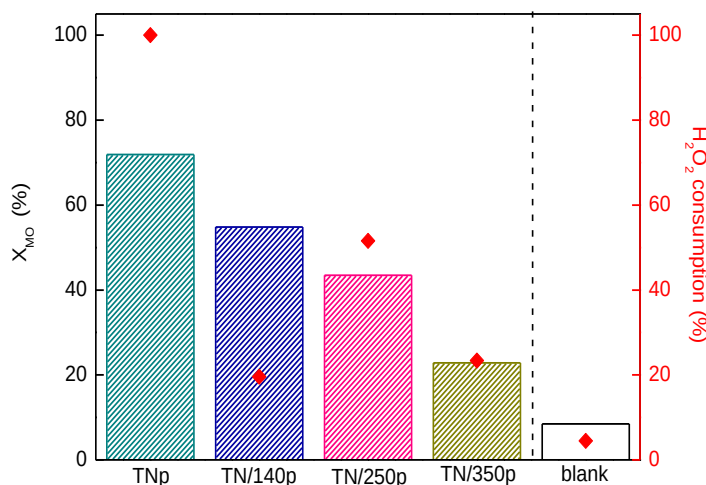


Figure 4.19: MO conversion and accompanied  $\text{H}_2\text{O}_2$  consumption for peroxide-treated TNp, TN/140p, TN/250p and TN/350p materials at 25°C. Test duration was 240 min.

The amount of deposited carbon species highly differs for each material (Table 1.8). TN/250p contains the lowest amount of accumulated carbon, namely 0.13 wt. %, in comparison with TN/140p and TN/350p that reach 0.30 wt. % and 0.38 wt. %, respectively. By comparing the amount of deposited carbon and  $\text{H}_2\text{O}_2$  consumption we can observe that TN/250p and TNp materials, which contain the lowest amount of carbon on the material's surface, have the highest  $\text{H}_2\text{O}_2$  consumption. By using DFT calculations and kinetic experiments Lousada et. al [6] have proven that a prerequisite for the  $\text{H}_2\text{O}_2$  decomposition, and radical formation, lies in the competitive absorbance on the  $\text{TiO}_2$  surface. Preferential H-bonding with surface -OH groups, as well as direct interaction between surface  $\text{O}_2$  atoms arising from  $\text{TiO}_2$  structure, could explain the lower amount of deposited carbon in the cases where higher  $\text{H}_2\text{O}_2$  consumption has been observed [6].

Table 4.8: MO conversion and accumulated carbon content for peroxide-treated TNp, TN/140p, TN/250p and TN/350p materials. MO conversion is given as a difference of MO removal occurred during CWPO and adsorption experiments.

| Sample  | $X_{\text{MO}}$ (%) | $C_{0,\text{TEOR}}$ (mg/L) | $C_{\text{ACCUMULATED}}$ (wt. %) |
|---------|---------------------|----------------------------|----------------------------------|
| TNp     | 72                  | 2.75                       | 0.23                             |
| TN/140p | 54                  |                            | 0.30                             |
| TN/250p | 43                  |                            | 0.13                             |
| TN/350p | 23                  |                            | 0.38                             |

## 4.3 Characterization of Acid and Peroxide-Treated TN Materials

### 4.3.1 Porosity, morphological and structural properties of acid and peroxide-treated TN materials

After excluding the contribution of the morphology and thermal treatment on the catalytic activity of peroxide-treated materials, the influence of different mineral acids on the

protonation step and ion-exchange capacity was examined. It has been proven that sulphate and phosphate groups increase the catalytic activity of  $\text{TiO}_2$ -based materials since their influence on the surface properties of the material, by altering their adsorption/desorption capacity, eases visible light activation and enhances the catalytic performance of surface peroxo species [51], [72], [79], [106], [115]. Therefore, as-synthesized  $\text{TiO}_2$ -based nanotubes were washed in  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$  and  $\text{HClO}_4$ , as well as left in a sodium substituted form, in order to examine the influence of different ionic species on the catalytic performance of peroxo species.

$S_{\text{BET}}$ ,  $V_p$  and  $d_p$  of as-prepared and peroxide-treated materials is listed in Table 4.9. From the obtained data we can observe that  $S_{\text{BET}}$  of as-prepared materials washed in 0.1 M acids lies in between 304-400  $\text{m}^2/\text{g}$ , which is in good correspondence with the  $S_{\text{BET}}$  values obtained for well-developed  $\text{TiO}_2$ -based nanotubes [51], [67]. In addition, we can observe that  $S_{\text{BET}}$  increases from 304>371>383>400  $\text{m}^2/\text{g}$  by following the acid strength order from the weakest acid  $\text{H}_3\text{PO}_4$ , followed by  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and  $\text{HClO}_4$  (values for TN and TNp can be found in Table 4.1). This shows that the acid strength and complete dissociation enables the formation of a high amount of relatively small  $V_p$  and  $d_p$ , which influences the  $S_{\text{BET}}$  of above-mentioned materials.

Table 4.9: Specific surface area ( $S_{\text{BET}}$ ), pore volume ( $V_p$ ) and average pore diameter ( $d_p$ ) of as-prepared and peroxide-treated ST, TN/P, TN 0.001, TN 0.01, TN/S, TN/ $\text{ClO}_4$  0.001, TN/ $\text{ClO}_4$  0.01 and TN/ $\text{ClO}_4$  0.1 materials.

| Sample                     | $S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ ) | $V_p$ ( $\text{cm}^3/\text{g}$ ) | $d_p$ (nm) |
|----------------------------|--------------------------------------------|----------------------------------|------------|
| ST                         | 230                                        | 0.75                             | 12.0       |
| STp                        | 233                                        | 0.81                             | 11.9       |
| TN/P                       | 304                                        | 1.24                             | 14.7       |
| TN/Pp                      | 318                                        | 0.96                             | 10.6       |
| TN 0.001                   | 230                                        | 0.85                             | 13.5       |
| TNp 0.001                  | 170                                        | 0.59                             | 12.9       |
| TN 0.01                    | 375                                        | 1.22                             | 11.6       |
| TNp 0.01                   | 406                                        | 1.31                             | 11.5       |
| TN/S                       | 371                                        | 1.21                             | 11.9       |
| TN/Sp                      | 428                                        | 1.40                             | 18.5       |
| TN/ $\text{ClO}_4$ 0.001   | 390                                        | 1.30                             | 11.8       |
| TN/ $\text{ClO}_4$ p 0.001 | 310                                        | 1.40                             | 15.0       |
| TN/ $\text{ClO}_4$ 0.01    | 369                                        | 1.18                             | 11.4       |
| TN/ $\text{ClO}_4$ p 0.01  | 412                                        | 1.60                             | 13.8       |
| TN/ $\text{ClO}_4$ 0.1     | 400                                        | 1.64                             | 15.5       |
| TN/ $\text{ClO}_4$ p 0.1   | 412                                        | 1.65                             | 14.2       |

Similar  $S_{\text{BET}}$  can be observed for materials washed in 0.01 M  $\text{HCl}$  and  $\text{HClO}_4$ , as well as for materials washed in 0.001 M  $\text{HClO}_4$ , which is in complete contrast with the material washed in 0.001 M  $\text{HCl}$ .  $S_{\text{BET}}$  of the latter is more in correspondence with  $S_{\text{BET}}$  of sodium substitute sample (ST), therefore apparently insufficient protonation has occurred which influenced the final properties of the TN 0.001 material. This is not surprising, since it is known that  $\text{HClO}_4$  is a ten times stronger acid than  $\text{HCl}$ , and even low concentration can achieve the same effect in the protonation degree. In addition, TN 0.001 and ST possess a high amount of lapsed structural  $\text{Na}^+$  ion present after the washing step [51], [66]. SEM/EDS analysis has confirmed that the amount of  $\text{Na}^+$  ions present in ST and TN 0.001 is about ~47 wt. % and ~6 wt. %, respectively. After peroxide treatment  $S_{\text{BET}}$  of the majority of materials increases due to, as already mentioned, partial disintegration during prolonged

exposure to  $\text{H}_2\text{O}_2$ . An exception has been made for STp, TNp 0.001 and TN/ $\text{ClO}_4$ p 0.001, where no changes or a slight decrease in the  $S_{\text{BET}}$  has been observed.

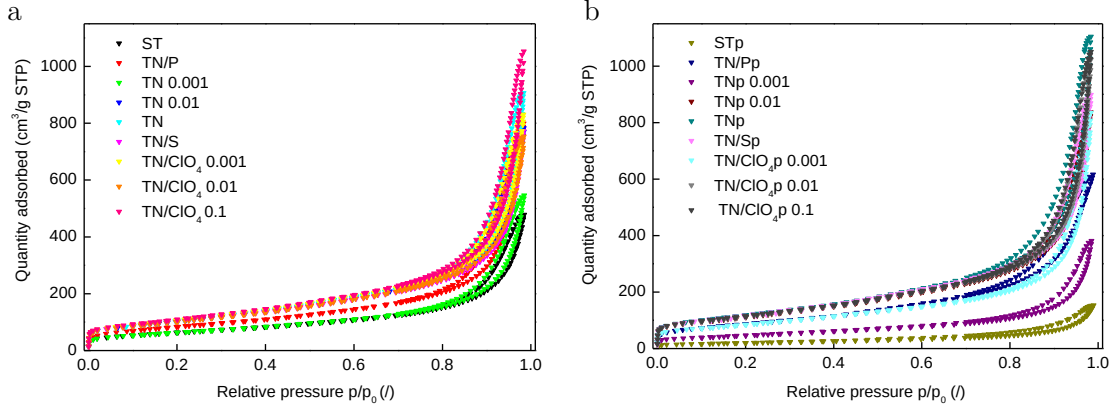


Figure 4.20:  $\text{N}_2$  adsorption-desorption isotherms of a) as-prepared and b) peroxide-treated ST, TN/P, TN 0.001, TN 0.01, TN, TN/S, TN/ $\text{ClO}_4$  0.001, TN/ $\text{ClO}_4$  0.01 and TN/ $\text{ClO}_4$  0.1 materials.

By taking into consideration the SEM analysis of the latter, we can observe that as-prepared, ST (Fig. 4.21a), and peroxide-treated, STp (Fig. 4.22a), material loses its primary morphology due to the thickening of the material and mild coherence of the structure [51], and those reflect on the  $V_p$  and inclination of  $\text{N}_2$  adsorption-desorption isotherms (Fig. 4.20).  $V_p$  of the ST material increases from  $0.75 \text{ cm}^3/\text{g}$  to  $0.81 \text{ cm}^3/\text{g}$  after peroxide treatment. Similar changes in the  $\text{N}_2$  adsorption-desorption isotherms are visible for TNp 0.001. A decrease in the  $V_p$  and  $d_p$ , which is the result of materials coherence, affects  $\text{N}_2$  adsorption-desorption, but it is not as pronounced to be observed in the SEM images (Fig. 4.21c2 and Fig. 4.22c2). In the case of the TN/ $\text{ClO}_4$ p 0.001 higher amount of the small pores exists, in comparison with the TNp 0.001, and therefore  $\text{N}_2$  adsorption-desorption isotherm is similar to the majority of peroxide-treated materials.

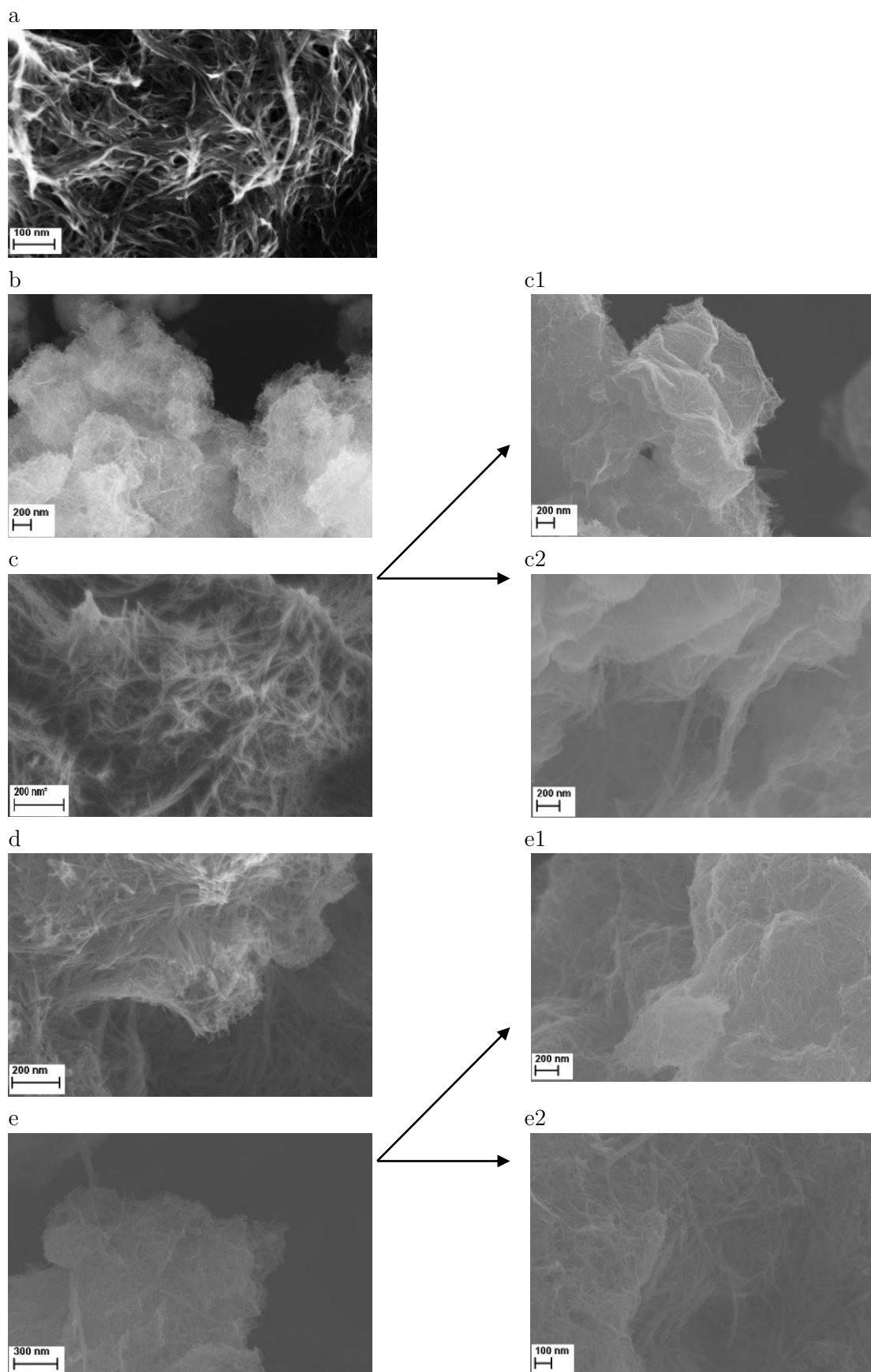


Figure 4.21: SEM images of as-prepared a) ST, b) TN/P, c) TN, c1) TN 0.01, c2) TN 0.001, d) TN/S, e) TN/ClO<sub>4</sub> 0.1, e1) TN/ClO<sub>4</sub> 0.01 and e2) TN/ClO<sub>4</sub> 0.001 materials.

