Improved photocatalytic activity of TiO$_2$ inverse opal nanostructures
IMPROVED PHOTOCATALYTIC ACTIVITY OF TiO$_2$ INVERSE OPAL NANOSTRUCTURES
Filipp Temerov

IMPROVED PHOTOCATALYTIC ACTIVITY OF TIO$_2$ INVERSE OPAL NANOSTRUCTURES

Publications of the University of Eastern Finland
Dissertations in Forestry and Natural Sciences
No 418

University of Eastern Finland
Joensuu
2021

Academic dissertation
To be presented by permission of the Faculty of Science and Forestry for public examination at the University of Eastern Finland, Joensuu, on February 19, 2021, at 12 o’clock noon.
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New energy sources are required for the development of modern society, for which heterogeneous photocatalysis is considered as a promising approach. The most studied heterogeneous photocatalyst is titanium dioxide (TiO₂). TiO₂ is a semiconductor material with a number of advantages such as absorption of the ultraviolet A (UVA) light, low cost, and nontoxicity. On the contrary, it has a large bandgap (3.2 eV) and a high recombination rate of photogenerated electron-hole pairs, which hinder its utilization for the visible light heterogeneous photocatalysis. Several strategies have been suggested to remove these obstacles including metal (Fe, Mn) and non-metal (N, S) doping, deposition of plasmonic nanostructures (Au, Ag, Pt nanoparticles (NPs)), coupling with other semiconductor (SiO₂, CeO, MoS), preparation of TiO₂ based nanostructures (nanotubes, nanosheets, interconnected structures), and combination of these methods. It is believed that visible light activated heterogeneous photocatalysis will find different applications such as CO₂ reduction, H₂ production, and degradation of pollutants, and eventually substitution of the current fossil fuel-based economy by a more sustainable solar-based economy.

In this thesis, TiO₂ inverse opal (IO) structures were developed that were functionalized with Au, Ag, Au/Ag nanoparticles (NPs). In addition, a double layer TiO₂ IO with AuNPs and TiO₂ IO with liquid flame spray (LFS) deposited AgNPs were fabricated. The photocatalytic activity was evaluated quantitatively using an in-house built gas-phase method based on the oxidation of C₂H₂ into CO₂ and H₂O. Traditionally, the photocatalytic activity has been evaluated by using a liquid-phase method that is based on a colour transformation of the used dye under illumination by visible or UVA light. However, this approach has a number of drawbacks: for instance, visible light can bleach the used dye inducing an error. Therefore, the developed gas-phase method is superior to the liquid phase method.
TiO$_2$ IO structures were prepared by a wet-chemical method and metal NPs (MeNPs) were deposited on surface either by slow evaporation or LFS method. The structures were characterized in detail by various microscopic (SEM, TEM, HRTEM) and spectroscopic (UV-vis, Raman, XPS, XRD, EDS) techniques confirming formation of TiO$_2$ IO structures and a firm anchoring of MeNPs with uniform distribution.

The results of photocatalytic activity showed that the TiO$_2$ IO structure had a higher photocatalytic activity compared to regular TiO$_2$ NPs. Deposition of MeNPs enhanced photocatalytic activity and visible light activation was also achieved. Energy transfer mechanisms were studied in the developed structures revealing that both hot electron transfer (HET) and plasmon-induced resonance energy transfer (PIRET) were responsible for the enhanced photocatalytic activity in TiO$_2$ IO with MeNP structures.

*Universal Decimal Classification: 544.526.5; 549.514.6*

*CAB Thesaurus: titanium dioxide; photocatalysis; nanoparticles; nanostructures; photonic crystals; catalysts – evaluation; metal coating; flame spraying.*
ACKNOWLEDGEMENTS

This work was carried out at the Department of Chemistry, the University of Eastern Finland between March 2018, and August 2020. The financial support provided by the Faculty of Science and Forestry of the University of Eastern Finland (SCITECO fellowship) and the Finnish Cultural Foundation is gratefully acknowledged. Special gratitude goes to the Anitta Etula travel grant from the Saastamoinen Foundation for the opportunity to have an international research experience.

First, my deepest gratitude goes to my supervisor Assoc. Prof. Jarkko J. Saarinen for granting me an opportunity to work in the field of Material Chemistry and Nanoscience. I thank you for your constructive criticism as well as the profound advice that helped us to conduct our research work.

Further, I would like to thank all collaborators who were involved in these research activities: Prof Tuula Pakkanen, Prof. Mika Suvanto, Prof. Jyrki Mäkelä, Dr. Elena Grachova, Dr. Bright Ankudze, Dr. Lena Ammosova, Dr. Andrey Beliaev, Dr. Janne Haapanen, Dr. Paxton Juuti, Dr. Santosh Kumar, MSc. Abid Zulfiqar and MSc. Khai Pham. Special thanks I address to Prof. Salvador Eslava for valuable discussions and advice.

I deeply acknowledge Prof. Jouko Peltonen and docent Erik Vartiainen for careful reading and a detailed review of this thesis. My special thankfulness is addressed to Dr. Sari Suvanto, Prof. Tapani Pakkanen, Prof. Igor Koshevoy, Prof. Geoffrey Waterhouse, Dr. Niko Kinnunen, Dr. Janne Hirvi, Dr. Pipsa Hirva, Dr. Jari Leskinen, Dr. Christian Jeppesen, Dr. Stanislav Petrovskii, Mr. Martti Lappalainen, Ms. Leila Alvila, Ms. Mari Heiskanen, Ms. Taina Nivajärvi, Mr. Urpo Ratinen, Ms. Päivi Inkinen, Ms. Tarja Virrantalo, Ms. Dmitry Semenov, and all administrative and technical staff of the Department of Chemistry, for their help and support throughout the years.

My appreciation goes to colleagues and friends: Dr. Kristina Kisel, MSc Mariia Beliaeva, MSc. Iida Partanen, MSc. Viktoriia Khistiaeva, MSc. Eija Uusi-Tarkka, MSc Ilja Moshnikov, MSc Hanna Paananen, MSc. Ksenia Plevak, MSc Anastasia Tarluk, MSc Aleksander Kochetov, MSc Olga Shromova, MSc Mikhail Korpusenko for productive discussions, and a great time we spent together.

I thank my parents for their support and faith in me.

Finally, all my love and appreciation go to my partner, best friend, and wife Diana. Your encouragement and motivation brought me where I am now.

Joensuu, 28th January 2021,
Filipp Temerov
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>4-MBA</td>
<td>4-mercaptobenzoic acid</td>
</tr>
<tr>
<td>ALD</td>
<td>atomic layer deposition</td>
</tr>
<tr>
<td>APS</td>
<td>ammonium persulfate</td>
</tr>
<tr>
<td>AR</td>
<td>antireflection</td>
</tr>
<tr>
<td>CA</td>
<td>contact angle</td>
</tr>
<tr>
<td>CB</td>
<td>conduction band</td>
</tr>
<tr>
<td>CFU</td>
<td>colony-forming unit</td>
</tr>
<tr>
<td>CTC</td>
<td>circulating tumour cell</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>DA</td>
<td>dopamine</td>
</tr>
<tr>
<td>DET</td>
<td>direct electron transfer</td>
</tr>
<tr>
<td>DSSC</td>
<td>dye-sensitized solar cell</td>
</tr>
<tr>
<td>EDS</td>
<td>electron disperse spectroscopy</td>
</tr>
<tr>
<td>Eg</td>
<td>energy bandgap</td>
</tr>
<tr>
<td>FCC</td>
<td>face-centered cubic</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>field emission scanning electron microscope</td>
</tr>
<tr>
<td>Jsc</td>
<td>short-circuit current density</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>GC-MS</td>
<td>gas chromatography-mass spectrometry</td>
</tr>
<tr>
<td>HCP</td>
<td>hexagonal closest packed</td>
</tr>
<tr>
<td>HER</td>
<td>hydrogen evolution reaction</td>
</tr>
<tr>
<td>HET</td>
<td>hot electron transfer</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HRTEM</td>
<td>high-resolution transmission electron microscopy</td>
</tr>
<tr>
<td>IO</td>
<td>inverse opal</td>
</tr>
<tr>
<td>LEMF</td>
<td>local electromagnetic field enhancement</td>
</tr>
<tr>
<td>LFS</td>
<td>liquid flame spray</td>
</tr>
<tr>
<td>LH</td>
<td>Langmuir-Hinshelwood</td>
</tr>
<tr>
<td>LSPR</td>
<td>localized surface plasmon resonance</td>
</tr>
<tr>
<td>LTALD</td>
<td>low-temperature atomic layer deposition</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MB</td>
<td>methylene blue</td>
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<tr>
<td>MeNP</td>
<td>metal nanoparticle</td>
</tr>
<tr>
<td>MG</td>
<td>malachite green</td>
</tr>
<tr>
<td>MH-LR</td>
<td>microcystin-LR</td>
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<tr>
<td>MO</td>
<td>methyl orange</td>
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<tr>
<td>MOF</td>
<td>metal-organic framework</td>
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<tr>
<td>NP</td>
<td>nanoparticle</td>
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<tr>
<td>NR</td>
<td>nanorod</td>
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<td>Acronym</td>
<td>Full Form</td>
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<tr>
<td>NT</td>
<td>nanotube</td>
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<tr>
<td>PBG</td>
<td>photonic bandgap</td>
</tr>
<tr>
<td>PDA</td>
<td>polydopamine</td>
</tr>
<tr>
<td>PEC</td>
<td>photoelectrochemical cell</td>
</tr>
<tr>
<td>PIRET</td>
<td>plasmon induced resonant energy transfer</td>
</tr>
<tr>
<td>PMMA</td>
<td>polymethyl methacrylate</td>
</tr>
<tr>
<td>PnP</td>
<td>proximity field nanopatterning</td>
</tr>
<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>PSPR</td>
<td>propagating surface plasmon resonance</td>
</tr>
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<td>PVD</td>
<td>physical vapor deposition</td>
</tr>
<tr>
<td>QD</td>
<td>quantum dot</td>
</tr>
<tr>
<td>R6G</td>
<td>rhodamine 6G</td>
</tr>
<tr>
<td>RET</td>
<td>resonant energy transfer</td>
</tr>
<tr>
<td>rGO</td>
<td>graphene oxide</td>
</tr>
<tr>
<td>RHE</td>
<td>reversible hydrogen electrode</td>
</tr>
<tr>
<td>ROS</td>
<td>reactive oxygen species</td>
</tr>
<tr>
<td>RTCVD</td>
<td>room temperature chemical vapor deposition</td>
</tr>
<tr>
<td>SDS</td>
<td>sodium dodecyl sulfate</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SERS</td>
<td>surface-enhanced Raman scattering</td>
</tr>
<tr>
<td>SHE</td>
<td>standard hydrogen electrode</td>
</tr>
<tr>
<td>SPR</td>
<td>surface plasmon resonance</td>
</tr>
<tr>
<td>TA</td>
<td>transient absorption</td>
</tr>
<tr>
<td>TCE</td>
<td>trichloroethylene</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TiBALDH</td>
<td>titanium(IV) bis(ammonium lactato) dihydroxide</td>
</tr>
<tr>
<td>TMAH</td>
<td>tetramethylammonium hydroxide</td>
</tr>
<tr>
<td>TRPAS</td>
<td>time-resolved photoacoustic spectroscopy</td>
</tr>
<tr>
<td>TSC</td>
<td>sodium citrate</td>
</tr>
<tr>
<td>TTIP</td>
<td>titanium (IV) isopropoxide</td>
</tr>
<tr>
<td>UVA</td>
<td>ultraviolet A</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>VB</td>
<td>valence band</td>
</tr>
<tr>
<td>VOCs</td>
<td>volatile organic compounds</td>
</tr>
<tr>
<td>XPS</td>
<td>x-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>x-ray diffraction</td>
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LIST OF ORIGINAL PUBLICATIONS

This thesis is based on data presented in the following articles, referred to by the Roman Numerals I-III.


AUTHOR’S CONTRIBUTION

I) The author has planned and carried out the experimental work and has written the original manuscript. Ankudze B. and Saarinen J. J. conducted supervision and editing of the original manuscript.

II) The original idea of the work belongs to the author. The experimental and characterization work has been carried out by Zulfiqar A. under supervision of the author. The author and Saarinen J. J. were editing and correcting the original manuscript. The supplementary cover art was produced the author.

III) The original idea of the publication belongs to the author. A significant part of experimental and characterization work was carried out by the author except LFS deposition (Juuti P. and Mäkelä J.M.), XPS measurements (Grachova E.V.), SEM microscopy (Pham K.) and HRTEM. Hydrogen evolution was measured under by author under supervision of Kumar S. and Eslava S. The original manuscript was written by the author and edited by Saarinen J. J.

Other related publications by the author during the study not included in this thesis:


CONTENTS

ABSTRACT ........................................................................................... 7
ACKNOWLEDGEMENTS ..................................................................... 9
LIST OF ABBREVIATIONS ................................................................ 10
LIST OF ORIGINAL PUBLICATIONS ................................................ 13
AUTHOR’S CONTRIBUTION ............................................................. 14
CONTENTS......................................................................................... 15
1 INTRODUCTION .............................................................................. 17
2 REVIEW OF LITERATURE .............................................................. 20
   2.1 Fundamentals of semiconductor photocatalysis ............................ 20
       2.1.1 General statement .......................................................... 20
       2.1.2 Mechanism of semiconductor photocatalysis ...................... 21
       2.1.3 Formation of reactive oxygen species ............................... 23
       2.1.4 Kinetics of semiconductor photocatalysis .......................... 23
   2.2 TiO₂ photocatalysis ................................................................... 24
       2.2.1 History of TiO₂ photocatalysis .......................................... 24
       2.2.2 Physical and chemical properties of TiO₂ ......................... 26
           2.2.2.1 Crystal structure ...................................................... 26
           2.2.2.2 Electronic structure .................................................. 26
       2.2.3 Concepts of TiO₂ Photocatalysis ....................................... 27
           2.2.3.1 Absorption of light .................................................. 27
           2.2.3.2 Charge separation and transfer ................................. 27
           2.2.3.3 Electron and hole trapping ...................................... 28
           2.2.3.4 Charge recombination ............................................ 28
       2.2.4 Selected application of TiO₂ photocatalysis ....................... 29
           2.2.4.1 Air and water purification ....................................... 29
           2.2.4.2 Water splitting ....................................................... 29
           2.2.4.3 CO₂ reduction ......................................................... 30
           2.2.4.4 Antibiological activity ............................................. 31
           2.2.4.5 Superhydrophilicity ............................................... 31
   2.3 Modification of TiO₂ for enhanced photocatalytic activity ............. 32
       2.3.1 Doping ............................................................................ 32
           2.3.1.1 Metal ion doping ...................................................... 33
           2.3.1.2 Non-metal ion doping .............................................. 34
       2.3.2 Nanostructured TiO₂ ........................................................ 34
           2.3.2.1 TiO₂ nanoparticles (0D) ............................................ 35
           2.3.2.2 TiO₂ nanotubes and nanofibers (1D) ....................... 36
           2.3.2.3 TiO₂ nanosheets (2D) .............................................. 36
           2.3.2.4 TiO₂ mesoporous structures (3D) ............................ 37
       2.3.3 TiO₂ heterostructures ......................................................... 37
           2.3.3.1 Coupling with another semiconductor ....................... 38
           2.3.3.2 Deposition of plasmon metal nanoparticles .............. 39
   2.4 TiO₂ inverse opal ................................................................. 42
       2.4.1 General information ......................................................... 42
       2.4.2 Properties of TiO₂ IO ...................................................... 42
       2.4.3 Preparation of TiO₂ IO ..................................................... 43
2.4.3.1 Sol-gel methods ........................................................................ 43
2.4.3.2 Chemical vapor deposition (CVD) ........................................ 44
2.4.3.3 Atomic layer deposition (ALD) .............................................. 44
2.4.3.4 Other methods ...................................................................... 44
2.4.4 Modification of TiO2 IO ..................................................................... 45
2.4.4.1 Metal and non-metal ion doping .......................................... 45
2.4.4.2 Metal nanoparticles deposition ............................................ 46
2.4.4.3 Heterojunction coupling ....................................................... 46
2.4.4.4 Other modifications .............................................................. 47
2.4.5 Application of TiO2 IO .................................................................. 47
2.4.5.1 Solar cells ............................................................................ 47
2.4.5.2 SERS detectors ................................................................... 48
2.4.5.3 Photocatalysis ...................................................................... 48
2.4.5.4 Other application .................................................................. 49
2.5 Methods for evaluation photocatalytic activity of TiO2 ......................... 49
2.5.1 Liquid-phase methods ................................................................. 49
2.5.1.1 Degradation of organic compounds ..................................... 50
2.5.1.2 Water splitting ...................................................................... 50
2.5.1.3 CO2 reduction ...................................................................... 51
2.5.2 Gas-phase methods .................................................................... 51
2.5.2.1 Degradation of organic contaminants .................................. 51
2.5.2.2 CO2 reduction ...................................................................... 52
3 EXPERIMENTAL PART .................................................................. 53
3.1 Development of gas-phase evaluation of the photocatalytic activity ... 53
3.2 Preparation of TiO2 inverse opals ..................................................... 54
3.2.1 Synthesis of polystyrene spheres ................................................ 54
3.2.2 Infiltration method ........................................................................ 55
3.2.3 Crack-free method ....................................................................... 56
3.3 Deposition of metal nanoparticles ..................................................... 57
3.3.1 Slow evaporation method ............................................................ 57
3.3.2 Liquid flame spray deposition method ........................................ 58
3.4 Characterization .............................................................................. 59
3.4.1 Photocatalytic activity evaluation ................................................. 60
3.4.1.1 C2H2 decomposition ............................................................. 60
3.4.1.2 H2 evolution .......................................................................... 60
4 RESULTS AND DISCUSSION ........................................................ 62
4.1 Validation of the gas-phase method .................................................... 62
4.2 Characterization of TiO2 IO, MeNPs and their heterostructure ........... 63
4.2.1 TiO2 IO with AgNPs, AuNPs and Au/AgNPs .................................. 63
4.2.2 Multilayer TiO2 IO with AuNPs .................................................. 68
4.2.3 TiO2 IO with AgNPs deposited by LFS ........................................ 74
5 CONCLUSIONS AND FUTURE PERSPECTIVE ............................ 83
6 BIBLIOGRAPHY .............................................................................. 85
1 INTRODUCTION

The continuous and rapid development of mankind undoubtedly has brought significant progress in many areas of daily life. However, this progress has also resulted in various side effects such as increased carbon dioxide (CO$_2$) emissions, air, and water pollutants. It is well known that the main source of CO$_2$ emission is combustion of fossil fuels and even though partial substitution has been accomplished by hydro, wind, nuclear, and solar energy generation, it does not fully solve the problem. To overcome the emerging issue, a new approach to reduce the CO$_2$ level is needed. Inspired by natural photosynthesis, where CO$_2$ and water (H$_2$O) convert to glucose and oxygen under solar irradiation, a similar strategy to artificially reduce CO$_2$ and convert it to valuable chemicals (solar fuels) has been investigated. In the early 1970s, heterogeneous photocatalysis and the seminal work of Fujishima and Honda (Fujishima & Honda, 1972) demonstrated water splitting into hydrogen (H$_2$) and oxygen (O$_2$) by irradiating titanium dioxide (TiO$_2$) electrode with an ultraviolet A (UVA) light in a photoelectrochemical (PEC) cell. This triggered a large interest in photocatalysis. The heterogeneous photocatalysis can be explained as a chemical transformation of a compound, induced by the absorption of electromagnetic radiation (UV or visible light), which is accelerated by the presence of a photocatalyst. In heterogeneous photocatalysis, the reactant and the photocatalyst are in different phases (e.g. solid and gas, or solid and liquid), and the photoreaction takes place on the photocatalyst surface.

The most typically used photocatalysts are semiconductors (usually metal oxides) due to their optical and electrical properties such as the bandgap structure, light absorption, and stability. The most studied semiconductor, TiO$_2$, possesses suitable properties such as a suitable bandgap structure for the absorption of UV light ($E_g \sim 3.2$ eV), long-term photostability, non-toxicity, and low-cost. The photocatalytic activation is realized upon absorption of a photon with energy larger than bandgap which results in a formation of electrons and holes in conduction (CB) and valence (VB) band, respectively. Subsequently, photoexcited carriers can transfer on the surface and take part in oxidation and reduction reactions. TiO$_2$ photocatalysis has been used in the energy and environmental sectors as air and water purification (Lee & Park, 2013; Peral et al., 1997), bacterial disinfection (Caballero et al., 2009), solar cells (Shankar et al., 2007), water splitting (Fujishima & Honda, 1972) and CO$_2$ reduction (Dhakshinamoorthy et al., 2012). However, TiO$_2$ has drawbacks that limit its utilization in a wider range of applications. First, the bandgap of TiO$_2$ is relatively large (~ 3.2eV) for visible light activation and can be excited only by UV irradiation (wavelength ($\lambda$) $<$ 385 nm). The solar spectrum consists only 3-5% in the UV range (Preto & Gomes, 2018). The fast recombination rate of photoexcited electron-hole pairs also limits the TiO$_2$ performance. Several strategies to improve
the photocatalytic activity of TiO₂ has been demonstrated such as doping the crystalline structure with metal or non-metal ions followed by the formation of additional energy levels in bandgap close to CB or VB facilitating the promotion of photoexcited electrons or holes, shifting of CB or VB, and reducing of bandgap energy (Asahi et al., 2001). TiO₂ can also be coupled as a heterostructure with various materials ranging from other semiconductors (Lakshmana Reddy et al., 2017; Wei et al., 2018), noble metal nanoparticles (MeNPs) (Gołabiewska et al., 2016), graphene derivatives (Tan et al., 2013), and metal-organic frameworks (MOF) (Li et al., 2018). By an accurate band structure alignment enhanced photocatalytic activity can be achieved. As an example, coupling TiO₂ with MeNPs allows efficient suppression of electron and hole recombination, acting as an electron sink, rapidly accepting photoexcited electrons from CB of TiO₂. In addition, photoexcited electrons can be injected from MeNPs to CB of TiO₂ via localized surface plasmon resonance (LSPR).

It is well-known that there is a large variety of TiO₂ based nanostructures that display improved photocatalytic activity compare to regular TiO₂ nanoparticles (NPs) namely nanorods (NRs) (Alfaro Cruz et al., 2019), nanotubes (NTs) (Zheng et al., 2019), nanoplates (Zhang et al., 2016), thin films (Singh et al., 2017) mesoporous structures (Yu et al., 2007). Lately, TiO₂ based hierarchical structures such as an inverse opal (IO) have attracted large attention due to their properties such as photonic bandgap (PBG), slow light effect, and localized photons (Yu et al., 2018). The PBG allows the propagation of light with only a specific wavelength due to the Bragg diffraction. The slow light effect enhances the absorption of light by multiple reflections of the light inside the IO structures leading to the generation of a large number of electron-hole pairs which enhance photocatalytic activity. TiO₂ IO consists of a three-dimensional porous ordered structure with a large specific surface area that can improve light-harvesting and advanced molecular transfer and diffusion (Huo et al., 2019). It is believed that improved TiO₂ photocatalysis can play an important role in the transformation from the current fossil fuel-based economy to a solar economy promoting both economically and ecologically sustainable development.

