Metal Oxide Composites with Carbon Materials

Synthesis, Characterisation and Preliminary Catalytic Applications

Karin Burström

Materials Engineering, master's level
2019

Luleå University of Technology
Department of Engineering Sciences and Mathematics
Table of contents

Table of contents ........................................................................................................................................ 1
Acknowledgements ................................................................................................................................. 2
List of Abbreviations ............................................................................................................................. 3
Introduction ............................................................................................................................................... 4
State of the art ........................................................................................................................................... 5
  Semiconducting metal oxides as photocatalysts ..................................................................................... 5
  Nanostructured TiO$_2$ and composites .................................................................................................. 7
  Bi-oxide core@shell nanocomposites ..................................................................................................... 7
Carbonaceous materials reduced at the nanoscale .................................................................................. 9
Photocatalytic water remediation .......................................................................................................... 10
Experimental section ............................................................................................................................. 12
  Synthesis of materials .......................................................................................................................... 12
    Commercial TiO$_2$ P25-rGO hybrid nanocomposites ....................................................................... 12
    TiO$_2$-rGO hybrid nanocomposites .................................................................................................... 12
    TiO$_2$-fCNTs hybrid nanocomposites ................................................................................................ 12
    SnO$_2$-ZnO core@shell nanostructures ............................................................................................... 12
    Electrodes for electrochemical characterisation .................................................................................. 13
Characterisation of materials .................................................................................................................. 13
  Optical, morphological and structural characterisation of materials .................................................... 13
  Electrochemical characterisation of materials ....................................................................................... 13
  Photocatalytic activity of materials, with respect to degradation of RhB ............................................. 14
Results and discussion ............................................................................................................................ 15
  Synthesis of materials .......................................................................................................................... 15
  Characterisation of materials ................................................................................................................ 16
    P25-rGO hybrid nanocomposites .......................................................................................................... 16
    TiO$_2$-rGO hybrid nanocomposites .................................................................................................... 20
    TiO$_2$-fCNT hybrid nanocomposites ................................................................................................ 24
    SnO$_2$-ZnO core@shell nanostructures ............................................................................................... 27
Conclusion ............................................................................................................................................... 33
Future Work ............................................................................................................................................. 34
References ............................................................................................................................................... 35
Acknowledgements
I would like to extend my personal thanks to my supervisors, Isabella Concina and Anton Landström, who have been supportive and generous with their time throughout this experience. In addition, the colleagues and friends I have met in my workplace have certainly made this journey into something I will always look back on with joy. Last but not least, thanks to my family for the endless patience and support.
List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB</td>
<td>conduction band</td>
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<td>C-mats</td>
<td>carbonaceous materials</td>
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<td>CNTs</td>
<td>carbon nanotubes</td>
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<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
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<tr>
<td>DSSCs</td>
<td>dye sensitised solar cells</td>
</tr>
<tr>
<td>EDX</td>
<td>energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>fCNTs</td>
<td>functionalised carbon nanotubes</td>
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<td>FTO-glass</td>
<td>fluorine-doped tin oxide glass</td>
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<td>K-M</td>
<td>Kubelka-Munck function</td>
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<td>MB</td>
<td>methyl blue</td>
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<td>MO</td>
<td>methyl orange</td>
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<td>MOx</td>
<td>metal oxide</td>
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<td>MWCNTs</td>
<td>multi wall carbon nanotubes</td>
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<td>NPs</td>
<td>nanoparticles</td>
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<tr>
<td>OM</td>
<td>optical microscopy</td>
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<td>rGO</td>
<td>reduced graphene oxide</td>
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<td>PL</td>
<td>photoluminescence spectrophotometry</td>
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<td>RhB</td>
<td>rhodamine B</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
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<tr>
<td>SWCNTs</td>
<td>single wall carbon nanotubes</td>
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<td>TNT</td>
<td>TiO$_2$ nanotubes</td>
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<tr>
<td>UV-Vis</td>
<td>UV-visible spectrophotometry</td>
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<td>VB</td>
<td>valence band</td>
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<td>W-H</td>
<td>Williamson-Hall analysis</td>
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<td>XRD</td>
<td>X-ray diffraction spectrophotometry</td>
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Introduction

The present work concerns the preparation of complex nanostructures of semiconducting wide band gap n-type metal oxides (MOx) with particular focus on TiO$_2$, SnO$_2$ and ZnO, aimed at enhancing their optoelectronic properties in view of functional applications.

The work carried out has been focused on the preparation of:

1. hybrid nanostructured composites, composed by carbonaceous materials (reduced graphene oxide, carbon nanotubes) and TiO$_2$ and SnO$_2$;

2. bioxide composites with a core@shell structure, composed by SnO$_2$ and ZnO.

As for the hybrid composites, the carbonaceous materials (C-mat) are herein exploited as a platform for the synthesis of nanostructured MOx and as an active scaffold to enhance charge transport properties.

Photocatalytic activity of the prepared composites is as well investigated, with particular reference to the degradation of a dye (rhodamine B, RhB), as a molecular model of organic water pollutants.

Research activities within the present investigation have been carried out in the light of green chemistry principles. Green chemistry is a notion developed in business and regulatory communities, as a natural product of the efforts to reduce human environmental impact. As defined by the American Chemical Society$^1$, it comprises the use of environment friendly materials and processes, the reduction of wastes and pollution, energy conservation and life cycle consideration. It is a non-political strive to improve on the effect that humans have on the planet.

The project is inserted in the frame of activities of the Experimental Physics subject on advanced functional materials for solar energy exploitation and will contribute to the on-going VINNER Marie Curie Fellowships under the project “Light Energy”.
State of the art

Semiconducting metal oxides as photocatalysts

A conducting crystalline material, for example a metal, has its valence electrons in the conductance band (CB), where they can be shared with other atoms in the vicinity. A metal can be said to have a “cloud” of electrons that can move across the material, ensuring the electric conductance of these materials. An insulator on the other hand, has an empty CB, its valence electrons residing in the valence band (VB). A semiconductor, for example the metal oxides that are interesting for this project, also has an empty CB, but, in contrast to the insulator, the gap between the VB and the CB is smaller, as displayed in Figure 1.

![Figure 1: Simplified illustration of the theory on energy bands.](image)

The band gap (displayed as $E_g$ in Figure 3 and with pink arrows in Figure 1) is measured in electron volt (eV), and in semiconductors it is of such size that an electron, forcibly in the VB, can be excited and jump into the CB.

![Figure 2: Illustration of (a) a direct band gap semiconductor and (b) an indirect semiconductor, depicted in reciprocal space.](image)

There are different types of band gaps, direct and indirect, as illustrated in Figure 2. A direct band gap implicates that the in energy lowest part of the CB is placed right over the in energy highest part of the VB, entailing a radiative recombination process. In an indirect band gap material, these peaks do not coincide, and the radiative recombination process entails the emitting of a phonon – or the involvement of a crystallographic defect, see Figure 2b. The radiative recombination of a direct band gap material is faster.

It should also be mentioned that the band gap of a semiconductor increases for decreasing particle size, namely the absorption edge blueshifts when particles size decreases $^2$.

A catalyst is a substance capable of speeding chemical reactions up, while remaining unchanged itself during the process. The term photocatalysis refers to a catalytic process promoted by light irradiation.
Semiconducting crystalline MOx can show photocatalytic properties, the mechanism of which is described for TiO$_2$ in Figure 3.

![Energy band diagram](image)

Figure 3: Energy band diagram representative of a spherical TiO$_2$ nanoparticle, also providing some explanation to the photoinduced redox reactions at the surface of such a particle.