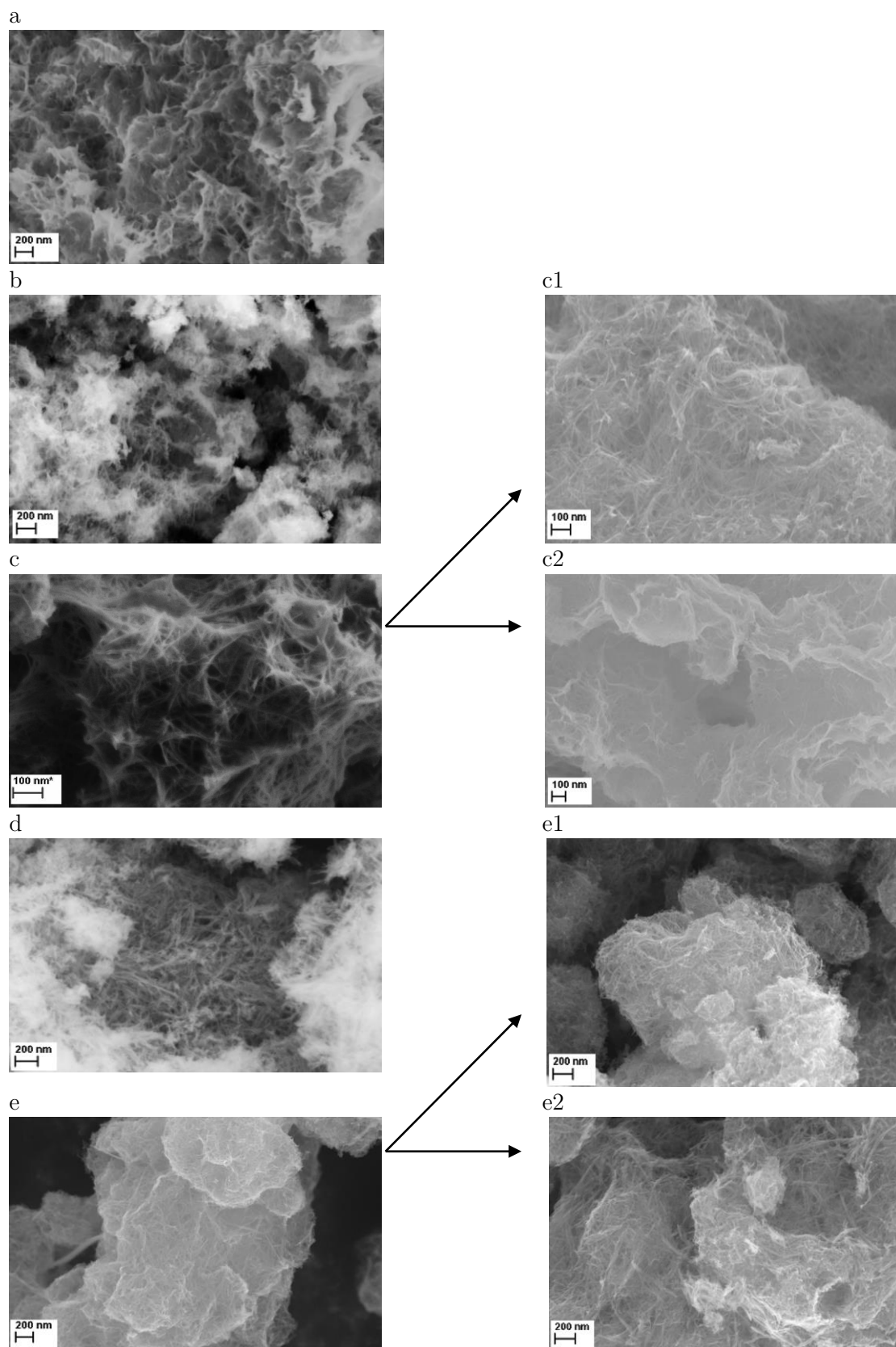


Figure 4.22: SEM images of peroxide-treated a) STp, b) TN/Pp, c) TNp, c1) TNp 0.01, c2) TNp 0.001, d) TN/Sp, e) TN/ClO<sub>4</sub>p 0.1, e1) TN/ClO<sub>4</sub>p 0.01 and e2) TN/ClO<sub>4</sub>p 0.001 materials.

The remaining materials show a preserved, well-developed and randomly oriented tubular structure prior (Fig. 4.21) and after peroxide treatment (Fig. 4.22). In addition to  $\text{Na}^+$  ions in as-prepared and peroxide-treated ST and TN 0.001, SEM/EDS analysis has revealed the presence of 1 wt. % of sulphur and 6 wt. % of phosphorus in the TN/S and TN/P, respectively. That is also confirmed by the FTIR/ATR analysis. The obtained FTIR/ATR spectra of as-prepared materials (Fig. 4.23a) reveals a small band at  $1135\text{ cm}^{-1}$  attributed to the S=O bond stretching, while the broad band at  $1009\text{ cm}^{-1}$  is associated with the stretching vibration of  $\text{PO}_4^{3-}$  groups [116], [117]. A strong band at  $894\text{ cm}^{-1}$  is the result of Ti-O-Na stretching present in the as-prepared and peroxide-treated ST material [118]. All of this suggests the functionalization of the material's surface, which can greatly affect the formation and catalytic activity of peroxo species [8], [17], [81]. By applying DFT calculation, Yoon et al. [17] have proven that competitive binding of phosphate dianion ( $\text{HPO}_4^{2-}$ ) can enhance the catalytic activity of surface peroxo species by creating  $\text{TiOO}-\text{H}(\text{HPO}_4)$  species whose catalytic activity is closer to those of  $\text{Ti}(\eta^2\text{-OOH})$  species, rather than to inactive  $\text{Ti}(\eta^2\text{-OO-})$  species. Nevertheless, calculations are made for TS-1 systems oriented towards the implementation in the cyclohexane oxidation. Wang et al. [8] have reported that  $\text{H}_2\text{SO}_4$  pre-treatment of  $\text{CeO}_2$  enhances the surface acidity of the material leading to higher decomposition of surface peroxo species into  $\bullet\text{OH}$  radicals, and enhanced catalytic activity in the CWPO of azo dyes AO7.

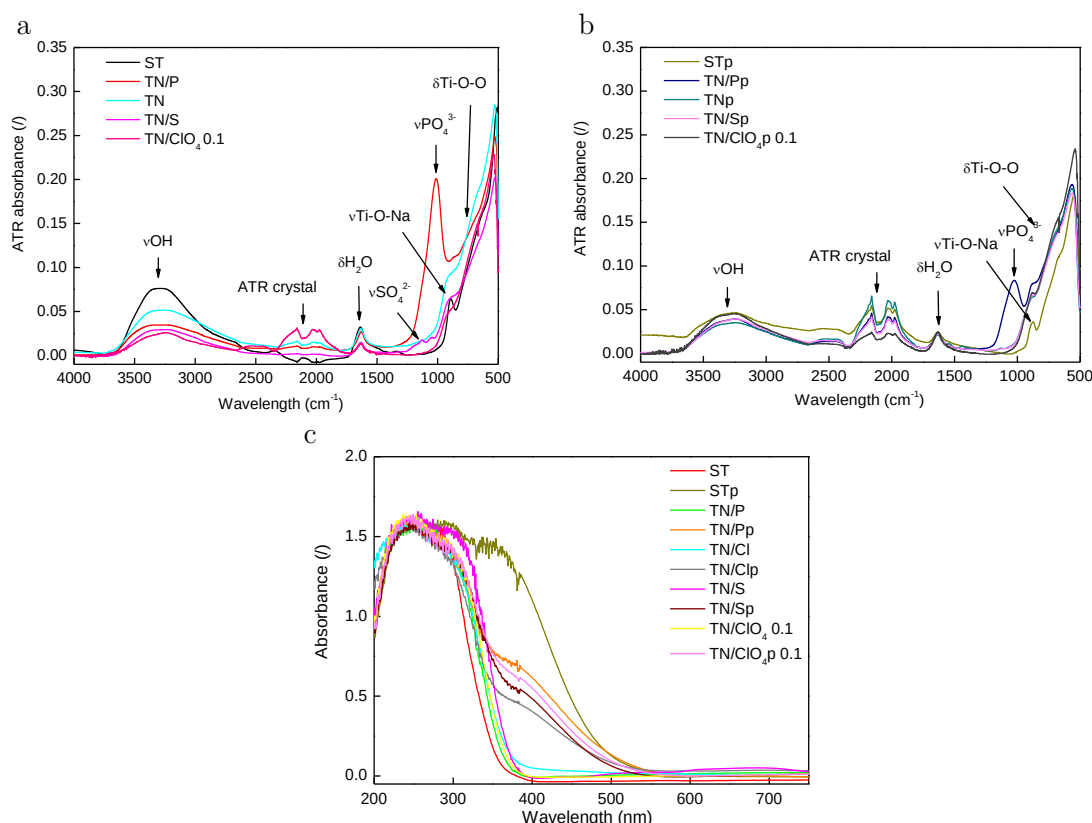


Figure 4.23: FTIR/ATR spectra of a) as-prepared and b) peroxide-treated ST, TN/P, TN, TN/S and  $\text{TN}/\text{ClO}_4\text{ 0.1}$  materials. c) UV/Vis DR spectra of as-prepared and peroxide-treated ST, TN/P, TN, TN/S and  $\text{TN}/\text{ClO}_4\text{ 0.1}$  materials.

The remaining FTIR/ATR assignment is already described in previous sections. Briefly, broad band at  $3420\text{ cm}^{-1}$  is attributed to the -OH stretching and H-bond vibrations, while the band positioned at  $1460\text{ cm}^{-1}$  confirms the presence of  $\text{H}_2\text{O}$  molecules [71], [102]. FTIR/ATR spectra of peroxide-treated materials is similar to those originating from as-

prepared materials with a slightly lower absorption band intensity due to partial washing of  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  from the surface (Fig. 4.23b).

The presence of surface peroxo species has been confirmed with UV/Vis DR analysis. From the obtained spectra (Fig. 4.23c) we can observe that the intensity of the band correlated with the  $\text{O}^{2-} \rightarrow \text{Ti}^{4+}$  LMCT is similar in all as-prepared materials, and only in the case of STp it shifts to the higher wavelength region. Although this kind of spectra can be attributed to the changes in the band gap energy [67], pH changes can also affect visible light absorption of surface peroxo species [81], and in some cases bridged  $\text{H}_2\text{O}_2$  and peroxo species [94], so it would be more accurate to state that these changes are just showing better interaction between surface peroxo species and the material itself. As it can be observed from  $\text{O}_2$  TPD/MS analysis, STp contains the highest amount of desorbed oxygen (Table 4.10), namely  $6.9 \times 10^{-6} \text{ mol/m}^2$ , so as-obtained spectra can be directly correlated with the LMCT interactions between the surface peroxo species and the material itself [85].

Similar spectra is obtained in the case of TNp 0.001 (Fig. 4.24c), which, as already mentioned, contains 6 wt. % of  $\text{Na}^+$  ions in the structure. Therefore, FTIR/ATR spectra (Fig. 4.24a,b) also contain a strong absorption band at  $894 \text{ cm}^{-1}$  as a result of Ti-O-Na stretching [118]. In addition, the FTIR/ATR spectra of TNp 0.01 material shows that the intensity of the band correlated with the presence of -OH groups is more pronounced than in the case of TNp, meaning that a higher amount of peroxo species should be formed on its surface. UV/Vis DR analysis has confirmed these observations. From Fig. 4.24c we can observe that the intensity of the absorbance peak at 420 nm, attributed to the presence of surface peroxo species, is more pronounced in the case of TNp 0.01 than in the case of TNp itself [51], [71].

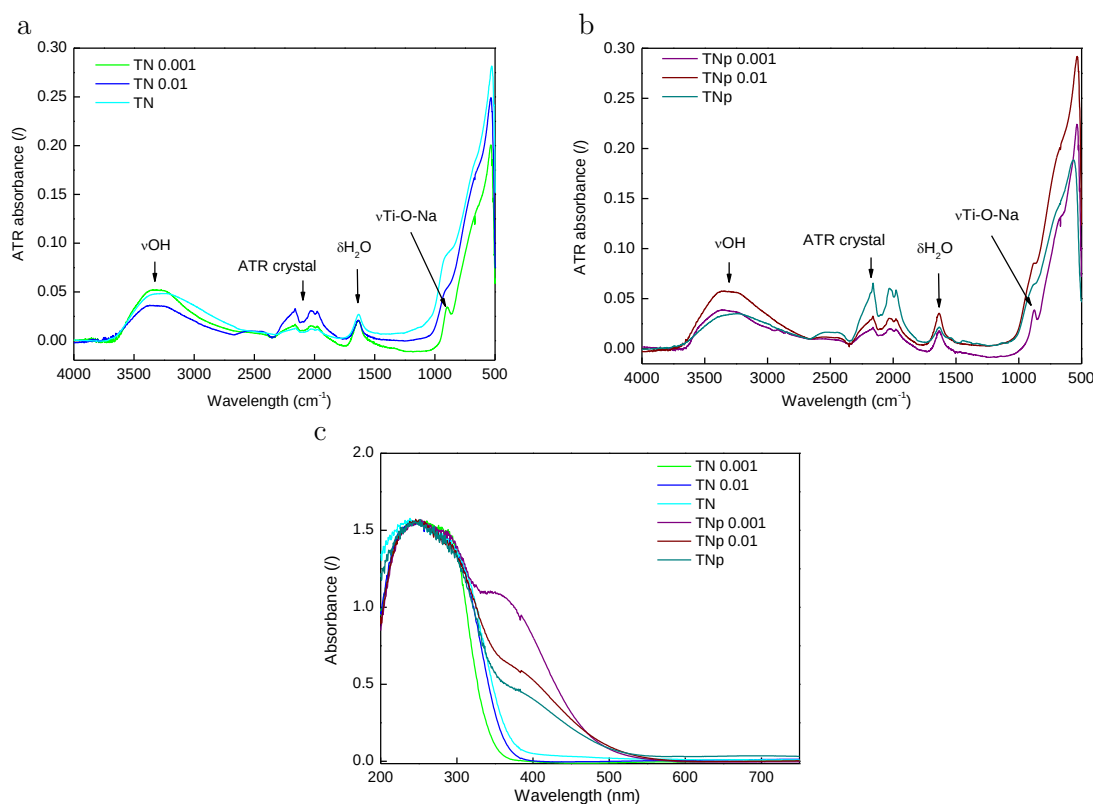


Figure 4.24: FTIR/ATR spectra of a) as-prepared and b) peroxide-treated TN 0.001, TN 0.01 and TN materials. c) UV/Vis DR spectra of as-prepared and peroxide-treated TN 0.001, TN 0.01 and TN materials.