Traditionally, the photocatalytic activity has been evaluated by an indirect liquid method based on the colour transformation of an optical dye such as methylene blue (MB) or methyl orange (MO) (Niu & Hao, 2013; Xu et al., 2014). However, for reliable, accurate, and quantitative photocatalytic activity results this is not sufficient as the incident light, particularly in the visible range, can itself bleach the used dye inducing an incorrect result (Yan et al., 2006). Moreover, NPs may easily detach from the substrate and transfer into the dye solution. Therefore, a better option to evaluate photocatalytic activity is the gas-phase oxidation of organic compounds. First, the mineralization of carbon compounds into CO₂ on top of
photocatalyst can be directly and quantitatively measured by detectors, following the CO₂ increase in the reaction chamber. Secondly, the gas-phase detection method does not induce any mechanical stresses on the surface of the photocatalyst.

The aims of this study were:

1. To develop a gas-phase photocatalytic activity evaluation based on mineralization and reduction of an organic compound to CO₂ and H₂O.
2. To fabricate and characterize TiO₂ IO with AuNPs, AgNPs, and Au/AgNPs deposited by slow evaporation method for improved photocatalytic activity and to study the effect of MeNPs on photocatalytic activity.
3. To fabricate and characterize multilayer TiO₂ IO structures with AuNPs deposited by slow evaporation method to improve photocatalytic activity.
4. To fabricate and characterize TiO₂ IO structures with liquid flame spray (LFS) deposited AgNPs to improved photocatalytic activity and to develop new nanoparticle deposition method for visible light photocatalytic activity.
5. To clarify the possible energy transfer processes responsible for the enhanced photocatalytic activity in TiO₂ IO/MeNPs photocatalysts.
2 REVIEW OF LITERATURE

2.1 FUNDAMENTALS OF SEMICONDUCTOR PHOTOCATALYSIS

2.1.1 General statement

Semiconductor photocatalysts (usually metal oxides) have a forbidden energy region (bandgap energy), where no energy levels are available, and no electrons can exist, between the top of the VB and the bottom of the CB. The VB and CB originate when a large number of atoms assemble and their wavefunctions of an electron in the nearest atoms start to overlap. According to the Pauli exclusion principle, the electrons in the same system cannot occupy the same quantum state. This results in splitting of the energy levels in the atomic orbital. The total number of electrons in a system is extremely large, and the difference between the energy states of the electrons becomes negligibly small, the electronic structure of the system can be considered as continuous bands (Hoffmann et al., 1995). The band structure of semiconductors is an expansion concept of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in molecules, which is VB and CB in semiconductors, respectively (Figure 2.1 A). There are two types of bandgaps in semiconductors: direct and indirect (Figure 2.1 B and C). The crystal structure of the semiconductor can be described by Bravais lattice and the reciprocal lattice is known as momentum or k-space. Momentum determines the type of transition of an electron from VB to CB. If the momentums for the VB and CB are equal the bandgap is regarded as direct and when momentums are not equal, the bandgap is known as an indirect. The photocatalytic properties of semiconductors are thus strongly affected by the bandgap structure.

Figure 2.1 (A) Formation of the electronic band structure of a semiconductor compound according to the growing of the monomeric units and (B) direct and (C) indirect bandgaps in semiconductors. Adapted from (Hoffmann et al., 1995).
The activation of the photocatalytic activity of semiconductors starts with the absorption of a photon with energy higher than the bandgap energy. This absorption process results in a transfer of an electron from VB to CB and the generation of a vacancy referred as a hole in VB (Figure 2.2 A). The photoexcited charge carriers (electron-hole pairs) can further diffuse to the surface and participate in reduction and oxidation reactions (Ong et al., 2016). The recombination of electrons and holes can also take place at the surface or in the bulk of semiconductors leading to a significant decrease in photocatalytic efficiency. There is a large variety of semiconductors with different bandgap structures. It is noteworthy that the relative position of the VB and CB is important because it determines the oxidation and reduction potential of the semiconductors (Figure 2.2 B). For example, in organic pollutant decomposition applications, semiconductor photocatalyst should be able to generate a hole in VB with a redox potential that is positive enough to oxidize and mineralize the target organic molecule.

Figure 2.2 (A) A schematic illustration of the charge separation in semiconductors upon absorption of electromagnetic irradiation with energy higher than the bandgap energy and (B) the band structure of TiO2 anatase and rutile, and reduction and oxidization potential of water at pH=7. Adapted from (Ong et al., 2016).

2.1.2 Mechanism of semiconductor photocatalysis

The generation of electrons and holes in the semiconductors is possible once a photon with energy higher than the bandgap of the semiconductor is absorbed (Figure 2.2) and Eq. (2.1). The transfer of photoexcited electrons and holes to the surface of the semiconductor may lead to bulk and surface recombination resulting
in heat production Eq. (2.2). The recombination process usually results in a low quantum efficiency for the photocatalytic process. However, this process can be gradually decreased if the photoexcited carriers are separated and trapped by defects, surface adsorbates, or other sites Eqs. (2.3)-(2.4). An adsorbed electron acceptor can be reduced by transferring to a photoexcited electron, while a hole can migrate to the surface where an electron from an absorbed donor species can combine with the surface hole oxidizing the donor species as given by Eqs. (2.5)-(2.6). After charge transfer from the adsorbed species to the semiconductor surface, a back-donation process can also take place (Linsebigler et al., 1995). The reaction scheme of a photocatalytic process is shown in figure 2.3 and the whole process is described by the Eqs (2.1)-(2.6):

\begin{align*}
\text{TiO}_2 + h\theta &\rightarrow e_{cR}^- + h_{\nu R}^+ \quad (2.1) \\
e_{cR}^- + h_{\nu R}^+ &\rightarrow \text{heat} \quad (2.2) \\
e_{cR}^- + Ti - OH &\rightarrow Ti^* + OH^- \quad (2.3) \\
h_{\nu R}^+ + Ti - OH &\rightarrow Ti - O^* + H^+ \quad (2.4) \\
e_{cR}^- + \text{Red} &\rightarrow \text{Red}^- \quad (2.5) \\
h_{\nu R}^+ + Ox &\rightarrow Ox^+ \quad (2.6)
\end{align*}

Figure 2.3. Processes in TiO$_2$ photocatalysis upon absorption of light: generation of electron-hole pairs, charge transfer, recombination of electron-hole pairs in the bulk or at the surface, and electron and hole induced oxidation or reduction at the surface. Adapted from (Linsebigler et al., 1995).
2.1.3 Formation of reactive oxygen species

The photoreactions occur on the solid semiconductor surface in heterogeneous photocatalysis. In the photooxidation of organic compounds, oxygen plays an important role. It can be easily reduced by the CB electrons to perhydroxyl / superoxide (HO₂• / O₂•⁻) in neutral pH to eventually form hydroxyl radical. The following Eqs. (2.7)-(2.13) summarize the process.

\[
\begin{align*}
\text{E}_\text{CB}^- + O_2 & \rightarrow HO_2^*/O_2^{*-} \\
HO_2^* & \Leftrightarrow O_2^{*-} + H^+ \\
2HO_2^* & \rightarrow O_2 + H_2O_2 \\
HO_2^* + O_2^{*-} & \rightarrow O_2 + HO_2^- \\
HO_2^- + H^+ & \rightarrow H_2O_2 \\
H_2O_2 + H_2 & \rightarrow O_2 \\
HO_2^* + H_2O_2 & \rightarrow HO^* + H_2O_2 + O_2
\end{align*}
\]

The hydroxyl radical (OH•) has a lifetime in the ns range being a highly reactive species with high (2.8V) oxidation potential. The hydroxyl radicals oxidize organic compounds without selectivity and are considered as the main oxidant product in a photocatalytic process. It is worth mentioning that the production of hydroxyl radical requires three photoexcited electrons, whereas only one hole is involved in the creation of a hydroxyl radical followed by another half-cell reaction. Therefore, the majority of the hydroxyl radicals are generated via hole reactions in the photocatalytic process. The hydrogen peroxide (H₂O₂) may also decompose to hydroxyl radicals by using a high energy UV light (λ < 300 nm).

2.1.4 Kinetics of semiconductor photocatalysis

The reaction rate of photocatalytic systems depends on the concentration of the photogenerated electron-hole pairs, wavelength and intensity of the used light source, and the recombination rate of electron-hole pairs. The photocatalytic reaction rate is determined by several factors such as electrical, optical, chemical, and structural properties of the semiconductor, absorbed rate of electron donors and acceptors, temperature, and pressure. The Langmuir–Hinshelwood (LH) kinetics is commonly used to describe heterogeneous photocatalytic processes (Liu et al., 2014). This model can be used to reflect the initial reaction rate with the reduction of any pollutant by the following equation.
\[
\frac{dC}{dt} = \frac{k KC_0}{1 + KC_0}, \tag{2.14}
\]

where \( C_0 \) is the initial concentration of the pollutant, \( K \) is the Langmuir adsorption constant or equilibrium constant for adsorption of the molecules onto semiconductor, \( k \) is a limiting rate constant which provides a measure of the reactivity of the photocatalytic surface with the pollutant.

For a standard photocatalytic condition, the concentration of organic pollutant is very low, thus \( KC_0 \) in equation (2.14) is much lower than 1, and it becomes

\[
\frac{dC}{dt} = \frac{k KC_0}{1 + KC_0} = k KC_0 = k_{app} C_0 \tag{2.15}
\]

where \( k_{app} \) is the apparent rate constant determined as the multiplication of \( k \) and \( K \). Integrating Eq. (2.15) from time 0 to \( t \), another form of the LH model can be obtained

\[
\ln \frac{C_0}{C_t} = k_{app} t, \tag{2.16}
\]

where \( C_0 \) is the initial concentration of organic pollutants before photocatalytic reaction, and \( C_t \) is the reactive concentration at time \( t \) during the photocatalytic reaction. From Eq. (2.16), \( k_{app} \) can be easily calculated for different photocatalytic reactions.

### 2.2 TiO\(_2\) Photocatalysis

An ideal candidate for an efficient semiconductor photocatalyst should have several features such as high photocatalytic activity, absorption at visible or/and UVA light, chemical and biological inertness, photostability, low cost, and non-toxicity. From a diverse variety of semiconductors, TiO\(_2\) has been the most studied being suitable for a wide range of environmental and energy photocatalytic applications (Fujishima et al., 2000).

#### 2.2.1 History of TiO\(_2\) photocatalysis

Carl Renz (Renz, 1921) first reported the photoactive effect of TiO\(_2\) by the darkening of the material under UV light. The photosensitization effect in TiO\(_2\) as a white pigment in paint and wallpapers was demonstrated by Goodeve and Kitchener (Goodeve & Kitchener, 1938). Gion (Gion, 1932) stated that TiO\(_2\) accelerates the
photooxidation of ammonia in solution. Kato and Masuo (Kato & Masuo, 1964) used TiO$_2$ as a photocatalyst for oxidation reaction of tetralin in the liquid phase under UV irradiation. Honda and Fujishima demonstrated photosensitization effect using a Pt metal electrode as a cathode and a TiO$_2$ based photoanode that was irradiated by UV light, for the electrolysis of H$_2$O into H$_2$ and O$_2$ (Fugishima & Honda, 1972). Under UV light irradiation of the TiO$_2$ electrode, the electrolysis of H$_2$O proceeded at a much lower bias voltage compared to the conventional electrolysis. This seminal work was a starting point in photocatalytic research, and nowadays more than 2,000 research works related to TiO$_2$ photocatalysis are published annually in peer-reviewed journals making TiO$_2$ photocatalysis an active research field. Figure 2.4 summarizes milestones in the development of TiO$_2$ photocatalysis.
2.2.2 Physical and chemical properties of TiO₂

2.2.2.1 Crystal structure

TiO₂ exists in the three naturally occurring crystal phases known as anatase, rutile, and brookite. All three TiO₂ phases are arranged of Ti⁴⁺ and six O²⁻ atoms forming a TiO₆ octahedron. The formation of crystal structures with different configurations for each of the three phases arises upon distortions in the octahedron of the phases. The bandgap values of anatase, rutile, and brookite are 3.2 eV, 3.0 eV, and 3.3 eV, respectively. Brookite is a rare natural phase and structurally more complex than the anatase and rutile. It is presented in nature in orthorhombic symmetry and forms very flat small tubular crystals with a colour ranging from yellow to brown-reddish. From the photocatalytic point of view, brookite has not been studied extensively owing to a rather high-temperature instability and large bandgap energy. The rutile and anatase phases are the most exploited for photocatalytic studies. Rutile is the most abundant and thermodynamically stable phase, while the other two phases are metastable and by elevation of temperature can irreversibly transfer into the rutile phase. It has a tetragonal unit cell (a =4.593 Å, c = 2.959 Å), having a structure constituted by a highly distorted octahedral TiO₆ with oxygen ions shared with other adjacent Ti ions. In nature, rutile-TiO₂ is black or reddish but it can also exist as transparent if free of impurities. Anatase crystalline phase is considered as the best candidate for the photocatalytic studies. It contains a tetragonal unit cell (a = 3.785 Å, c = 9.514 Å) resembling an elongated octahedron. The anatase phase is a more distorted structure because every polyhedron shares 4 edges with the adjacent one, particularly the tetragonal elementary cell contains 4 units. The anatase crystals are relatively small ranging from blue sapphire to yellow-brown colours. Unlike rutile and brookite, anatase TiO₂ possesses an indirect bandgap that results in an extended lifetime of photogenerated electrons and holes compared to the rutile or brookite phases (Carp et al., 2004; Etacheri et al., 2015).

2.2.2.2 Electronic structure

The bandgap and relative position of the redox potential of CB and VB determine the photocatalytic properties of TiO₂. The band position is an important parameter that indicates the thermodynamic possibility for the photocatalytic reaction that can be carried out with the electrons and holes. In the anatase TiO₂, the redox potential of a hole is +2.53 V, while the photoexcited electron is −0.52 V (versus standard hydrogen electrode (SHE), pH=7). Therefore, the photocatalytic reduction can be accomplished only if the redox potential of the photoexcited electrons is negative enough to reduce the oxidant while photooxidation takes place if the redox potential of the photoexcited holes is more positive than that of the reductant
(Fujishima et al., 2000). TiO₂ has a relatively positive VB position having a strong oxidative capability (Carp et al., 2004). For example, two half-reactions should be realized for water splitting: first, the reduction of H₂O to H₂ (−0.413 V vs. SHE) and secondly, the oxidation of H₂O to O₂ (+0.83 V vs. SHE). This process is allowed on TiO₂ because the redox potentials of photogenerated carriers are strong enough to reduce (−0.52 V < −0.413 V) and oxidize (+2.53 V > +0.83 V) water (Figure 2.2 B).

2.2.3 Concepts of TiO₂ photocatalysis

The photocatalysis of TiO₂ obeys the overall mechanism for photocatalysis of semiconductors. In particular, taking TiO₂ in the anatase crystalline phase (E₉~3.2 eV) as an example, the photocatalytic reaction can be triggered upon absorption of a photon with energy higher than the bandgap (λ < 387 nm). The negatively charged electron from the VB transfers to the CB, leaving behind a positively charged hole in VB. Photoexcited electrons and holes can experience bulk or surface recombination, trapping, and diffusion to the surface of TiO₂ and taking part in the oxidation and reduction reactions.

2.2.3.1 Absorption of light

The bandgap energy determines the absorption properties of TiO₂. In the anatase crystalline phase, TiO₂ can efficiently absorb only UV light (λ < 390 nm). For sunlight excitation, the absorption in the UV range limits the efficiency of TiO₂ photocatalysis. However, there are several methods to alter the optical properties of TiO₂ and to shift light absorption into the visible part of the spectrum (Section 2.3).

2.2.3.2 Charge separation and transfer

Light absorption results in photoexcited electrons and holes in CB and VB, respectively. The charge separation is a fast process in the fs range that contributes to the quantum efficiency of photocatalysis. However, only less than 10% of photoexcited electrons or holes can be transferred to the surface of TiO₂ to participate in photocatalytic reactions, while the remaining ~90% of them recombine rapidly after charge separation (Hoffmann et al., 1995). Therefore, improvement of the charge separation efficiency is one of the main approaches to enhance the photocatalytic activity of TiO₂.
2.2.3.3 Electron and hole trapping

One possibility to suppress the recombination rate of photoexcited electrons and holes is electron and hole trapping (Tachibana et al., 2012). The recombination can be delayed, with a carrier lifetime in μs scale, making charge transfer of electrons to molecular oxygen competitive with the recombination. Thermalization and trapping dynamics of the photogenerated charge carriers in TiO₂ NPs excited by 266 and 355 nm irradiation have been studied (Tamaki et al., 2009). The photogenerated electrons and holes are rapidly trapped (within <100 fs) upon 355 nm excitation. The trapping time decreased to ~200 fs for the free electrons in the CB of TiO₂ with 266 nm excitation. During the electron and hole trapping, Ti⁴⁺ cations were reduced to Ti³⁺ and O₂⁻ anions oxidized to O⁻ states, respectively. The electron traps were localized as Ti³⁺ sites at the lattices of TiO₂ that were ~0.1–1 eV below the CB edge of TiO₂ (Henderson, 2011). The electron traps were assumed to be trapped at the surface of TiO₂ (Diebold, 2002). Others studies suggested that electrons were trapped in the bulk (subsurface) of TiO₂ (Nakaoka & Nosaka, 1997) and other, that electrons were trapped on the undercoordinated Ti³⁺ cation sites at the surface (Qu & Kroes, 2006). The opposite process of electron trapping is electron detrapping, and normally it takes place when polaronic hopping is involved in a “trap-to-trap” hopping process (Deskins & Dupuis, 2007) or when trapped electrons become free. The hole traps are most likely located at Ti³⁺–O⁻ site with the hole remaining at an undercoordinated lattice oxygen atom. It remains under investigation whether two coordinated bridging oxygen (O₆) or three coordinated oxygen (oxo type) is favorable for hole trapping. Theoretical studies demonstrated that the near-surface region is preferable for hole trapping (Kerisit et al., 2008). However, due to the lack of suitable hole donors, all studies of hole trapping dynamics start from photogenerated holes in the TiO₂ VB.

2.2.3.4 Charge recombination

The charge recombination is one of the main limitations of TiO₂ photocatalysis. Generally, the recombination process in TiO₂ follows two pathways: radiative and nonradiative recombination. During radiative recombination, the energy is released as a photon while nonradiative recombination takes place through the emission of multiple phonons. It is believed that the nonradiative recombination pathway is the main recombination process in TiO₂ photocatalysis (Qian et al., 2019). The nonradiative pathway is dominant if the lifetime of nonradiative recombination is shorter than the radiative. The experimental detection of nonradiative recombination is nearly impossible since it occurs via the emission of phonons. However, time-resolved photoacoustic spectroscopy (TRPAS) revealed that in the colloidal anatase TiO₂ nearly 60% of the electron and hole recombination took place.
via the nonradiative pathway (Leytner & Hupp, 2000). Furthermore, the charge carrier dynamic decay in rutile and anatase TiO$_2$ was studied by a combination of time-resolved photoluminescence spectroscopy, transient absorption (TA) spectroscopy, and photoconductivity (Yamada & Kanemitsu, 2012). The lifetimes of photoexcited carriers were found to be a few tens of ns (24 ns and 48 ns for electron and hole, respectively) for rutile TiO$_2$, while in anatase TiO$_2$, the holes decayed rapidly (a few ns) and electrons were populated in the CB for more than a few μs. These results highlight that the long-living electrons in CB are responsible for the high photocatalytic activity in anatase TiO$_2$.

2.2.4 Selected applications of TiO$_2$ photocatalysis

2.2.4.1 Air and water purification

The quality of air and water is vitally important for everyday life and the sustainable development of society. TiO$_2$ photocatalysis has been employed for removing organic pollutants in water and air. TiO$_2$ has been known for successful air removal of hazardous volatile organic compounds (VOCs) such as NO (Devahasdin et al., 2003), NO$_2$ (Li et al., 2004), SO (Shelimov et al., 2008), chloroform (Yamazaki et al., 2005), acetone (Reyes-Coronado et al., 2008), benzene (Jacoby et al., 1996), phenol (Palmisano et al., 1994), and formaldehyde (Obbe & Brown, 1995). As an example, Palmisano and co-workers (Palmisano et al., 1994) demonstrated gas-phase oxidation of phenol compounds on anatase TiO$_2$ powder whereas Coronado et al. (Coronado et al., 2003) achieved 100% mineralization of acetone over TiO$_2$ thin film. TiO$_2$ has also been used in aqueous solutions for removal of inorganic ions (Guillard et al., 2003; Wong & Chu, 2003), heavy metals (Angelidis et al., 1998; Kabra et al., 2004), organic pollutants (Pelaez et al., 2009), and bio-organisms (Wanag et al., 2018). The highly toxic hepatotoxin microcystin-LR (MH-LR) frequently found in surface waters can be easily decomposed under visible light irradiation on nitrogen-doped TiO$_2$. Moreover, decomposition of MH-LR was enhanced upon the simultaneous doping of TiO$_2$ with nitrogen and fluorine. When the ratio was increasing towards fluorine, a higher MC-LR degradation rate was observed (Pelaez et al., 2009).

2.2.4.2 Water splitting

Since the seminal work of Fujishima and Honda (Fujishima & Honda, 1972), photocatalytic water splitting into H$_2$ and O$_2$ using TiO$_2$ is attractive for clean and natural energy production. For water splitting, the positions of CB and VB are important as discussed earlier. However, splitting water into H$_2$ and O$_2$ on pure TiO$_2$ is not easy in the aqueous suspension system. Therefore, TiO$_2$ modification has
been a central concept for enhanced water splitting applications. For efficient water splitting Wang et al. (Wang et al., 2020) preparedCu₂O/TiO₂ heterojunction photocathodes. The stability of Cu₂O photocathode was significantly improved by the formation of heterojunction with the TiO₂ protection layer. A greater photovoltage and reduced the recombination of photoexcited electrons and holes were performed by an as-prepared photocathode. The photocathode current density of ~3.71 mA/cm² at 0 V vs. RHE was procured while the onset potential for hydrogen evolution reaction (HER) was altered from 0.37 to 0.54 V_RHE. Cui and co-workers (Cui et al., 2020) reported an ultrathin NiFe-MOF/TiO₂ hybrid-photoanode prepared by the sacrifice template method for PEC water splitting. The synthesized NiFe-MOF/TiO₂ heterostructure exhibited a good PEC performance including the enhanced photocurrent density and efficiency of electrons and holes injection, good durability, and charge separation.