If a photon of energy equal to or exceeding the band gap hits the semiconductor, an electron is excited from the VB to the CB, making the system conductive. The excited electron leaves a positive charge, a hole, behind in the VB, and together they form what is called an exciton pair. This pair can recombine within nanoseconds, entailing the dissipation of the absorbed photon energy. Other possible fates for the exciton pair are to get trapped in a metastable surface state or react with the surrounding material.

In photocatalytic water remediation, the exciton pair is to induce a redox reaction in the surrounding environment, thus promoting the degradation of the targeted pollutant. However, the kinetics of recombination is 10-1000 times faster than that of a redox reaction, so it is critical that recombination is prevented, inhibited or at least slowed down $^3$.

The exciton pair can for instance generate highly reactive oxidative radicals, like OH$^-$ and HO$_2^-$, in aqueous solutions, able to degrade organic pollutants at the interface catalyst/environment. This is the reaction path suggested for instance by Epifani et al.$^4$ for the photocatalytic degradation of RhB using a bioxide core@shell structure, SnO$_2$@V$_2$O$_5$. 
**Nanostructured TiO\(_2\) and composites**

The primary focus of this thesis is TiO\(_2\), and how to modify and improve its photocatalytic properties with the use of carbonaceous materials (C-mats). A separate section on C-mats can be seen further down, here only the composite system and TiO\(_2\) in its own merit will be discussed.

Anatase and rutile TiO\(_2\) have indirect band gaps. These two are the main constituents of P25\(^5\), which is widely known as a benchmark material for semiconductor photocatalysis\(^6\)-\(^8\). P25 has a band gap value of 3.3 eV\(^9\), and anatase TiO\(_2\), which is the most prominent photocatalysis actor of P25, has a band gap value of 3.2 eV\(^10\).

In 2015, Trapalis et al.\(^10\) made TiO\(_2\)-rGO composites from Ti(OC\(_3\)H\(_7\))\(_4\) with the same method adapted in this project. The composites were tested for photocatalytic NO\(_x\) removal, using visible light as energy source, and outperformed both pure TiO\(_2\) and TiO\(_2\) composites with surface stabilised graphene. Composites with an rGO content of 0.1 % were found to be the most efficient. Calza et al.\(^9\) made TiO\(_2\)-rGO composites from commercial P25 and tested its photocatalytic efficiency on risperidone, an antipsychotic drug. The TiO\(_2\)-rGO achieved reduction of toxicity and mineralisation faster than the pure P25, including reduction of intermediate biproducts from mineralisation.

C-mats such as carbon nanotubes (CNTs) have also been composited with TiO\(_2\), for example by Korhaghi et al. in 2017\(^11\), who used multi wall CNTs (MWCNTs) treated with nitric-sulfuric acid (1:1 volume ratio) to promote functional groups on the CNTs. This composite tested fourfold better than pure TiO\(_2\), when comparing their photocatalytic skill in degrading methyl orange (MO) under UV-light. The improvement was attributed to lowered charge recombination and enlarged surface area for the composite, and the best results were obtained for 30 wt% CNT. Another group, Xu et al.\(^12\), prepared TiO\(_2\)-CNT composites to test them on gas phase photocatalytic degradation of benzene, as well as liquid phase photocatalytic degradation of MO. These authors used 60 wt%, 80 wt% and 95 wt% CNTs, in relation to TiO\(_2\), and obtained better results for the composites than for the pristine material, the best result coming from the 95 wt% composite. The theory presented is that CNTs work as an electron reservoir, keeping the exciton pairs from recombining, and that CNTs support the structure and morphology of the TiO\(_2\) NPs during and after synthesis, assuring a large surface area and prohibiting agglomeration of NPs.

Other forms of nanostructured TiO\(_2\) have also had some success in photocatalysis research, such as TiO\(_2\) nanotubes (TNTs). Payan et al.\(^13\) made nanocomposites comprising single wall CNTs (SWCNTs) and TNTs: the use of TNTs instead of TiO\(_2\) NPs was intended to reduce agglomeration of TiO\(_2\) and improve interfacial contact between TiO\(_2\) and C-mats. Although some agglomeration was still present, the authors claim a very good result, indeed their composite tested better than bare TNTs or SWCNTs in photocatalytic degradation of 4-chlorophenol. The inclusion of SWCNTs is theorised having improved the composite by increasing the surface area, reducing exciton pair recombination and enhancing photocatalytic activity by including longer wavelengths.

**Bi-oxide core@shell nanocomposites**

The secondary focus of this study is a bi-oxide system with core@shell structured nanocomposites, SnO\(_2\)@ZnO, and the effect that this type of structure can have on photocatalytic properties. In a core@shell system, the excited electron is transferred from the VB in the shell to the CB in the shell, leaving behind a positive charge, a hole, in the VB of the shell. The same electron is then injected into the semiconductor with a lower band gap edge of CB, the core – in this case SnO\(_2\), and holes are injected in the opposite direction – into the higher band gap edge of VB, consequently in the shell. Thus, the excitons are separated, and recombination is inhibited\(^7\).

The difference between contact type and core@shell type mainly lies in the selectivity of the core@shell type heterostructure, which will only work as an oxidative agent, whereas the contact type heterostructure can be both oxidative and reductive agent\(^7\). The fabrication of core@shell structures allows for some special functionalities. A shell can protect the catalytic core substance from
photocorrosion, which is a problem for semiconductors of moderate to low band gap values, for example CdS\textsuperscript{14}. The core@shell structure induces an intimate contact between substances, which is preferable for charge transfer\textsuperscript{14,15}.

Numerous methods of manufacturing core@shell nanostructures are suggested in literature. Atomic layer deposition was performed by Ma et al.\textsuperscript{14} in the study previously mentioned, yielding a very thin layer of ZnO on a CdS core. The layer thickness was easily controlled by the number of deposition cycles applied. The thin layer is stated to guarantee transparency, so that the active photocatalyst can absorb light, yet protection towards photocorrosion. Core@shell nanoparticles can also be manufactured by wet chemistry, Huy et al.\textsuperscript{15} fabricated TiO\textsubscript{2}@MgFe\textsubscript{2}O\textsubscript{4} by two methods, parting either from annealed TiO\textsubscript{2} nanoparticles, or from its precursor, a TiO\textsubscript{2} powder obtained from a wet chemical hydrolysis process. The resulting core@shell nanoparticles showed similar properties, the one stemming from the TiO\textsubscript{2} precursor displaying a slightly higher rate of photocatalytic degradation of 2,4-dichlorophenoxyacetic acid. Das et al.\textsuperscript{16} manufactured core@shell Ag@ZnO NPs for solar light assisted water remediation. The shell was intended to prevent leaching of reactive metal ions into the purified water, to extend the shelf life of the catalyst and to inhibit the decrease of active surface area by dopant atoms. In addition to fulfilling these requirements, the core@shell NPs had a higher photocatalytic efficiency with regards to disinfection of water polluted by bacteria \textit{E. coli} and \textit{S. aureus}, than both pure ZnO NPs and Degussa P25.

Troian-Gautier\textsuperscript{17} \textit{et al.} studied the effect that a MOx@MOx core@shell structure can have on the lifetime of injected electrons from photinduced reactions. They compared TiO\textsubscript{2} to core@shell SnO\textsubscript{2}-TiO\textsubscript{2} thin films and found that the core@shell structures had a larger activation energy barrier for interfacial back-electron transfer; 32 kJ/mol for SnO\textsubscript{2}-TiO\textsubscript{2}, and 22 kJ/mol for TiO\textsubscript{2}. The theory that best fitted the results was a low energy trap state model with recombination from the TiO\textsubscript{2} rutile polymorph shell.