From O<sub>2</sub> TPD/MS analysis TNp 0.01 and TNp contain  $2.0 \times 10^{-5}$  mol/m<sup>2</sup> and  $1.4 \times 10^{-5}$  mol/m<sup>2</sup> of peroxo species, respectively, although there are no observable differences in complete TGA weight loss (Fig. 4.25a), namely ~17 wt. % and ~16 wt. % for TN 0.01 and TN, respectively. Similar weight loss is also at 140°C and 300°C. In the first temperature region weight loss issues ~13 wt. % and ~12 wt. %, while in the second temperature region ~16 wt. % and ~15 wt. % for TN 0.01 and TN, respectively. Apparently, such small differences can influence the amount of formed surface peroxo species, although other parameters are rather more important which will be discussed in the upcoming section. The highest weight loss is observed in the case of TN 0.001 material with ~19 wt. % loss at 750°C, ~17 wt. % at 300°C and ~15 wt. % at 140°C. Therefore, peroxide-treated TNp 0.001 contains the highest amount of surface peroxo species (Table 4.10) among HCl washed material samples. This can be attributed to the presence of Na<sup>+</sup> which contributes to higher hydration degree and peroxo species content [119].

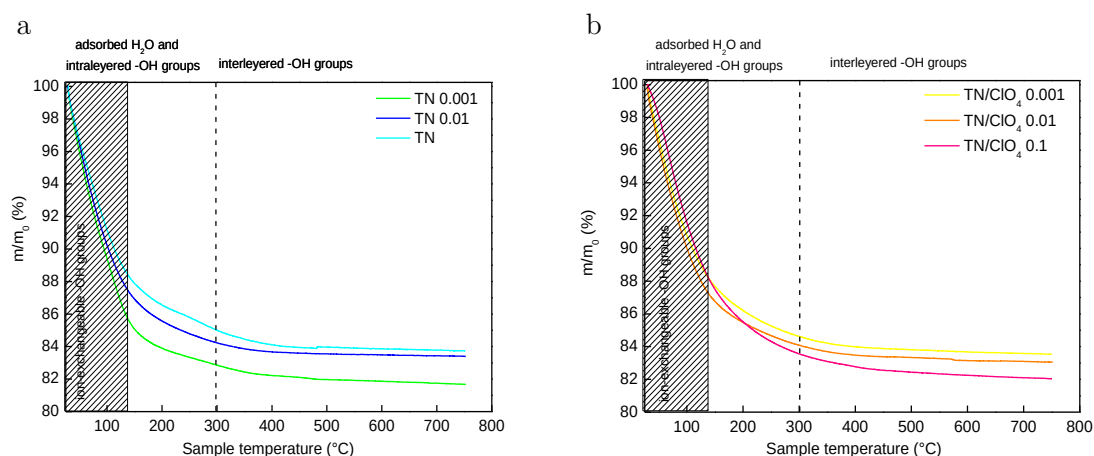


Figure 4.25: TGA profiles of as-prepared a) TN 0.001, TN 0.01, TN and b) TN/ClO<sub>4</sub> 0.001, TN/ClO<sub>4</sub> 0.01, TN/ClO<sub>4</sub> 0.1 materials.

TGA spectra of HClO<sub>4</sub> washed materials (Fig. 4.25b) are in good correspondence with those of HCl. In the first temperature region, up to 140°C, weight loss is ~12>13<12 wt. % for TN/ClO<sub>4</sub> 0.001, TN/ClO<sub>4</sub> 0.01 and TN/ClO<sub>4</sub> 0.1, respectively. In the second temperature region (T=300°C) weight loss is approximately ~15>14>13 wt. %, while complete weight loss, up to 750°C, is ~16>17>18 wt. % for the above-enumerated materials, respectively. In correspondence with complete TGA weight loss is the amount of oxygen desorbed from the peroxide-treated materials during O<sub>2</sub> TPD/MS analysis, namely  $1.6 \times 10^{-5} < 2.3 \times 10^{-5} < 2.6 \times 10^{-5}$  mol/m<sup>2</sup> for TN/ClO<sub>4</sub> 0.001, TN/ClO<sub>4</sub> 0.01 and TN/ClO<sub>4</sub> 0.1, respectively. Nevertheless, by means of UV/Vis DR (Fig. 4.26c) analysis TN/ClO<sub>4</sub>p 0.001 and TN/ClO<sub>4</sub>p 0.01 possess an absorption peak at 420 nm with a similar intensity, while in the case of TN/ClO<sub>4</sub>p 0.1, this peak has a lower intensity. This is direct evidence that by means of the UV/Vis DR technique, it is not possible to quantify the amount of surface peroxo species, or distinctively know which peroxo species are present, but rather only to confirm the presence of surface peroxo species and their interaction (LMCT) with the surface of the material. FTIR/ATR spectra of as-prepared (Fig. 4.26a) and peroxide-treated (Fig. 4.26b) materials are similar to those previously described, with no visible presence of foreign ions.

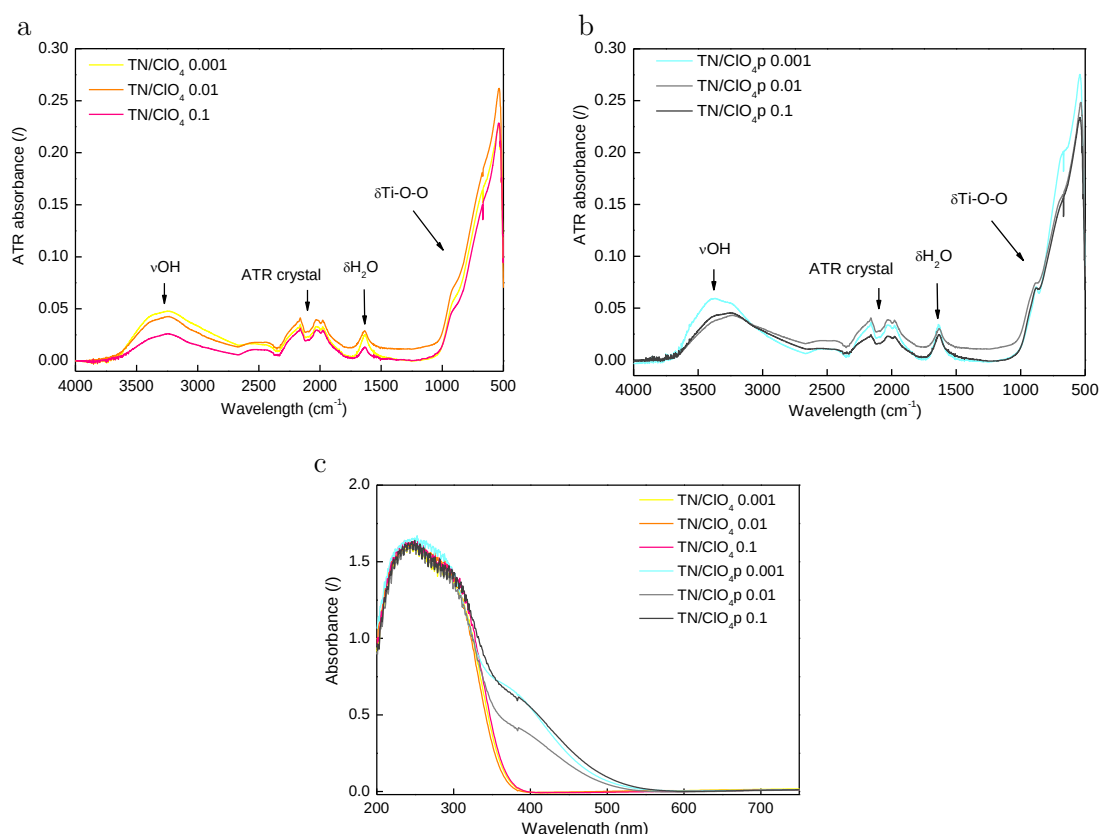


Figure 4.26: FTIR/ATR spectra of a) as-prepared and b) peroxide-treated TN/ClO<sub>4</sub> 0.001, TN/ClO<sub>4</sub> 0.01 and TN/ClO<sub>4</sub> 0.1 materials. c) UV/Vis DR spectra of as-prepared and peroxide-treated TN/ClO<sub>4</sub> 0.001, TN/ClO<sub>4</sub> 0.01 and TN/ClO<sub>4</sub> 0.1 materials.

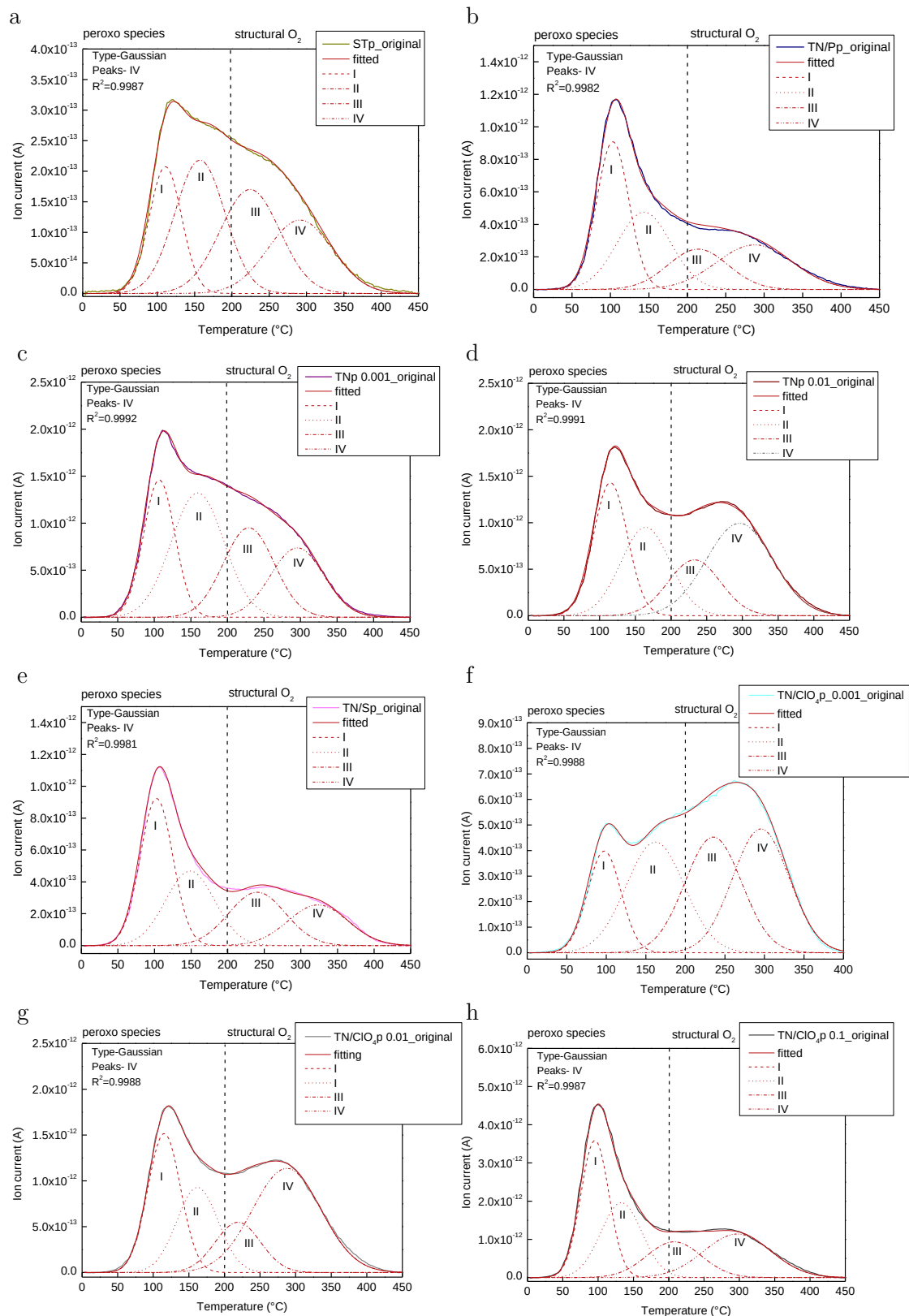
Quantification of surface peroxo species, by means of oxygen desorbed during O<sub>2</sub> TPD/MS analysis, has shown that the amount of O<sub>2</sub> per m<sup>2</sup> of the materials surface highly varies. Obtained values are listed in Table 4.10. As already mentioned, STp and TNp 0.001, which contain Na<sup>+</sup> in their structure, have the highest amount of desorbed O<sub>2</sub>, which can be due to the stabilizing effect of Na<sup>+</sup>. Sodium ions enable stronger electrophilic interaction with surface peroxo species, therefore increasing their number on the catalyst surface [120]. In addition, from the SEM images, as well as from N<sub>2</sub> adsorption-desorption isotherms, it has been confirmed that the morphology of above-mentioned materials completely changes and this desorbed O<sub>2</sub> can also be attributed to those structurally bonded which is, as already proposed in Section 4.1.2., desorbed in the region above 200°C. TNp and TN/Sp contain exactly the same amount of O<sub>2</sub>, namely 1.4\*10<sup>-5</sup> mol/m<sup>2</sup>, although it has been proposed that the presence of SO<sub>4</sub><sup>2-</sup> should increase the amount of surface peroxo species [17]. In contrast, peroxide-treated material washed in H<sub>3</sub>PO<sub>4</sub> (TN/Pp) contains a higher amount of O<sub>2</sub> than the sample washed in the 0.1 M HClO<sub>4</sub> (which is the strongest acid and should provide the highest protonation degree), so apparently the presence of PO<sub>4</sub><sup>3-</sup> on the surface of the material affects the formation and stability of surface peroxo species, as shown by Wang et al. [8]. TN/HClO<sub>4</sub>p 0.001 has a similar amount of desorbed O<sub>2</sub>, such as in the case of TNp and TN/Sp, therefore showing that ten times stronger acid diluted to the lowest concentration (0.001 M) can provide the same effect as 0.1 M HCl and H<sub>2</sub>SO<sub>4</sub>.