2.2.4.3 CO₂ reduction

The CO₂ reduction or artificial photosynthesis is a modern pathway of TiO₂ photocatalysis aiming to reduce CO₂ emission and providing solutions to the energy crisis by solar fuels. Theoretically, the bandgap structure of TiO₂ is suitable to perform redox reactions, because the relative positions of the maximum of VB and minimum of CB allow reduction of CO₂ to formic acid, methanol, and methane and oxidation of H₂O to form H⁺. The selectivity of the product is based on the number of electrons involving a particular reaction. Therefore, the production of CH₄ is challenging. However, compared to other reactions, it has a more positive reduction potential (Figure 2.2 B). Koči and co-workers (Kočí et al., 2011) used various wavelengths (254, 365, and 400 nm) for photocatalytic reduction of CO₂ on TiO₂. The yield was highest by 254 nm excitation followed by 365 nm excitation, and no reaction was observed by 400 nm excitation. Furthermore, the yield of products was low because the photogenerated electron-hole pairs interacted with adsorbed species in longer timescale (ns to μs) compared to the recombination time (ns) decreasing their redox reactions. Thus, modification of TiO₂ for application in solar-driven CO₂ photoreduction must be achieved. Tahir and Amin (Tahir & Amin, 2015) prepared indium (In)-doped TiO₂ NPs by a sol-gel method. The In-doped TiO₂ NPs displayed improved photocatalytic activity for CO₂ reduction with H₂O vapour. The pristine TiO₂ produced (carbon monoxide) CO as the main product while In-doped TiO₂ increased the CH₄ yield. The yield of In-doped TiO₂ was 7.9 times greater than the pristine TiO₂. In addition, C₂H₄, C₂H₆, C₃H₆, and C₃H₈ were also identified in the product mixture. Interfacial charge transfer of photogenerated electrons and holes between In and TiO₂ resulted in an improved charge separation with reduced recombination rate followed by an enhanced photoactivity in In-doped TiO₂ NPs.
2.2.4.4 Antimicrobial activity

TiO$_2$ photocatalysis can also be used for the inactivation of microorganisms due to simultaneous redox reactions. It was demonstrated that TiO$_2$ NPs have strong disinfecting activity against gram-negative (Escherichia coli (strain LE392, HB101, K12)) and gram-positive bacteria (Streptococcus (GS5, LM7, OMZ175)) (Bekbölet & Araz, 1996; Massard et al., 2013; Ng et al., 2010; Saito et al., 1992; Sakai et al., 1994; Sulek et al., 2019). Photoinactivation of pathogens occurs upon oxidation of the cell wall components, which can lead to reactive oxygen species (ROS) inside the cell. Further, ROS intrudes into DNA replication and respiratory cycles, leading to loss of cell viability and death. Gram-negative bacteria are more vulnerable to photocatalytic inactivation than gram-positive bacteria (Regmi et al., 2018; Van Doorslaer et al., 2015). The efficiency of photocatalytic inactivation of bacteria is highly affected by the crystal phase and particle size of the TiO$_2$. Small anatase TiO$_2$ NPs have a higher affinity to the cell surfaces and produce more oxidative damage to the cells. Photosterilization of E. coli $10^2$ on TiO$_2$ immobilized acetyl cellulose membrane was demonstrated in the pioneering work of Matsunaga and co-workers (Matsunaga et al., 1988) with 99% inactivation rate under a solar simulator. For visible light activation, Karunakaran et. al. (Karunakaran et al., 2011) prepared a 2% cadmium (Cd) doped TiO$_2$ (Cd-TiO$_2$) for effective photocatalytic disinfection of E. coli population $\sim2 \times 10^{11}$ colony-forming unit (CFU) ml$^{-1}$ in 40 min. Using a facile hydrothermal-calcination method Li and co-workers (Li et al., 2015) synthesized a graphitic carbon nitride (g-C$_3$N$_4$)/TiO$_2$ composite photocatalyst with improved photocatalytic bacterial disinfection activity. The as-prepared hybrid photocatalyst consisted of micron-sized TiO$_2$ spheres wrapped with lamellar g-C$_3$N$_4$ for improved visible light absorption and effective separation of photoexcited carriers. Using g-C$_3$N$_4$/TiO$_2$ composite photocatalyst, $10^7$ CFU ml$^{-1}$ of E. coli K12 in water can be entirely deactivated in 180 min under visible light irradiation.

2.2.4.5 Superhydrophilicity

There are two distinct photoinduced phenomena on the TiO$_2$ surface: the first one is photocatalytic activity and the second one is the high wettability of water (superhydrophilicity). Even though they take place simultaneously on the same TiO$_2$ surface they are fundamentally different processes. The superhydrophilicity effect was accidentally discovered when TiO$_2$ thin film was irradiated by UV light illumination (Rong et al., 1997). The photoexcited electrons were supposed to reduce the Ti$^4+$ cations to the Ti$^3+$ state, while photoexcited holes oxidize the O$_2^-$ anions, ejecting oxygen atoms and creating oxygen vacancies. Water molecules inhibit oxygen vacancies and created adsorbed OH groups that resulted in surface hydrophilicity. The longer the exposure time on the surface, the smaller the contact
angle for water can be observed. This phenomenon was extensively studied and utilized in industry for two applications: antifogging surfaces and self-cleaning materials. As an example of antifogging surfaces, Watanabe, and co-workers (Watanabe et al., 1999) studied the photoinduced hydrophilicity in different crystalline phases of TiO$_2$. They found out that the water was deposited as a very thin layer and evaporated quickly when its water amount was small. On the other hand, the sheet-like layers were formed when water volume was higher. The commercial application of this phenomenon for side-view mirrors in automobiles was implemented. The TiO$_2$ coated surfaces can retain clean under solar illumination reducing service costs and utilization of detergents. Zhang et. al. (Zhang et al., 2005) reported the fabrication of the core-shell TiO$_2$-SiO$_2$ NPs by an electrostatic attraction method for antireflection (AR) and self-cleaning purposes. SiO$_2$ was used to provide a substrate layer structure with a low refractive index while TiO$_2$ NPs were coated on top of the SiO$_2$ layer providing a self-cleaning, superhydrophilic layer. The self-cleaning properties of the TiO$_2$-SiO$_2$ NPs were studied by the water contact angle (WCA) on octadecyldimethylchlorosilane modified coatings under UV light disclosing good surface wetting.

2.3 MODIFICATION OF TiO$_2$ FOR ENHANCED PHOTOCATALYTIC ACTIVITY

The main limitations of TiO$_2$ in photocatalytic applications are the large bandgap (~3.2 eV for anatase TiO$_2$) and a high recombination rate of photoexcited electrons and holes. There are many pathways to overcome these major drawbacks and enhance the photocatalytic activity of TiO$_2$ followed by improved optical and electrical properties for solar-driven photocatalytic applications. (Fujishima et al., 2000).

2.3.1 Doping

TiO$_2$ bandgap alteration can be achieved through the bulk chemical modification process of doping. The doping can be realized by metal or non-metal substitutes in the lattice structure of TiO$_2$ for extension of its optical absorption into the visible region by replacing the Ti$^{4+}$ or the O$^{2-}$ ions. The doping process is usually performed to reduce the bandgap value by lowering the upper edge of the CB (metal doping) or raising the lower VB edge (non-metal doping) (Figure 2.5).
2.3.1.1 Metal ion doping

Many metal ion-doped TiO$_2$ structures have been fabricated for enhanced visible-light photocatalytic activity ranging from alkaline earth Ca$^{2+}$, Sr$^{2+}$ and Ba$^{2+}$ (Al-Salim et al., 2000), Fe$^{3+}$ (Kang, 2003), Cr$^{6+}$ and Co$^{3+}$ (Wang et al., 2004), Mo$^{5+}$ (Wilke & Breuer, 1999) to rare-earth ions such as La$^{3+}$, Er$^{3+}$, Pr$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$ (Xu et al., 2002). A general understanding is that semiconductor doping with metal ions will lead to the introduction of an additional 3d energy level, leading to a reduction of the bandgap. There are three main strategies for the preparation of metal ion-doped TiO$_2$ structures: ion implantation, high-temperature treatment, or wet chemistry pathway. A systematic study (Choi et al., 1994) of TiO$_2$ NPs prepared by the sol-gel method doped with 21 metal ions was carried out to study their photocatalytic activity by photocatalytic oxidation and reduction of chloroform and carbon tetrachloride, respectively. It was discovered that the introduction of metal ion dopants into the TiO$_2$ structure essentially influenced the photocatalytic activity, recombination rates of photogenerated charge carriers, and interfacial electron transfer rates. Su and co-workers (Su et al., 2012) prepared high-quality polycrystalline Fe-doped TiO$_2$ porous films for visible light photodecomposition of methylene blue (MB). They showed that impurity concentration had a large effect on the photodecomposition of MB complemented with a higher photocurrent density under visible light irradiation in Fe-doped TiO$_2$ structures without impurities. In summary, doping of TiO$_2$ with metal ions is a promising approach for visible-light-driven photocatalysis. Depending on the target application of TiO$_2$ based photocatalyst, the concentration of the metal ion and implantation method should be considered.
2.3.1.2 Non-metal ion doping

The best-known non-metal ions for TiO$_2$ doping are C (Irie et al., 2003), F (Yurddaskal et al., 2018), S (Umebayashi et al., 2003), B (Zhao et al., 2004), and P (Lin et al., 2005). Doping with nitrogen (N) has attracted large interest since the first breakthrough in 1986 (Sato, 1986). It was observed that upon calcination of TiO$_2$ with NH$_4$Cl, the absorption of TiO$_2$ was shifted towards the visible region. The as-prepared compound (NO$_x$-doped TiO$_2$), demonstrated visible-light-driven photocatalysis for the oxidation of CO, oxygen isotope equilibration, and ethane. Asahi and co-workers (Asahi et al., 2001) fabricated an N-doped TiO$_2$ photocatalyst by sputtering a TiO$_2$ target in an N$_2$/Ar gas mixture followed by calcination of TiO$_2$ powder in an NH$_3$/Ar atmosphere. The N 1s XPS spectra showed an N atom peak at 396 eV that was suggested to substitute oxygen atom in the TiO$_2$ lattice. The as-prepared yellowish TiO$_2$ powder absorbed visible light ($\lambda < 500$ nm) and exhibited larger photocatalytic activity for decomposition of acetaldehyde and MB solution under visible light. Irie et al. reported a fabrication of carbon (C)-doped TiO$_2$ by calcination of TiC powder (Irie et al., 2003). By precise control of the temperature, C-doped TiO$_2$ in anatase or rutile crystalline phases were produced. The as-prepared C-doped TiO$_2$ photocatalyst was yellowish with extended absorption to the visible part of the spectra. The C 1s XPS spectra revealed a carbon peak at 281.8 eV corresponding to an exchanged carbon. The C-doped TiO$_2$ showed photocatalytic decomposition of gaseous 2-propanol under visible light. Normally, to produce visible light active non-metal doped TiO$_2$ photocatalyst, the following conditions should be met. First, the dopant should produce additional energy levels in the bandgap just above the VB of TiO$_2$ which can absorb visible light. Second, the new energy levels should overlap with band states of TiO$_2$ to allow efficient photogenerated carriers to transfer to the active sites at the surface.

2.3.2 Nanostructured TiO$_2$

The fabrication of various morphological configurations of TiO$_2$ is beneficial for photocatalytic applications. It is well known that size, dimension, crystalline phase, specific surface area, the exposed surface facets, and the pore volume have a major impact on the photocatalytic activity. Therefore, the development of improved TiO$_2$ structure by modifying these parameters is one of the key strategies in photocatalytic research. For example, zero-dimensionality (0D) structures possess a relatively high specific surface area, which facilitates the decomposition of organic pollutants. One-dimensional (1D) materials such as nanotubes (NTs) or nanofibers have a low recombination rate of photoexcited charge carriers due to the short distance for electrons and holes diffusion and superior light-scattering properties. For two-dimensional (2D) structures like nanosheets and thin films, high adhesion
and smooth surfaces are typical features. Three-dimensional (3D) nanostructures contain an interconnecting or mesoporous structure that exhibits good carrier mobility and can be utilized in environmental applications (Figure 2.6).

![Diagram of structural dimensionality of TiO$_2$](image)

**Figure 2.6 Schematic illustration of structural dimensionality of TiO$_2$. Adapted from (Nakata & Fujishima, 2012).**

### 2.3.2.1 TiO$_2$ nanoparticles (0D)

The photocatalytic reaction takes place at active sites on the surface of TiO$_2$ and hence it is effective to expand the exposure time of the photocatalyst surface to the light and the environment (Verbruggen et al., 2012). This can be achieved by producing NPs with a high surface-to-volume ratio with a shorter charge carrier diffusion length that reduces electron and hole recombination. The properties of TiO$_2$ NPs are determined by the preparation method and have a crucial role in photocatalysis. Numerous approaches can be applied to prepare TiO$_2$ NPs such as sol-gel process, spray pyrolysis, sonochemical and microwave-assisted methods, hydro/solvothermal methods, chemical vapor deposition (CVD), and physical vapor deposition (PVD) (Nyamukamba et al., 2018). The Degussa P25 is an industrial TiO$_2$ nano-sized powder with an average particle size of around 20-25 nm which is one of the most used commercial photocatalysts. Maira et al. (Maira et al., 2000) demonstrated that for photocatalytic oxidation of trichloroethylene (TCE) optimal size of TiO$_2$ NPs was 7 nm. The larger TiO$_2$ NPs were considered to be less efficient due to high scattered fraction and thus lower absorption of the light. On the other hand, the photocatalytic activity of TiO$_2$ NPs with a size of less than 7 nm was also reduced. The “quantum size effect” was in control of this phenomenon, since upon discretization of the band structure it undergoes a blue shift, leading to inefficient absorption of incoming photons (Brus, 1986; Lin et al., 2006). There are
some other approaches to synthesize more sophisticated architectures of TiO$_2$ NPs such as hollow nanospheres (Li et al., 2007) or sphere-in-sphere structures (Kondo et al., 2008) which show the additional benefit of improved light utilization by multiple reflections and scattering inside the NPs.

2.3.2.2 TiO$_2$ nanotubes and nanofibers (1D)

The 1D TiO$_2$ materials, such as nanofibers and NTs have optical and electrical properties suitable for photocatalytic reactions. The higher surface-to-volume ratio allows a significant recombination rate delay of photoexcited carriers and enhanced interfacial electron and hole transfer rates. The different methods such as sol-gel and template-assisted methods, hydro/solvothermal, and electrochemical approaches (Ghicov & Schmuki, 2009; Hoyer, 1996; Kasuga et al., 1998, 1999; Macak et al., 2007; Sander et al., 2004; Xia et al., 2003) were used for the fabrication of 1D TiO$_2$ nanostructures. TiO$_2$ 1D nanomaterials have been utilized in energy and environmental application including photocatalysis, gas sensing (Kim et al., 2006; Park et al., 2010), solar cells (Song et al., 2005), and batteries (Nam et al., 2010). It was shown that the photocatalytic activity of TiO$_2$ NTs has a higher performance than a regular nanoparticulate layer (Degussa P25 nanopowder, 20–30 nm) (Macak et al., 2007). One possible application of TiO$_2$ NTs in photocatalytic applications is the fabrication of free-standing flow-through membranes (Albu et al., 2010) that allow well-defined photocatalytic interactions and longer interaction times combined with filtration capability. Solar cells are another attractive application of TiO$_2$ NTs. Roy et. al. (Roy et al., 2010) reported an effective fabrication of high aspect ratio TiO$_2$ NTs. An ordered TiO$_2$ NTs layer exhibited a record for dye-sensitized solar cells (DSSCs) efficiency (5.2%) under solar illumination.

2.3.2.3 TiO$_2$ nanosheets (2D)

TiO$_2$ nanosheets are flake-shaped structures with a thickness of 1–10 nm and cross-sectional dimensions to a few microns, flat surface, and high surface aspect ratio (Shibata et al., 2007). This results in good adhesion to substrates, low turbidity, and high-quality smoothness (Ao & Lee, 2004). The photocatalytic applications of TiO$_2$ nanosheets have been realized in superhydrophilicity and photocatalytic decomposition of organic molecules (Leary & Westwood, 2011). TiO$_2$ nanosheets have found applications as self-cleaning and anti-fouling materials. Han et al. (Han et al., 2009) reported preparation of TiO$_2$ nanosheets with a thickness of 8 nm and studied their photocatalytic performance in the decomposition of methyl orange (MO). It was demonstrated that TiO$_2$ nanosheets had an improved decomposition rate of MO than P25 TiO$_2$ NPs. Furthermore, Ao and Lee reported the fabrication of
TiO$_2$ nanosheets based self-cleaning glass (Ao & Lee, 2004), where TiO$_2$ nanosheets were deposited on microscopic glass with further calcination. Strong adhesion and good hardness of TiO$_2$ nanosheets with glass were realized. The self-cleaning properties were analyzed by dip-coating of the microscopic glass with TiO$_2$ nanosheet in an MB solution. As a result, MB was not attached to the microscopic glass with TiO$_2$ nanosheet, indicating high self-cleaning properties.

### 2.3.2.4 TiO$_2$ mesoporous structures (3D)

The 3D mesoporous structures have great potential for practical photocatalytic applications with large surface-to-volume ratios with efficient diffusion pathways. The photons along with pollutant species can penetrate the highly porous framework offering efficient purification, separation, or storage. Generally, a templating strategy has been applied to produce a mesoporous TiO$_2$ based structure. This approach involves deposition of TiO$_2$ in or inside the foreign template following by its chemical or temperature removal and formation of an interconnected highly porous TiO$_2$ network. As an example, Ahn and co-workers (Ahn et al., 2013) fabricated 3D monolithic nanoshell titania by proximity field nanopatterning (PnP) and low-temperature atomic layer deposition (LTALD) methods. First, TiO$_2$ was uniformly deposited on the 3D polymer template by the ALD technique. Then, the polymer template was removed by high-temperature treatment along with the conversation of TiO$_2$ to the anatase crystalline phase. The photocatalytic activity of 3D nanoshell TiO$_2$ was 3 times higher than that of thin-film P25 TiO$_2$ NPs owing to larger light absorption and pore structure that enhanced the accessibility of the reactants, unlike the P25 film. Moreover, due to a monolithic form of 3D TiO$_2$ nanoshell, photocatalytic activity showed recyclable performance degradation compared to P25 TiO$_2$ NPs.

A particular case of TiO$_2$ based mesoporous and interconnected structures is TiO$_2$ based photonic crystals or IO. These structures have a highly ordered periodic structure, high surface areas, and PBG that allow for precise control of emission and photon localization (Liu et al., 2009; Ren et al., 2006). Section 2.4 is devoted to a detailed discussion of TiO$_2$ based IO structures.

### 2.3.3 TiO$_2$ heterostructures

Fabrication of TiO$_2$ based heterostructures is carried out to obtain several advanced optical and electrical properties such as visible light absorption, improved interfacial charge transfer, and extended selectivity towards synthesis or decomposition of target compounds. As a sensitizer, numerous materials can be
used such as semiconductors, graphene-based and plasmonic structures. The band alignment between two materials should be carefully considered before preparation, making an electron and hole transfer from one structure to another thermodynamically favorable.

2.3.3.1 Coupling with another semiconductor

Bringing two independent semiconductors into close electrochemical contact will result in the formation of a semiconductor heterojunction with improved charge separation, low recombination rate, absorption of the visible light, and enhanced photocatalytic activity. The semiconductor heterojunctions can be divided into three groups depending on the bandgap potentials: type I (straddling gap), type II (staggered gap), and type III (broken type) as shown in Figure 2.7 (Kumar et al., 2019).

![Figure 2.7 The charge transfer processes in type I, II, and III heterojunctions (paring two different semiconductors). Adapted from (Kumar et al., 2019).](image)

In type I heterojunction, the VB of semiconductor A is more positive, while CB is more negative than VB and CB of semiconductor B, respectively. Thus, the holes from VB of A to VB of B semiconductor and photogenerated electrons transfer from CB of A semiconductor to CB of B semiconductor. One disadvantage of type I heterojunction is that photogenerated electrons and holes can be stored on one of the semiconductor materials leading to low photocatalytic activity. In type II heterojunction, the CB of semiconductor B is less positive than CB of semiconductor A and VB of B semiconductor is more negative than VB of semiconductor A. Thus, the photogenerated electrons transfer from CB of semiconductor B to CB of semiconductor A along with holes from VB of semiconductor A to VB of semiconductor B, resulting in the efficient charge separation, reduced
recombination, and formation of distinct oxidation and reduction sites. Type III heterojunction exhibits broken band positions. The photogenerated electrons in the CB of semiconductor A recombine with holes of semiconductor B, favoring the accumulation of electrons in CB of semiconductor B and hole in VB of semiconductor A, improving photocatalytic activity.

TiO₂ based heterojunctions have been extensively investigated for photocatalytic applications. There are many examples such as CdS/TiO₂ photocatalysts for the degradation of aqueous pollutants (Li et al., 2018), IrO₂/TiO₂ for solar water splitting (Ryu et al., 2014), SnO₂/TiO₂ and VO₃/TiO₂ for gas-phase oxidation of organic pollutants (Fuerte et al., 2002; Shang et al., 2004). Xie et al. (Xie et al., 2014) synthesized TiO₂/BiVO₄ heterojunction by depositing BiVO₄ NPs into the TiO₂ sol. The photogenerated charge carriers in TiO₂/BiVO₄ heterojunction had an extended lifetime and greater separation than in pristine BiVO₄ resulting in an elevated photocatalytic activity for PEC oxidation of water and improved photodegradation of phenol.