Both SnO\textsubscript{2} and ZnO have previously been investigated separately for their photocatalytic properties and shown interesting results\textsuperscript{18-20}. The advantage that SnO\textsubscript{2} and ZnO present contra TiO\textsubscript{2} is a natural abundance and larger band gaps. SnO\textsubscript{2} is also very stable towards photocorrosion\textsuperscript{21,22}, and ZnO presents a higher charge carrier mobility than TiO\textsubscript{2}\textsuperscript{20}. If one would obtain a composite combining the strengths of the two materials, its efficiency is expected to compare to, or surpass, that of benchmark P25 when it comes to photocatalysis.

Coupling of SnO\textsubscript{2} and ZnO in a contact type bi-oxide nanocomposite was performed by Uddin et al. in 2012, who fabricated a heterogeneous nanostructured powder for photocatalytic degradation of methylene blue (MB). The powder had a band gap value in between that of ZnO and SnO\textsubscript{2} respectively, and it displayed a higher photocatalytic efficiency than the MOx pure. It was theorised that it is the separation of excitons – electrons escaping into the SnO\textsubscript{2} and holes into the ZnO, upon their creation, that, via decrease in recombination, is the reason for this increase in photocatalytic activity\textsuperscript{7}.

Core@shell type SnO\textsubscript{2}-ZnO nanocomposites have been fabricated in different configurations, for example nanowires\textsuperscript{23}, nanorods, and nanoflowers\textsuperscript{24}. Li \textit{et al}.\textsuperscript{25} fabricated, by double precipitations and calcinations, spherical core@shell nanoparticles, that were investigated for their photocatalytic skill by decolouration of MO under irradiation at a wavelength of 365 nm. For comparison, a contact type nanostructured composite with the same MOx was also fabricated by co-precipitation and tested. The consequent result was that the core@shell nanocomposite was more efficient in photocatalysis, presumably because of enhanced charge separation. However, the difference in photocatalytic activity was very small, the authors claimed that some heterojunctions between the two MOx would have been formed during the co-precipitation, but that the core@shell structures ensured more of these heterojunctions and thus a higher photocatalytic efficiency. They found the optimal ratio of Zn to Sn to be 1:2 for this purpose.
Carbonaceous materials reduced at the nanoscale

Reduced graphene oxide

Graphene is a material which has been given much attention since its observation and characterisation by Novoselov et al. in 2004. It is a single-layer two-dimensional crystal structure, based on carbon atoms in a hexagonal lattice. Graphene experimental specific surface area is about 1 500 m$^2$g$^{-1}$, and its electrical conductivity about 2 000 Scm$^{-1}$.$^{26}$ A charge carrier mobility of over 200 000 cm$^2$V$^{-1}$s$^{-1}$ has been measured for a single layer of suspended graphene.$^{27}$ Graphene oxide (GO) is easier to produce in bulk$^{27}$ but has a lower charge carrier mobility. To be able to retrieve some of this important property, the GO is reduced to form reduced graphene oxide (rGO) – a good conductor that adheres easily to other chemicals.$^{28}$ Figure 4 illustrates the difference between these C-mats.

Figure 4: Illustration of the difference between (a) graphene, (b) graphene oxide and (c) reduced graphene oxide.$^{28}$ The markers illustrate different atoms/functional groups as follows: carbon (black), epoxy (red), carbonyl (blue), hydroxyl (green), carboxyl (light blue).

According to literature, coupling of rGO with a MOx photocatalyst has been found to increase its photocatalytic activity$^{29-32}$. Various theories exist to explain this phenomenon. For example, an rGO scaffold allows for a larger specific surface area of the composite material, increasing the number of possible adsorption sites$^{20,31}$. The high carrier mobility of rGO could induce the separation of exciton pairs upon their creation, and thus inhibit recombination by increasing the distance between the charges.$^{20,31}$ Recombination being one of the more leaned-upon theories to explain the low efficiency of MOx photocatalysts, inhibiting it has become a crucial field of research.

However, adding too much rGO to a MOx composite results in another effect; the agglomeration of rGO in films or stacks. This stacking will make the composite take on a graphite like structure, and so the unique properties of rGO are not put to use. The phenomenon also induces shadowing the MOx, thus reducing its light absorption efficiency.$^{33}$

Carbon nanotubes

CNTs were discovered in wakes of fullerenes, long before graphene, and can be considered its forebear.$^{31}$ They have the same sp$^2$-hybridised structure, with the difference that CNTs can be described as rolled up graphene sheets, as shown in Figure 4 (graphene) compared to Figure 5 (CNTs). There are two types of CNTs, single-wall (SWCNTs) and multi-wall (MWCNTs), their architectural difference being displayed in Figure 5. MWCNTs are several concentric tubes, whereas SWCNTs are single tubes. Diameters of SWCNTs range from below 1 nm to a couple of nm, and length can be up to several tens of microns, in powder format.$^{34}$ Grown on substrates, the length of the CNTs can be extended to mm. It has been shown that SWCNTs can have a greater effect on photocatalytic properties of semiconductors, as compared to MWCNTs.$^{35}$ This is motivated by the larger active interphase between the constituents, creating more of the sought synergistic effects, as well as the SWCNTs providing a better dispersion and scaffold for the TiO$_2$. However, the lower price of MWCNTs motivates research into making an efficient MWCNT-MOX photocatalyst.$^{12}$
CNTs have excellent mechanical properties\(^3\), making them interesting as fillers in composites. Their electrical properties are also outstanding, with a maximum current density of \(10^{13}\) A/m\(^2\)\(^3\). In this respect, they are viable for use in photocatalysts, with the aim to increase conductivity, induce charge separation and ultimately decrease exciton recombination\(^3\), much like the previously discussed rGO. CNTs has also been known to reduce MOx crystallite size and prevent the agglomeration of MOx nanoparticles in a composite\(^1\). This effect is explained by surface defects on the CNTs allowing for MOx grains to grow on the CNTs in a more controlled manner, in contrast to a dispersion of CNTs in a MOx lattice.

One significant issue with CNTs is their reluctance to disperse in liquids, which depends on the strong van der Waals interactions between \(\pi\)-bonds. This drawback can be remediated by the use of surfactants or by functionalisation of the CNTs themselves, the first having the disadvantage of needing to be removed after fulfilling its purpose\(^3\). Functionalisation of CNTs also improves the contact surface between composite constituents and prevents aggregation in the respect that the limit concentration of CNTs in the composite, before aggregation starts, can be increased\(^3\).

Zhang et al.\(^3\) compared the effect of adding graphene or CNTs to a semiconductor photocatalyst in 2011. It was found that graphene coupled with TiO\(_2\) results in a more efficient photocatalyst for conversion of alcohols to corresponding aldehydes, than CNTs coupled with the same MOx. However, the two composites showed similar results when the TiO\(_2\) NPs were integrated randomly on the surface of the C-mats, indicating that morphology of the resulting composite is crucial for the effect of these additives. The authors suggest that the random integration of TiO\(_2\) NPs on graphene sheets a) does not take advantage of the “structure-directing” properties of the substance, thus rendering it less useful than its potential, and b) results in a less than maximum interfacial contact between graphene and MOx, thus not fully utilizing the exceptional charge transfer abilities of graphene.

Weng et al.\(^3\) reported a similar result, i.e. the structure of the photocatalyst is of high importance. The authors coupled rGO and melamine-functionalised rGO with CdS. By the melamine functionalisation, the electrical conductivity of rGO was largely diminished, yet in combination with CdS gave an even higher photoactivity than the unfunctionalised rGO could induce in the composite. Those authors were able to conclude that electrical conductivity is not the main reason for rGO improving on a semiconductor photocatalyst, but the achieved structural effect has a larger impact.