Table 4.10: Amount of oxygen obtained by means of TPD/MS analysis and surface acidity expressed as LAS and BAS for as-prepared and peroxide-treated ST, TN/P, TN 0.001, TN 0.01, TN, TN/S, TN/ClO<sub>4</sub> 0.001, TN/ClO<sub>4</sub> 0.01 and TN/ClO<sub>4</sub> 0.1 materials.

| Sample                                              | LAS<br>(mmol/g) | BAS<br>(mmol/g) | BAS/LAS<br>(/) | O <sub>2</sub><br>(mol/g)*10 <sup>-4</sup> | O <sub>2</sub><br>(mol/m <sup>2</sup> )*10 <sup>-6</sup> |
|-----------------------------------------------------|-----------------|-----------------|----------------|--------------------------------------------|----------------------------------------------------------|
| ST                                                  | /               | /               | /              | /                                          | /                                                        |
| STp                                                 | /               | /               | /              | 16.5                                       | 6.9                                                      |
| TN/P                                                | 1.097           | 0.223           | 0.20           | /                                          | /                                                        |
| TN/Pp                                               | 0.145           | 0               | 0              | 8.8                                        | 2.8                                                      |
| TN 0.001                                            | 0.521           | 0.061           | 0.03           | /                                          | /                                                        |
| TNp 0.001                                           | 0.922           | 0.038           | 0.04           | 12.4                                       | 7.3                                                      |
| TN 0.01                                             | 0.722           | 0.00(3)         | 0              | /                                          | /                                                        |
| TNp 0.01                                            | 1.019           | 0.00(5)         | 0              | 8.1                                        | 2.0                                                      |
| TN                                                  | 0.067           | 0.00(3)         | 0              | /                                          | /                                                        |
| TNp                                                 | 1.008           | 0.446           | 0.44           | 6.0                                        | 1.4                                                      |
| TN/S                                                | 1.355           | 0.189           | 0.14           | /                                          | /                                                        |
| TN/Sp                                               | 1.873           | 0.292           | 0.16           | 6.2                                        | 1.4                                                      |
| TN/ClO <sub>4</sub> 0.001                           | 0.885           | 0.00(1)         | 0              | /                                          | /                                                        |
| TN/ClO <sub>4</sub> p 0.001                         | 0.318           | 0.037           | 0.11           | 5.1                                        | 1.6                                                      |
| TN/ClO <sub>4</sub> 0.01                            | 1.031           | 0.055           | 0.05           | /                                          | /                                                        |
| TN/ClO <sub>4</sub> p 0.01                          | 0.443           | 0.219           | 0.49           | 9.5                                        | 2.3                                                      |
| TN/ClO <sub>4</sub> 0.1                             | 0.050           | 0.051           | 0.98           | /                                          | /                                                        |
| TN/ClO <sub>4</sub> p 0.1                           | 1.301           | 0.018           | 0.01           | 10.8                                       | 2.6                                                      |
| TN/ClO <sub>4</sub> p 0.01_5 <sup>th</sup><br>cycle | /               | /               | /              | 5.3                                        | 1.3                                                      |

By fitting the obtained O<sub>2</sub> TPD/MS profiles (Fig. 4.27) it has been observed that also four different desorption peaks are present. Accompanied peak position, amplitude and FWHM are listed in Table 4.11, while the information regarding the TNp sample can be found in Section 4.1.2. (Fig. 4.6b, Table 4.2). In the case of all peroxide-treated materials, the first peak lies in the temperature region from 95–115°C, followed by the second peak between 133–162°C, the third between 207–240°C and the fourth between 287–323°C. Nevertheless, accompanied integrated areas, as well as the shape O<sub>2</sub> TPD/MS curve, vary drastically. Profiles belonging to STp (Fig. 4.27a) and TNp 0.001 (Fig. 4.27c) are concentrated in the I and II temperature region, without a nicely defined shape. As already mentioned, we can assume that this region is attributed to the surface peroxo species, which is in good correspondence with the obtained UV/Vis DR spectra showing stronger LTMC in both cases. In contrast to them, TN/ClO<sub>4</sub>p 0.001 (4.27f) has a completely different curve shape, therefore desorbed O<sub>2</sub>, as we assume, can be attributed to the structural O<sub>2</sub> or peroxo species located between the inner layers of the tubular shells where interlayered -OH groups are placed (as mentioned and described in Section 4.1.2.). Although SEM analysis did not show morphological changes, S<sub>BET</sub> of the peroxide-treated materials decreases drastically from 390 m<sup>2</sup>/g to 310 m<sup>2</sup>/g, accompanied with an increase of d<sub>p</sub> from 11.8 nm to 15.0 nm, confirming partial disintegration of the material and loss of small pores. Therefore, peroxide treatment of the TN/ClO<sub>4</sub> 0.001 has caused disintegration of the material and this can occur only if the atomic structure of the material can be changed [120]. In the case of remaining materials O<sub>2</sub> TPD/MS profiles are quite similar, especially in the case of TNp and TN/ClO<sub>4</sub>p 0.01, as well as TN/Sp and TN/ClO<sub>4</sub>p

0.1. Therefore, we can assume that similar changes in the materials have been induced, from the surface peroxo species formation to the textural properties as already described.



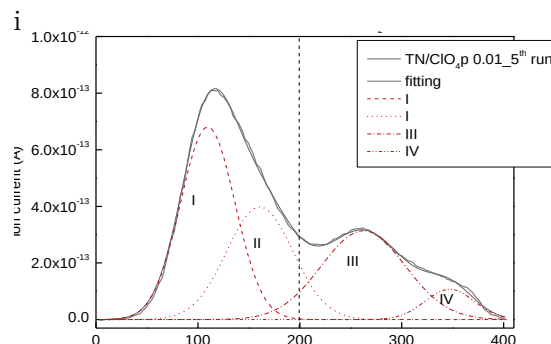


Figure 4.27: Fitted O<sub>2</sub> TPD/MS profiles for peroxide-treated a) STp, b) TN/Pp, c) TNp 0.001, d) TNp 0.01, e) TN/Sp, f) TN/ClO<sub>4</sub>p 0.001, g) TN/ClO<sub>4</sub>p 0.01 and h) TN/ClO<sub>4</sub>p 0.1 materials. i) Fitted O<sub>2</sub> TPD/MS profiles for peroxide-treated TN/ClO<sub>4</sub>p 0.01 used in 5 consecutive runs. Dashed lines represent Gaussian fits.

In the case of TN/ClO<sub>4</sub>p 0.01 sample, which has shown a slightly better catalytic activity (see Section 4.3.2.), O<sub>2</sub> TPD/MS spectra was also measured after 5 consecutive runs (Fig. 4.27i). Prior to use the amount of desorbed O<sub>2</sub> was  $2.3 \times 10^{-6}$  mol O<sub>2</sub>/m<sup>2</sup>, and it decreased for 56 % ( $1.3 \times 10^{-6}$  mol O<sub>2</sub>/m<sup>2</sup>) during 5 consecutive runs. Nevertheless, from the fitted O<sub>2</sub> TPD/MS spectra it can be observed that this decrease mostly occurs in the second temperature region (above 200°C), while in the lower temperature region the amount of desorbed O<sub>2</sub> remains almost constant. This is especially observed in the case of the first peak with the amount of desorbed O<sub>2</sub> of  $5.9 \times 10^{-7}$  mol O<sub>2</sub>/m<sup>2</sup> and  $5.2 \times 10^{-7}$  mol O<sub>2</sub>/m<sup>2</sup> prior and after the use, respectively. Since there were no observed changes in the catalytic activity, this part can be attributed to the catalytically active peroxo species.

Surface acidity for all materials, presented as BAS and LAS, is listed in Table 4.10 (values for TNp material can be found in Section 4.1.2., Table 4.2). From the obtained values we can observe that, as already mentioned, applied peroxide treatment usually increases BAS and LAS values due to tearing of surface -OH groups. The formation of peroxo species can influence the increase of BAS, while exposed unoccupied Ti<sup>4+</sup> are responsible for the enhancement of LAS [106]. Nevertheless, we cannot exclude the possibility that the remaining surface -OH groups, as well as surface lattice oxygen, do not contribute to the BAS, similar as in the CeO<sub>2</sub> systems [121]. In the case of sodium substituted ST and STp materials no distinctive peaks have been obtained during pyridine adsorption DRIFT analysis, therefore no values for LAS and BAS have been presented. Kitana et al. [107] have shown that the protonation step in the preparation of TiO<sub>2</sub>-based nanotubes is necessary in order to create surface LAS and BAS, therefore the removal of Na<sup>+</sup> ions from the structure of the material is a necessary step for the increase of surface acidity. HCl washed materials all follow the increase in the LAS and BAS, which is expected due to the effects described above, while HClO<sub>4</sub> washed material samples mostly show a decrease in either LAS and BAS after peroxide treatment, similar to the H<sub>3</sub>PO<sub>4</sub> washed material. The presence of PO<sub>4</sub><sup>2-</sup> surface impurities increases BAS of the as-prepared sample, which are after H<sub>2</sub>O<sub>2</sub> treatment partially removed and “neutralized” in the presence of surface peroxo species by forming complexes described by Yoon et al. [17]. Surface (TiOO-H(HPO<sub>4</sub>)) complex can be responsible for the BAS decrease in the peroxide-treated TN/Pp material [122]. In the case of HClO<sub>4</sub> materials peroxide treatment is influencing the increase in BAS and decrease in LAS which can be both due to the prevalent presence of surface peroxo species and exposed surface bulk O<sub>2</sub> in comparison to unoccupied Ti<sup>4+</sup> sites. H<sub>2</sub>SO<sub>4</sub> washed material has the most pronounced LAS prior and after peroxide treatment due to the presence of surface-bonded SO<sub>4</sub><sup>2-</sup>. Namely, the existence of covalent S=O bonds

is responsible for the generation of surface acidity and therefore sulfonation, or washing in  $\text{H}_2\text{SO}_4$ , are some of the most applied ways to ensure the creation of LAS and BAS on the surface of  $\text{TiO}_2$ -based materials [123].

Table 4.11: Peak fit parameters for Gaussian fits of peroxide-treated ST, TN/P, TN 0.001, TN 0.01, TN, TN/S,  $\text{TN}/\text{ClO}_4$  0.001,  $\text{TN}/\text{ClO}_4$  0.01 and  $\text{TN}/\text{ClO}_4$  0.1 materials and accompanied integrated area.

| Sample                                        | Peak | Position | Amplitude            | FWHM | Area (%) |
|-----------------------------------------------|------|----------|----------------------|------|----------|
| STp                                           | I    | 111      | $2.1 \cdot 10^{-13}$ | 51   | 19       |
|                                               | II   | 157      | $2.2 \cdot 10^{-13}$ | 79   | 31       |
|                                               | III  | 224      | $1.7 \cdot 10^{-13}$ | 94   | 28       |
|                                               | IV   | 291      | $1.2 \cdot 10^{-13}$ | 102  | 22       |
| TN/Pp                                         | I    | 103      | $9.1 \cdot 10^{-13}$ | 49   | 32       |
|                                               | II   | 143      | $4.8 \cdot 10^{-13}$ | 82   | 28       |
|                                               | III  | 214      | $2.5 \cdot 10^{-13}$ | 92   | 17       |
|                                               | IV   | 287      | $2.7 \cdot 10^{-13}$ | 117  | 23       |
| TNp 0.001                                     | I    | 107      | $1.5 \cdot 10^{-12}$ | 50   | 23       |
|                                               | II   | 159      | $1.3 \cdot 10^{-12}$ | 85   | 34       |
|                                               | III  | 229      | $9.5 \cdot 10^{-13}$ | 82   | 24       |
|                                               | IV   | 295      | $7.4 \cdot 10^{-13}$ | 86   | 19       |
| TNp 0.01                                      | I    | 115      | $1.4 \cdot 10^{-12}$ | 56   | 25       |
|                                               | II   | 164      | $9.5 \cdot 10^{-13}$ | 81   | 24       |
|                                               | III  | 233      | $6.0 \cdot 10^{-13}$ | 86   | 16       |
|                                               | IV   | 296      | $9.9 \cdot 10^{-13}$ | 110  | 35       |
| TNp                                           | I    | 107      | $9.6 \cdot 10^{-13}$ | 51   | 39       |
|                                               | II   | 159      | $4.7 \cdot 10^{-13}$ | 62   | 23       |
|                                               | III  | 213      | $3.1 \cdot 10^{-13}$ | 51   | 13       |
|                                               | IV   | 262      | $4.9 \cdot 10^{-13}$ | 63   | 25       |
| TN/Sp                                         | I    | 103      | $9.2 \cdot 10^{-13}$ | 53   | 35       |
|                                               | II   | 149      | $4.7 \cdot 10^{-13}$ | 79   | 26       |
|                                               | III  | 240      | $3.4 \cdot 10^{-13}$ | 91   | 22       |
|                                               | IV   | 323      | $2.5 \cdot 10^{-13}$ | 93   | 17       |
| TN/ $\text{ClO}_4$ p 0.001                    | I    | 98       | $3.9 \cdot 10^{-13}$ | 49   | 14       |
|                                               | II   | 162      | $4.3 \cdot 10^{-13}$ | 87   | 28       |
|                                               | III  | 235      | $4.5 \cdot 10^{-13}$ | 85   | 28       |
|                                               | IV   | 296      | $4.8 \cdot 10^{-13}$ | 84   | 30       |
| TN/ $\text{ClO}_4$ p 0.01                     | I    | 115      | $1.5 \cdot 10^{-12}$ | 54   | 26       |
|                                               | II   | 162      | $9.3 \cdot 10^{-13}$ | 68   | 21       |
|                                               | III  | 218      | $5.5 \cdot 10^{-13}$ | 75   | 13       |
|                                               | IV   | 287      | $1.1 \cdot 10^{-12}$ | 113  | 40       |
| TN/ $\text{ClO}_4$ p 0.1                      | I    | 95       | $3.6 \cdot 10^{-12}$ | 47   | 33       |
|                                               | II   | 133      | $1.9 \cdot 10^{-12}$ | 68   | 26       |
|                                               | III  | 207      | $9.4 \cdot 10^{-12}$ | 91   | 16       |
|                                               | IV   | 297      | $1.1 \cdot 10^{-12}$ | 112  | 25       |
| TN/ $\text{ClO}_4$ p 0.01_5 <sup>th</sup> run | I    | 109      | $6.8 \cdot 10^{-13}$ | 62   | 40       |
|                                               | II   | 160      | $3.9 \cdot 10^{-13}$ | 76   | 27       |
|                                               | III  | 262      | $3.1 \cdot 10^{-13}$ | 96   | 27       |
|                                               | IV   | 346      | $1.0 \cdot 10^{-13}$ | 56   | 6        |

### 4.3.2 Catalytic performance of acid and peroxide-treated TN materials in the CWPO of MO

Catalytic performance of all as-prepared and peroxide-treated materials was tested in the CWPO of 50 mg/L MO solution under ambient conditions. Results are shown in Fig. 4.28. The MO conversion increased over peroxide-treated materials (Fig. 4.28b) in the following order  $3 > 39 > 43 > 54 > 72$  % for STp, TN/Pp, TN/Sp, TN/ClO<sub>4</sub>p 0.1 and TNp, respectively. The lowest MO conversion, occurring in the case of STp, is negligible improvement in comparison to the MO conversion occurred in the presence of unmodified (Fig. 4.28a) ST material, as well as in blank experiments, therefore this material shows no catalytic activity. As already mentioned, STp contains a high amount of Na<sup>+</sup> ions in the structure and its electrophilic centres can neutralize negatively charged peroxy species [120]. In addition, a relatively low  $S_{\text{BET}}$  of 233 m<sup>2</sup>/g can slow down the usually efficient transport of MO, H<sub>2</sub>O<sub>2</sub> and degradation products to and from the surface of material [51], [71]. Therefore, the highest amount of peroxy species and desorbed O<sub>2</sub>, quantified by means of O<sub>2</sub> TPD/MS analysis, does not enable this material to perform the best in the CWPO experiments. The amount of deposited carbon (Table 4.12) is therefore relatively low, namely 0.02 wt. %.