2.3.3.2 Deposition of plasmonic metal nanoparticles

TiO₂ functionalized with plasmonic MeNPs shows improved photocatalytic efficiency under visible light due to SPR properties or functioning as an electron trap, stimulating interfacial charge transfer, and hindering the recombination of photogenerated charge carriers. Typical metals used for plasmonic activation of the TiO₂ are noble metals such as Pt, Pd, Au, and Ag (Albiter et al., 2015; Barakat et al., 2014; Lei et al., 2015; Quesada et al., 2018). When MeNPs come in contact with the TiO₂, a redistribution of electric charge is observed and Fermi levels of the TiO₂ and MeNPs reach a thermodynamic equilibrium which depends on the values of the TiO₂ electrons affinity and the work function of the MeNPs. The electrons start to migrate from the TiO₂ to the MeNPs resulting in a negative charge on the MeNPs surface and a positive charge on the TiO₂ surface which further leads to an upward bending of the CB and VB of the TiO₂ forming a Schottky barrier. Since TiO₂ is having an electron deficit at the point of electrical contact with MeNPs, a space charge layer forms in the region which determines the degree of CB and VB bending and the height of the Schottky barrier (Figure 2.8).
The MeNPs can efficiently enhance the photocatalytic activity of TiO$_2$ either acting as an electron trap, accepting photoexcited electrons from CB of TiO$_2$, and reducing the recombination rate or via plasmonic properties of MeNPs. The SPR is a collective oscillation of the free electrons in CB on the metal-induced by an electromagnetic wave with a suitable wavelength (Figure 2.9). There are two types of SPR, one is a propagating surface plasmon resonance (PSPR) which occurs in bulk metals, and an LSPR which can be observed on the surface of MeNPs. The PSPR can be seen when the propagation of electron density waves induces positive and negative charges along the metal surface due to the plasmonic effect (Lu et al., 2009). The LSPR can be observed in MeNPs where the oscillation is confined to a finite volume. The electric field across MeNPs is considered uniform if the wavelength of incident light is larger than the MeNPs creating a dipole. The electric field generates the oscillation of electrons, creating a plasmon state. When the frequency of incident light is equal to the plasmon frequency, the resonance conditions are achieved. The plasmonic properties of the MeNPs are highly dependent on the selected metal, size, shape, and local environment (Noguez, 2007). The selected metals should have pronounced SPR properties in the visible range of the spectrum, such as Au, Ag, and Cu. Alternatively, the fabrication of metal alloy NPs can tune SPR properties. The particle size determines the SPR wavelength; by increasing particle size, the intensity of the absorption band gets broader and taller (Liz-Marzán, 2006). Besides spherical particles, many other nanosized morphologies such as nanorods (Eustis & El-Sayed, 2006; Hu et al., 2006), nanocubes (Sherry et al., 2005), and nanowires (Ditlbacher et al., 2005) exhibit SPR effects. A general trend for the plasmonic nanostructures architectures is the greater the deviation from spherical shape, the greater the SPR shifts to the red region.
The plasmon nanostructures can improve the photocatalytic activity of TiO$_2$ by three major energy transfer mechanisms: (i) direct or hot electron transfer (DET or HET), (ii) local electromagnetic field enhancement (LEMF), and (iii) resonant energy transfer (RET) (Linic et al., 2011). The DET (HET) process occurs when MeNPs and TiO$_2$ form a Schottky barrier. Upon light excitation, photoexcited electrons can overcome the Schottky barrier and migrate to CB of TiO$_2$. Several works (Silva et al., 2011; Tsukamoto et al., 2012) have demonstrated the effectiveness of this mechanism. The LEMF energy transfer process can be achieved via a radiative transfer between MeNPs and TiO$_2$. The intense charge accumulation on the MeNPs surface leads to the generation of an electric field. Its intensity decays exponentially with increasing distance from the MeNPs and the photogenerated electrons and holes are formed in the close vicinity of MeNPs. And since the field intensity reduces with distance, more electron and hole pairs are produced near the semiconductor surface (Linic et al., 2011). As a result, the short charge carrier diffusion lengths reduce charge recombination and lead to greater photocatalytic activity. Awazu and co-workers displayed evidence for this mechanism (Awazu et al., 2008). They prepared coated AgNPs with SiO$_2$ insulator layers to prevent direct contact with TiO$_2$ so to exclude the possibility of DET mechanism. As a result, under the proposed mechanism, the photocatalytic activity increased with decreasing thickness of the SiO$_2$ insulator layer. The RET energy transfer mechanism can be considered as long as the plasmonic band overlaps with the semiconductor light absorption. The RET directly produces charge carriers in semiconductors via the relaxation process of localized surface plasmon dipoles. Taking an example of Cushing and co-workers (Cushing et al., 2015) work, where two compounds Au/SiO$_2$/TiO$_2$ and Ag/SiO$_2$/TiO$_2$ were prepared so that the plasmonic band of Ag was partly overlapping with the absorption of TiO$_2$ while...
there was no overlapping between Au and TiO$_2$. The SiO$_2$ layer was used to prevent the DET from the metal surface to TiO$_2$. Ag/SiO$_2$/TiO$_2$ demonstrated RET energy transfer in visible light range while Au/SiO$_2$/TiO$_2$ structure, owing to the lack of plasmonic and absorption overlap did not show photocatalytic activity.

2.4 TiO$_2$ INVERSE OPAL

2.4.1 General information

IO is a three-dimensional porous ordered structure with a large specific surface area and has the optical properties of photonic crystals. TiO$_2$ IO consists of only 25% by the volume of the TiO$_2$ itself while the remaining 75% is occupied by air in the pores. The pores are arranged in a face-centered (FCC) or hexagonal closest packed (HCP) structure and each pore is surrounded by twelve nearest neighbor pores. From the photocatalytic point of view, TiO$_2$ IO contains all properties attributed to pristine TiO$_2$ but complemented with flexible size pore structure, large surface area, and advanced optical properties.

2.4.2 Properties of TiO$_2$ IO

TiO$_2$ IO contains photonic crystal properties such as PBG (Yablonovitch, 1993), the slow light effect (Curti et al., 2017), super prism effect (Kosaka & Kawashima, 1998), and negative refractive effect (Cubukcu et al., 2003). The PBG can be considered as a frequency band in the 3D structures where propagation of the electromagnetic wave in space direction with certain frequencies is forbidden. The slow light effect or slow photons normally can be observed when photons propagate through the 3D structure with a strongly reduced group velocity which leads to a delay and multiple light scattering inside the structure. A significant improvement of the photocatalytic activity results in the overlapping of frequency edge (high and low) of the low photons with the electronic bandgap of the IO structure. In photonic crystals, a slight change of the incident light angle can result in a large light path swing due to the sharp alteration of group velocity, i.e. the super prism effect. And when the electromagnetic waves are refracted at an interface of 3D structure in the opposite direction to the normal (left-handed materials) is known as the negative refractive effect.
2.4.3 Preparation of TiO$_2$ IO

The fabrication procedure of TiO$_2$ IO normally follows the colloidal crystal template method which comes down into three steps: (i) assembly of template, (ii) infiltration of TiO$_2$ based precursor and (iii) removal of the template by calcination or chemical treatment (Figure 2.10). The assembly of the template is carried out by polystyrene (PS), polymethyl methacrylate (PMMA), or silica (SiO$_2$) microspheres by self-assembly method, centrifugal sedimentation, or dip coating. The infiltration of the TiO$_2$ based precursor is an important factor in the preparation of TiO$_2$ IO structures. There is a variety of infiltration methods ranging from deposition techniques as ALD to widely used sol-gel methods. The final step is calcination or chemical etching is conducted to remove the template and to simultaneously convert TiO$_2$ to the targeted crystalline phase.

![Figure 2.10 Template assisted preparation of the TiO$_2$ IO structure using the PS sphere as a template (Publication III).](image)

2.4.3.1 Sol-gel methods

The sol-gel methods are popular and widely used approaches for the preparation of TiO$_2$ IO (Galusha et al., 2008; Wu et al., 2013). It is a relatively simple synthetic procedure without the use of special instruments, which allows accurate control of reaction conditions, low synthesis temperature, and high regularity of the product. The TiO$_2$ based precursor, which is used for the infiltration, undergoes hydrolysis and condensation to form a stable and transparent sol. Upon aging, the sol inside the 3D template becomes a gel. Subsequently, after drying and calcination TiO$_2$ IO structure is observed. The precursor usually consists of Ti-based materials (mainly titanium alkoxides), an inorganic acid (usually hydrochloric acid (HCl)) as a catalyst, and an organic solvent (isopropyl alcohol or ethanol). As an example, Wu and co-workers (Wu et al., 2013) prepared a high-quality TiO$_2$ IO by the template-
assisted method using PS spheres template and HCl and titanium (IV) isopropoxide (TTIP) for photocatalytic degradation of dyes. Qi et al. (Qi, et al., 2014) synthesized TiO$_2$ IO by using TiO$_2$ based precursor based on TTIP, HCl along with ethanol and acetylacetone. The precursor solution was then filled into the PS opal template and after calcination, TiO$_2$ IO structures were obtained. Utilizing PS spheres with different sizes, the TiO$_2$ IO structures with various PBG were observed.

2.4.3.2 Chemical vapor deposition

The CVD method has been successfully applied for the infiltration of the TiO$_2$ precursor into a colloidal template in the gas phase. Moon and co-workers (Moon et al., 2009) demonstrated the fabrication of TiO$_2$ IO by room temperature chemical vapor deposition (RTCVD) under atmospheric pressure. They used PS spheres as a template for precursor deposition followed by exposure to water and titanium tetrachloride (TiCl$_4$) vapours with subsequent calcination of the colloidal template. The filling parameters were controlled by the number of depositions of TiCl$_4$ vapour. This method allows a very uniform formation of the TiO$_2$ IO structure with an adjustable filling rate.

2.4.3.3 Atomic layer deposition

Recently, ALD has attracted attention for the preparation of the high-quality TiO$_2$ IO structure. King et al. (King et al., 2005) demonstrated this technique for the uniform fabrication of the TiO$_2$ IO structure. They reported a low-temperature fabrication of TiO$_2$ IO on the SiO$_2$ colloidal template (200 to 440 nm) by the ALD infiltration method using TiCl$_4$ and H$_2$O precursors at 100 $^\circ$C, followed by sintered for 2 h at 400 $^\circ$C, and template removal by hydrofluoric acid. The obtained TiO$_2$ IO structure possessed an exceptionally smooth surface (less than 1 nm root-mean-square (RMS) roughness) and filling fractions of the SiO$_2$ colloidal template was about 88%. Furthermore, Liu and co-workers (Liu et al., 2011) prepared a TiO$_2$ IO structure with an even higher filling fraction up to 96%. This structure was used as a photoanode for solar cell applications enhancing the light-harvesting of DSSCs.

2.4.3.4 Other methods

TiO$_2$ IO structures have also been synthesized by electrochemical methods such as electrodeposition. Yan et al. (Yan et al., 2006) demonstrated the filling of the PS template with TiO$_2$ by the cathodic electrodeposition method. The FTO glass with
assembled PS template was used as a working electrode, calomel electrode as a reference electrode and aluminum foil as the counter electrode. After the electrochemical experiment, drying, and removal of the PS template, TiO$_2$ IO structures with high filling factors were obtained. Matsushita and co-workers (Matsushita et al., 2007) prepared smooth TiO$_2$ IO structures in a large area (> 5 cm$^2$) using a spin-coating technique. A precursor (ethanol solution of titanium (IV) tetrabutoxide) was spin-coated on the PS template with a spinning rate 500 rpm) during 2-20 s. After the disposal of the PS template, smooth TiO$_2$ IO structures were observed. The TiO$_2$ IO structures can be produced over large areas (< 1 cm) by the crack-free method. It combines the template self-assembly steps with precursor infiltration into one process in which the colloidal template is assembled directly from the sol-gel solution, generating solid IO films with no overlayer, large (from mm to cm) surface area without cracks. The work of Hatton and co-workers (Hatton et al., 2010) on the assembly of large-area, highly ordered, crack-free IO films gave an insight into this procedure and opened new perspectives for the preparation of the TiO$_2$ IO structures.

2.4.4 Modification of TiO$_2$ IO

2.4.4.1 Metal and non-metal ion doping

The metal or non-metal ion doping is an approach to introduce metal or non-metals to the TiO$_2$ IO structure and improve optical and photocatalytic properties. Li and Shang (Li & Shang, 2008) demonstrated a physical and chemical modification of TiO$_2$ IO by fabrication nitrogen-doped (N-TiO$_2$) IO. First, they fabricated the PS template and further spin-coated TiO$_2$ based precursor with tetramethylammonium hydroxide (TMAH). The N-doped TiO$_2$ IO had larger absorption capacity and visible light photocatalytic activity compared to an untreated TiO$_2$ IO. Yang and co-workers (Yang et al., 2011) prepared Yb$^{3+}$, Er$^{3+}$ co-doped TiO$_2$ IO by a similar approach as above. The PS templates (220, 400, or 460 nm) were filled with titanium butoxide (Ti(OC$_4$H$_9$)$_4$), Yb$_2$O$_3$, and Er$_2$O$_3$. The Er$^{3+}$ ions are upconversion luminescence rare earth metal ions and Yb$^{3+}$ is usually used to increase the absorption cross-section for improved photocatalytic activity. Luminescence was suppressed by overlapping PBG with the Er$^{3+}$ emission band. Li et. al. (Li et al., 2018) for the first time reported the fabrication of bifunctional Ni-doped TiO$_2$ IO for application as photocatalyst and surface-enhanced Raman scattering (SERS) active substrate. This approach enhanced SERS sensitivity for the detection of 4-mercaptobenzoic acid (4-MBA) down to a concentration of $1 \times 10^{-11}$ M and increased photocatalytic activity under simulated sunlight decomposing 95% of the MB within 90 min.
2.4.4.2 Metal nanoparticle deposition

The MeNPs deposition to the TiO₂ IO structure is an effective way to improve the photocatalytic activity of TiO₂ IO since MeNPs work as electron traps promoting the separation of photo-generated electrons and holes or through the LSPR. The most common MeNPs for decoration of TiO₂ IO structures are Au, Ag, and Pt. Boppella and co-workers (Boppella et al., 2017) reported deposition of AuNPs on the TiO₂ IO structure with incorporated reduced graphene oxide (rGO). The TiO₂ IO/rGO/Au composite exhibited a 14-fold enhanced PEC performance under visible light and a 2.5-fold enrichment in the applied bias photon-to-current efficiency compared to pristine TiO₂ due to enhanced charge transfer and light absorption. Furthermore, using TiO₂ IO/rGO/Au as a photoelectrode an H₂ evolution rate of 17.8 μmol/cm² was achieved that was 2.5 times greater than with TiO₂ sample. Chen et al. (Chen et al., 2014) reported the preparation of the TiO₂ IO structure with AgNPs deposited by pulsed current deposition technique for enhanced photocatalytic degradation of MB. The pulsed current deposition process was effectively suppressing the agglomeration of AgNPs due to the high nucleation rate followed by a uniform deposition of small AgNPs (10-15 nm). The as-prepared TiO₂ IO/AgNPs composite displayed an enhanced photocatalytic activity towards degradation of MB due to LSPR properties of AgNPs and reduced electron-hole pair recombination rate. Huo and co-workers (Huo et al., 2019) prepared a composite photocatalyst by coupling TiO₂ IO, PtNPs, and rGO for photocatalytic purification of water. The TiO₂ IO was prepared by a conventional template-assisted method while PtNPs and rGO were impregnated by the in situ reduction method. The visible-light photocatalytic activity was evaluated by photodecomposition of MO and TiO₂ IO/PtNPs/rGO composite displayed a 6-fold enhanced activity compared to pristine TiO₂ IO. The significantly enhanced photocatalytic activity of composite was ascribed to the synergetic effect of the slow photon effect of IO structure and elevated light absorption and charge separation upon the decoration of the PtNPs and rGO.

2.4.4.3 Heterojunction coupling

TiO₂ IO coupling with another semiconductor followed by the alignment of the band structures can result in the photogenerated electrons and holes being shuttled to the CB or VB of another semiconductor, extending the lifetime and improving the photocatalytic properties. Alessandri and co-workers (Alessandri et al., 2009) prepared a CeO/TiO₂ IO composite. First, CeO IO structure was prepared by the template-assisted method and then by ALD TiO₂ film was cast in CeO IO. The CeO/TiO₂ IO composite showed a better photocatalytic activity by the degradation of MB compared to TiO₂ and CeO alone. Li et al. (Li et al., 2017) fabricated
TiO$_2$/MoS$_2$ core/shell IO (TiO$_2$/MoS$_2$ IO) structure through the ALD method by deposition of TiO$_2$ and MoS$_2$ on a PS template. By changing the diameter of the PS sphere in the template as well as the thickness of MoS$_2$ layer in TiO$_2$/MoS$_2$ IO composite enhanced photocatalytic activity was obtained.

2.4.4.4 Other modifications

Other modification methods include, for example, an electrode based on TiO$_2$ IO with CdS quantum dots (QDs) for PEC H$_2$ production (Cheng et al., 2012). The structure was fabricated by a template-assisted method and CdS QDs were sensitized by a successive ionic layer adsorption and reaction (SILAR) approach. Under simulated solar-light photocurrent density of 4.84 mA cm$^{-2}$ was achieved for the TiO$_2$ IO with 288 nm pore size as photoanode at 0 V vs. Ag/AgCl bias. Chen and co-workers (Chen et al., 2018) prepared TiO$_2$ IO/CsPbBr$_{1.5}$I$_{1.5}$ QDs/ Nafion composites for a visible light-triggered PEC sensor for dopamine (DA) detection. The CsPbBr$_{1.5}$I$_{1.5}$ QDs were self-organized into the framework of the TiO$_2$ IO by the slow volatilization of cyclohexane. The resulting compound exhibited increased absorption of the visible light, shifting to 640 nm, covering the whole visible region. Moreover, immediate response for DA detection with a linear range (0.1 μM– 250 μM) and a low detection limit (0.012 μM) along with high sensitivity and selectivity was observed.

2.4.5 Application of TiO$_2$ IO

2.4.5.1 Solar cells

Liu et. al. (Liu et al., 2011) studied the PEC performance of the TiO$_2$ IO photoanodes with different pore sizes for application in DSSCs. The energy conversion efficiency of the DSSCs was recorded at 2.22% by utilizing the TiO$_2$ IO with 288 nm pore size as a photoanode and a dye as a sensitizer. The PEC performance was associated with the decreased lattice size of the TiO$_2$ IO electrode along with the enlarged surface area for dye loading. Kim and Moon (Kim & Moon, 2012) used Nb$_2$O$_5$-coated TiO$_2$ IO electrodes in DSSCs. Maximum efficiency of 7.23% was detected during photovoltaic measurement for a 3.3 wt % Nb$_2$O$_5$/TiO$_2$ IO structure. The introduction of Nb$_2$O$_5$ significantly enhanced the short-circuit current density (J$_{SC}$) by improving electron injection. The effectiveness of the 1D NRs-planted TiO$_2$ IO structure as an electrode for DSSCs was shown by Park and co-workers (Park et al., 2014). The NRs were hydrothermally grown on the surface of the TiO$_2$ IO structure. The NR/TiO$_2$ IO electrode demonstrated a significant increase in J$_{SC}$ with a photocurrent of 14.84 mA cm$^{-2}$ and total efficiency of 6.38%. The enhanced
performance was due to increased light absorption and electron transport properties of the NR/TiO$_2$ IO electrode.

### 2.4.5.2 SERS detectors

SERS technology is usually applied to the detection of various chemical compounds. The most common SERS materials are noble metals like Au, Ag, and Cu. However, the SERS activity of TiO$_2$ IO has also been reported by Qi et al. (Qi et al., 2014). The highly sensitive detection was regulated by the position of PBG upon the improvement of light-matter coupling. The maximum sensitivity was accomplished by adequate adjusting of the pore sizes and follow the slow light effect. Additionally, TiO$_2$ IO showed recyclability by optical irradiation. Furthermore, Zhao and co-workers (Zhao et al., 2015) fabricated Ag coated TiO$_2$ IO films with high SERS enhancement factors by an electroless deposition process. They demonstrated that the major factors, which determine the magnitude of the SERS signal, were the TiO$_2$ IO pore size and the number of Ag-loading cycles. The highest SERS enhancement for a rhodamine 6G (R6G) with the detection limit of $10^{-10}$ mol l$^{-1}$ was observed for Ag-decorated TiO$_2$ IO. Moreover, a detection limit of $10^{-9}$ M was attained.

### 2.4.5.3 Photocatalysis

The majority of TiO$_2$ IO applications fall to photocatalytic applications. As an example, Sordello et al. (Sordello et al., 2011) studied the photocatalytic activity of TiO$_2$ IO, P25 TiO$_2$ NPs, microporous TiO$_2$ IO, and disordered TiO$_2$ IO. The results indicated that the photocatalytic activity of the TiO$_2$ IO was higher compared to the others due to the highly porous ordered structure and slow light effect. Besides conventional dye degradation, TiO$_2$ IO was utilized to produce solar fuels such as CO, CH$_4$, and H$_2$ production. Jiao and co-workers (Jiao et al., 2017) used TiO$_2$ IO decorated with PtNPs with an average size of 2.5 nm for the photocatalytic reduction of CO$_2$ in the water. Loading of PtNPs into TiO$_2$ IO boosted the photocatalytic reduction of CO$_2$ to CH$_4$ (2.416 mmol), which was 3.2 times higher than TiO$_2$ IO and 2.4 times higher than powder P25 TiO$_2$. The enhanced photocatalytic activity can be assigned to the improved visible light absorption and reduced recombination rate of the photogenerated charge carriers. Kim et al. (Kim et al., 2013) produced TiO$_2$ IO with AuNPs and investigated the PEC H$_2$ generation. The combination of TiO$_2$ IO structure properties and LSPR of AuNPs considerably improved the performance of PEC H$_2$ generation that was 2.58 times higher than in P25 TiO$_2$ photoelectrode.
2.4.5.4 Other application

TiO₂ IO structures have found applications in photonic and energy storage devices and in biological applications. For example, McNulty and co-workers (McNulty et al., 2017) tested rutile TiO₂ IO for Li-ion batteries that displayed a high-rate capability, long life cycles, and high stability of the structure due to the porous and ordered TiO₂ IO structure. When 75 mA g⁻¹ current was applied, the reversible battery capacities were ~ 170 mA g⁻¹ after 100 cycles and 140 mA h g⁻¹ after the 1000 cycles, with a retaining capacity of around 82.4%. Xu et. al. (Xu et al., 2017) designed a bionic TiO₂ IO structure for an effective immunocapture of circulating tumour cells (CTCs) by structuring a magnetic Fe₃O₄/C₆/silane NPs with anti-EpCAM (antiepithelial cell adhesion molecule) and TiO₂ IO structure. TiO₂ IO properties can be accurately controlled for imitating components of the living cell while anti-EpCAM antibodies were further modified on the TiO₂ IO interface by coupling with polydopamine (PDA). The CTCs capture effectiveness achieved a remarkable factor of 20 for the TiO₂ IO interface compared to flat glass followed by an improvement of the MCF-7 cells capture efficiency. The maximum efficiency of 92% with 1 mL h⁻¹ for CTCs capture was achieved for the TiO₂ IO structure with a pore size of 415 nm.

2.5 METHODS FOR EVALUATION PHOTOCATALYTIC ACTIVITY OF TiO₂

Generally, the heterogeneous photocatalytic activity can be evaluated by two approaches: liquid and gas-phase methods. The liquid phase method implies that photocatalytic reaction takes place on the interface of solid and liquid while in the gas phase it occurs on the solid-gas interface. Historically, photocatalytic activity has been evaluated by liquid phase methods. However, the gas phase method is more accurate, quantitative, and induces no mechanical stress on the surface.