**Photocatalytic water remediation**

The term water remediation refers to the act of purifying water from one or several pollutants. One way of achieving this is by the use of heterogeneous photocatalysis\(^4\). TiO\(_2\) is a well-documented substance
for this purpose, for example reduced at the nanoscale\textsuperscript{9}, and Degussa P25\textsuperscript{®} is commonly accepted as the benchmark material\textsuperscript{6,7,31}.

Heterogeneous photocatalysis includes various reactions, the goal is often to purify a gas or a liquid, air or water for example. According to Herrmann\textsuperscript{40}, the catalytic reaction can be divided into the following steps: transfer of the reactants (pollutants) in the fluid phase to the surface of the catalyst, adsorption, reaction in the adsorbed stage, desorption of products, and removal of products from the interphase region. The photocatalytic reaction concerns the third step: reaction in adsorbed state. There can also be some photoinduced adsorption or desorption of reactants, although mainly oxygen is concerned\textsuperscript{40}.

Several organic and inorganic pollutants have been object of studies devoted to find a suitable photocatalyst to eliminate them from water. Herein it is worth citing RhB, phenols\textsuperscript{30}, CO\textsubscript{2}\textsuperscript{41}, Cr(VI)\textsuperscript{20}, and heavy metals\textsuperscript{3}. Their degradation should result in the complete mineralisation of the pollutant, i.e. its transformation into some less harmful chemical, for example CO\textsubscript{2} and ethanol for organic pollutants or Cr(III) for Cr(VI).
Experimental section

Synthesis of materials

Materials were used as received from the suppliers, without any further purification or treatment, unless otherwise specified below.

Commercial TiO$_2$ P25-rGO hybrid nanocomposites

For comparison purposes, composites with commercial P25 (Sigma Aldrich) and rGO were prepared by making of pastes suitable for tape casting wherein different amounts of rGO were added to P25 powder. Typically, 2.9 g of ethyl cellulose (Sigma Aldrich) was mixed with 1 g of P25 and an amount of rGO dispersed in chloroform. 8 ml of α-terpineol (90 %, Sigma Aldrich), 3.3 ml of deionised water, and 16.9 ml of ethanol were added. The mixture was stirred for 24 hours, or until a homogeneous paste was obtained. This paste was partitioned; one part was used to prepare electrodes, according to the description below, and the other part was dried in 500 °C for 30 minutes.

TiO$_2$-rGO hybrid nanocomposites

Hybrid nanocomposites were prepared according to the synthetic method previously described by Trapalis et al. Specifically, when synthesising pure TiO$_2$, 1 g of Pluronic F127 (Sigma Aldrich) was dissolved in 113 ml of ethanol and 64 µl of HNO$_3$ 65 %. The mixture was stirred for 10 minutes, while dropwise addition of 7.3 ml of Ti(OC$_2$H$_5$)$_4$ (Sigma Aldrich) was carried out. A white precipitate immediately formed when the Ti-precursor was added. The mixture was then transferred into autoclaves and heated at 180°C for 2 hours, in a conventional oven. The product was washed several times in deionised water, dried and ground to a fine powder.

When synthesising hybrid composites, a specific amount of rGO dispersed in chloroform (≥99 %, Sigma Aldrich) was added to the reaction mixture prior the addition of precursor, and the solution was let stirring for 1 hour after the addition of precursor. With this exception, no changes were made to the synthetic procedure.

TiO$_2$-fCNTs hybrid nanocomposites

Hybrid nanocomposites with MWCNTs were prepared from commercial anatase TiO$_2$ pastes (Dyesol® TiO$_2$ Paste DSL 18NR-T, Sigma Aldrich) with average nanoparticle size 4 nm.

Commercial MWCNTs were functionalized with p-methoxyphenyl substituents by Prof. E. Menna and co-workers at the University of Padova (hereafter called fCNTs). The functionalisation was carried out through in situ generation of diazonium salts of p-methoxyaniline, in the presence of isopentyl nitrate. The fCNTs were dispersed in chloroform (≥99 %, Sigma Aldrich) prior to any use.

To prepare 1 g of composite, 5 g of paste was weighed and diluted with 1.5 ml of ethanol, after which dispersed MWCNTs were added. The mixture was stirred for 24 hours, until homogeneous colour and texture of the paste were observed. Annealing was done at 500 °C for 30 minutes. Before annealing, the pastes could be used for preparing electrodes, according to the description below.

SnO$_2$-ZnO core@shell nanostructures

SnO$_2$ NPs were synthesised according to a procedure previously described by Milan et al. In a typical reaction, 3.6 g Sn (IV) Cl$_2$·5H$_2$O (98 %, Sigma Aldrich) were dissolved in 100 ml ethanol, and 5 ml of NH$_3$·H$_2$O (25 %, Merck) were added dropwise over 10 minutes, whereupon a white flocculate immediately formed. The dispersion was left in room temperature under constant stirring, for 20 minutes, then dried at 80 °C on a hot plate. The dried raw product was scraped into a crucible and annealed for one hour at 500 °C.

The subsequent application of a thin ZnO shell on the SnO$_2$ NPs was performed by Dr. M. Epifani at the National Research Council in Italy in the frame of a scientific collaboration, by precipitation method.
Electrodes for electrochemical characterisation

Electrodes were fabricated by tape casting on a conductive substrate (fluorine-doped tin oxide glass (FTO-glass), with an active area of approximately 15x15 mm²). For paste preparation, unless this step was included in the synthetic process, 65 mg of ethyl cellulose (Sigma Aldrich) was mixed with 180 µl of α-terpineol (90 %, Sigma Aldrich), 80 µl of distilled water and 380 µl of ethanol, and 30 mg of sample was added. The solution was let stirring overnight.

The FTO-glass substrates were thoroughly washed in water and soap, ethanol and acetone, then sonicated in acetone for 15 minutes, and again washed in acetone. The paste was tape cast on the conductive side of the substrates in three layers. Each layer was dried for 10-15 minutes on a hotplate at 120 °C, before the next layer was applied. Annealing was done in an annealing hot plate oven, at 500 °C for 30 minutes.

Characterisation of materials

Optical, morphological and structural characterisation of materials

Scanning electron microscopy (SEM) was carried out in a FEI Magellan 400. X-ray diffraction (XRD) patterns were recorded on a Siemens D5000. Evaluation of crystallite sizes was done by the Williamson-Hall plot (Equation 1).

\[ B \cos \theta = C \varepsilon \sin \theta + \frac{K \lambda}{L} \]  

Equation 1

The width B measured is the full width at half maximum (FWHM), θ is half of the angle at which this maximum occurs (Bragg angle), K is the constant of proportionality (or the Scherrer constant) and λ is the X-ray wavelength, 154 Å. The particles are assumed spherical, K = 0.89. L is the diameter of the NPs. C is a constant and ε the internal strain of the particles. Thus, the size component can be taken from the intercept, and the strain component from the inclination.

An Edinburgh Instruments FLS 980 was used for photoluminescence spectrophotometry (PL). With Equation 2, band gap was determined, and quenching phenomena investigated. h is Planck’s constant, c is the speed of light, and λ is the wavelength at which the band gap was detected.

\[ E = \frac{hc}{\lambda} \]  

Equation 2

UV-visible spectra (UV-vis) were recorded in an Agilent Cary 5000. For liquids, quartz cuvettes of 1.5 ml were used, and for powders, a holder with a quartz window. The band gap can be calculated with the Kubelka-Munk function (K-M), applied to the slope of the reflectance data. R in Equation 3 is the reflection.

\[ F = \frac{(1 - R)^2}{2R} \]  

Equation 3

F in Equation 3 is plotted against the energy of the applied irradiation, calculated with Equation 2. By performing a linear fit on the drop in F, the band gap is taken as the intercept.