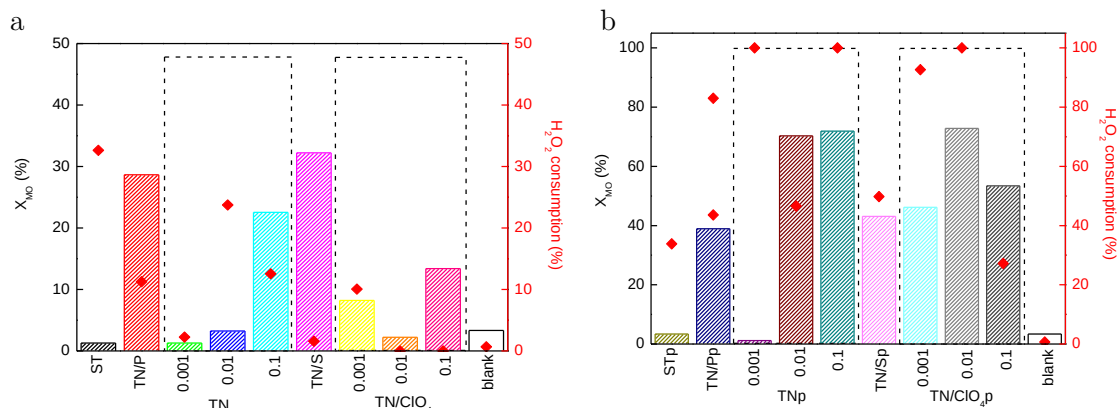


Figure 4.28: MO conversion and H<sub>2</sub>O<sub>2</sub> consumption obtained at 25°C for a) as-prepared and b) peroxide-treated ST, TN/P, TN 0.001, TN 0.01, TN, TN/S, TN/ClO<sub>4</sub> 0.001, TN/ClO<sub>4</sub> 0.01 and TN/ClO<sub>4</sub> 0.1 materials. Test duration was 240 min and a stoichiometric amount of H<sub>2</sub>O<sub>2</sub> was used.

TN/Pp and TN/Sp show better performance in comparison to STp, but SEM/EDS and FTIR/ATR analyses have confirmed the presence of SO<sub>4</sub><sup>2-</sup> (~1 wt. % of sulphur) and PO<sub>4</sub><sup>3-</sup> (~6 wt. % of phosphorous) ions on the material's surface. That can influence the formation and activity of peroxy species, as well as the surface acidity of the surface. As already mentioned, H<sub>2</sub>SO<sub>4</sub> treatment is usually applied in order to increase the surface acidity of TiO<sub>2</sub>-based materials, which, although it is favourable in some reaction [123], causes high MO removal in the presence of as-prepared materials and this is mostly due to adsorption since H<sub>2</sub>O<sub>2</sub> consumption is negligible (Fig. 4.28a). pH<sub>pzc</sub> for as-prepared materials is at ~2.8 and ~2.9 for TN/S and TN/P, respectively, while starting pH of the reaction solution is around ~5.2. In that manner the surface of the material should be positively charged [51] which can attract a negatively charged sulphonic group of the MO molecule. An especially high amount of surface deposited carbon, namely 0.47 wt. %, is observed for TN/Sp, while TN/Pp contains only 0.16 wt. % given as a difference between the fresh and used material.

Catalytic performance of peroxide-treated TN/ClO<sub>4</sub>p 0.1 material was therefore the highest in comparison with above-mentioned materials, with only ~13 % of MO removal

achieved in the presence of as-prepared TN/ $\text{ClO}_4$  0.1. Obtained catalytic performance was closest to the one observed with the use of TNp, therefore additional materials washed in 0.001 M and 0.01 M HCl and  $\text{HClO}_4$  were made additionally. STp, TN/Pp and TN/Sp were also ruled due to the presence of foreign ions which influence the overall catalytic activity and exclude the contribution of only peroxo species. From the obtained MO conversion values we can observe that catalytic activity of TNp 0.001, as well as of TN 0.001, was rather similar to those of STp and ST. This is not surprising since TN 0.001 and TNp 0.001 also contain  $\text{Na}^+$  in their structure, as well as really low  $S_{\text{BET}}$  of  $230 \text{ m}^2/\text{g}$  and  $170 \text{ m}^2/\text{g}$  for TN 0.001 and TNp 0.001, respectively. In addition, TNp 0.001 material contains an even higher amount of desorbed  $\text{O}_2$  and surface peroxo species in comparison to STp (Table 4.10), but  $\text{H}_2\text{O}_2$  consumption in the presence of TNp 0.001 is 100 %, which can be due to the smaller amount of  $\text{Na}^+$  in the structure of the materials, therefore possible induced formation of new peroxo species can occur. In contrast, a TN/ $\text{ClO}_4$ p 0.001 material achieves  $\sim 46$  % of MO conversion, while the contribution of the as-prepared TN/ $\text{ClO}_4$  0.001 is only  $\sim 8$  %. Washing in 0.001 M  $\text{HClO}_4$  enables sufficient ion-exchange therefore  $\text{Na}^+$  ions have not been detected in the as-prepared and peroxide-treated materials. The amount of desorbed  $\text{O}_2$  is much lower, namely  $1.6 \cdot 10^{-5} \text{ mol O}_2/\text{m}^2$ , but  $S_{\text{BET}}$  is almost twice higher ( $310 \text{ m}^2/\text{g}$ ), with the large  $V_p$  of  $1.40 \text{ cm}^3/\text{g}$  and  $d_p$  of  $15.0 \text{ nm}$ . Nevertheless, the amount of the deposited carbon is also rather high,  $0.48 \text{ wt. \%}$ , meaning that partially degraded products have a higher tendency to adsorb on the catalyst surface [47], in combination with competitive  $\text{H}_2\text{O}_2$  adsorption which resulted in an almost  $\sim 95$  %  $\text{H}_2\text{O}_2$  conversion [6]. TNp 0.01 and TN/ $\text{ClO}_4$ p 0.01 achieve  $\sim 70$  % and  $\sim 73$  % of MO conversion, which is similar to those of TNp. In addition, the contribution of the support (as-prepared materials) is only  $\sim 3$  % and  $\sim 2$  %, but by comparing the amount of deposited carbon TNp 0.01 contains  $0.49 \text{ wt. \%}$ , while TN/ $\text{ClO}_4$ p 0.01 only  $0.28 \text{ wt. \%}$ . Therefore, the activity of the TN/ $\text{ClO}_4$ p 0.01 sample is closer to that of the first catalytically most active material, TNp. They are both optimally dissolved during peroxide treatment achieving similar  $S_{\text{BET}}$ ,  $V_p$  and  $d_p$  of peroxide-treated materials (Table 4.1 and Table 4.9). A similar effect can be seen in BAS/LAS ratio of 0.44 and 0.49 for TNp and TN/ $\text{ClO}_4$ p 0.01, respectively. Although UV/Vis DR peak is comparable for both materials, meaning similar LMTC, the amount of desorbed  $\text{O}_2$  and surface peroxo species is almost twice higher, namely  $2.3 \cdot 10^{-5} \text{ mol O}_2/\text{m}^2$ , in the case of TN/ $\text{ClO}_4$ p 0.01. In addition, adsorption in the presence of TN/ $\text{ClO}_4$ p 0.01 material was only  $\sim 1$  % during 4 h experiments, which is  $\sim 3$  % lower than in the case of the TNp material.

Due to the fact that both materials exhibited similar textural, morphological and surface properties, as well as catalytic activity in the CWPO of MO conducted at  $25^\circ\text{C}$  with a stoichiometric amount of  $\text{H}_2\text{O}_2$ , a detailed analysis was done in order to gain insight between  $\text{H}_2\text{O}_2$  usage and MO conversion. Experiments were carried out at  $25^\circ\text{C}$  with 50 % and 100 % of  $\text{H}_2\text{O}_2$  surplus (Fig. 4.29a). Activity of the TNp material decreases as the amount of  $\text{H}_2\text{O}_2$  in starting suspension increases, probably due to the degradation of surface peroxo species and enhanced carbon deposition, as seen in Table 4.12. In addition,  $\text{H}_2\text{O}_2$  consumption decreases with the increase of the initial  $\text{H}_2\text{O}_2$  amount, which in combination with a high amount of deposited carbon confirms the competitive adsorption on the catalyst surface and that the oxidation of the organic substances through radical mechanism in the presence of surface peroxo species is more efficient with a low  $\text{H}_2\text{O}_2$  amount (in comparison with the organic pollutant) [6], [17]. In contrast, catalytic activity of the TN/ $\text{ClO}_4$ p 0.01 material increased with the increase of the starting amount of  $\text{H}_2\text{O}_2$ . Nevertheless,  $\text{H}_2\text{O}_2$  consumption decreases and the amount of deposited carbon increases also showing competitive adsorption on the catalyst surface. Therefore, the sample was also tested at  $40^\circ\text{C}$  with a double stoichiometric amount of  $\text{H}_2\text{O}_2$ . In the first 90 min of the reaction 94

% of MO conversion was achieved, while the amount of deposited carbon was only 0.32 wt. %. Therefore, by increasing the temperature for 15°C enhanced adsorption/desorption of the reactants and degradation products from the materials surface was achieved. Results from the IC analysis have confirmed that 6.12 mg/L of  $\text{SO}_4^{2-}$  and 2.95 mg/L of  $\text{NO}_3^-$  are formed during MO degradation, meaning that ~40 wt. % and ~31 wt. % of the S and N containing parts of the molecule have been successfully converted into ionic products. As shown in Fig. 4.29b, catalytic stability of the TN/ $\text{ClO}_4$  0.01 was tested during 5 consecutive runs with 100 % surplus  $\text{H}_2\text{O}_2$  at 40°C. The achieved MO conversion, as well as  $\text{H}_2\text{O}_2$  consumption remained unchanged. ~93 % of MO conversion and ~40 % of  $\text{H}_2\text{O}_2$  consumption was achieved in each consecutive run, with the cumulative amount of deposited carbon of 1.2 wt. %.

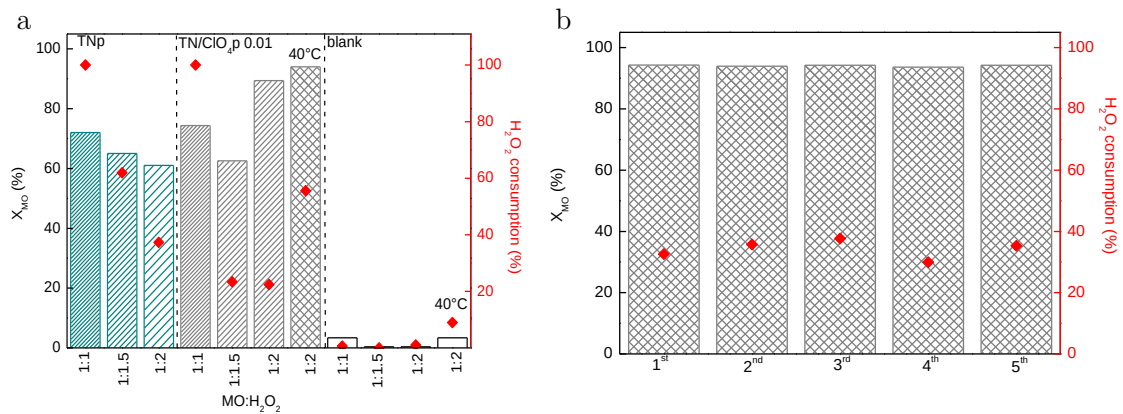


Figure 4.29: MO conversion and accompanied  $\text{H}_2\text{O}_2$  consumption for peroxide-treated a) TNp and TN/ $\text{ClO}_4$ p 0.01 materials tested with a different initial amount of  $\text{H}_2\text{O}_2$  at 25°C and 40°C during 240 min and b) TN/ $\text{ClO}_4$ p 0.01 material during 5 consecutive runs at 40°C with 100 % surplus  $\text{H}_2\text{O}_2$  during 90 min.