2.5.1 Liquid-phase methods

The first successful evaluation of photocatalytic activity was demonstrated in the seminal work of Fujishima and Honda (Fujishima & Honda, 1972) in which water splitting was carried out on the TiO₂ electrode. Various parameters such as pH, temperature, viscosity, and concentration can have an influence on this method.
2.5.1.1 Degradation of organic compounds

Colourful organic dye solutions such as MB, MO, or malachite green (MG) have been used as an indicator of a photocatalytic reaction. The photocatalytic activity can be evaluated by how fast the used dye solution degrades with the solution becoming transparent. Generally, UV-vis spectroscopy is used for the analysis of the dye solution before and after the reaction. However, the utilization of the dyes is doubtful because the incident light itself can bleach the used dye and induce a significant inaccuracy of the result. The liquid phase photodegradation of MG induced by UV light on TiO$_2$ NPs was demonstrated by Chen and co-workers (Chen et al., 2007). The photodegradation rate of MG dye enhanced, upon increasing pH. After 4 h of UV irradiation, 99.9% of MG was photodegraded. The TiO$_2$ surface was not favourable for the cationic dye adsorption because the photodegradation mechanism was beneficial for cleavage the whole conjugated MG structure, and thus the photocatalytic efficiency was hindered under acidic conditions. Under alkaline conditions, the cationic dye MG can be relatively easily adsorbed onto the TiO$_2$ surface since the photodegradation mechanism was favourable to a generation of a series of N-de-methylated intermediates of the MG dye, leading to the enhanced photodegradation. Yan et. al. (Yan et al., 2006) examined the visible light photocatalytic activity of sulfur (S) doped TiO$_2$ in the liquid phase by the degradation of MB. Their results demonstrated that as a probe molecule for semiconductor photocatalysis, MB is not appropriate, because the photoinduced reaction by absorption of MB may lead to the understanding that semiconductor material had a visible-light photocatalytic activity.

2.5.1.2 Water splitting

The water-splitting process consists of two subprocesses: H$_2$ and O$_2$ generation. Thus, the photocatalytic activity of a given photocatalyst can be evaluated by the production of either H$_2$ or O$_2$. Normally gas chromatography (GC) is used for a qualitative analysis of gas mixture produced by photocatalyst. The photocatalytic reaction takes place in a sealed reactor, which is connected to the GC. Abe and co-workers (Abe et al., 2001) designed a Pt-loaded anatase TiO$_2$ and rutile TiO$_2$ photocatalyst for H$_2$ and O$_2$ evolution, respectively. The photocatalytic reaction was carried out in a closed gas-circulating system in a reactor with inner irradiation type and on-line GC. The gas evolution of H$_2$ and O$_2$ was 180 $\mu$mol h$^{-1}$ and 90 $\mu$mol h$^{-1}$ for an alkaline (pH=11) NaI aqueous suspension under UV irradiation, respectively.
2.5.1.3 CO₂ reduction

The photocatalytic activity of CO₂ reduction, as well as water splitting, can be evaluated by reduction products such as CO, CH₄ and others depending on the target product using a similar setup consisting of a photoreactor with inner or outer irradiation and GC analyzer. In a typical CO₂ reduction experiment, a mixture of the dispersed photocatalyst in a solution is introduced to the photoreactor. CO₂ gas is further bubbled through the reaction mixture to saturate it. The photocatalytic reduction is launched when the irradiation source is on and upon a certain interval of time, gas products are taken and analyzed by GC. As an example, Liu and co-workers (Liu et al., 2012) have studied photocatalytic CO₂ reduction on TiO₂ nanocrystal polymorphs (anatase, rutile, and brookite). For TiO₂ anatase and brookite, the main products were CO and CH₄ which was 10 times higher compared to the defect-free surfaces. TiO₂ brookite with defects was photocatalytically more active than anatase and rutile, due to lower formation energy of surface oxygen vacancies. They observed that CO₂ photoreduction was not detected on defect-free TiO₂. The photoreduction of CO₂ to CO undertook different reaction pathways on oxygen-deficient TiO₂ anatase and brookite through different intermediates such as CO₂ on anatase and HCOOH or CO₂ on brookite.

2.5.2 Gas-phase methods

The gas-phase photocatalytic activity evaluation methods have several advantages over the liquid phase methods such absence of additional mechanical stresses on the photocatalyst surface and superfluous dyes, superior permeability of light irradiation. Gas-phase photoreactor with GC or GC mass-spectrometry (GC-MS) is typically used. The photocatalyst is introduced inside the photoreactor, and the photoreactor is filled with a designed gas or a gas mixture. The light exposure initiates the gas phase photocatalytic reaction and the gas mixture is analysed by GC or GC-MS with certain time intervals.

2.5.2.1 Degradation of organic contaminants

Yamazaki and co-workers (Yamazaki et al., 2005) examined the gas phase photodecomposition of chloroform with TiO₂ pellets produced by the sol-gel method. As a result, full mineralization of chloroform into CO₂ and HCl was completed within 3.5 h. However, the conversation rate was dramatically decreased because the Cl⁻ ions were accumulated on the surface of TiO₂. The photocatalytic activity was retained after washing TiO₂ pellets with water. It is worth mentioning that the gas phase photocatalytic activity of TiO₂ pellets was higher than commercially available Degussa P25. Keshmiri et al. (Keshmiri et al., 2006)
compared the gas-phase photocatalytic activity of TiO$_2$ porous films produced by the sol-gel method and standard Degussa P25 for the decomposition of TCE and toluene. The result showed that both photocatalysts had similar photocatalytic activity, but the photocatalytic oxidation rate of TCE was considerably higher than for toluene. Summarizing their findings, TiO$_2$ porous films is an alternative for industrial use of Degussa P25, with good mechanical integrity, abrasion resistance, and comparable photocatalytic efficiency.

### 2.5.2.2 CO$_2$ reduction

Yu and co-workers (Yu et al., 2016) demonstrated photoreduction of CO$_2$ to CH$_4$ by Ag/TiO$_2$ composite under UV and visible light. The high photocatalytic activity of as-prepared Ag/TiO$_2$ composite was attributed to LSPR properties of AgNPs and trapping of photoexcited electrons. The diverse organic chemical products were detected during the photocatalytic reduction of CO$_2$, including CH$_4$ and CH$_3$OH as well as a small amount of C$_2$ and C$_3$ species such as acetaldehyde and acetone. Beigi et al. (Beigi et al., 2014) prepared CdS/TiO$_2$ nanocomposites with different loading amounts of CdS for UV and visible light CO$_2$ gas-phase reduction to CO and CH$_4$. The photocatalytic reaction was taking place in a batch gaseous reactor. A significant improvement in photocatalytic activity was observed for CdS/TiO$_2$ nanocomposites compared to TiO$_2$ due to the addition of CdS and the small size of TiO$_2$ NPs. The highest photocatalytic performance under visible light was observed with 45% CdS/TiO$_2$ with 13 nm average crystal size producing 10 $\mu$mol g$^{-1}$ and 1.5 $\mu$mol g$^{-1}$ of CO and CH$_4$, respectively.
3 EXPERIMENTAL PART

3.1 DEVELOPMENT OF GAS-PHASE EVALUATION OF THE PHOTOCATALYTIC ACTIVITY

There are several methods for evaluating photocatalytic activity such as CO₂ reduction (Liu et al., 2012), H₂ evolution (Lin & Shih, 2015), and decomposition of organic pollutants or dyes (Li et al., 2008; Silva & Faria, 2009). These methods can be divided into two groups: liquid and gas-phase methods. Liquid phase methods were historically the first, and they were based on the colour transformation of the used dye under UV or visible irradiation. However, these methods suffer from some drawbacks such as bleaching of the dye by the incident light and producing additional stress on the top surface of photocatalysts (Yan et al., 2006). For these reasons the gas phase method was selected for engineering since it does not induce mechanical stress on the photocatalyst surface. This was especially important for LFS deposited NPs that are only loosely bound onto the substrate by weak van der Waals forces. An in-house built gas-phase reactor was developed for reliable, reproducible, and quantitative photocatalytic activity characterization as shown in figure 3.1 A. The reactor shell was made of a stainless-steel cylinder with a diameter of 145 mm and a volume of 15.4 cm³. The bottom was sealed whereas the top contained a flange connection with UVA transparent quartz glass functioning as a lid. Inside the reactor was a movable mesh sample holder. The CO₂ concentration detector (Vaisala GMP343), temperature and humidity sensor (Thorlabs TSP01), and pressure meter (Wika PGT10, USB mode) with USB connection to the PC for a real-time measurement were assembled in the reactor.

The measurement flow chart is shown in figure 3.1 B. The fundamental principle of this method is the oxidation of organic molecules to CO₂ and H₂O in the gas phase. Acetylene (C₂H₂) was chosen as an organic test molecule because it is a simple molecule, a common pollutant in automobile exhaust gases, cost-effective, and commercially available. First, acetylene and technical air were flowed into the mixing chamber for homogeneous mixing. The mixture of gases was flowed inside the reactor continuously until the CO₂ concentration became constant and the reactor valves 3 and 4 were shut simultaneously. The photocatalytic reaction was initiated by UV or visible light excitation through the UVA transparent quartz glass reactor window. The results of C₂H₂ oxidation into CO₂ were measured continuously by an optical CO₂ concentration detector.
3.2 PREPARATION OF TiO$_2$ INVERSE OPALS

The preparation of IO structures contains three steps: self-assembly of the template usually by polystyrene (PS) or poly (methyl methacrylate) (PMMA) spheres, infiltration, and hydrolysis of precursor solution into the template, and removal of the template. The modified method called “crack-free”, in which the first and second steps are joined, was also used for the preparation of TiO$_2$ IO.

3.2.1 Synthesis of polystyrene spheres

The PS spheres were used as building blocks for the opal templates since the preparation of PS is a rather simple and high yield process (Erola et al., 2015). Synthesis of PS spheres was completed in two steps: first, negatively charged PS spheres with a diameter of 200 nm were synthesized as seeds for the PS spheres with 400 nm diameter. 200 nm PS spheres were synthesized by a free-radical batch emulsion polymerization. 200 mg of sodium dodecyl sulfate (SDS) as a capping agent was added to 160 ml of deionized water in a reaction vessel. The reaction mixture was heated up to 70°C and stirred using an anchor-like mixer at 500 rpm. Then, 20 g of styrene was added to the reaction mixture and the reaction proceeded for 30 min at the same temperature. Further, 20 ml of deionized water with 200 mg of ammonium persulfate (APS) was added into the reaction vessel as an initiator. The reaction continued 20 h under nitrogen atmosphere.
The prepared 200 nm PS spheres were used for the preparation of 400 nm PS spheres. The polymerization reaction was continued by adding 30 ml of as prepared 200 nm PS spheres and 150 ml distilled water in a three-neck round flask. Additionally, 25 mg SDS was added to the reaction mixture, and the system was purged with nitrogen gas until the temperature was raised to 70°C. Next, 20 ml deionized water with 28 mg APS solution was introduced into the reaction mixture. After that, 21.6 g styrene was slowly added into the flask via a syringe for 10 min. The polymerization reaction was continued at 70 ºC for 20 h after the injection of styrene under the nitrogen atmosphere.

3.2.2 Infiltration method

400 nm PS spheres were self-assembled on pre-treated (washed with ethanol and water several times) microscopic slides by vertical deposition. Namely, 1 ml of 400 nm PS spheres was added to 20 ml of ultra-pure water in a small beaker. Pre-treated microscopic slides were vertically immersed into the beaker and set by the clips 5 mm above the bottom of the beaker. The whole system was carefully transferred to the laboratory oven in which liquid evaporated in a temperature range of 60-65 °C for 48 h. During the evaporation, the PS spheres were deposited on the microscopic slides due to capillarity and electrostatic forces. TiO₂ sol was prepared for further infiltration into the PS template by mixing TTIP (1 ml), ethanol (1 ml), and 0.1M hydrochloric acid (HCl) (3 ml). The precursor solution was diluted two times with ethanol (to reduce the concentration) and was stirred for one hour before use. Finally, the self-assembled PS templates on microscopic slides were gently submerged into the TiO₂ precursor solution for 5 min. After that, they were carefully taken out and dried in the fume hood for 24 h to complete hydrolyzation and formation of solid TiO₂ (Figure 3.2). When the hydrolysis had been completed, microscopic slides with PS and TiO₂ were calcinated in the high-temperature oven to remove PS spheres and convert TiO₂ into the anatase crystalline phase.

![Figure 3.2 Schematic representation of formation of TiO₂ IO by infiltration method (Publication I).](image-url)
3.2.3 Crack-free method

The crack-free method is an advanced method for the preparation of IO structures. The infiltration method has some drawbacks such as the formation of overlayers, big cracks, and the concentration of precursors should be strictly controlled (Cai et al., 2014). These problems can be solved by using a crack-free method in which deposition of PS spheres and infiltration of the precursor is a simultaneous process. This approach also allows formation of multi-layered structures such as sandwich structures with different PS sphere diameters. Fabrication of TiO$_2$ IO by the crack-free method was completed in two steps: first, self-assembly of PS spheres along with TiO$_2$ precursor solution, and second, calcination of obtained structure. In the first step, by mixing the titanium(IV) bis(ammonium lactato) dihydroxide (TiBALDH) (1 ml), ethanol (1.5 ml), and 0.1 M HCl (1 ml) and stirring for 30 min before use, TiO$_2$ precursor solution was prepared. Next, 450 μl of PS spheres 400 nm (or 200 nm) and 200 μl of TiO$_2$ precursor solution were added to 25 ml of ultrapure water and was sonicated for 30 min. Finally, the pre-treated microscopic glass slides were vertically introduced inside the beaker with the PS spheres and TiO$_2$ precursor solution. The deposition was performed by slow evaporation method in the laboratory oven at 68 ºC for 48 h. The self-assembled templates were further pre-heated at 100 ºC for 1 h to make a strong binding (necking) between PS spheres. Then, the PS template was completely removed by high-temperature treatment (a two step procedure: temperature was first increased from room temperature to 250ºC (hold time at 250ºC of 120 min) that was followed by heating from 250ºC to 550ºC in 300 min (final hold time at 550ºC of 300 min) along with the conversation of TiO$_2$ into the anatase phase that resulted in crack-free TiO$_2$ IO structures. Moreover, a double-layered IO structure was also designed. For that, after the pre-heating step, the second layer of 200 nm (or 400 nm) PS spheres was deposited, by the same approach and followed calcination procedure revealed double-layered IO structure with different pore sizes (Figure 3.3).
3.3 DEPOSITION OF METAL NANOPARTICLES

3.3.1 Slow evaporation method

The fundamental principle of the slow evaporation method is that MeNP solution is slowly evaporating and MeNPs can easily and firmly be anchored on the top layers of the structure due to large capillarity forces and large pores in IO structure. Three types of noble MeNPs, namely gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), and gold-silver nanoparticles (Au/AgNPs) were produced and used for deposition into TiO$_2$ IO. All MeNPs were prepared by a similar hydrothermal reduction method using sodium citrate (TSC) as a reduction agent (Gicheva & Yordanov, 2013; Han et al., 2016; Zhou et al., 2017). Synthetic routs of MeNPs share a common pattern; MeNPs precursor (HAuCl$_4$·3H$_2$O and/or AgNO$_3$) aqueous solution was heated up to the boiling point to initiate the growth of MeNPs. Then, upon vigorous boiling, TSC was added to trigger the reduction of NP growth. The reaction mixture was kept boiling for 15 min to form a uniform MeNPs population. The experimental details of the synthesis of individual MeNPs are summarized in Table 3.1.
Table 3.1. Summarized experimental data for the synthesis of MeNPs.

<table>
<thead>
<tr>
<th>MeNPs</th>
<th>Precursors concentration</th>
<th>Reduction agent (TSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuNPs</td>
<td>10 ml of HAuCl₄·3H₂O (0.1%) in 100 ml of ultrapure water</td>
<td>2 ml (1%)</td>
</tr>
<tr>
<td>AgNPs</td>
<td>1 ml of AgNO₃ (0.1 M) in 60 ml of ultrapure water</td>
<td>3 ml (2%)</td>
</tr>
<tr>
<td>Au/AgNPs</td>
<td>1 ml of HAuCl₄·3H₂O (0.01 M) and 1 ml of AgNO₃ (0.01 M) dissolved in 78 ml of ultrapure water</td>
<td>8 ml (0.1 M)</td>
</tr>
</tbody>
</table>

For a typical MeNPs deposition procedure, 1 or 2 ml of MeNPs solution was diluted in 20 ml of ultrapure water in a small beaker followed by 30 min of sonification for the homogeneous mixture. Microscopic glass slides with TiO₂ IO structures were carefully immersed into the beakers and retained so that they did not touch the bottom and walls of the beaker. The solution was slowly evaporated in the fume hood or the laboratory oven for 40-48 hours. TiO₂ IO structures with MeNPs were washed with deionized water and ethanol.

3.3.2 Liquid flame spray (LFS) deposition of nanoparticles

LFS allows the deposition of different metal and metal oxide NPs on large-area substrates (Teisala et al., 2010). It consists of a high-temperature flame in which an organometallic precursor evaporates, nucleates, and forms solid NPs of the final material. For the first time, the deposition of AgNPs by the LFS method was demonstrated on top of TiO₂ IO (Figure 3.4). The deposition process was performed using a rotating carousel where the amount of AgNPs was simply controlled by the number of times the microscopic slides with TiO₂ IO went through the flame. The LFS nozzle was placed 20 cm above the surface of the microscopic slide. The AgNO₃ dissolved in water (250 mg ml⁻¹ of pure silver) was used as a precursor for the AgNPs. The precursor was injected into the flame with a feed rate of 2 ml min⁻¹. The flame consisted of combustion gases such as H₂ and O₂ which were supplied with gas flow rates of 20 l min⁻¹ and 10 l min⁻¹, respectively. Additionally, nitrogen gas was introduced to the flame with a gas flow rate of 5 l min⁻¹ as an inert sheath gas to modify the flame according to burner design “KP” (Haapanen et al., 2015).
Moreover, the LFS deposition technique was used for the deposition of TiO$_2$ NPs for the evaluation of the gas-phase method. Four samples (2×15x and 2×30x) were prepared for validation of the gas phases method. TiO$_2$ NPs were deposited on microscopic glass slides using a rotating carousel and its amount was determined by the number the microscopic slides went through the flame. The LFS nozzle was 20 cm above the microscopic glass surface. The H$_2$ with gas flow rates of 50 l min$^{-1}$ and O$_2$ with gas flow rates of 50 l min$^{-1}$ were utilized as combustion gases. The precursor, TTIP (50 mg ml$^{-1}$) in 2-propanol, with a feed rate of 2 ml min$^{-1}$ was injected into the flame.

### 3.4 CHARACTERIZATION

The characterization of produced materials was performed with various techniques and methods. The main instruments for our research work were microscopes. The morphology and structure of the PS spheres, MeNPs, and surface and cross-section of TiO$_2$ IO were characterized using the field emission scanning electron
microscope (FE-SEM, Hitachi S-4800, Japan) and high-resolution transmission electron microscope (HRTEM, JEM-2100F, Jeol, Japan). Microscopic methods were complemented with energy disperse X-ray spectroscopy (EDS) by Noran system Six (NSS) software. The PerkinElmer Lambda 900 UV/Vis/NIR spectrometer fitted with a 150 mm integrating sphere was used to measure the diffuse absorbance spectra of the solid structures as well as the absorption spectra of MeNPs in an aqueous solution. X-ray photoelectron spectroscopy XPS (Thermo Scientific ESCALAB 250Xi system with an AlKα X-ray source) was applied to determine the oxidation states of individual elements in the TiO₂ IO with AgNPs structures. To confirm the crystalline nature of the TiO₂ IO and TiO₂ IO with MeNPs Raman spectroscopy and X-ray diffraction (XRD) were used. Raman spectra were collected by a programmed microscope with WireTM 3.4 software using a 785 nm excitation laser with 1 mW power, an integration time of 10 s with a measurement range of 100-800 cm⁻¹. The crystalline properties were characterized by XRD (Bruker AXS D8 Advance device using Cu Kα as radiation source), measured between 12° and 90° at 2θ scale with a step size of 0.3° min⁻¹.

3.4.1 Photocatalytic activity evaluation

The photocatalytic activity evaluation was performed using a gas-phase method based on the decomposition of organic molecules. TiO₂ IO with LFS deposited AgNPs were also characterized by the H₂ evolution test.

3.4.1.1 C₂H₂ decomposition

The evaluation of photocatalytic activity by decomposition of C₂H₂ was carried out in an in-house build photoreactor. The microscopic glass slides with TiO₂ IO were placed on the movable mesh sample holder. When the lid was sealed, the mixture of gases (C₂H₂ and technical air) started to flow through the reactor. Once the CO₂ concentration reached a plateau, UV (100 W UVP Black-Ray®B-100AP High Intensity) or visible (450 W Xe lamp OSRAM, with PMMA UV cut-off filter) light irradiation was turned on. C₂H₂ was decomposed on the surface of TiO₂ IO under UV or visible light irradiation producing CO₂ and H₂O. The CO₂ concentration was monitored in real-time by a CO₂ detector (Vaisala GMP343, diffusion mode).

3.4.1.2 H₂ evolution

The photocatalytic H₂ evolution tests were performed in a gas-closed quartz glass reactor system (125 ml). Microscopic glass slides were placed into the reactor on a sample holder. Deionized water (10 ml) was poured on the bottom of the reactor.
High purity He gas (10 ml min⁻¹) was purged for 2 h to remove air from the reactor system. Once the air had been removed, a 300 W Xe arc lamp adjusted to 1 sun (AM 1.5 G filter) initiated the reaction. The water vapours served as a proton source for H₂ evolution during the irradiation. The photocatalytic system was equipped with a Shimadzu GC-MS-2030 gas chromatograph fitted with Barrier Ionization Detector and regularly 500 μl of the gas mixture was withdrawn from the reactor for quantitative analysis of products. The observed products were calibrated with a standard gas mixture and determined by the retention time.
4 RESULTS AND DISCUSSION

4.1 VALIDATION OF THE GAS-PHASE METHOD

The developed gas-phase evaluation method was tested for producing reliable results with a high degree of repeatability. TiO$_2$ NPs thin films with different thicknesses were produced by the LFS deposition method. The samples were named 15x and 30x which correlate to the number of times microscopic slides went through the flame, (15x corresponds to the thickness of the layer in the range of 600-700 nm). The photocatalytic activity was measured for these samples and for their combination (15x, 15x/15x, 30x, and 30x/30x) three times. The results are shown in Figure 4.1 A. The sample 15x had the lowest activity (0.7 ppm min$^{-1}$) because of the lowest amount of TiO$_2$ NPs. A combination of sample 15x/15x showed a higher activity compared to a single 15x, increasing more than two times (1.7 ppm min$^{-1}$) and became comparable with photocatalytic activity of a single 30x sample (1.5 ppm min$^{-1}$), indicating on the comparable amount of TiO$_2$ NPs. The highest photocatalytic activity was assigned to a 30x/30x sample (2.3 ppm min$^{-1}$). These results demonstrated the dependence between the number of TiO$_2$ NPs and photocatalytic activity. Moreover, control tests were performed for the complete validation of the method. The sample with the highest activity (30x/30x) was chosen for the control test since it had the highest response for the photocatalytic reaction. Figure 4.1 B illustrates the summarised bar chart of the control tests. In the dark conditions (absence of the UV light) photocatalytic activity was not observed, even though the reactor was filled with C$_2$H$_2$ and technical air. Next, photocatalytic activity was not recorded in the absence of C$_2$H$_2$ (UV light was on), which indicated that the only source of CO$_2$ was C$_2$H$_2$. And once C$_2$H$_2$ and UV light were present together, photocatalytic activity was observed.