Electrochemical characterisation of materials

Cyclic voltammetry (CV) was carried out in a ModuLab XM electrochemical station (Solartron Analytical). Experiments were performed in a three electrodes configuration, with the investigated composite as working electrode, a platinum foil as the counter electrode and a micro Ag/AgCl electrode as the reference electrode. The experiment was performed in a 0.1 M Na₂SO₄ aqueous solution. CV was performed in ascending order of scan rate and using a staircase type of loading.
Photocatalytic activity of materials

Rhodamine B (RhB) was used as a molecular model for determining the water remediation capabilities of the composites. 10⁻⁵ M aqueous solutions were prepared and used as testing solutions. 50 mg of catalyst were added to 100 ml of the testing solution, the concentration of catalyst was thus 0.5 g/L. This mixture was let stirring in the dark for 30 minutes to allow for absorption/desorption equilibria to take place. Then the reaction mixture was irradiated with the solar light simulator, and 0.5 ml aliquots were taken out at known times, diluted with 2 ml H₂O and centrifuged. The corresponding absorption spectra were recorded, and the concentration of pollutant was determined by use of the calibration curve in Figure 6, previously built up by measuring the absorption of solutions with known concentrations of RhB and using the Lambert-Beer law.

Figure 6: Calibration curve for RhB, used in photodegradation tests for calculating the concentration of pollutant from absorption spectra. Squares are data points, and the line is the fitted calibration curve. Interception of the y-axis is at x= -4.1*10⁻⁴, the slope is 106866 and R² is 99.999%.
Results and discussion

Synthesis of materials

A list of synthesised materials is reported in Table 1.

<table>
<thead>
<tr>
<th>Label</th>
<th>Mass content rGO</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25-1</td>
<td>0</td>
</tr>
<tr>
<td>P25-2</td>
<td>1 %</td>
</tr>
<tr>
<td>P25-3</td>
<td>0.01 %</td>
</tr>
<tr>
<td>P25-4</td>
<td>0.05 %</td>
</tr>
<tr>
<td>P25-5</td>
<td>0.1 %</td>
</tr>
<tr>
<td>Ti-1</td>
<td>0</td>
</tr>
<tr>
<td>Ti-3</td>
<td>0.01 %</td>
</tr>
<tr>
<td>Ti-4</td>
<td>0.05 %</td>
</tr>
<tr>
<td>Ti-5</td>
<td>0.1 %</td>
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</tbody>
</table>

<table>
<thead>
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</tr>
<tr>
<td>TC-3</td>
<td>0.01 %</td>
</tr>
<tr>
<td>TC-4</td>
<td>0.05 %</td>
</tr>
<tr>
<td>TC-5</td>
<td>0.1 %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Label</th>
<th>Atomic ratio SnO₂:ZnO</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Pure SnO₂</td>
</tr>
<tr>
<td>SZ-1</td>
<td>20:1</td>
</tr>
<tr>
<td>SZ-2</td>
<td>10:1</td>
</tr>
</tbody>
</table>

In the original recipe for Ti-composites, rGO was dispersed in water before being added to the TiO₂ precursor. Here rGO was instead dispersed in chloroform, to follow the same synthetic approach used with fCNTs.
Characterisation of materials

**P25-rGO hybrid nanocomposites**

SEM analysis of two composites based on P25 NPs is shown in Figure 7. NPs (average particle size around 20 nm) are clearly visible, while no direct imaging of rGO is possible. Direct imaging of C-mats dispersed in MOx nanostructures is difficult, supporting a conformal coverage by the semiconductor nanoparticles.

![SEM images of (a) P25-2 (1 % rGO) and (b) P25-5 (0.1 % rGO).](image)

XRD patterns of P25-composites, reported in Figure 8, showed that 74% of the crystalline material was anatase, and the remainder rutile. This is consistent with the normal ratio of 3:1 anatase to rutile, declared for P25 by the supplier. The anatase had an average crystallite size of 36 nm and the rutile 48 nm, according to Scherrer analysis (Equation 1). These results indicate that the crystallites have grown during processing, from their original 21 nm diameter.

![XRD spectra of P25-5 (0.1% rGO), representative of all P25-composites. Figure includes the XRD patterns for anatase (red bars) and rutile (blue bars) taken from the Empyrean package database (September 2011).](image)
Analysis of electrochemical measurements is the key to understanding some electrical behaviours of the materials. For example, accumulation of charges in the materials is investigated by applying different CV scan speeds and comparing the current response to loading and unloading of voltage. There is also information about the rate of recombination of excitons pairs, which is supposed to be slowed by addition of C-mats. The electrochemical behaviour of the materials can explain some functional results and possibly indicate improvements.

Cyclic voltammograms of the P25-based samples are reported in Figure 9a and b. A comparison of the voltammetry features of the materials shows a faradaic behaviour with almost no charge accumulation for the samples constituted by bare TiO$_2$ and the 0.1 wt% rGO composite, while some charge accumulation can be seen in case of the 1 wt% rGO composite.

Analysis of the voltammograms recorded at different scan speeds (1 wt% rGO composite is reported in Figure 9b as example, the other specimens featuring the same trends) shows that charge accumulation is favoured at slow scan speed, being also that the current onset is positioned at higher voltages. This feature may suggest that charge accumulation within the materials is a slower process compared to diffusion favoured by the electrolyte, and that mass transport is the limiting factor in charge transport.

Current density is linearly proportional to the square root of scan speed for all the materials (Figure 9c), thus suggesting a diffusion-controlled charge exchange within the circuit.

![Figure 9. Electrochemical characterization of TiO2 P25-based materials. (a): cyclic voltammograms (scan speed: 50 mV s$^{-1}$) of all the samples; (b): cyclic voltammograms at all the investigated scan speeds for sample P25-5; (c) trend of maximum current density vs. the square root of scan speed; (d) capacitance of the materials according to the rGO content. (a) and (c): red markers: bare P25; grey markers: P25-5 (0.1% rGO); black markers: P25-2 (1% rGO).](image)

Analysis of capacitance vs. rGO content (reported in Figure 9d) highlights a clear trend: capacitance increases with the increase of rGO content in the composites. An addition of 0.1 wt% rGO induces an
increase of the capacitance of almost three times as compared to pristine P25, from 0.09 mF for pristine P25 to 0.25 mF for P25-5. It is remarkable to notice that adding more rGO does not result in any relevant further increase of capacitance; indeed, the composite featuring 1 wt% rGO shows 0.03 mF more than the composite with 0.1 wt% rGO does.

This type of behaviour could hint at a percolation limit; as previously mentioned, rGO can start stacking in the event of too large quantities being present. This stacking inhibits the increase of contact with the MOx upon rGO addition and has been seen to inhibit some of the characteristics of rGO. Essentially, the product closes in on a graphite structure.

Typical spectra from photocatalytic degradation of a solution with 10⁻⁵ M RhB is represented in Figure 10. Each line in the diagram of epresents the UV-Vis spectrum of an aliquot taken from the reaction mixture at a specific time. RhB has an important absorption peak at 554 nm. The highest peak values at 554 nm are reached in the first couple of aliquots, after which the value of this peak starts to diminish, representing the decrease in RhB concentration in the reaction mixture. At the same time the peak starts shifting to lower wavelengths, a so-called hypsochromic shift, which has previously been interpreted as N-deethylation of the RhB into other species⁴.

Figure 10: Typical spectra from photocatalytic degradation of RhB, each curve representing an aliquot removed at a specific time.