Table 4.12: MO conversion and accumulated carbon content for peroxide-treated STp, TN/Pp, TNp 0.001, TNp 0.01, TNp, TN/Sp, TN/ $\text{ClO}_4$ p 0.001, TN/ $\text{ClO}_4$ p 0.01 and TN/ $\text{ClO}_4$ p 0.1 materials tested in the CWPO of MO. MO conversion is given as a difference of MO removal occurred during CWPO and adsorption experiments.

| Sample                     | MO: $\text{H}_2\text{O}_2$ | T (°C) | $X_{\text{MO}}$ (%) | $C_{0,\text{TEOR}}$ (mg/L) | $C_{\text{ACCUM.}}$ (wt. %) |
|----------------------------|----------------------------|--------|---------------------|----------------------------|-----------------------------|
| STp                        |                            |        | 3                   |                            | 0.02                        |
| TN/Pp                      |                            |        | 39                  |                            | 0.16                        |
| TNp 0.001                  | 1:1                        |        | 1                   |                            | 0.11                        |
| TNp 0.01                   |                            |        | 70                  |                            | 0.49                        |
|                            |                            |        | 72                  |                            | 0.23                        |
| TNp                        | 1:1.5                      | 25     | 64                  | 2.75                       | 0.18                        |
|                            | 1:2                        |        | 61                  |                            | 0.30                        |
| TN/Sp                      | 1:1                        |        | 43                  |                            | 0.47                        |
| TN/ $\text{ClO}_4$ p 0.001 |                            |        | 46                  |                            | 0.48                        |
|                            |                            |        | 73                  |                            | 0.28                        |
| TN/ $\text{ClO}_4$ p 0.01  | 1:1.5                      |        | 66                  |                            | 0.50                        |
|                            | 1:2                        | 40     | 89                  |                            | 1.10                        |
|                            |                            |        | 93                  |                            | 0.32                        |
| TN/ $\text{ClO}_4$ p 0.1   | 1:1                        | 25     | 54                  |                            | 0.41                        |

### 4.3.3 Peroxo species formation, interaction and proposed surface structure for TN/ $\text{ClO}_4$ 0.01 material

Based on the highest catalytic activity, as-prepared and peroxide-treated TN/ $\text{ClO}_4$  0.01 material was submitted to detailed examination in order to define the geometry of peroxo species, their formation and interaction with  $\text{H}_2\text{O}_2$ .

First, morphological and structural analysis of as-prepared TN/ $\text{ClO}_4$  0.01 material was done. TEM analysis (Fig. 4.30a) has confirmed that as-prepared TN/ $\text{ClO}_4$  0.1 has a hollow multiwall nanotubular structure several micrometers long with an outer diameter of  $\sim 10$  nm, therefore more uniform than in TN material whose diameter varies between  $\sim 3$ – $10$  nm (Fig. 4.2a). In addition, although  $\text{TiO}_2$ -based nanotubes obtained through hydrothermal synthesis method are characterized with the open end structure [51], we can observe deviations in the case of TN/ $\text{ClO}_4$  0.01. Close ends can be found in some tubular fragments. Accompanied SAED pattern has confirmed that TN/ $\text{ClO}_4$  0.01 does not possess an ordered crystallographic structure, therefore showing similarities with the TN in which only faint diffraction rings attributed to the amorphous structure are observed [102], [120].

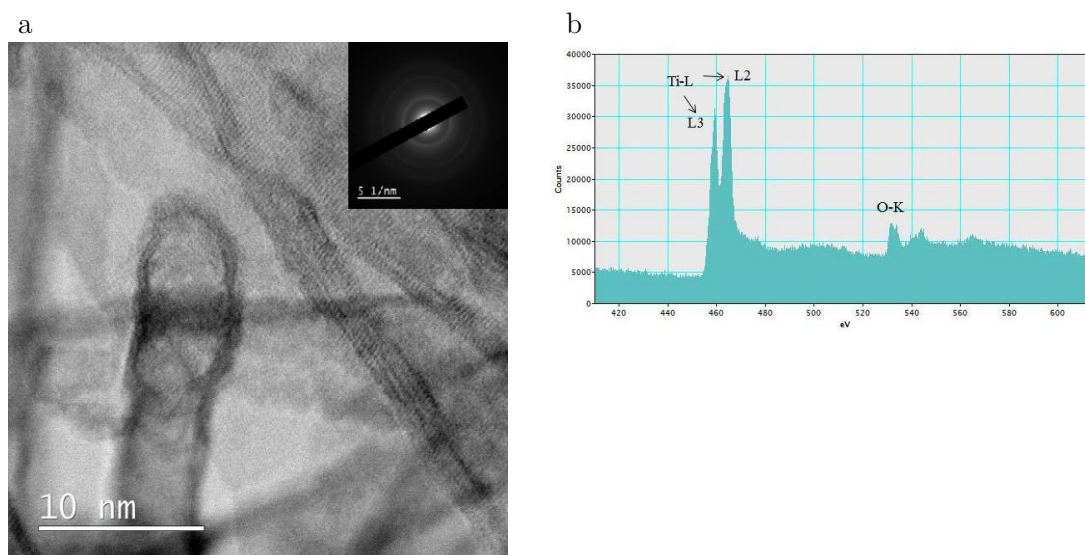


Figure 4.30: a) TEM image with accompanied SAED pattern and b) EELS spectra of as-prepared TN/ $\text{ClO}_4$  0.01 material.

By comparing EELS spectra of the TN/ $\text{ClO}_4$  0.01 material (Fig. 4.30b) with the one obtained from the TN material (Fig. 4.2b) we can confirm that they are both similar. Only Ti-L edge (L3 and L2), with the adsorption energy of around 460 eV, and O-K peak with the adsorption energy at 532 eV are observed [102]. XRD diffraction pattern (Fig. 4.31) shows only faint diffraction peaks at  $25.2^\circ$  and  $47.9^\circ$ , characteristic of [101] and [200] reflections of anatase  $\text{TiO}_2$  (JCPDS 01-071-1168). These peaks can be attributed to the partially unconverted P25 precursor or anatase formed during hydrothermal synthesis, which is completely equal to those observed for TN and TNp material (Fig. 4.3). Therefore, TN and TN/ $\text{ClO}_4$  0.01 are characterized with identical morphology and probably atomic structure, with apparently different surface properties as shown in Section 4.3.1.

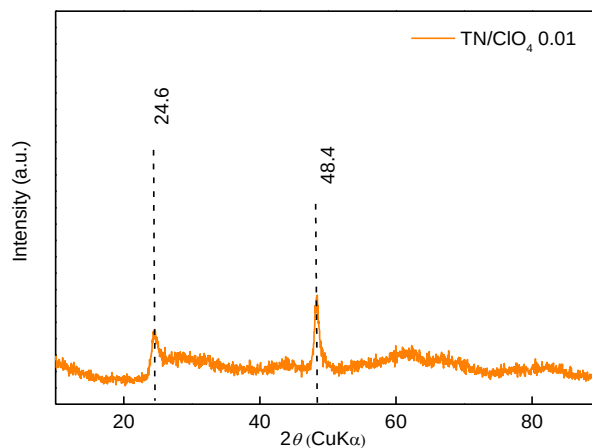


Figure 4.31: XRD diffraction pattern of as-prepared TN/ClO<sub>4</sub> 0.01 material.

As shown in Section 4.3.1., by applying FTIR/ATR, DRIFT and UV/Vis DR analyses, as-prepared and peroxide-treated TN/ClO<sub>4</sub> 0.01 materials show similar surface properties related to the presence of -OH groups and peroxo species, such as TN and TNp. The only difference lies in the amount of O<sub>2</sub> desorbed during O<sub>2</sub> TPD/MS analysis. In order to gain additional information of formed peroxo species (which cannot be confirmed with UV/Vis DR analysis) and their interaction with H<sub>2</sub>O<sub>2</sub> *in-situ* Raman analysis of as-prepared and peroxide-treated TN/ClO<sub>4</sub> 0.01 material has also been applied. TN/ClO<sub>4</sub> 0.01 Raman spectra (Fig. 4.32) is similar to those of TN, therefore it will be briefly described. Firstly, characteristic band for amorphous TiO<sub>2</sub> and of anatase are located at 466 cm<sup>-1</sup>, 277 cm<sup>-1</sup>, 185 cm<sup>-1</sup> and 146 cm<sup>-1</sup> [104], while band assigned to stretching and vibration of Ti-O bonds (-OH/H<sub>2</sub>O) is present at 670 cm<sup>-1</sup>. This band is strongly expressed in the case of TN/ClO<sub>4</sub> 0.01, rather than TN (Fig. 19), which can be an indication of a higher amount of adsorbed H<sub>2</sub>O and surface -OH groups (intra and interlayered) or their stronger interaction with the surface. As already mentioned, TGA analysis of both materials (Fig. 4.25) has shown that complete weight loss is similar, namely ~17 wt. %, but in the first temperature region (up to 140°C where ion-exchangeable groups decompose) it is higher for 1 wt. % in the case of TN/ClO<sub>4</sub> 0.01 material.

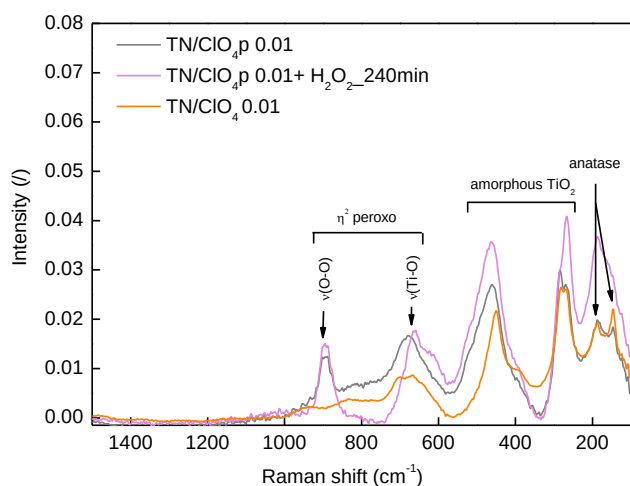


Figure 4.32: *In-situ* Raman spectra of as-prepared and peroxide-treated TN/ClO<sub>4</sub> 0.01 material exposed to 0.15 M H<sub>2</sub>O<sub>2</sub> during 240 min. Laser excitation was 1064 nm.

After peroxide treatment the Raman spectra of TN/ClO<sub>4</sub>p 0.01 is different than the one for TNp. First, the intensity of the band characteristic for amorphous TiO<sub>2</sub> increases

like in the case of TNp. As already mentioned, this can occur due to partial disintegration of the sample. In addition, the intensity of the band associated with stretching and vibration of Ti-O bonds also increases, probably as a result of side-on bonding between peroxo species and  $\text{Ti}^{4+}$  centres that is confirmed with the appearance of the new band near  $890\text{ cm}^{-1}$  attributed to O-O vibrations of  $\eta^2$  species [104], [105]. After 4 h interactions with  $0.15\text{ M H}_2\text{O}_2$  solution band at  $670\text{ cm}^{-1}$  reduces and redshifts which confirms the formation of side-on ( $\eta^2$ ) peroxo species at the expense of  $\text{H}_2\text{O}_2$  consumption [105]. In the spectrum belonging to TNp material (Fig. 4.28) shifting is even more pronounced. The band occurs at  $618\text{ cm}^{-1}$  which can be explained as a formation of  $\eta^2$  species which are more prone to degradation during CWPO runs or are more labile bonded to the  $\text{Ti}^{4+}$ . For the TN/ $\text{ClO}_4\text{p}$  0.01 material the same band is redshifted for only  $30\text{ cm}^{-1}$  which can correspond to the stronger interaction between  $\eta^2$  peroxo species and  $\text{Ti}^{4+}$  centres. The presence of  $\eta^1$  peroxo species on the surface of TN/ $\text{ClO}_4\text{p}$  0.01 material had not been detected in the acquired Raman spectra, probably due to overwhelming different peroxo species with the Raman enhancement.

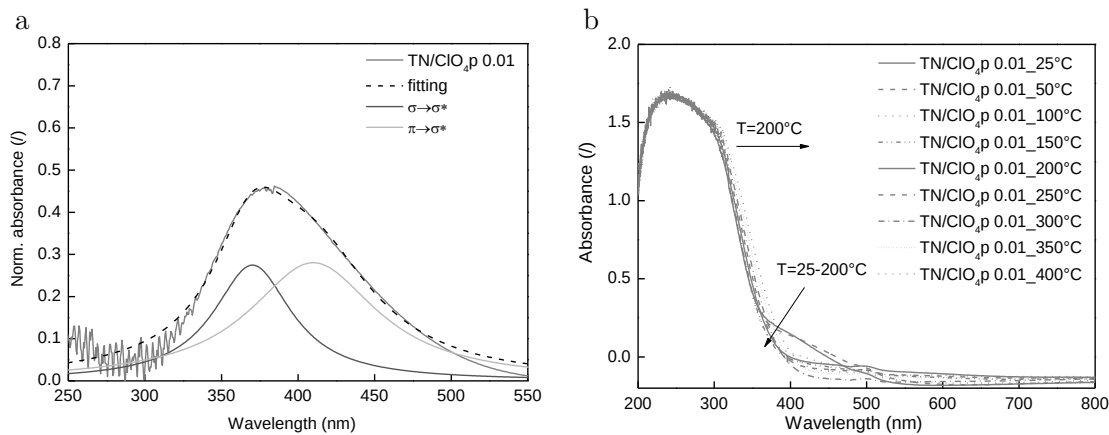


Figure 4.33: a) Fitted UV/Vis DR spectra of peroxide-treated TN/ $\text{ClO}_4\text{p}$  0.01 material. Curves represent subtracted values between peroxide-treated and as-prepared materials. b) UV/Vis DR spectra of peroxide-treated TN/ $\text{ClO}_4\text{p}$  0.01 material showing thermal instability of the peroxo species in the temperature region up to  $400^\circ\text{C}$ .

By subtracting and fitting UV/Vis DR spectra of as-prepared and peroxide-treated TN/ $\text{ClO}_4$  0.01 material (Fig. 4.33a), two peaks, representing  $\sigma \rightarrow \sigma^*$  and  $\pi \rightarrow \sigma^*$  transition, are present. By comparing it with fitted UV/Vis DR of TNp sample (Fig. 4.9a) we can observe that fitted curves are shifted towards higher wavelengths, confirming weaker LMCT between peroxo species and  $\text{Ti}^{4+}$  in the case of TN/ $\text{ClO}_4\text{p}$  0.01. This is also confirmed with UV/Vis DR analysis combined with gradual heating (Fig. 4.33b). Absorbance peak at  $420\text{ nm}$  diminished already at  $100^\circ\text{C}$ , which is  $50^\circ\text{C}$  lower than in the case of TNp sample (Fig. 4.9b). Nevertheless, at  $200^\circ\text{C}$  both materials perceive a shift in the region attributed to the structural LMCT of  $\text{O}^{2-} \rightarrow \text{Ti}^{4+}$  [71].

In order to completely define the changes induced during peroxide treatment, as well as geometry of the surface peroxo species, as-prepared and peroxide-treated TN/ $\text{ClO}_4\text{p}$  0.01 materials have been subjected to NMR analysis.  $^1\text{H}$  MAS NMR analysis of as-prepared TN/ $\text{ClO}_4$  0.01 (Fig. 4.34a) has revealed several characteristic proton resonance peaks fitted at  $\delta$  1.16 ppm, 1.23 ppm, 3.87 ppm, 4.77 ppm and 5.97 ppm attributed to hydrogen species bonded to the surface of materials. Fitted peaks at  $\delta$  5.97 ppm and  $\delta$  3.87 ppm confirm strong surface H-bonding between non-ion-exchangeable protons, and they are usually found in perovskite-type titanates with resonance at  $\delta$  3.8 ppm and 6.2 ppm [77]. Fitted peak at  $\delta$  4.77 ppm is assigned to physically adsorbed  $\text{H}_2\text{O}$  whose chemical shift lies in

between  $\delta$  4.0–4.7 ppm [77], while the remaining fitted peaks at  $\delta$  1.16 ppm and  $\delta$  1.23 ppm can be assigned to the terminal -OH groups bonded to the surface of amorphous  $\text{TiO}_2$  and they are more likely to be coordinated to only one Ti atom [124].