Figure 4.1 (A) Photocatalytic activity results of TiO$_2$ thin films and (B) control test of the developed gas phase method.

62
4.2 PREPARATION AND CHARACTERIZATION OF TiO₂ IO, MeNPs AND THEIR HETEROSTRUCTURE

This section deals with TiO₂ IO structures functionalized with MeNPs such as TiO₂ IO with AuNPs, AgNPs, and Au/AgNPs, multilayer TiO₂ IO with AuNPs, and TiO₂ IO with AgNPs deposited by LFS and their application for gap-phase photocatalysis.

4.2.1 TiO₂ IO with AgNPs, AuNPs and Au/AgNPs

Table 4.1. Summary of the preparation and characterization methods used in the discussion section.

<table>
<thead>
<tr>
<th>Preparation of TiO₂ IO</th>
<th>Infiltration method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deosition of metal nanoparticles (AuNPs, AgNPs and Au/AgNPs)</td>
<td>Slow evaporation method</td>
</tr>
<tr>
<td>Evaluation of photocatalytic activity</td>
<td>Organic pollutant decomposition</td>
</tr>
</tbody>
</table>

The preparation of TiO₂ IO with AgNPs, AuNPs, and Au/AgNPs was the first approach. First, the PS self-assembled template was prepared and characterized. Figure 4.2 A demonstrates an SEM image of the self-assembled PS spheres on a microscopic glass slide deposited by the vertical slow evaporation method. A highly ordered close-packed structure was observed with an average sphere diameter of approximately 400 nm. TiO₂ IO was prepared by the infiltration method. The calcination procedure was used to remove PS template and to convert TiO₂ to anatase crystalline phase by a given protocol: rising from room temperature to 250°C in 250 min (holding time at 250°C of 120 min) and heating from 250°C to 550°C in 300 min (holding time at 550°C of 300 min). The calcination process strongly affects the morphology of the prepared TiO₂ IO structures (Amano et al., 2011). SEM image in Figure 4.2 B illustrates a highly ordered porous TiO₂ IO structure with an average pore size of around 350 nm. This decrease in size by 12-13% of their original size was assigned to the temperature contraction during the calcination process. The crack formation was also observed, originating from the shrinking and infiltration process. However, the structure was free of overlayers from the top view. It is worth mentioning that cracks and defects may affect the photocatalytic activity performance (Chen et al., 2007).
The MeNPs can enhance the photocatalytic activity of TiO$_2$ by reducing the recombination rate of electrons and holes, functioning as an electron sink accepting photogenerated electron from CB of TiO$_2$ (Li et al., 2016) or by LSPR via injection of the photogenerated electron to CB of TiO$_2$ (Gołabiewska et al., 2016). The MeNPs (AuNPs, AgNPs, and Au/AgNPs) were prepared by the hydrothermal reduction method. Figure 4.3 summarizes the morphological, elemental, and optical properties of as-prepared MeNPs. Transmission electron microscopy (TEM) micrographs (Figure 4.3 A, C, E) demonstrate AuNPs, AgNPs and Au/AgNPs, respectively. The average sizes of MeNPs were around 40 ± 5 nm. Agglomerated MeNPs were also observed with an average diameter of 80 ± 10 nm. The EDS analysis (Figure 4.3 B, D, F) was further conducted to verify the elemental composition of MeNPs and each element in the Au/Ag NPs. The mapping profiles clearly illustrate that AuNPs and AgNPs fully consisted of metallic Au and Ag, respectively (red and yellow dots). Both Au and Ag metals were evenly distributed in the particle (red and yellow dots together) for Au/Ag NPs. The optical properties of MeNPs are important since at certain wavelengths MeNPs get excited and display LSPR properties. Figure 4.3 G presents the normalized UV-vis absorption spectra of AuNPs, AgNPs and Au/AgNPs. AuNPs and AgNPs had characteristic absorption peaks at about 520 nm and 430 nm, respectively. The redshift occurred from AgNPs towards AuNPs absorption peak for Au/Ag NPs when the ratio of gold to silver had been increasing. Au/AgNPs displayed an LSPR absorption peak at 475 nm that matched well with the composition of bimetallic NPs.
The composite of MeNPs-TiO$_2$ IO structures was characterized to confirm a contact between the MeNPs and TiO$_2$ IO structures. Figure 4.2 C, D, E display SEM images of TiO$_2$ IO with AuNPs, AgNPs, and Au/AgNPs, respectively. It is evident that MeNPs were uniformly distributed and firmly anchored, forming a close contact with the TiO$_2$ IO framework. MeNPs with the smaller diameter mainly covered the ridges of the top layer of the TiO$_2$ IO, while agglomerated MeNPs were deposited inside the pores. The three photocatalysts had a similar morphology as TiO$_2$ IO retaining the diameter of the pores around 350 nm indicating that the deposition process did not alter the structural or morphological properties of TiO$_2$ IO. The diffusion reflectance spectra of TiO$_2$ IO with MeNPs (Figure 4.2 F) were measured normal to FCC (111) plane. Pristine TiO$_2$ IO showed absorption in the UV region (380-385 nm), which well-matched with the intrinsic bandgap of the TiO$_2$. Upon deposition of MeNPs, reflectance spectra were changing; a broad peak appeared at 400-600 nm, which was specified as the sub-bandgap state of the special TiO$_2$ IO well-ordered structure (Lai et al., 2010). However, the peaks of MeNPs LSPR overlap with the sub-band of TiO$_2$ (Liu et al., 2014).
The photocatalytic activity results are presented in Figure 4.4. The photocatalytic activity increased with the deposition of MeNPs. Pristine TiO$_2$ IO had the lowest activity (0.38 ppm min$^{-1}$). It is noteworthy that the photocatalytic activity of the TiO$_2$ IO structure was higher than regular TiO$_2$ NPs due to the slow light effect (Chen et al., 2014). When AgNPs were deposited on TiO$_2$ IO, the photocatalytic activity was increased up to 39% compared to pristine TiO$_2$ IO (0.53 ppm min$^{-1}$). Deposition of AuNPs resulted in an enhancement of 53% (0.57 ppm min$^{-1}$) whereas the highest activity was observed with Au/AgNPs (0.6 ppm min$^{-1}$) with a 62% increase compared to pristine TiO$_2$ IO. The wider and stronger absorption as in bimetallic Au/AgNPs compared to single MeNPs (AuNPs and AgNPs) resulted in a greater coupling with the incident light and thus, increased photocatalytic activity. Furthermore, Figure 4.4 B represents activity tests of TiO$_2$ IO with Au/AgNPs confirming stability and reproducibility of results for more than 250 min.

![Figure 4.4 A](image1.png) ![Figure 4.4 B](image2.png)

**Figure 4.4 (A) Plot of photocatalytic activity results of the MeNPs-TiO$_2$ IO and (B) activity test for Au/Ag NPs-TiO$_2$ IO (Publication I).**

The MeNPs had a significant contribution to the photocatalytic activity. There are three major electron transfer processes responsible for improved photocatalytic activity in MeNPs/Semiconductor heterojunction: HET, near-field electromagnetic enhancement, and plasmon resonant photon scattering (Ye et al., 2017). When wavelengths of the plasmon resonance and the semiconductor absorption overlap the near-field electromagnetic enhancement can be observed (Kulkarni et al., 2010). The resonant photon scattering typically arises in the large plasmonic nanostructures (diameter more than 50 nm) (Burda et al., 2005; Cushing et al., 2012). For HET, MeNPs should be in close contact with a semiconductor, forming a Schottky barrier, by which photoexcited electrons can be transferred to the CB of the adjacent semiconductor. On this basis, HET is the most probable electron transfer process in the MeNPs/TiO$_2$ IO systems (Figure 4.2 C, D, and E).
Figure 4.5 Schematic diagram of the HET process in TiO$_2$ IO with MeNPs and equations of reactions mechanism (Publication II).

The fundamental principle of the HET process can be perceived by the scheme represented in figure 4.5. When MeNPs absorb visible light, electrons get photoexcited and metal ions ($M^+$) form due to the LSPR effect (Eq. (4.1)). By the Schottky barrier, photoexcited electrons can be transferred from MeNPs to CB of TiO$_2$ IO. The transport of photoexcited electrons improved the charge separation between the photoexcited electrons and metal ions were facilitated under LSPR electric field (Eq. (4.2)). To generate superoxide anion radicals (O$_2$••), injected electrons can react with the abundant molecular oxygen (Eq. (4.3)) with further protonation producing (HO$_2$••) radicals (Eq. (4.4)). The H$_2$O$_2$ can be produced via the interaction of HO$_2$•• radicals and the trapped electrons (Eq. (4.5)) following the formation of hydroxyl radicals (OH•) (Eq. (4.6)). Although these active oxygen species take part in the degradation and mineralization of C$_2$H$_2$, simultaneously, the metal ions themselves can directly decompose C$_2$H$_2$ into CO$_2$ (Chen et al., 2014). The overall mechanism reactions are presented in Eqs. (4.1)-(4.7).

\[ \text{MeNPs} + h\theta \rightarrow \text{MeNPs}^\ast \] (4.1)
\[ \text{MeNPs} + \text{TiO}_2 \rightarrow \text{MeNPs}^\ast(h^+) + \text{TiO}_2(e^-) \] (4.2)
\[ \text{TiO}_2(e^-) + O_2 \rightarrow \text{TiO}_2 + O_2^- \cdot \] (4.3)
\[ O_2 + H^+ \rightarrow H_2O \] (4.4)
\[ H\text{O}_2 + H^+ + e^- \rightarrow H_2\text{O}_2 \] (4.5)
\[ H_2\text{O}_2 + e^- \rightarrow OH^- +•OH \] (4.6)
\[ \text{MeNPs}^\ast(3h^+) + 2OH + 2C_2H_2 + 2O_2 \rightarrow \text{MeNPs} + 2CO_2 + 2H_2O \] (4.7)
4.2.2 Multilayer TiO$_2$ IO with AuNPs

Table 4.2. Summary of the preparation and characterization methods used in the discussion section.

<table>
<thead>
<tr>
<th>Preparation of TiO$_2$ IO</th>
<th>Crack-free method</th>
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<tbody>
<tr>
<td>Deposition of metal nanoparticles (AuNPs)</td>
<td>Slow evaporation method</td>
</tr>
<tr>
<td>Evaluation of photocatalytic activity</td>
<td>Organic pollutant decomposition</td>
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</table>

A multilayer TiO$_2$ IO structure was developed and functionalized with AuNPs for gas-phase photocatalytic activity. PS spheres with an average diameter of 200 nm or 400 nm, and TiBALDH as a precursor were used (Figure 3.3, Section 3.2.3). Two double-layered TiO$_2$ IO structures were fabricated, namely 200/400 and 400/200. Here the first number stands for the diameter of the PS spheres used in the first layer, which was prepared by the crack-free method. The PS spheres and the TiO$_2$ precursor were self-assembled in FCC structure by a vertical slow evaporation method (Figure 4.6 A). Before the deposition of the second PS layer, the first layer was pre-heated in a laboratory oven at 100 °C for 1h to reinforce the structure by slightly melting PS spheres and producing a strengthened contact between the PS spheres and glass surface. Because of the high surface tension between PS layers, the formation of the second PS layer was partially uneven and irregular (Figure 4.6 B) (Cai et al., 2011). After calcination using the same protocol as in section 4.2.1, TiO$_2$ IO multilayers were obtained.

Figure 4.6 SEM images of the self-assembled PS template of (A) top and (B) cross-sectional views (Publication II).
Figure 4.7 A and B present the top view SEM images of TiO$_2$ IO 200/400. The average pore size of the top layer (400 nm) is 290 nm. Figure 4.7 E illustrates the SEM cross-section image of TiO$_2$ IO 200/400, confirming the formation of a double-layer structure. TiO$_2$ IO structure was cracked with spatula for cross-sectional SEM images from the exposed side-view. Similarly, figure 4.7 C and D show top views of the TiO$_2$ IO 400/200 demonstrating a highly ordered porous structure with an average pore size around 130 nm, while figure 4.7 F displays a cross-section image. The average thickness of both multilayer TiO$_2$ IO structures was 4.3 ± 2.0 μm. The high-temperature process caused a large shrinkage in the structures: 27% for TiO$_2$ IO 200/400 and 35% for TiO$_2$ IO 400/200, respectively. Both structures had an ordered structure of more than 10 μm indicating the suitability of the applied precursor solution and calcination process. However, due to shrinkage, formation of small cracks was inevitable.

Figure 4.7 SEM images of TiO$_2$ IO 200/400 (A, B) and TiO$_2$ IO 400/200 (C, D) and cross-sectional images of TiO$_2$ IO 200/400 (E) and TiO$_2$ IO 400/200 (F) (Publication II).
Crystalline properties of the multilayer structures were studied using XRD and Raman spectroscopy. The Raman spectrum (Figure 4.8 A) shows characteristic anatase crystalline phase peaks at 133 cm$^{-1}$ $E_g(1)$ matched to the bending vibration of the O–Ti–O bond, while peaks at 384 cm$^{-1}$ $B_{1g}$, 504 cm$^{-1}$ $A_{1g}$, and 631 cm$^{-1}$ $E_g(2)$ corresponded to the Ti–O–Ti bending. The XRD analysis (Figure 4.8 B) of TiO$_2$ IO double-layer structures also demonstrated characteristic peaks corresponded to the anatase crystalline phase of TiO$_2$ at $2\theta$ angles of 25.3° (1 0 1), 37.8° (0 0 4), 48.0° (2 0 0), 53.9° (1 0 5), 55.1° (2 1 1), 62.7° (2 0 4), 68.7° (1 1 6), 70.3° (2 2 0), and 75.0° (2 1 5). The obtained crystalline data was in agreement with the Joint Committee on Powder Diffraction Standards (JCPDS 21-1272) (Yang et al., 2017). The analysis of XRD and Raman spectroscopy data confirmed the existence of the anatase crystalline phase in the double layer structures after the calcination process.

AuNPs were prepared by the hydrothermal method reported in section 4.2.1 and deposited to multilayer structure for quantitative evaluation of photocatalytic activities between decorated and undecorated structures. Figure 4.9 A shows a TEM micrograph of the AuNPs population, with an average diameter of 18 ± 2 nm (Figure 4.9 D). The optical properties of AuNPs were studied by UV-vis absorption spectroscopy. The LSPR absorption peak of AuNPs was located at 520 nm accordingly with the size distribution (Figure 4.9 B). The elemental composition of AuNPs was examined by EDS detecting characteristic peaks of gold at 2.2 keV and 9.8 keV and confirming the successful formation of metallic AuNPs (Figure 4.9 C). Additional copper peaks were also observed because of the copper grid which was used as a support in the EDS analysis.
The prepared AuNPs were deposited on the top layer in TiO$_2$ IO 200/400 and 400/200 by slow vertical evaporation method (Section 3.3.1). Figure 4.10 A and B illustrate TEM micrographs of TiO$_2$ IO 400/200. It is evident that the structure consisted of two TiO$_2$ IO layers with different pore diameters and a higher magnification micrograph confirmed a successful deposition of AuNPs inside the first layer of the pores. AuNPs were evenly distributed within the layer and firmly anchored to the framework of TiO$_2$ IO. The size of AuNPs did not change upon deposition and remained around 20 nm. Additionally, EDS was used to reconfirm the compositional properties of AuNPs and TiO$_2$ IO after deposition (Figure 4.10 C). The characteristic peaks of gold at 2.2 keV and 9.8 keV and titania at 4.7 keV and 5 keV were demonstrating efficient and successful impregnation of metallic AuNPs to TiO$_2$ IO structure.
Figure 4.10 (A) TEM micrograph of TiO$_2$ IO 400/200 with AuNPs, (B) TEM high-magnification micrograph of AuNPs inside the framework of TiO$_2$ IO, and (C) EDS spectrum of TiO$_2$ IO 400/200 with AuNPs (Publication II).

Figure 4.11 A demonstrates photocatalytic activity measurement of all prepared samples, namely TiO$_2$ IO 200, TiO$_2$ IO 400, TiO$_2$ IO 200/400, TiO$_2$ IO 400/200, TiO$_2$ IO 200/400 with AuNPs, and TiO$_2$ IO 400/200 with AuNPs. The lowest photocatalytic activities were observed with single-layered TiO$_2$ IO structures of 1.31 and 1.35 ppm min$^{-1}$ for TiO$_2$ IO 200 and TiO$_2$ IO 400, respectively. Addition of a second layer improved photocatalytic activity performance; 1.95 and 2.16 ppm min$^{-1}$ for TiO$_2$ IO 200/400 and TiO$_2$ IO 400/200, respectively. This increase can be related to the synergetic action of slow light effects in two different pore size structures (Chen et al., 2014). The photocatalytic activity was increased by the deposition of AuNPs, and the highest photocatalytic activities of 2.11 ppm min$^{-1}$ and 2.42 ppm min$^{-1}$ were observed for TiO$_2$ IO 400/200 and TiO$_2$ IO 200/400, respectively. The increased photocatalytic activity was attributed to the synergetic effect of the IO structure and LSPR of AuNPs. Figure 4.11 B shows visible light activation of the TiO$_2$ IO 400/200 with AuNPs (0.21 ppm min$^{-1}$) and TiO$_2$ IO 200/400 with AuNPs (0.27 ppm min$^{-1}$). It was also observed that the photocatalytic activity of a double-layered structure with a top layer made of 400 nm was higher than the structures with a 200 nm top layer. The observed results were in line with the literature, as the TiO$_2$ IO structures
with larger size are more stable and have a higher photocatalytic performance compared to IO structures with a smaller size (Zhou et al., 2018). Figure 4.11 C shows cyclic activation of the TiO$_2$ IO 200/400 with AuNPs. After three cycles (90 min) photocatalytic activity remained stable with no detected changes. In double layer TiO$_2$ IO structures functionalized with AuNPs, the energy transfer mechanism with a major contribution for enhanced photocatalytic activity was HET, because of the formation of a Schottky barrier in contact between AuNPs and TiO$_2$ IO. A schematic illustration and a detailed description of that process are shown in Figure 4.5 and section 4.2.1. The mechanism reactions are given by Eqs (4.1)-(4.7).

Figure 4.11 Results of photocatalytic activity evaluation of (A) TiO$_2$ IO-based structures under UV light, (B) TiO$_2$ IO 200/400, and TiO$_2$ IO 400/200 with AuNPs under visible light, and (C) cyclic activation tests for TiO$_2$ IO 200/400 with AuNPs under UV irradiation (Publication II).
### 4.2.3 TiO$_2$ IO with LFS deposited AgNPs

Table 4.3. Summary of the preparation and characterization methods used in the discussion section.

<table>
<thead>
<tr>
<th>Preparation of TiO$_2$ IO</th>
<th>Infiltration method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition of metal nanoparticles (AgNPs)</td>
<td>Liquid flame spray (LFS)</td>
</tr>
<tr>
<td>Evaluation of photocatalytic activity</td>
<td>Organic pollutant decomposition and H$_2$ evolution test</td>
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A wide range of MeNPs deposition methods on TiO$_2$:IO structures is available such as slow evaporating method (as discussed earlier), atomic layer deposition (Assaud et al., 2015), spin coating (Hamdi, 2016), and pulsed current deposition (Chen et al., 2014). Here, the deposition of AgNPs on TiO$_2$:IO structures for enhanced photocatalytic activity was, for the first time, demonstrated by the LFS method. AgNPs were chosen for the deposition due to low cost, LSPR, and nontoxicity. The TiO$_2$:IO structures were prepared by a similar approach as discussed in section 3.2.2, and 4.2.1. Four TiO$_2$:IO samples were deposited with AgNPs 5x, 10x, 20x, 30x (where the abbreviation corresponds to the number of times TiO$_2$:IO passed through the flame) and one TiO$_2$:IO sample without AgNPs. Figure 4.12 A shows a self-assembled PS template with an average size of 350 nm having a highly ordered structure with FCC plane (111) orientation. Figure 4.12 B presents a well-ordered and crack-free TiO$_2$:IO without AgNPs with an average pore size around 200-250 nm, indicating a 28-42% PS shrinkage in calcination. Figures 4.12 C, D, E and F display TiO$_2$:IO structures with AgNPs 5x, 10x, 20x and 30x, respectively. The average pore size remained the same after LFS deposition process (~250 nm), reflecting that LFS high-temperature flame did change neither the morphology nor crystallinity of the structure. Increasing the LFS deposition from 5x to 30x was followed by an increased AgNP amount and average size. The average size of the AgNPs 5x was 25-35 nm that was increased up to 55-65 nm for AgNPs 10x, 65-75 nm for AgNPs 20x, and 80-90 nm for 30x. LFS deposited AgNPs did not block the pores and were mainly collected on the ridges of the top rows of pores. Based on figure 4.12, LFS deposition method allowed a rather uniform deposition of AgNPs on TiO$_2$:IO structure.
Figure 4.12 SEM images of (A) PS self-assembled spheres, (B) TiO\textsubscript{2} IO with AgNPs 5x, (C) TiO\textsubscript{2} IO with AgNPs 10x, (D) TiO\textsubscript{2} IO with AgNPs 20x, and (F) TiO\textsubscript{2} IO with AgNPs 30x (Publication III).

HRTEM micrograph was used to investigate the distribution and impregnation of AgNPs to TiO\textsubscript{2} IO. Figure 4.13 presents HRTEM micrographs of the TiO\textsubscript{2} IO framework with embedded AgNPs emphasizing the contact between the two structures. The lattice fringes with a d-spacing of 0.352 represented the (101) plane of anatase TiO\textsubscript{2} and 0.224 nm displayed the (111) plane of metallic AgNPs. Figure 4.13 shows the EDS spectra with characteristic absorption peaks of silver 3 keV and titania 4.7 and 5 keV, confirming the enduring of the elemental composition of the composite structures after the deposition process.
The optical properties of the structures were measured by UV diffuse absorption spectroscopy. Figure 4.14 displays normalized UV-vis diffuse absorbance spectra of TiO$_2$ IO with AgNPs measured normal to the FCC (111) plane. TiO$_2$ IO without AgNPs showed a broadband (380-600 nm, red area) due to slow photon effect via multiple light scattering inside the IO structure and intrinsic absorbance of TiO$_2$ starting from 370 nm. The enhanced absorbance of visible light was attributed to the plasmonic excitation of AgNPs along with the slow light effect of the IO structure (Tarannum et al., 2019). The absorbance reached its maximum in TiO$_2$ IO with AgNPs 30x in the visible range. Additionally, a new peak was starting to appear at 375 nm (blue area) in TiO$_2$ IO with AgNPs 20x and 30x due to a quadrupole resonance effect in AgNPs (Barman et al., 2017). A redshift of the PBG occurs upon the deposition of the AgNPs. The redox state of the AgNPs may be responsible for this feature as plasmon absorption of AgNPs can lower the reflectance intensity of TiO$_2$ IO whereas Ag$_2$O does not have an effect on it. Moreover, a photoinduced reversible transformation between AgNPs and Ag$_2$O upon UV/Vis irradiation can also induce reversible changes in the intensity of the PBG (Liu et al., 2014). Furthermore, the PBG of TiO$_2$ IO was calculated according to Bragg’s law:

$$\lambda_{max} = \frac{2D\sqrt{2}}{3} \sqrt{\frac{n_{TiO_2}^2 f + n_{air}^2 (1 - f)}{n_{TiO_2}^2 f + n_{air}^2 (1 - f) - \sin^2 \theta}} \quad (4.8)$$

where $\lambda_{max}$ is the stopband position for the first order Bragg diffraction, $D$ is the pore size of TiO$_2$ IO, $n_{TiO_2}$ and $n_{air}$ are the refractive indexes (2.5 and 1.0003, respectively), $f$ is the TiO$_2$ IO phase volume percentage of 0.26 based on the FCC geometry, (Chen et al., 2014; Qi, et al., 2014) and $\theta$ is the incident angle of light that can be taken as 0. According to Eq. (4.8), the stopband of the TiO$_2$ IO was calculated in the range of 500-630 nm. Considering the average pore size around 200-250 nm the result well agrees with the experimental data (Figure 4.14).
Figure 4.14 Normalized UV-vis diffuse absorbance spectra of TiO$_2$ IO structures with AgNPs (Publication III).