Hypsochromic shift has previously been described by Epifani et al.⁴ for photodegradation of RhB with MOx NPs. Those authors based their statements on the work of Watanabe et al.⁴² who monitored RhB degradation by photocatalysis with suspended CdS powder in aqueous dye solution. They found that RhB (N,N,N',N'-tetraethylrhodamine) degrades stepwise by N-deethylation to TER (N,N,N'-triethylrhodamine), DER (N,N-diethylrhodamine), MER (N-ethylrhodamine) and finally rhodamine, all of which have different maximum absorption peaks in UV-Vis spectrophotometry; 554 nm, 539 nm, 522 nm, 510 nm and 498 nm respectively. By formal quantum efficiency measurements, Watanabe et al. were able to deduce that the degradation of RhB proceeds either by the excitation of the CdS, or by light absorption of the dye molecule, and that the latter was by far the more prominent pathway. RhB is stable in aqueous solution when irradiated with light of wavelength <350 nm. The authors also pointed out that although light absorption on RhB is the main degradation pathway in this system, any surface is not enough to degrade the RhB – the presence of a photoreactive substance is needed.
Figure 11 describes the photocatalytic performance of the composites prepared from commercial P25. The performance of the P25 was expected to be enhanced by the addition of rGO (see section State of the Art), but this was not the case – not for very small, nor for larger quantities of rGO.

The performance of the P25 was expected to be enhanced by the addition of rGO (see section State of the Art), but this was not the case – not for very small, nor for larger quantities of rGO.

Since there is no significant difference in photocatalytic functionality between the samples with 0.1 % and 1 % added rGO, it could be theorised that a limit of rGO content is reached. Adding more only adds to an already growing stack of rGO sheets, which will make no change to the functionality. Indeed, since there is no obvious decrease in photocatalytic performance either, it could be theorised that this limit occurs even before 0.1 wt%. This lack of improvement could also be due to the method of manufacturing, since previous authors have managed to add such amounts of C-mats as was attempted here, and attained measurable improvement as to photocatalytic skill⁹.
A hypsochromic shift is evidenced in the degradation of RhB, as was mentioned in the Experimental section. For P25-rGO composites, there is no clear relation between rGO contents and rate of shift, as can be seen in Figure 12. The fastest shift is achieved with the highest amount of rGO, 1 wt%; after 120 minutes the solution has the same composition of RhB species as the composite featuring 0.1 wt% rGO achieves after 180 minutes. The pristine P25 never reaches this composition.

**TiO$_2$-rGO hybrid nanocomposites**

Figure 13 shows two representative images of TiO$_2$-rGO composites, manufactured from the precursor Ti(OC$_3$H$_7$)$_4$. In Figure 13a, some aggregations are showing, possibly this is the rGO sheets covered in NPs. Figure 13b is a close-up, where it is shown how well the rGO is covered in NPs, and that they seem small and reasonably similar in appearance. There is no visible rGO in any of the SEM images.

XRD results, reported in Figure 14, show the presence of anatase phase, and no traces of rutile phase. W-H analysis yields a crystallite size of 42.4 nm for the pristine material, although the linear fit is not
very accurate, $R^2 \approx 0.2$. For Ti-2 (1 wt% rGO), W-H yields a smaller crystallite size, 34.8 nm, however the linear fit is more accurate, $R^2 \approx 0.5$.

![XRD pattern](image)

**Figure 14**: XRD pattern of TiO$_2$-rGO composites: pristine material and composite with 1 wt% rGO. Figure includes the pattern for anatase (red bars) taken from the Empyrean package database (September 2011).

The difference in crystallite size, as evidenced by W-H analysis, is small comparing the pristine material to the composite, even though this composite has the largest amount of rGO added, among the composites synthesised here. Considering that the linear fit is not perfect, it is reasonable to say that addition of rGO does not affect the crystallite size of TiO$_2$.

In Figure 15 is reported the results of cyclic voltammetry analysis of TiO$_2$-rGO materials. From the voltammograms the same trend could be discerned as was discussed for P25-materials, a higher current onset for slower scan speeds. Here represented in Figure 15b is only the results of Ti-1, but the remaining samples follow the same trend. Thus, it seems again that mass transport is the limiting factor in charge transport.

From Figure 15c, it is clear that current onset is also higher for a lower amount of rGO, which could indicate that the charge transfer capabilities of rGO are being harnessed in the composites. In this case, that means that charge accumulation is lower in the composites than the pristine material.
In addition, the current density reported in Figure 15c and d is higher than the values recorded for P25-rGO composites. For the pristine materials, P25-1 attained a peak value of 1.7 μA/cm², whereas Ti-1 attained 14.2 μA/cm². The proposed reason for this interesting result is the presence of rutile crystals in P25 – indeed, P25 consists to about ⅓ of rutile crystals, as was evidenced by the XRD pattern in Figure 8.

The capacitance of the TiO₂-rGO composites is reported in Figure 15a. The capacitance seems unchanged for a small addition of rGO; the fact that a composite with 0.01 wt% rGO presents a lower capacitance than pristine TiO₂ is considered an experimental artefact. However, the composite featuring 0.05 wt% rGO showed a capacitance of about 2.5 times the value pertaining to pristine TiO₂ – 0.73 mF for Ti-3 compared to 0.29 mF for Ti-1. This finding indicates that the rGO capability of storing electrical charge is preserved in the composites, once a proper amount of C-mat is dispersed in the MOx crystal lattice. This may be extremely relevant for functional applications; indeed, these stored charges might be made available for chemical reactions at the composite surface.

It is also relevant that TiO₂-rGO composites manufactured from precursor material seems to have higher capacitance values overall, as compared to P25-rGO composites. Already the pristine material shows a difference, with Ti-1 presenting a capacitance of 0.29 mF and P25-1 presenting 0.09 mF; the capacitance is more than three times larger for Ti-1 as compared to P25-1. This difference could again be attributed to the presence of rutile phase in P25 – anatase is the better electron charge storage, compared to rutile.
As for composites, only a trend can be derived from the presented results, since the rGO contents do not coincide between the two substances. However, it can be deduced that Ti-rGO composites seem to have a larger capacitance than P25-rGO composites, and that the addition of rGO seems to have a greater impact on the Ti-rGO materials. Figure 16 is inserted for visualisation, although no direct comparison can be made. Another possible reason, excepted the mentioned difference in crystal structure, is related to a better adhesion of TiO$_2$ particles to the rGO sheets, which should favour the “electrical talk” between the two materials. Indeed, previous studies\textsuperscript{31} have found that materials manufactured with the C-mat present during NP formation showed a better adhesion between NPs and C-mat, than materials combining prepared NPs and C-mat.

At present, the actual reason behind the differences in capacitance observed is not fully clarified, but the results would indicate that the composite Ti-rGO should be more suitable for photocatalysis from an electrical perspective. Photocatalytic testing yielded the graph in Figure 17.
Figure 17: Photocatalytic performance of pristine TiO$_2$ (black markers), and composite with 0.01 wt% rGO (red markers). The experiment was conducted in an aqueous solution of 10$^{-5}$ M RhB, and the irradiation was manufactured sunlight. Lines are a guide for the eye.

Compared to P25, the pristine TiO$_2$ is not as efficient a photocatalyst. It also seems that the addition of 0.01 wt% rGO has little effect on the photocatalytic skill of the material.

The deethylation is not very progressed with the Ti-materials, although the pristine material seems a little bit more efficient – the main constituent after 180 min of photocatalysis, is the first bi-product of RhB deethylation, TER, which has its peak at 539 nm (the lowest wavelength measured here is 538 nm). Compared to RhB deethylated by P25 which reached as low as 529 nm after 180 min, and where consequently DER is more prominent, having its peak at 522 nm.