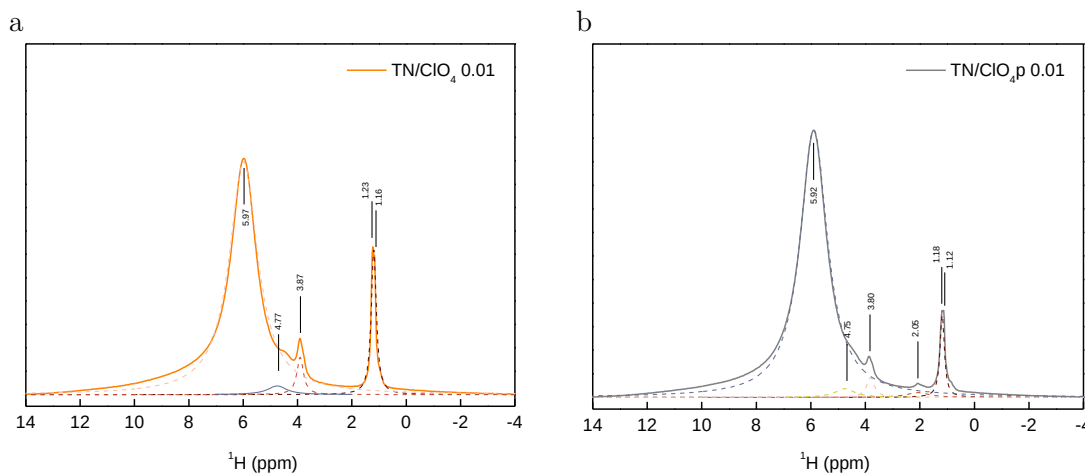


Figure 4.34: Fitted  $^1\text{H}$  MAS NMR spectra of a) as-prepared and b) peroxide-treated  $\text{TN}/\text{ClO}_4$  0.01 material. Dashed lines represent Gaussian fits.

After peroxide treatment (Fig. 4.34b) all proton resonance peaks slightly shifted in the higher field region confirming stronger interaction with the surface of the material. In addition, intensity of the signal attributed to the terminal -OH groups drastically decreases giving the confirmation that peroxy species are formed on the -OH rich surfaces by replacing terminal -OH groups. By fitting obtained  $^1\text{H}$  MAS NMR spectra one additional peak, with the chemical shift of  $\delta$  2.05 ppm, is observed. It can be assigned to terminal -OH groups bonded to the anatase [125], therefore confirming partial disintegration and presence of anatase in the final material.

Similar  $^1\text{H}$  MAS NMR spectra has been obtained after treatment with  $^{17}\text{O}$ -enriched  $\text{H}_2\text{O}_2$  ( $\text{H}_2^{17}\text{O}_2$ ). Appearance of the new three peaks (Fig. 4.35a) with the chemical shift at  $\delta$  0.12, 0.75 and 7.60 ppm can be attributed to the organic residues arising from the antraquinone oxidation process used for the synthesis of  $\text{H}_2^{17}\text{O}_2$ . Peaks occurring in the lower field region are attributed to the aromatic protons, while the peak occurring in the higher field region is arising from the adsorbed aromatic residue occurring from the hydrolysis of toluene [125].  $^{17}\text{O}$  NMR spectra obtained after treatment with  $\text{H}_2^{17}\text{O}_2$  can be divided into four regions (Fig. 4.35b). First, two fitted signals occurring in the higher field region between  $\delta$  -100 ppm and 150 ppm can be attributed to the surface-bonded  $\text{H}_2\text{O}$  and -OH groups in the water environment, which usually have weaker interactions with the  $\text{TiO}_2$  surface [126]. Narrow fitted signal at  $\delta$  75 ppm is attributed to the powdered  $\text{Al}_2\text{O}_3$  originating from the  $\text{ZnO}_2$  spinners used during the NMR analysis [127]. This signal can arise when high density material is tightly stuffed up in the spinner. Second region between  $\delta$  200–400 ppm is composed of two signals, namely broad signal with the lowest chemical shift occurring at  $\delta$  276 ppm, attributed to the peroxy species [128], and narrow signal at  $\delta$  390 ppm, attributed to the  $\text{ZnO}_2$  spinners [127]. Chemical shift for  $\eta^2$  peroxy species is usually observed at  $\delta$  263 ppm, although due to the broadness of the signal, and its low intensity, the chemical shift attributed to  $\eta^1$  peroxy species, usually occurring at  $\delta$  233 ppm [128], can easily be overlapped. In addition, although the chemical shift at  $\delta$  390 ppm is attributed to the  $\text{ZnO}_2$  spinners, a chemical shift attributed to the four-coordinated oxygen species ( $\text{O}_{4\text{Ti}}$ ) usually found in TS-1 systems and titanium-oxo clusters also arises in this region [129], [130].  $\text{O}_{4\text{Ti}}$  species are usually a result of surface-coordinated acetylacetonate (acac) ligand used during material synthesis [126], so since traces of organic solvents are

visible in the  $^1\text{H}$  MAS NMR spectra, we can assume that the as-observed chemical shift can also be the result of the organic ligand bonded to two-coordinated ( $\text{O}_{2\text{Ti}}$ ) bridging oxygen atoms. The signal with the chemical shift at  $\delta$  515 ppm, in the region between  $\delta$  460–600 ppm, is attributed to three-coordinated oxygen species ( $\text{O}_{3\text{Ti}}$ ) [130], [131] whose chemical shift is usually found in this region. The remaining high intensity signal with the chemical shift at  $\delta$  730 ppm confirms the presence of two-coordinated oxygen atoms ( $\text{O}_{2\text{Ti}}$ ) formed at the surface or in the inner cluster bridges ( $\text{O}_{\text{Ti}}$ ) of  $\text{TiO}_2$ -based nanotubes [126], [129].

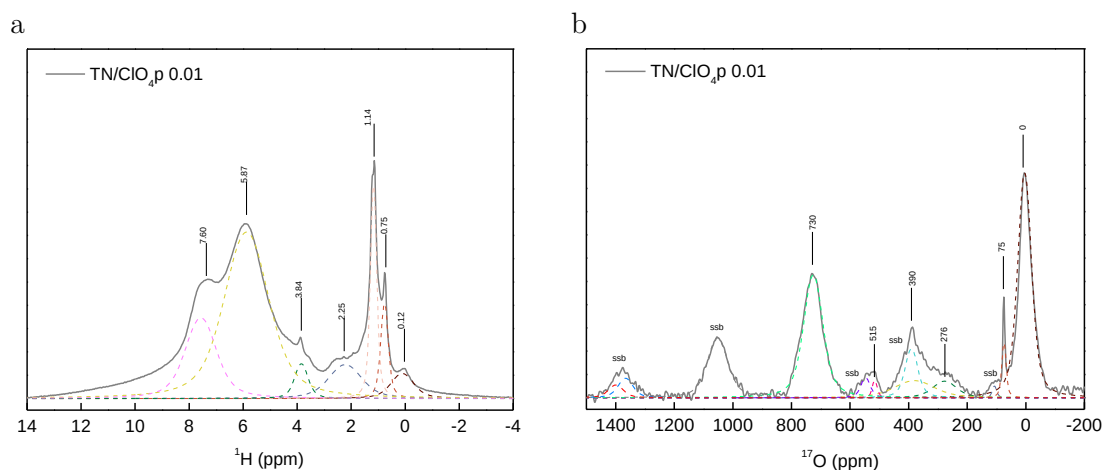


Figure 4.35: Fitted a)  $^1\text{H}$  MAS NMR and b)  $^{17}\text{O}$  NMR spectra of  $\text{H}_2^{17}\text{O}_2$ -treated TN/ $\text{ClO}_4\text{p}$  0.01 material. ssb denotes spinning sidebands. Dashed lines represent Gaussian fits.

By combining the result from  $^1\text{H}$  MAS and  $^{17}\text{O}$  NMR analysis, as well as temperature-dependant UV/Vis DR analysis, with the  $\text{O}_2$  TPD/MS profiles obtained for TN/ $\text{ClO}_4\text{p}$  0.01 material measured after 5 consecutive runs, we can assign the first two peaks, present in the temperature region up to  $200^\circ\text{C}$ , to the  $\eta^2$  and  $\eta^1$  peroxy species. Since it is known that  $\eta^1$  peroxy species show higher thermal stability, the first  $\text{O}_2$  TPD/MS peak is attributed to  $\eta^2$  peroxy species, while the second one is attributed to  $\eta^1$  peroxy species. The remaining two peaks evolved above  $200^\circ\text{C}$  can be attributed to the  $\text{O}_{2\text{Ti}}$  intra/interlayered oxygen species formed in the place of intra/interlayered terminal -OH groups. In addition, since the concentration of  $\text{O}_{2\text{Ti}}$  species drastically decreases during 5 consecutive runs, we assume that these species are not catalytically active (MO conversion and  $\text{H}_2\text{O}_2$  consumption are constant), but they can serve either as a place for new peroxy species formation. Therefore, by combining all the results obtained for TN/ $\text{ClO}_4\text{p}$  0.01 material we can ascribe high catalytic activity to the  $\eta^2$  peroxy species. Schematic presentation of TN/ $\text{ClO}_4\text{p}$  0.01 surface labelled with  $\text{H}_2^{17}\text{O}_2$  is shown in Fig. 4.36.

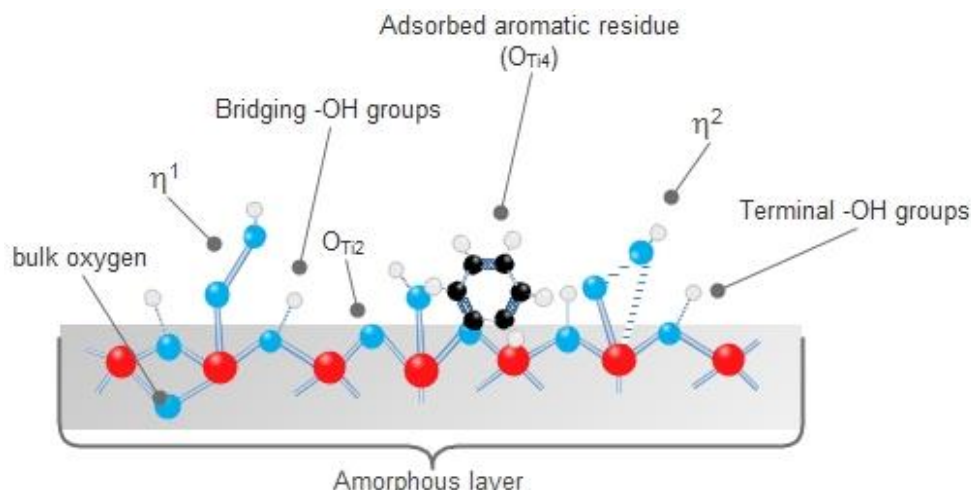


Figure 4.36: Graphical illustration of  $\text{H}_2^{17}\text{O}_2$  labelled TN/ $\text{ClO}_4\text{p}$  0.01 surface. Red, blue, gray and black spheres represent Ti, O, H and C atoms, respectively.

#### 4.3.3.1 Tentative reaction mechanism for $\text{H}_2\text{O}_2$ decomposition over TN/ $\text{ClO}_4\text{p}$ 0.01 material

Based on the obtained results, possible reaction pathways for  $\text{H}_2\text{O}_2$  decomposition over TN/ $\text{ClO}_4\text{p}$  0.01 material are proposed.

From the *in-situ* Raman, TGA and  $^1\text{H}$  MAS NMR analysis we can observe that the prerequisite for peroxo species formation on the amorphous  $\text{TiO}_2$ -based nanotubes relies on the fact that the surface is abundant with -OH groups, where special importance is given to terminal -OH groups which serve as a place for peroxo species formation. These -OH groups can be both intra and interlayered. With  $^{17}\text{O}$  NMR analysis these species are characterized as  $\eta^2(\text{Ti}-\text{OOH})$ , although the possibility of the  $\eta^1(\text{Ti}-\text{OOH})$  existence cannot be excluded, as seen with the Raman analysis (on the TNp sample). UV/Vis DR analysis, combined with the gradual heating of the sample, has confirmed that peroxo species decompose up to 100–150°C, meaning that oxygen desorption up to 200°C, measured by means of  $\text{O}_2$  TPD/MS analysis, can be ascribed to peroxo species. Higher thermal stability of  $\eta^1$  over  $\eta^2$  has been confirmed by others [17], so the first peak is attributed to  $\eta^2$  species, while the second one is attributed to  $\eta^1$  species. Oxygen desorption, connected with the first and second peak, lies in the temperature range of 95–116°C and 130–175°C, respectively. As it can be seen, it slightly varies in each sample which can be attributed to the difference in morphology and acid treatment.

In addition, the presence of four-coordinated ( $\text{O}_{4\text{Ti}}$ ) and three-coordinated ( $\text{O}_{3\text{Ti}}$ ) oxygen species has been detected by means of  $^{17}\text{O}$  NMR analysis. Prior ones can be attributed to bonded aromatic residue [126], while the former ones can be attributed to the structure itself [129]. Two-coordinated ( $\text{O}_{2\text{Ti}}$ ) oxygen atoms have been attributed to the bridging oxygen atoms arising from the disrupted material's structure [126], [129]. By combining UV/Vis DR with gradual heating and  $^{17}\text{O}$  NMR analysis we assume that oxygen species liberated in the temperature region above 200°C can be attributed to structural bonded oxygen which is apparently successfully exchanged during peroxide treatment. This can occur due to the partial disintegration of the sample which occurs during peroxide treatment [71], [120].