Raman spectroscopy and XRD were further used for crystalline characterization. Raman spectrum with all samples is shown in Figure 4.15 A demonstrating characteristic anatase bands. The peak at 145 cm$^{-1}$ $E_{g1}$ was attributed to O–Ti–O bond bending vibration and peaks at 196, 395, 516, and 639 cm$^{-1}$ corresponded to $E_{2g}$, $B_{1g}$, $A_{1g}$, and $E_{g3}$ Ti–O–Ti bending, respectively (Huo et al., 2019). The new band appeared at 230 cm$^{-1}$ as the AgNPs contents had increased. The new peak was assigned to the bending vibration mode of Ag–OCO$^-$ and was observed only in TiO$_2$ IO with AgNPs 20x and 30x samples, indicating the interaction of the TiO$_2$ with the Ag through the carboxylic group i.e. by the Ag–OCO bond (Grouchko et al., 2011). The origin of carbon in the structures can be assigned to the incomplete removal of the PS template (Mohapatra et al., 2017). The residual carbon content (e.g. sole) in the structures, under the high-temperature LFS flame, might evaporate and form carboxylic compounds on top of AgNPs and since the exposure time to the flame was the longest in TiO$_2$ IO with AgNPs 20x and 30x, the new band appeared in spectra of these structures. XRD pattern for the TiO$_2$ IO with AgNPs is presented in Figure 4.15 B. All patterns confirmed exclusively anatase phase formation by characteristic peaks of TiO$_2$ at $2\theta = 25.3^\circ$ (1 0 1), 37.8$^\circ$ (0 0 4), 48.0$^\circ$ (2 0 0), 53.9$^\circ$ (1 0 5), 55.1$^\circ$ (2 1 1), 62.7$^\circ$ (2 0 4), 68.7$^\circ$ (1 1 6), 70.3$^\circ$ (2 2 0), and 75.0$^\circ$ (2 1 5) which were in agreement with the Joint Committee on Powder Diffraction Standards File number JCPDS 21-1272, displaying a body-centered tetragonal phase. Moreov
Furthermore, XPS was used to determine the chemical composition and confirm the effective integration of AgNPs into TiO₂. Figure 4.16 A illustrates the XPS survey spectrum of TiO₂ IO with AgNPs 30x. The spectrum has four distinctive peaks: C 1s, O 1s, Ti 2p, and Ag 3d. The origin of carbon was discussed before, and a small amount of carbon could also come from the XPS instrument itself. Two characteristic peaks at 459 and 465 eV were assigned to Ti 2p₃/₂ and Ti 2p₁/₂ (Figure 4.16 B), indicating Ti⁴⁺ state (Chen et al., 2014; Zhang et al., 2013). Two XPS oxygen species were recorded at the O 1s spectrum (Figure 4.16 C) at 530 eV that corresponds to the lattice oxygen of TiO₂ and peak at 532.2 eV attributing to adsorbed oxygen and/or surface hydroxyl species (i.e. Ti−OH) (Wang et al., 2014). The characteristic peak of Ag 3d₅/₂ was found at 368 eV and the Ag 3d₃/₂ was centered at 374 eV (Figure 4.16 D). 6.0 eV was the difference between the binding energy of Ag 3d₅/₂ and 3d₃/₂ which is a specific feature of the metallic Ag 3d state (Chen et al., 2013).
Figure 4.16 (A) XPS survey scan spectrum and high-resolution XPS spectra of (B) Ti 2p, (C) O 1s, (D) Ag 3d of TiO$_2$ with AgNPs 30x (Publication III).

The photocatalytic activity for TiO$_2$ IO with LFS deposited AgNPs was evaluated using a gas-phase organic pollutant decomposition and H$_2$ evolution test. Figure 4.17 A shows the results of the photodegradation of C$_2$H$_2$ into CO$_2$ in the presence of UVA light. TiO$_2$ IO without AgNPs had the lowest activity (1.86 ppm min$^{-1}$). The photocatalytic activity was doubled (2.78 ppm min$^{-1}$) compared to pristine TiO$_2$ IO, by deposition of AgNPs 5x. It is worth highlighting that even a relatively small amount of AgNPs improved photocatalytic activity by 50%.) An increasing number of deposited AgNPs induced enhanced photocatalytic activity by 67% (3.09 ppm min$^{-1}$), 91% (3.55 ppm min$^{-1}$), and 106% (3.82 ppm min$^{-1}$) with AgNPs of 10x, 20x, and 30x, respectively compared to pristine TiO$_2$ IO. The LFS deposition of the nanocomposites with a higher number of AgNP deposition than 30x was not carried out because the AgNPs with the size of more than 100 nm would induce additional issues such as enhanced scattering and blockage of the pores which eventually would have an undesirable effect on photocatalytic activity. The photocatalytic activity was also evaluated under visible light (Figure 4.17 B). TiO$_2$ IO without AgNPs did not show photocatalytic activity because of the large electric bandgap. TiO$_2$ IO with AgNPs 30x displayed the highest performance of 0.86 ppm min$^{-1}$. As the number of deposited AgNPs went up from 5 to 10 and 20 times,
photocatalytic activity increased accordingly: 0.38 ppm min\(^{-1}\) 0.48 ppm min\(^{-1}\), and 0.7 ppm min\(^{-1}\). The AgNPs on TiO\(_2\) IO structures significantly enhanced light absorption due to LSPR in AgNPs (Figure 4.14) (Huo et al., 2019; Wei et al., 2015). The stability of TiO\(_2\) IO with AgNPs 30x was investigated by a cyclic activation under UVA and visible light (Figure 4.17 C and D). It was observed that the TiO\(_2\) IO with AgNPs 30x did not exhibit a significant loss of activity after three cycles (90 min).

![Graphs showing photocatalytic activity results](image)

Figure 4.17 Photocatalytic activity results (A) under UVA light and (B) under visible light and stability tests (C) under UVA light and (D) under visible light for TiO\(_2\) with AgNPs 30x (Publication III).

Finally, photocatalytic activity was also evaluated through the H\(_2\) evolution test. The bar chart in figure 4.18 represents an H\(_2\) evolution performance under solar simulated irradiation. TiO\(_2\) IO without AgNPs did not induce H\(_2\) production due to large electric bandgap (Christopher et al., 2010), whereas all TiO\(_2\) IO structures with AgNPs demonstrated rather high yields of H\(_2\) without the use of a hole scavenger (Jo et al., 2018). H\(_2\) evolution of the structures was increasing with the number of AgNP deposition, i.e. 14.9 \(\mu\)mol cm\(^{-2}\) h\(^{-1}\), 20 \(\mu\)mol cm\(^{-2}\) h\(^{-1}\), 24.6 \(\mu\)mol cm\(^{-2}\) h\(^{-1}\), and 32.9 \(\mu\)mol cm\(^{-2}\) h\(^{-1}\) for TiO\(_2\) IO with AgNPs 5x, 10x, 20x, and 30x, respectively.
There are several possible electron transfer mechanisms in MeNPs/semiconductor systems. The HET process was assigned as the major electron transfer process in previous sections and undoubtedly, it is present in TiO$_2$ IO with AgNPs. However, based on experimental results and previously reported literature, PIRET is suggested as the main mechanism for the improved photocatalytic activity in TiO$_2$ IO with AgNPs as shown in figure 4.19 A. Considering the work of Christopher et al., (Christopher et al., 2010), the direct injection of electrons from AgNPs to CB of TiO$_2$ in the TiO$_2$/AgNPs system is ruled out. The electron transfer from AgNPs to TiO$_2$ results in the formation of electron-deficient AgNPs that are too weak oxidizers and are not able to accept electrons from water or C$_2$H$_2$ respectively (Varapragasam et al., 2019). According to Christopher experiments (Christopher et al., 2010), a strong plasmonic field creates at the interface of TiO$_2$ and AgNPs that can enable electronic excitation from the VB of TiO$_2$ to Ti$^{3+}$ defect states and further transition to the CB of TiO$_2$ and from there to AgNPs via spatial charge separation suppressing recombination process (Cushing et al., 2015; Li et al., 2015).

PIRET is observed in large plasmonic nanostructures (diameter > 50 nm) (Burda et al., 2005) and upon overlapping of the absorption edge tail of TiO$_2$ with the plasmonic band of AgNPs (Cushing et al., 2015). In the present work, the size of AgNPs was found to be more than 50 nm and overlap of the absorption of TiO$_2$ and AgNPs was recorded. Therefore, the photocatalytic degradation of C$_2$H$_2$ to CO$_2$ and H$_2$O had proceeded via the PIRET pathway as shown in figure 4.19 A. By spatial charge separation between TiO$_2$ and AgNPs photoexcited electrons can be transferred to the abundant molecular oxygen, to produce superoxide anion radicals (O$_2$•-) (Hirakawa et al., 2001) while further protonation outcomes in the
formation of (HO$_2$•) radicals. Through the mixing of HO$_2$• radicals with the proton and electron H$_2$O$_2$ can be produced (Christopher et al., 2010). Alternatively, holes in the VB of TiO$_2$ can directly interact with water to produce •OH. The degradation and mineralization of C$_2$H$_2$ can be accomplished by these ROS (Figure 4.19 A and Eq. 4.9 and 4.10) (Chen et al., 2014).

$$TiO_2^+ + h\phi \rightarrow TiO_2 (e^- + h^+) \quad (4.9)$$

$$AgNPs + TiO_2 (e^- + h^+) \rightarrow AgNPs^- (e^-) + TiO_2 (h^+) \quad (4.10)$$

Since the electron-deficient AgNPs are too weak to oxidize water to O$_2$ the H$_2$ evolution mechanism also follows the PIRET pathway (Figure 4.19 B) (Awazu et al., 2008; Varapragasam et al., 2019). TiO$_2$ IO produces photoinduced charge carriers via both direct and non-radiative excitation under UV light and PIRET excitation under visible light. The photoexcited electrons can be trapped by AgNPs reducing the recombination of the electron-hole pairs and accelerating efficient charge separation. In TiO$_2$, the oxidation potential of the holes is +2.7 V vs. SHE, (pH=7) which is sufficient for a successful water splitting (+0.83 V vs. SHE). The electrons in AgNPs can participate in hydrogen formation from 2H$^+$ as demonstrated in Figure 4.19 B and Eqs. (4.11) and (4.12):

$$TiO_2 (h^+) + H_2O \rightarrow \frac{1}{2} O_2 + 2H^+ \quad (4.11)$$

$$AgNPs^- (e^-) + 2H^+ \rightarrow H_2 + AgNPs \quad (4.12)$$

![Figure 4.19 Schematic representation of electron transfer mechanisms in TiO$_2$ IO with AgNPs systems (A) PIRET and (B) hydrogen evolution (Publication III).](image)
5 CONCLUSIONS AND FUTURE PERSPECTIVE

A reliable, reproducible, and quantitative gas-phase method for photocatalytic activity characterization was developed based on the photodegradation of C\textsubscript{2}H\textsubscript{2}. The method was successfully verified by a simple photocatalytic reaction with reproducible results and comprehensive data. This method was utilized in the following works with more sophisticated photocatalysts.

The TiO\textsubscript{2} IO structures with MeNPs were fabricated by infiltration and crack-free methods and their gas-phase photocatalytic activities were evaluated. The infiltration method was applied for the preparation of single-layer structures, while the crack-free method was found to be helpful for the preparation of double-layer structures. The noble MeNPs were prepared by the hydrothermal reduction method resulting in a uniform and homogeneous population.

First, TiO\textsubscript{2} IO structures with AuNPs, AgNPs, and Au/AgNPs were prepared. The decoration of TiO\textsubscript{2} IO with MeNPs was achieved via a slow evaporation process. The as-prepared structures were characterized by microscopic and spectroscopic methods proving the information of the successful deposition of MeNPs. The gas-phase photocatalytic activity was evaluated by the developed method. The results pointed out that the deposition of MeNPs enhanced photocatalytic activity. The highest activity was observed with Au/AgNPs due to the synergetic action of Au, Ag, and IO structure. The double layer TiO\textsubscript{2} IO based structures with AuNPs were also fabricated. Composites were prepared by a crack-free method by subsequent one by one deposition of two layers. The characterization demonstrated the successful production of a double layer structure with different pore sizes. The structures were functionalized with AuNPs by a slow evaporation method. The gas-phase photocatalytic oxidation of C\textsubscript{2}H\textsubscript{2} demonstrated that a double-layer structure had an enhanced photocatalytic activity compared to a single layer due to the extended slow light effect. Moreover, deposition of AuNPs allowed visible light photocatalytic activity due to the LSPR effect. In these structures, the enhanced photocatalytic activity was achieved majorly by HET, because the formation of the Schottky barrier was observed.

Finally, the TiO\textsubscript{2} IO structures with LFS deposited AgNPs were fabricated. The LFS deposition process resulted in uniform coverage of the TiO\textsubscript{2} IO with AgNPs. The obtained composites were thoroughly investigated by advanced microscopic and spectroscopic techniques revealing a high-quality TiO\textsubscript{2} IO structure with rather uniformly distributed AgNPs. The photocatalytic activities of TiO\textsubscript{2} IO with AgNPs
were evaluated by gas-phase photooxidation of C₂H₂ and H₂ evolution. The results demonstrated larger photocatalytic activity of the composite due to the LSPR effect of LFS deposited AgNPs and PBG properties of the TiO₂ IO structure. The photocatalytic activity in AgNPs/TiO₂ IO composites was enhanced by the PIRET process since only this process enables the formation of the holes with an oxidation potential enough for water splitting.

The gas-phase photocatalytic activity results are summarized in the Table 5.1, providing a comprehensive comparison of all produced TiO₂ IO with MeNPs.

Table 5.1. Summary of the photocatalytic activity results of all prepared TiO₂ IO with MeNPs under UV and visible light excitation.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Photocatalytic activity (ppm min⁻¹)</th>
<th>Increase of photocatalytic activity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UV</td>
<td>Visible light</td>
</tr>
<tr>
<td>Paper I</td>
<td>Pristine TiO₂ IO</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>TiO₂ IO with AgNPs</td>
<td>0.53 (39.5)</td>
</tr>
<tr>
<td></td>
<td>TiO₂ IO with AuNPs</td>
<td>0.57 (50.0)</td>
</tr>
<tr>
<td></td>
<td>TiO₂ IO with Au/AgNPs</td>
<td>0.60 (57.9)</td>
</tr>
<tr>
<td></td>
<td>TiO₂ IO 200</td>
<td>1.31</td>
</tr>
<tr>
<td></td>
<td>TiO₂ IO 400</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>TiO₂ IO 200/400</td>
<td>1.95 (48.8)</td>
</tr>
<tr>
<td></td>
<td>TiO₂ IO 400/200</td>
<td>2.16 (60.0)</td>
</tr>
<tr>
<td></td>
<td>TiO₂ IO 400/200 with AuNPs</td>
<td>2.11 (61.1)</td>
</tr>
<tr>
<td></td>
<td>TiO₂ IO 200/400 with AuNPs</td>
<td>2.42 (79.3)</td>
</tr>
<tr>
<td>Paper II</td>
<td>TiO₂ IO without AgNPs</td>
<td>1.86 (0.00)</td>
</tr>
<tr>
<td></td>
<td>TiO₂ IO with AgNPs 5x</td>
<td>2.78 (49.5)</td>
</tr>
<tr>
<td></td>
<td>TiO₂ IO with AgNPs 10x</td>
<td>3.09 (67.0)</td>
</tr>
<tr>
<td></td>
<td>TiO₂ IO with AgNPs 20x</td>
<td>3.55 (91.0)</td>
</tr>
<tr>
<td></td>
<td>TiO₂ IO with AgNPs 30x</td>
<td>3.82 (106.0)</td>
</tr>
</tbody>
</table>

Further work on improving the photocatalytic activity of TiO₂ IO can be turned towards the preparation of multicomponent structures such as a combination of TiO₂ IO with graphene-based nanostructures, perovskites, or bismuth oxides. By adequate adjustment of the band structures, TiO₂ IO based multicomponent structures can be used in photocatalysis, CO₂ reduction, water splitting, PEC application, and solar cells.
6 BIBLIOGRAPHY


VISIBLE LIGHT PHOTOCATALYSIS

TIO₂ INVERSE OPAL
Multilayer TiO$_2$ Inverse Opal with Gold Nanoparticles for Enhanced Photocatalytic Activity

Abid Zulfiqar, Filipp Temerov, and Jarkko J. Saarinen

ABSTRACT: Three-dimensional highly ordered multilayer titanium dioxide (TiO$_2$) inverse opal (TIO) structures with two pore sizes were fabricated over a large surface using a self-convective method. The fabricated TIO multilayers were functionalized with gold nanoparticles (AuNPs) by immersing the samples in solution with gold nanoparticles. The photocatalytic activity of TiO$_2$ was enhanced by 85% via plasmonic activation of AuNPs that increased the lifetime of photogenerated holes and electrons. The improved photocatalytic activity was characterized with both UVA and visible light irradiation using an in-house built gas-phase photoreactor.

1. INTRODUCTION

Recently, semiconductor-based photocatalysts have attracted large attention due to their significant potential for solving environmental problems. Titanium dioxide (TiO$_2$) is a chemically and biologically stable, cost-effective, and nontoxic photocatalytic material that has several applications from oxidation of harmful organic compounds and production of hydrogen gas by photoelectrochemical dissociation of water. It can be used for purification of air and polluted water with self-cleaning of the surface. TiO$_2$ has found applications in optical filters for dielectric mirrors, dye-sensitized solar cells, and agriculture including the degradation and detection of pesticide residues, germination, and growth of plants by controlling different diseases. It also has applications in the surface-enhanced Raman scattering (SERS). However, the rather large band gap of TiO$_2$ limits its use as photocatalytic activation requires light in the UVA region (only 3–5% of the solar energy is in the UVA range). Additionally, recombination of photogenerated electrons and holes can reduce its quantum efficiency. The concept of photonic crystals (PCs) was proposed by Yablonovitch and John in 1987 with specific physical properties such as light localization, a slow light effect, and photonic band gap (PBG) properties. PBG inhibits the propagation of light with a specific wavelength due to the coherent Bragg diffraction. The slow light effect enhances the absorption of light by increasing the reflections of light inside the PCs. Many electron–hole pairs can be generated upon overlapping the slow photon wavelength and the TiO$_2$ electronic excitation wavelength for enhanced photocatalytic activity. Various structures have been studied for fabrication of PCs such as opal and inverse opal (IO) photonic crystal structures. Opal PCs can be prepared by self-assembly of colloidal particles, whereas IO PCs can be formed by filling the opal PCs with a material having a high refractive index followed by removal of the self-assembled particles. IO PCs are three-dimensional porous structures that have a large specific surface area and optical properties associated with PCs. PCs have an artificial periodic structure, which work for light in a similar manner as the semiconductor behaves for electrons. Because of these similarities, they have the characteristic band gap but in the photon wavelength range (photonic band gaps, PBGs). The presence of PBG permits the PCs to control the flow of light by inhibiting the transmission of light for a specific wavelength in one, two, or more directions within the PBG materials.

TiO$_2$ IO (TIO) PCs can offer a large surface area for adsorbing the pollutant molecules. An alternative way to improve photocatalytic activity is to incorporate metal and nonmetal nanoparticles (NPs) and noble metal NPs such as gold and silver into the TIO structure. Loading TIO with noble metal NPs can significantly enhance the lifetime of photogenerated holes and electrons, which, as a result, increase the photocatalytic activity of TiO$_2$. The TiO$_2$ morphology and surface characteristics have also a significant role in the improved photocatalytic activity. Furthermore, noble metal NPs exhibit localized surface plasmon resonance (LSPR), which can couple visible light for photocatalytic activation of TiO$_2$.

In the present study, TIO multilayers were produced using a crack-free method that was functionalized with gold NPs (AuNPs) for improved photocatalytic activity of TiO$_2$. 

Received: February 25, 2020
Accepted: April 23, 2020
Published: May 4, 2020

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https://dx.doi.org/10.1021/acsomega.0c00833
ACS Omega 2020, 5, 11595–11604
Generally, TIO structures can be fabricated in three sequential steps: (1) self-assembly of monodisperse colloidal particles, (2) infiltration of the assembled opal template with a TiO2 precursor solution, and (3) calcination of the opal template. However, fabrication of TIO structures using conventional methods face several challenges. First, the TiO2 precursor is sensitive to moisture, resulting in difficulties to control the degree of precursor infiltration. Second, the use of excess precursor amount can form overlayers on the surface of TIO since it is problematic to control the precursor infiltration, and these overlayers can decay the optical properties. TIO were fabricated using a sol–gel precursor solution for the infiltration of interstitial spaces of a self-assembled polystyrene (PS) template. The problem with overlayers of precursor solution on top of TIO was solved using a lift-off technique. However, the lengthy procedure was not able to completely remove the precursor overlayers. A sandwich-vacuum method was used to remove the precursor overlayers. This was carried out successfully, but it also induced large cracks into the PS template. Hence, there is a clear demand for a more efficient method to fabricate high-quality crack-free TIO structures. Here, large-area, crack-free multilayer TIO structures were fabricated using the titanium-(IV)-bis-lactato-bisammonium dihydroxide (TIBALDH) precursor. The advantage here is a more uniform distribution of TiO2 precursor solution in the interstitial spaces of opal PS that produces a high-quality ordered IO structure suitable for the fabrication of the uniform crack-free IO structure.