Pristine P25 would reach an RhB concentration of 32 % compared to initial concentration after 60 min, whereas it takes the pristine TiO$_2$ manufactured from precursor 180 min to reach a similar value, 29 % compared to initial concentration. It seems that the mixture of crystal structures in P25, anatase and rutile, is beneficial for photocatalytic skill. There is very little difference in size, according to the XRD measurements – both the P25-rGO composites, and the Ti-rGO composites measured around 40 nm. However, the pristine P25 should, according to the manufacturer, have a diameter of about 21 nm, which increased some for the composites, as seen in XRD measurements. In that case, since the pristine material is the best photocatalyst, it is reasonable to say that such a small diameter of NPs is beneficial for photocatalytic skill of TiO$_2$.

TiO$_2$-fCNT hybrid nanocomposites

Representative SEM imaging of TC-composites is reported in Figure 18. Imaging was done on tape casted FTO-glass electrodes, in part to increase the visibility of the images by enhancing the adhesion between the conductive support and the sample – tape casted electrodes show an enhanced adhesion with respect to powder adhering to carbon tape, and in part because imaging of CNTs is quite difficult due to their complete coverage by NPs.
In Figure 18a and d, the conformal coverage of fCNTs by the TiO$_2$ particles is clearly visible: no fCNTs can be detected in the uncracked active surfaces. The fCNTs are only visible in the cracks on the surface, as depicted in Figure 18b and c. They are mostly found in bundles, emerging from a “sea” of TiO$_2$ NPs, which adhere well to the fCNTs. A proper adhesion is mandatory to enable charge transfer between the two substances.

It seems that bundling is more consistent in the composite featuring five times more fCNTs, which indeed sounds reasonable. In fact, the fCNT visible in Figure 18b is the only one found in TC-3 containing 0.01 wt% fCNT.

In Figure 18d is a close-up of the uncracked surface of the active layer, illustrating the appearance of NPs. According to the manufacturer, these NPs should have an average size of 4 nm, however this image seems to disagree. NPs do not appear spherical, but instead cylindrical, in that case having two defining sizes – diameter and length. By measuring directly on the images, an average crystal length is found at 39 nm. The diameter is more difficult to discern from these images, XRD patterns are required for more information. The fact remains that the size and appearance of NPs are not completely homogeneous. Comparing them to for example P25 NPs (Figure 7), they appear much larger and less homogeneous.

CV scans of TiO$_2$-fCNT composites are presented in Figure 19. On a side-note, when manufacturing these electrodes, it was necessary to scrape off some of the active layer, that showed poor adhesion to the substrate, leaving some area of bare FTO-substrate which was subsequently submerged in the electrolyte and possibly contributed to the results. The electrodes concerned were those carrying TC-3
and TC-4, approximately half of the submerged conductive surface was covered in TiO$_2$-fCNT composite.

![Graph](image)

**Figure 19:** Voltammograms of al TC-samples (scan speed 50 mV/s), (a) survey, and (b) detail.

Notably there is an exponential increase in current for all the samples, and there are some clear differences in the batch. Pristine TiO$_2$ (TC-1) and the composite featuring the highest amount of fCNTs (0.1 wt% for TC-5) show an almost identical behaviour, although capacitance measurements, obtained from cyclic voltammetry, shows a slightly higher result for the composite.

The samples start to show an increase in current density at different polarisation voltages; -0.1 V for TC-1 and TC-5, and 0.3 V for TC-3 and TC-4. This could mean that there is a shift of Fermi level, something that has been reported previously. At increasing scan speed, charge accumulation was recorded in all cases. On the other hand, the shape of voltammograms suggest a close to faradaic behaviour, in turn implying that charge loss is dominating.

It is noteworthy that TC-3 featuring 0.01 wt% fCNT, reports maximum current density values that surpass the other composites, and the pristine material, by far. For instance, the highest value of current density for TC-3 is 7.6 $\mu$A/cm$^2$, which is more than eight times higher than the second highest value, 0.92 $\mu$A/cm$^2$ recorded for the pristine material. That such a low amount of C-mat dispersed in a MOx scaffold is ideal with respect to electrical behaviour is in agreement with previous findings.

Figure 20 shows the capacitance of TC-composites vs. fCNT contents. The sample featuring 0.01 wt% fCNT exhibits the highest capacitance, about five times higher than that of the others – 0.054 mF for TC-3, compared to 0.015 mF for TC-4 and 0.008 mF for the pristine material.
The lower capacitance recorded from composites featuring an amount of fCNTs higher than 0.01 wt% suggests some agglomeration of fCNTs at higher concentrations, as was seen in SEM images. Agglomeration, instead of an even dispersion, of fCNTs would decrease the contact area between C-mat and MOx, and thus diminish the probability of harnessing the properties of the C-mat. It is interesting that the capacitance of TC-composites is about 10 or 30 times lower than for the other TiO$_2$-composites. Pristine Dyesol® TiO$_2$ has a capacitance value of 0.0081 mF, pristine P25 TiO$_2$ measures 0.090 mF and pure TiO$_2$ manufactured from precursor material measures 0.29 mF. It has been proposed that rutile is a less efficient charge storage, compared to anatase, but this cannot be the reason for Dyesol® TiO$_2$ NPs having such low capacitance, since they are 99.9 % anatase. In the frame of these results, it would seem that from an electrical point of view, the Ti-rGO composites should be the best suited for photocatalytic water remediation.

There is no significant trend in photocatalytic skill when adding fCNTs to the Dyesol® TiO$_2$. There is a small decrease in skill, again pointing to the superiority of the pristine material, but the amount of fCNT does not seem to influence this decrease. In fact, the decrease itself is so small, that it could be interpreted as an experimental artefact. There is however a palpable change in the hypsochromic shift. It seems that the more efficient prompter of deethylation of RhB is the pristine material, the data suggests that after 180 min, the main constituent of pollutant is a mixture of the first and second biproducts, TER and DER. This result equals that of P25-composite with 0.1 wt% rGO, although the pristine P25 outperforms them both, reaching this stage after 120 min of reaction time.

SnO$_2$-ZnO core@shell nanostructures
SnO$_2$@ZnO core@shell structures were synthesised by applying a thin shell of ZnO on prepared SnO$_2$ NPs. SEM images are displayed in Figure 21.
The SnO$_2$ NPs were determined to be spherical and have a diameter of 9-12 nm. In Figure 21b, the homogeneity in shape and size of the NPs can be seen. It looks like the NPs in SZ-1 and SZ-2 are a little bit larger than the pristine SnO$_2$, which would be logical if the NPs were covered in a layer of MOx. In Figure 21e an area that looks melted is marked with an arrow. This could be a separate phase of ZnO, these areas do not show up at all in the pristine SnO$_2$, see Figure 21a. The separate phase is discovered.

Figure 21: SEM images of (a and b) pristine SnO$_2$ NPs, (c and d) SZ-1 with a molecular ratio SnO$_2$:ZnO 20:1, and (e and f) SZ-2 with a molecular ratio of 10:1.
also for the SZ-1, which features half the amount of ZnO as compared to SZ-1, but they are scarce, and smaller, than for SZ-2.

XRD patterns of the materials are presented in Figure 22. It was confirmed that there is no zincite phase present, so the layer of ZnO is likely amorphous. This is what was expected for such a small addition of MOx. By W-H analysis, the crystallite size and internal strain in the system is found not change with the addition of ZnO, also confirming the amorphous nature of the ZnO.

From Figure 22 there is no clear difference between the pristine SnO$_2$ NPs and the core@shell NPs. The graph displays the substance featuring more ZnO, it is implied that there is no change for the SZ-1 either.