Nevertheless,  $\text{O}_2$  TPD/MS analysis has shown that high catalytic activity of the TN/ $\text{ClO}_4\text{p}$  0.01 is attributed to thermally unstable yellow-coloured  $\eta^2$  peroxo species which is in correspondence with the results reported by others [17], [83], [90], [95]. In the liquid-

phase catalytic reactions  $\eta^2$  peroxo species are always in the equilibrium with  $\eta^1$  peroxo species, which can be easily hydrolyzed into  $\eta^2$  due to structural instability [17], [83]. It is worth mentioning that thermoneutral transformation of  $\eta^1$  into  $\eta^2$  occurs at the temperatures above 65°C, which is 25°C higher than the CWPO operating temperature employed in 5 consecutive runs using TN/ClO<sub>4</sub>p 0.01 material, so we assume constant equilibrium between  $\eta^1$  and  $\eta^2$  species [17]. In the equilibrium state energetically favourable intermolecular homolysis of the O-O peroxide bond occurs through oxidation of H<sub>2</sub>O<sub>2</sub> to the  $\bullet$ OOH radical (Fig. 4.37, step 1). In this step the formation of the surface titanium oxyl (Ti-O $\bullet$ ) radical species occurs simultaneously (Fig. 4.37, step 2) [17]. Newly formed Ti-O $\bullet$  species can participate in the termination reaction, where  $\bullet$ OOH is oxidized to H<sub>2</sub>O, Ti(OH) and O<sub>2</sub> (Fig. 4.34, step 3) [17]. It is calculated that this process occurs as thermoneutral, so we assume that the termination reactions are present to some extent but they do not define the catalytic stability of the TN/ClO<sub>4</sub>p 0.01 during 5 consecutive runs. Parallel to the termination reaction, a thermoneutral process of water molecules adsorption, onto Ti<sup>4+</sup>, occurs [17]. Based on the result obtained with <sup>1</sup>H MAS NMR analysis, we can assume that the prerequisite for the peroxo species formation are terminal -OH groups, which can be formed during step 3, therefore we assume that the creation of the peroxo species can occur after the termination reaction.

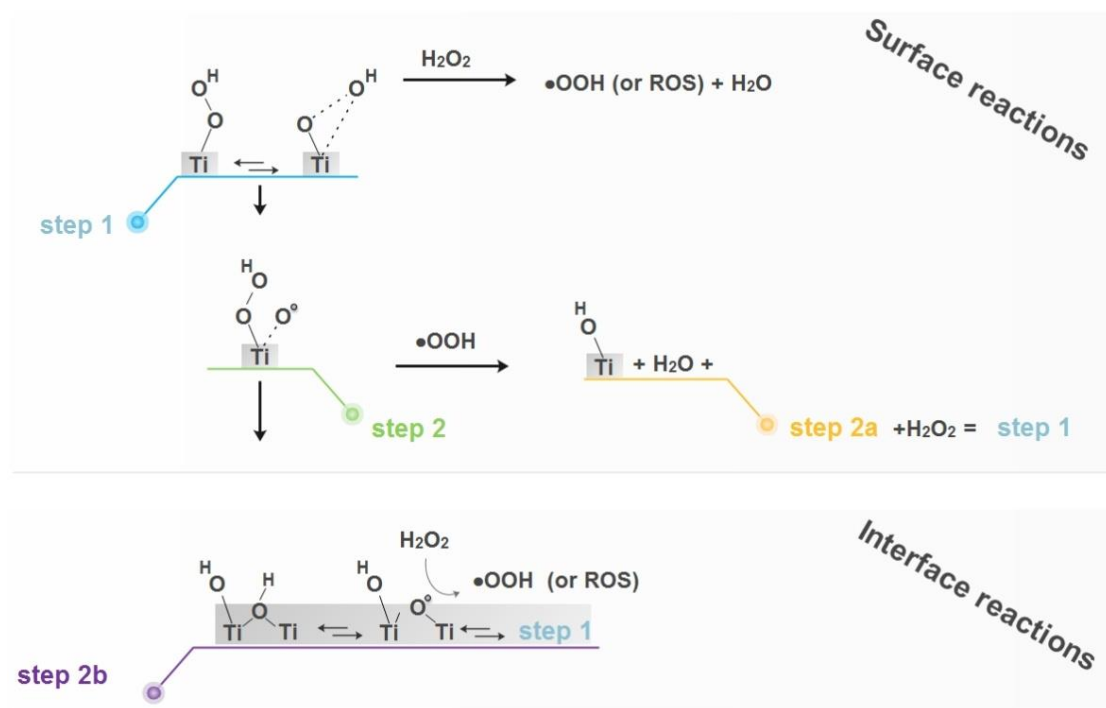


Figure 4.37: Schematic illustration of a possible H<sub>2</sub>O<sub>2</sub> decomposition pathway and surface/interface reactions for TN/ClO<sub>4</sub>p 0.01 material in the CWPO of MO.

With O<sub>2</sub> TPD/MS analysis it has been confirmed that oxygen desorbed after 200°C, for what we assume is attributed to the bridging OTi<sub>2</sub> species, is consumed during 5 consecutive runs. Since the amount of  $\eta^2$  peroxo species remains almost constant, namely 5.9\*10<sup>-7</sup> mol O<sub>2</sub>/m<sup>2</sup> and 5.2\*10<sup>-7</sup> mol O<sub>2</sub>/m<sup>2</sup> prior and after five consecutive runs, we assume that O<sub>Ti2</sub> species do not contribute to the catalytic activity but rather serve as centres for new peroxo species formation. Montoya et al. [132] have observed that bridging O<sub>Ti2</sub> species lead to the generation of bridging oxygen radicals (Ti-O<sub>br</sub>•) in the photocatalytic reactions. Set forth radicals have a considerably weaker interaction with Ti<sup>4+</sup> than terminal Ti-O• radicals, which can be formed during step 2, therefore causing “coordination loss” from

two-coordinated  $O_{Ti2}$  to one-coordinated  $O_{Ti}$ . Such highly labile coordinated bridging oxygen radical can increase reactivity of the surface towards increased consumption of protons which can be, as we assume, withdrawn from  $H_2O_2$  [132]. We assume that in this step, the creation of bridging -OH groups can occur, which can serve as a place for the creation of surface peroxo species (Fig. 4.37, step 4). We also cannot exclude the possibility for the formation of the bridging  $-OH\bullet$  radicals [132], but we assume that this does not influence the overall catalytic activity since no observed increase in the catalytic activity of the TN/ $ClO_4p$  0.01 sample occurs.

Therefore, we propose that  $\eta^2$  peroxo species are the main species responsible for the catalytic activity of TN/ $ClO_4p$  0.01 in the CWPO of MO, while  $O_{Ti2}$  gives additional structural stabilization to the material. In addition, due to the complexity of the system, and radical reactions as well, we cannot exclude the possibility for the formation of a wide variety of ROS, especially  $O_2\bullet$  and  $O_2^{2-}\bullet$ , which are proposed to be formed at neutral pH [1], [3], [18].

## Chapter 5

# Confirmation of Hypotheses

Based on the obtained relevant experimental data, the following hypotheses have been confirmed and disconfirmed:

1. Hypothesis No1: As already stated 1D nanotubular morphology enables efficient transport of the product and reactants from the surface of the material, as well as uniform distribution of the material into the reaction system, therefore peroxo-treated TiO<sub>2</sub>-based nanotubes morphology has shown prevalent activity in comparison with nanosheets, nanorods and rice-like morphology. We can also assume that this morphology enables more efficient introconversion of surface two-coordinated oxygen species into Ti(O•-) radicals and enables their better interaction with the H<sub>2</sub>O<sub>2</sub> during the formation of new peroxo species. S<sub>BET</sub>, V<sub>p</sub> and d<sub>p</sub> of TiO<sub>2</sub>-based nanotubes is a little higher, so apparently the accessibility to the reaction sites is enhanced, therefore this type of the morphology is crucial in order to obtain satisfying catalytic activity in the CWPO of MO. In addition, it has been observed that materials obtained through the hydrothermally conversion of P25 are more prone to disintegration, therefore the type of the precursor apparently influences the structure of the material, its stability during peroxide treatment and catalytic performance. It would be better to obtain different morphologies using the same precursor in order to gain better insight into the morphological influence.
2. Hypothesis No2: Low temperature thermal treatment can induce partial reduction of Ti<sup>4+</sup> sites, which is observed in the change of the material's colour, although this did not increase the catalytic activity of the peroxide-treated material. Therefore, peroxo species formed on the surface of TiO<sub>2</sub>-based nanotubes should be the only catalytically active sites. In addition, with the partial thermal treatment, the amount of the bonded peroxo species drastically decreases and apparently no structurally bonded O<sub>2</sub> is formed during peroxide treatment, which affects the overall catalytic performance. Reaction mechanisms in the presence of the peroxide-treated TiO<sub>2</sub>-based materials are different than those found in the CeO<sub>2</sub> materials.
3. Hypothesis No3: Peroxo species formed on the surface of TiO<sub>2</sub>-based materials can only be formed in the materials abundant with surface -OH groups, especially terminal -OH groups. Nevertheless, it is hard to distinguish between intra/interlayered and ion-exchangeable protons, therefore we assume that all of them can be involved in the peroxo species formation.
4. Hypothesis No4: Protonation step greatly influences the complete surface and structural properties of the TiO<sub>2</sub>-based nanotubes, therefore it influences the degree of the disintegration, strength of the bonding and the amount of the peroxo species formed. The protonation step, in our own personal opinion, is a crucial factor for

achieving satisfactory catalytic activity and interaction between surface peroxo species, structural two-coordinated oxygen and  $\text{H}_2\text{O}_2$  during CWPO runs.

5. Hypothesis No5: From the  $^{17}\text{O}$  NMR analysis we proposed that only  $\eta^1(\text{Ti-OOH})$  and  $\eta^2(\text{Ti-OOH})$  peroxo species can be found on the surface of peroxide-treated  $\text{TiO}_2$ -based materials, with the catalytic activity ascribed mostly to the  $\eta^2$  peroxo species. We assume that these species can be found in hydrated form, and that they influence the absorption in the visible region.
6. Hypothesis No6: Peroxide treatment, as well as protonation step, induces significant changes in structural, textural and surface properties of materials, therefore, high catalytic activity cannot be exclusively ascribed only to peroxo species. In other words,  $\eta^2$  peroxo species are catalytically active but their performance is aided with the presence of the two-coordinated structural oxygen.



## Chapter 6

### Conclusion

The importance of developing a novel stable metal-free catalyst, which will be able to operate under mild conditions, is a bold challenge for researchers. Hence, the presented study was focused on the development of metal-free  $\text{TiO}_2$ -based materials which will be used as a catalyst in the CWPO of MO under mild conditions.

From the obtained results it can be seen that amorphous peroxide-treated  $\text{TiO}_2$ -based nanotubes decorated with the surface peroxo species can provide an alternative way for the  $\text{H}_2\text{O}_2$  in the CWPO of MO under mild conditions. The formation and activity of the peroxo species are not only driven by the development of adequate morphology, but also by structural and surface properties of the material. Materials abundant with surface -OH groups, as proven with  $^1\text{H}$  MAS NMR terminal -OH groups, are the main factor governing the peroxo species formation. Partial thermal treatment of the materials, which can allow partial reduction of  $\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$ , will ameliorate their performance due to the loss of surface -OH groups and the creation of the lower amount of the surface peroxo species. The presence of structural  $\text{Na}^+$  ions will allow higher peroxo species formation, but it will ameliorate the catalytic performance of these materials. Treatment with different acids will enable sufficient ion-exchange, although the presence of different surface ionic species can lower the peroxo species performance. In addition, acid strength and concentration will affect the degree of protonation and disintegration of the material, therefore optimal concentration and acid type should be used. Too low concentration does not enable efficient proton exchange, while too strong acid increases the adsorption and partial disintegration of the material. Therefore, it affects the formation process and activity of the peroxo species.

Optimum acid concentration, and highest catalytic activity, is visible in the case  $\text{TiO}_2$ -based nanotubes were washed in 0.01 M  $\text{HClO}_4$  and treated with  $\text{H}_2\text{O}_2$  (TN/ $\text{HClO}_4$ p 0.01 material). At  $T=40^\circ\text{C}$ , with a double stoichiometric amount of  $\text{H}_2\text{O}_2$ , MO conversion reached  $\sim 93\%$  during 1 h of the experiment, accompanied with only  $\sim 1\%$  of adsorption. Combined  $^1\text{H}$  MAS and  $^{17}\text{O}$  NMR analysis has revealed that  $\eta^1$  and  $\eta^2$  peroxo species are formed during peroxide treatment and it has been revealed that terminal -OH groups are the main factors for their formation. By combining  $\text{O}_2$  TPD/MS and temperature dependant UV/Vis DR analysis it has been proposed that  $\text{O}_2$  desorbed up to  $200^\circ\text{C}$  is attributed to the peroxo species, while the remaining  $\text{O}_2$  comes from structurally bonded oxygen. By fitting  $\text{O}_2$  TPD/MS spectra thermally labile  $\eta^2$  peroxo species have been proposed as catalytically active species since their concentration remains constant during 5 consecutive runs. Structural oxygen has been attributed to the presence of two-coordinated intra/interlayered oxygen species detected by means of  $^{17}\text{O}$  NMR analysis. Their structural liability and drastic decrease in the 5 consecutive runs, without affecting the overall catalytic activity, leads to the assumption that terminal  $\text{Ti}-\text{O}\cdot^-$  radicals and

-OH groups are formed during the CWPO experiment and they can provide a place for the formation of peroxo species.

The results altogether show that the catalytic activity of the high specific surface area peroxide-treated amorphous  $\text{TiO}_2$ -based nanotubes relies on the complete substantial change of the materials properties; however, catalytic activity is well correlated with the presence of  $\eta^2$  peroxo species aided with the presence of two-coordinated oxygen species which serve as structural stabilizing agents.

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## Publications Related to the Thesis

### Journal Articles

- N. Drašinac, B. Erjavec, G. Dražić, and A. Pintar, “Peroxo and gold modified titanium nanotubes for effective removal of methyl orange with CWPO under ambient conditions”, *Catal. Today*, vol. 280, pp. 155–164, 2017.
- Drašinac Pajić, Nina, Djinović, Petar, Dražić, Goran, Grdadolnik, Jože, Šket, Primož, Cerkovnik, Janez, Pintar, Albin, “Structural stabilization and characterization of active peroxo species on TiO<sub>2</sub>–nanotube based materials in mild catalytic wet peroxide oxidation process”, *Applied catalysis. A. General*, vol. 562., pp. 276-283, 2018.

### Conference Paper

- N. Drašinac, B. Erjavec, and A. Pintar, “Peroxo and gold modified titanium nanotubes for effective removal of methyl orange with CWPO under ambient conditions” in Book of proceedings: Athens, 2015.

### Other Publications

- D. Dolar, N. Drašinac, K. Košutić, and D. Ašperger, “Adsorption of hydrophilic and hydrophobic pharmaceuticals on RO/NF membranes: Identification of interactions using FTIR”, *J. Appl. Polym. Sci.*, vol. 134, pp. 17-21, 2017.
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