Tauc plots for these materials, retrieved from UV-vis analysis, are shown in Figure 23. Both composites (SZ-1 and SZ-2) show two separate materials present namely SnO$_2$ and ZnO, which was expected. In Figure 23b is the Tauc plot for SZ-2, with the slopes indicating the presence of SnO$_2$ and ZnO marked, the behaviour is clearer in the composite featuring more ZnO, but also visible for SZ-1. The two band gaps showing is intriguing, because it could mean that the amorphous ZnO shell is transparent, although it could also indicate an insufficient coverage of SnO$_2$.

\[ \text{Figure 22: XRD patterns of pristine SnO}_2 \text{, and the core@shell systems with ZnO with a ratio SnO}_2 \text{ to ZnO of 10:1.} \]
According to the extrapolated slopes in Figure 23b, the two band gap values measured are 3.45 eV and 3.36 eV for SZ-2. According to literature, the band gap for SnO$_2$ and ZnO are 3.7 and 3.2 respectively\(^7\), which means that the band gaps for SZ-2 are slightly different than the original materials. The distance between them seems contracted.

A PL scan of pristine SnO$_2$ is shown in Figure 24. By Equation 2, its band gap was calculated to 3.5 eV.

The PL scans for SZ-1 and SZ-2 are shown in Figure 25. For comparison with the pristine material, take note of the black curve, which in both spectra in Figure 25 are taken at 300 nm, and the fact that the scans are in different scales.
In Figure 25a, SZ-1 is displaying its first peak, the band gap peak, at 439 nm. This peak increases at longer emission wavelengths. It points to more light being absorbed and re-emitted at these wavelengths. There seems to be two peaks, or rather bumps, marked with arrows in Figure 25b, on the magenta line representing the scan at 380 nm. These are present also in Figure 25a, magenta and blue lines, however less pronounced. The first bump is attributed to the band gap, the second one is likely an experimental artefact. The large peak between 550 nm and 700 nm is attributed to the ZnO NPs.

Figure 26: Photocatalytic performance of pristine SnO₂ (black markers), SZ-1 (red markers), and SZ-2 (green markers). The experiment was conducted in an aqueous solution of 10⁻⁵ M RhB, and the irradiation was manufactured sunlight. Lines are a guide for the eye.
Photocatalytic performance of SZ-composites is displayed in Figure 26. The pristine material does not show any photocatalytic skill. The composites show a slight improvement in comparison, however the measurements are dubious since the amount of RhB seems to increase compared to initial concentration (SZ-1, red line of Figure 26). SZ-2 shows a degradation of about 10% compared to initial concentration, but this increase in skill is not very convincing, as it could be the ZnO present acting on its own, rather than improvement stemming from the core@shell structure.

There was no significant hypsochromic shift recorded for the core@shell NPs, nor was there any difference between the samples. A test with a mixture of SnO$_2$ and ZnO NPs in the same ratio, should give information about whether the advantages of the structure are harvested or not.

It is theorised that NPs are in fact saturated with RhB, which would seriously reduce their efficiency towards photocatalysis. In fact, preliminary trials with pristine SnO$_2$ NPs and a solution with a $10^{-4}$ M RhB were conducted and showed some remediation of the pollutant.
Conclusion

When it comes to photocatalytic skill, the primary focus of this study, it seems that the P25-composites are the ones more affected by the addition of C-mats – even though this effect was negative in the sense that the photocatalytic degradation of RhB decreased. Neither Ti- nor TC-composites show great difference in behaviour in this respect, when adding C-mats. However, chemical capacitance was increased by addition of rGO, yet again the addition of CNTs does not seem to have affected the composite greatly.

The core@shell nanocomposites need more investigation. We have seen no improvement of photocatalytic skill, even though characterisation indicates that composites indeed differ from the original NPs on optical and morphological, and sometimes structural, levels.

It can be noted that the band gap energy for bare SnO$_2$ seems to vary somewhat according to the testing technique – with reflectance and K-M it was found to be 3.8 eV, but with PL it was found lower, at 3.5 eV. There are pros and cons of both techniques. PL seems the more direct way of finding the band gap, however the peak from which it is calculated is less easily defined. As for the reflectance measurements, the K-M takes more than one peak value into consideration, an approximation is made from the extrapolation of a slope. It could be mentioned that the $R^2$ value for these extrapolations never dropped below 0.99.

Another note is that there is evidently some error margin in the photocatalytic tests. This has not been investigated systematically, but one can see from, for example, Figure 26, that RhB concentration seems to be increasing as the test is running, which is effectively impossible. Thus, we can assume a margin of at least the difference between the normalised concentration at $t = 0$ and the maximum normalised concentration attained. Except for the human factor, the sampling of testing solution should be the biggest source for errors. The needle used is thoroughly washed in between each sample, but RhB is a very strong dye and it is possible that some is transferred between samples. Using an autopipette with disposable tips would improve on this.
Future Work

It is theorised that enhancing the dispersion of fCNTs before adding them to the MOx could improve on the result, this could possibly be achieved by further sonication or a change of dispersant. However, changing the dispersant would most probably elevate the toxicity of the process, compare chloroform to for example dimethylformamide, which is a common dispersant. In spite of this argument, it would be interesting to see the difference that an improved dispersion could have, perhaps it would be possible to increase the percolation limit for stacking or bundling of C-mats.

To continue the photocatalytic experiment until it stabilises; instead of letting a time frame rule the experiment, one would let the chemical reaction decide when it is done, could give clues about what happens to the remaining products. According to Watanabe\textsuperscript{42}, the best mineralisation is achieved by simultaneous hypsochromic shift and decrease in UV-Vis absorption. Those authors conducted the experiment for 5 hours, here 2 or 3 hours are the limits. It would also serve a comparative purpose to use a more diluted RhB solution, for example 10^{-6} M, especially for core@shell NPs, since we have preliminary results that indicate a better result at this concentration.

As mentioned, structure could be very important to the functionality of the composite. Structure has been investigated by SEM and XRD here, but transmission electron microscopy would give information, especially about the core@shell nanocomposites, that we have not seen. It is of course pertinent to confirm that the desired structure is achieved for these particles in particular. In addition, it would as mentioned be interesting to see what photocatalytic performance a mixture of SnO\textsubscript{2} and ZnO NPs at the same ratio as in the core@shell NPs could have. Comparing that to the results from SZ-1 and SZ-2 would tell us if ZnO is in fact acting on its own in the core@shell NPs, or if the result achieved here is due to the structure of the NPs.

Preliminary light absorption tests have been conducted on some TiO\textsubscript{2}-rGO composites, hinting at UV-light in fact being absorbed on the NPs. This would indeed inhibit the photon participation in photocatalysis, and thus lower the photocatalytic performance of the materials. A more dedicated study of this phenomena is required.

Some aspects have not been dealt with at all during this project, for example investigation of specific surface area of composites, which could be very interesting. Sequestration investigations would also further the research. A problem here is the separation of particles; after photocatalytic reaction there are two types of residues – one pale pink powdery residue that sinks to the bottom of the beaker and is easily separated from the solution by centrifugation, and one bright pink flaky type of residue that floats and has yet been very difficult to effectively remove from the solution. A suggestion to resolve this problem is lowering the surface tension before separating particles and solution or using a filter system instead of centrifugation. The latter was experimented with here but failed, and thus needs more attention or a different strategy.

On another note, Zhuang \textit{et al.}\textsuperscript{44} examined RhB photocatalytically degraded over TiO\textsubscript{2} bilayer films, and found by total organic carbon measurements that the sample providing the highest degree of mineralisation was the one displaying both a hypsochromic shift and a decrease in absorbance – which our samples do. It would thus be interesting to verify the hypothesis of Zhuang and to investigate further the changes that C-mats induce in this respect.

Once a reliable photocatalyst is found, it would be interesting to see how it behaves when recycled. For designing a lasting water remediation system, this is of outmost importance.
References


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