Photocatalytic activity of TIO has been traditionally measured by a color change using optical dyes such as methyl orange or methylene blue. However, the incident light itself can bleach the dyes, and these methods can generate an erroneous result. Furthermore, the NPs may detach from the surface of TIO and transfer into the solution during the sample immersion into the dye-containing solution. To overcome these barriers, a better way to evaluate the photocatalytic activity is by gas-phase mineralization of organic compounds such as acetylene (C2H2) oxidation into carbon dioxide (CO2). Additionally, gas-phase detection methods also remove all mechanical stresses from the micro- and nanostructures.

This paper summarizes the fabrication of TIO multilayers with AuNPs having an enhanced light absorption. The open templates for TIO multilayers were fabricated by the deposition of one-size PS followed by a different-size PS using a crack-free method. TIO multilayers were obtained by calcining the PS templates. The fabricated TIO multilayers were functionalized with AuNPs (Au-TIO) that were deposited both on the walls and cavities of TIO multilayers by vertically immersing the glass substrate containing the TIO into the AuNP solution. The photocatalytic activity measurement was carried out using the in-house built gas-phase photoreactor under both UVA and visible light activation.

2. RESULTS AND DISCUSSION

2.1. Characterization of TIO Multilayers. The PS colloidal spheres, in the presence of the TiO2 precursor, were self-assembled as a face-centered cubic (FCC) form by using the vertical deposition method, as shown in Figure 1a. The samples were preheated at 100 °C before the deposition of the other-size PS colloidal particles to ensure a contact between the assembled PS sphere and glass surface before the deposition of the second layer of PS. The deposition of the second layer, as shown in Figure 1, was partially uneven due to high surface tension between the first and second deposition of PS. Figure 2 presents an SEM image of 3D uniform TIO multilayers in the anatase crystalline phase that were obtained upon calcination of the opal templates.

Highly ordered multilayers were successfully fabricated in a large area (10 μm) with minor cracks, as shown in Figure 2a,c. Structures in larger area than 10 μm showed the cracks that were created during the calcination process with shrinkage of the IO structures. This may decrease the photocatalytic activity of the materials. Due to shrinkage, TIO 200/400 and TIO 400/200 after calcination showed air void diameters about 73 and 65% compared to the original 400 and 200 nm PS sphere diameters, respectively.
structure from 200 nm PS particles. The cross-sectional images of both surfaces showed a 4.3 ± 2.0 μm thickness of the TIO surfaces, which depended on the used PS concentration (Figure 2e,f). A TiO₂ precursor solution with a volume ratio of 1:1.5:1 used for the fabrication of TIO was observed to be the best ratio for the synthesis of IO structures. Uniform IO structures were achieved without precursor overlayers.

The anatase crystalline form of TIO structures was further confirmed by Raman spectroscopy. The peak at 133 cm⁻¹ (E₉(1)) presented in Figure 3a corresponds to the bending vibration of the O−Ti−O bond, whereas the other peaks at 384 cm⁻¹ (B₁g), 504 cm⁻¹ (A₁g), and 631 cm⁻¹ (E₉(3)) indicate the Ti−O−Ti bending. The anatase crystalline phase of TIO multilayers was also studied using the XRD spectroscopy. The XRD pattern of TIO multilayers is presented in Figure 3b. Five diffraction peaks at 2θ angles of 25.5, 37.9, 48.0, 53.0, 55.0, 62.7, 68.7, 70.0, and 75.0° can be assigned to the crystal planes (JCPDS 21-12768) of (101), (004), (200), (105), (211), (204), (116), (220), and (215), respectively. The comparison of Raman and XRD spectra confirmed that the anatase crystalline form of TIO was formed upon calcination at 550°C. The calcination temperature also affects the photocatalytic results of the material. IO structures obtained at low temperature possess the smaller crystallite grains due to a low degree of structure contraction. The smaller crystallite grains of IO structures can increase the photocatalytic activity of TiO₂ due to more catalytic active sites, large surface area, and their ability to reduce the chances of recombination of photogenerated holes and electrons.

2.2. Characterization of AuNPs. AuNPs were prepared using the hydrothermal reduction method. The size of the AuNPs can be controlled by varying the temperature, concentration of substances, and pH of the solution. AuNPs with an average size of 18 ± 2 nm were synthesized by

Figure 3. (a) Raman spectrum of TIO structures and (b) XRD spectrum of TIO structures.

Figure 4. (a) STEM image of AuNPs, (b) UV−vis spectrum of AuNPs, (c) EDS spectrum of AuNPs, and (d) size distribution of AuNPs.
using 1% solution of sodium citrate as a reducing agent. The reducing agent solution was added to a dilute aequous solution of HAuCl₄·3H₂O at 100 °C. Figure 4d shows the average diameter of AuNPs around 18 ± 2 nm that was measured using the STEM. Figure 6d confirms that AuNPs were prepared without any capping agent, i.e., by lowering the temperature, not only smaller-size particles were accumulated but also larger-size particles were produced with diameters ranging from 19 to 22 nm. Surface plasmon resonance (SPR) in AuNPs was analyzed by UV—visible (UV—vis) absorption spectroscopy. The normalized absorption spectrum of AuNPs is given in Figure 4b. The SPR absorption peak of synthesized AuNPs was observed around 520 nm in the visible range that depends on the size of particles. In the literature, nanoparticles with a diameter around 20 nm were observed to have a sharp absorption peak around 520 nm. This is also in agreement with our size distribution shown in Figure 4d. Larger nanoparticles have a larger optical cross section and scatter more light that results in the absorption spectrum shifts toward longer wavelengths (red shift). The synthesis of round-shaped AuNPs was confirmed by the STEM images and by a single peak in the UV—vis spectrum of AuNPs, whereas Au nanorods displayed two peaks in the UV—vis spectrum.

The EDS spectrum in Figure 4c verifies the presence of Au atoms in the solution and successful synthesis of AuNPs. A typical optical absorption band peak at 2.2 keV reflects the successful formation of AuNPs, whereas the other absorption band peaks were detected for copper grid that was used for the EDS analysis.

2.3. AuNP-Functionalized TIO Multilayers. Deposition of AuNPs into the TIO multilayers improved photocatalytic activity of TIO by enhancing separation of the photogenerated electron-hole pairs. Furthermore, AuNPs increase the absorption of visible light. The size of NPs has an effect on photocatalytic activity of the semiconductor material. Similarly, location of absorption peaks in the visible range also depends on the NP size. Both TIO samples were dipped in the same concentration of AuNP solutions. The same AuNP content was assumed in all samples as it is difficult to measure quantitatively the actual AuNP loading content from SEM and STEM images. This could be carried out using inductively coupled plasma (ICP) mass spectrometry or ICP-optical emission spectroscopy. The AuNPs were uniformly dispersed and firmly anchored on the walls and inside the pores of TIO structures, as displayed in Figure 5a. Large accumulated NPs were located inside the cavities of porous structures that were observed from SEM images in Figure 5b.

Au-TIO was characterized using STEM to confirm both the multilayer nature of IO structures as well as loading of AuNPs. Figure 6a clearly shows a uniform fabrication of TIO with two different diameters corresponding to 200 and 400 nm PS spheres. EDS mapping of Au-TIO confirms the coexistence of Ti and O in the sample (blue and red in Figure 6b,c, respectively).

The presence of AuNPs inside the porous TIO was confirmed by the STEM and EDS spectrum. Figure 7a shows a distribution of AuNPs inside the pores and on the surface of TIO, which can be clearly seen in a high-magnification STEM image shown in Figure 7b. The EDS spectrum in Figure 7c of Au-TIO verified the existence of Ti, O, and Au.

2.4. Photocatalytic Activity. Figure 8 presents a schematic for photocatalytic activity mechanisms of TiO₂ loaded with AuNPs upon the absorption of photons. The photocatalytic reaction in a pure semiconductor starts when a photon with energy equal or higher than the semiconductor band gap is absorbed. TiO₂ has a band gap around 3.2–3.3 eV that corresponds to 390–400 nm within the UVA range. Electron paramagnetic resonance (EPR) studies have confirmed that the photoexcited electrons from the conduction band (CB) and photogenerated holes from the valence band (VB) get separated from each other and trap at different atomic sites. EPR studies have also suggested the role of O₂⁻ in the adsorbed organic molecules or their intermediates. VB holes can act in two ways: First, they can contribute to direct oxidation or alternatively via formation of hydroxyl radicals with the reaction to water molecules. Detailed mechanisms of hydroxyl radical formation have been debated in the literature: both direct hole oxidation and electron scavenging involving oxygen molecule reduction to superoxide anion radicals (O₂⁻) have been discussed. Therefore, TiO₂ can be used for generating reactive oxygen species for oxidation of organic molecules. In our case, we used acetylene as a target molecule. Adsorption of alkenes and alkynes is typically poor on the oxide surface, and hence, an intermediate is probably formed that binds on the oxide surface. Based on redox potential of the organic molecules, they may convert to the product through cation radical formations by the reduction of h⁺. Water or hydroxyl ions (‘OH) may also reduce the h⁺ to convert to hydroxyl radicals (·OH), which can then oxidize C₂H₂ molecules.

Photocatalytic activities of all samples under UVA irradiation were evaluated by the rate of CO₂ production through
photodegradation of C₂H₂, and the results are shown in Figure 9a. Photocatalytic activities of AuNP-loaded multilayers were compared to multilayers without AuNPs as well as with single-layer IO structures. All samples displayed photocatalytic activity under UVA irradiation. TIO 200, TIO 400, TIO 400/200, TIO 200/400, Au-TIO 400/200, and Au-TIO 200/400 produced CO₂ with rates of 1.31, 1.35, 1.95, 2.16, 2.11, and 2.42 ppm/min, respectively. Loading with AuNPs increased the photocatalytic activity by 8 and 12% for Au-TIO 400/200 and Au-TIO 200/400 compared to samples without AuNPs, respectively.

Photocatalytic activities of AuNP-loaded samples were also evaluated under visible light irradiation as AuNPs absorb visible light (Figure 4b) and can excite the Au-TIO composite. Samples without AuNPs under visible irradiation did not have photocatalytic activity since TiO₂ requires UVA light activation due to a large band gap. Figure 9b shows the photocatalytic activities of Au-TIO 400/200 and Au-TIO 200/400 under visible light that produced CO₂ with rates of 0.21 and 0.27 ppm/min, respectively. It can be concluded that IO structures with larger pores on top (200/400 samples) with and without AuNPs showed a larger photocatalytic activity compared to IO structures with small pores on top (400/200 samples) both under UVA and visible light. It is known that larger-size IO structures are more stable and have a higher efficiency for photocurrent compared to smaller-size IO structures. Furthermore, multilayer TIO structures loaded with AuNPs displayed photocatalytic activity under visible light via the plasmonic coupling of AuNPs with visible light. Finally, reproducibility and stability of the results were confirmed for Au-TIO 200/400 with UVA light irradiation shown in Figure 9c. The results confirm that the Au-TIO 200/400 photocatalyst was stable with no catalyst deactivation after three cycles. The cyclic photodegradation of C₂H₂ confirmed that pore structures were stable, and the response was unchanged during the process. It was also confirmed from the SEM image that AuNPs remain intact to IO structures after the cyclic degradation, as presented in Figure 9d.

SEM, TEM, and EDS analyses together with photocatalytic activities of Au-TIO 200/400 and Au-TIO 400/200 confirmed the deposition of AuNPs into the TIO multilayers. There was a significant difference in the photocatalytic activities of TIO multilayers with and without AuNPs.

The AuNPs play a significant role in enhanced photocatalytic activity of the TIO structures by increasing the separation of photogenerated holes and electrons. The energy diagrams of the Au-TIO structure are presented in Figure 8. Absorption of photons by the metal NPs can excite plasmonic electron oscillations in which hot electrons can transfer into the CB of the semiconductor via the formed Schottky barrier followed by extra electrons in the CB of the semiconductor. Typical Schottky barrier heights in the Au-TiO₂ interface are in the range from 0.23 to 1.0 eV, depending on the sample morphology and crystalline structure.
AuNPs, due to the SPR effect, interact with visible light leading to the production of photogenerated metal ions ($M^+$) and excited electrons (Figure 8). The photoexcited electrons then transfer from AuNPs to the CB of the TiO surface (eq 2). The transfer of photoexcited electrons to TiO structures is followed by separation of photoexcited electrons and $M^+$ (Figure 8). The injected electrons can be used for conversion of molecular oxygen into superoxide anion radicals ($O_2^-$) (eq 3), and the protonation $O_2^-$ radicals leads to the formation of $H_2O_2$-radicals (eq 4). The combination of trapped electrons on the surface of TiO structures and $H_2O_2$-radicals produces the $H_2O_2$ that forms the hydroxyl radicals ($·OH$) (eqs 5 and 6). All these active species and $M^+$ play their role in the oxidation of $C_2H_2$ (eq 7).

A detailed reaction mechanism is given below by eqs 1−7

$$\text{MeNPs} + h\nu \rightarrow \text{MeNPs}^*$$

$$\text{MeNPs}^* + \text{TiO}_2 \rightarrow \text{MeNPs}^+ (h^+) + \text{TiO}_2 (e^-)$$

$$\text{TiO}_2 (e^-) + O_2 \rightarrow \text{TiO}_2 + O_2^-$$

$$O_2^- + H^+ \rightarrow H_2O$$

$$H_2O + H^+ + e^- \rightarrow H_2O_2$$

$$H_2O_2 + e^- \rightarrow O^- + \cdot OH$$

$$\text{MeNPs}^+ (3h^+) + 2\cdot OH^- + 2C_2H_2 + 2O_2$$

$$\rightarrow \text{MeNPs} + 2CO_2 + 2H_2O$$

It is worth emphasizing the role of three holes in eq 7 that are required for the reaction to take place, as demonstrated by Imanishi et al.\textsuperscript{56}

3. CONCLUSIONS

High-quality TiO multilayers were fabricated in a large area using a convective self-assembly method for enhanced photocatalytic activity of TiO\textsubscript{2}. Light absorption was increased by functionalizing TiO multilayers with AuNPs that further improved photocatalytic activity by extending the lifetime of excited holes and electrons. Under UVA irradiation, up to 85\% increase in the photocatalytic activity was observed compared to TiO\textsubscript{2} structures. The TiO functionalized with AuNPs displayed photocatalytic activity also in visible light that was nonexistent with conventional solutions due to the TiO\textsubscript{2} band gap in the UVA range.
The fabricated TiO multilayers can extend the applications of photocatalysis from differential drug release and solar cells to optical filters. It was observed that photocatalytic activity of TiO can be tuned by changing the pore size of IO structures by using a combination of different pore sizes in IO periodic structures. Finally, functionalization with AuNPs can extend photocatalytic activity into the visible wavelengths, opening new avenues for the TiO applications with enhanced performance.

4. EXPERIMENTAL SECTION

4.1. Materials. Styrene (99%, Acros Organics), ammonium persulfate (APS, 98%, Sigma-Aldrich), and sodium dodecyl sulfate (SDS as a capping agent, 98.5%, Sigma-Aldrich) were used for the synthesis of polystyrene (PS) spheres. A Millipore water purification system was used for deionized water. Ethanol (99.5%, ETAX Aa), titanium(IV)-bis-lactato-bisammonium dihydroxide (TiBALDH, 50% aqueous solution, Sigma-Aldrich), and hydrochloric acid (37%, VWR Chemicals) were used for the preparation of TiO precursor solution. Gold(III) chloride trihydrate (HAuCl₃·3H₂O, ≥99.9%, Alfa Aesar) and sodium citrate (TSC, ≥99%, Sigma-Aldrich) were used for the formation of gold nanoparticles. Glass plates (Thermo Scientific) were used as a substrate for the fabrication of TiO IO multilayers.

4.2. Synthesis of PS Spheres. Synthesis of polystyrene spheres was carried out using the procedure by Erola et al. with minor modifications. The synthesis of 200 nm PS spheres was carried out in the first step and used as seeds for the synthesis of 400 nm PS spheres. For the synthesis of 200 nm PS spheres, 160 mL of distilled water was added in a reaction vessel followed by an addition of 200 mg of SDS as a capping agent. The reaction solution was stirred at 70 °C using an anchor-like stirrer at 500 rpm. The reaction mixture was stirred for another 30 min at the same temperature after the addition of 20 g of styrene. An initiator was prepared by dissolving 200 mg of APS in 20 mL of deionized water and added into the reaction mixture. The reaction was proceeded for 20 h under a nitrogen atmosphere. For the preparation of 400 nm PS spheres, the polymerization reaction was proceeded by adding 30 mL of prepared 200 nm PS colloidal spheres and 150 mL of distilled water in a three-neck round flask followed by an addition of 25 mg of SDS. The temperature of the reaction mixture was raised up to 70 °C under the nitrogen atmosphere, and 28 mg of APS solution in 20 mL of deionized water was poured into the reaction mixture. Styrene (21.6 g) was slowly injected into the flask once the solution temperature reached 70 °C that took approximately 10 min. The reaction mixture was allowed to polymerize at 70 °C for 20 h after the injection of styrene.

4.3. Preparation of Crack-Free TiO Multilayers. Fabrication of high-quality TiO multilayers was carried out in two steps: (1) convective self-assembly of PS colloidal crystals (CCs) using the TiO precursor solution and (2) calcination of self-assembled PS CCs to remove PS and to convert the TiO into anatase crystalline phase with the highest photocatalytic activity among the other crystalline phases of TiO. PS with average diameters of 200 and 400 nm were used in this study. In the first step, for convective self-assembly of PS CCs, the TiO precursor solution was freshly prepared 30 min before use. The hydrolyzed TiO precursor solution was prepared by mixing the TiBALDH, ethanol, and 0.1 M HCl with a volume ratio of 1:1.5:1, respectively, and stirred for 30 min. The deposition of PS CCs was performed using the vertical deposition method. Four hundred fifty micro liters of 200 nm PS spheres and 25 mL of water were added in a beaker followed by the addition of 200 μL of precursor solution. The mixture of PS and precursor solution in water was ultrasonicated for 30 min. The glass substrates were prewashed with ethanol followed by deionized water were vertically suspended inside the beaker, containing the ultrasonicated PS and precursor solution. The deposition of PS/TiO CCs on glass substrates was allowed by evaporating the solvent in the oven at 68 °C for 40 h. After the deposition of 200 nm PS/TiO CCs on glass substrates, the samples were preheated at 100 °C for 1 h to make a strong binding between the PS template and glass slide by partially melting the PS. After preheating, 450 μL of 400 nm PS spheres was deposited on top of the bottom layer using the same approach as for 200 nm PS sphere deposition. In the second step, the deposited PS/TiO CCs were calcined for the fabrication of inverseopal multilayers. The deposited films were calcined in air from room temperature to 250 °C in 250 min that was kept constant for 120 min. The temperature was further increased from 250 to 550 °C in 300 min and retained for 300 min to fully remove the PS spheres and to convert TiO into the anatase crystalline phase (Figure 10). TIO 200/400 multilayers were obtained upon cooling the samples to room temperature. TIO 400/200 multilayers with the bottom layer from 400 nm PS spheres and the upper layer from 200 nm PS spheres were also prepared using the same protocol but deposited with reversed order.

4.4. Synthesis of AuNPs. AuNPs were synthesized using a hydrothermal reduction method. For a typical process, 10 mL of aqueous solution of HAuCl₃·3H₂O (0.1%) was dissolved in 100 mL of deionized water that was boiled. Solution of sodium citrate (1%, 2 mL) was mixed with the first solution and stirred for 15 min. The AuNPs were synthesized in solution upon cooling the reaction mixture to room temperature.

4.5. Deposition of AuNPs into TiO Multilayers. An aqueous solution of the prepared AuNPs was diluted by adding 2 mL of aqueous solution of AuNPs in 20 mL of deionized water and ultrasonicated for 30 min. After the ultrasonication, the
glass substrates with TIO multilayers were vertically immersed into the AuNP solution. The solvent was allowed to evaporate for 40 h at 65 °C. As a result, AuNPs were deposited into the pores of TIO multilayers, as shown in Figure 11.

Figure 11. Schematic illustration for deposition of AuNPs in TIO multilayers.

4.6. Characterization. The morphology and structure of TIO multilayers and Au-TIO multilayers were recorded using a Hitachi S-4800 field emission scanning electron microscope (FE-SEM). Cross-sectional images of the TIO multilayer were taken by scratching a small surface from glass substrates and dispersing that on a carbon tape.

The absorption spectrum of AuNPs was recorded using a PerkinElmer Lambda 900 UV/Vis/NIR spectrometer. The crystalline phase and morphology of Au-TIO were further characterized by X-ray diffraction (XRD) with NORAN System SIX (NSS) software. The size of the deposited AuNPs was measured using an excitation laser of 785 nm with a 1 mW power with an integration time of 10 s with a measurement range of 100–800 cm⁻¹. The crystalline nature of the TIO material was characterized with a Bruker AXD D8 Advance device using Cu Kα as the radiation source. The diffraction pattern was measured between 2θ and 90° at the 2θ scale with a step size of 0.3°/min.

4.7. Gas-Phase Photocatalytic Activity Measurement. Photocatalytic activity of TIO 200 (from 200 nm PS), TIO 400 (from 400 nm PS), TIO 200/200 (200 nm followed by 400 nm), TIO 400/200 (400 nm followed by 200 nm), Au-TIO 200/200, and Au-TIO 200/400 were evaluated by oxidizing of acetylene (C₂H₂) into carbon dioxide (CO₂). Such an approach has been demonstrated for the characterization of photocatalytic activity. A large range of hydrocarbons such as C₂H₂, ethylene, and propene are present in automobile exhaust gases, which can be removed by photocatalytic oxidation. Hence, the photodegradation of C₂H₂ was selected for this work to measure the photocatalytic efficiency of the TIO multilayer.

The photocatalytic activities were measured using an in-house built (University of Eastern Finland, Department of Chemistry, Joensuu campus) gas-phase photoreactor, as described in detail in ref 52. It was assumed that all samples had the same surface area. TIO samples on glass substrates (3.3 × 2.6 cm) were placed into the reaction chamber, and a constant concentration of CO₂ was maintained by purging the mixture of C₂H₂ and technical air through the reactor system. The samples were excited using a 450 W xenon lamp (OSRAM). A filter composed of PMMA glass was used to block the UVA portion of incident light with a cutoff filter (λ < 400 nm removed). The visible light source was fixed 10 cm above the reactor chamber. The photocatalytic activity was evaluated by the production rate of CO₂. It is noteworthy that photodegradation of C₂H₂ can also produce other compounds in small number, which can be detected by gas chromatography (GC) and thermal analysis techniques. CO₂ concentration was measured using an optical CO₂ detector (Vaisala GMP343) fixed into the reactor chamber.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

F.T. wishes to thank the Finnish Cultural Foundation for a research grant. J.J.S. acknowledges the Faculty of Science and Forestry at the University of Eastern Finland for the financial support (grant no. 579/2017).

REFERENCES


Optimization for visible light photocatalytic water splitting: gold-by slow photon effect induced strong light absorption.

ACS Omega
http://pubs.acs.org/journal/acsodf

Localizaion effect between titania and photonic crystals on enhanced comparison of activities of Au-TiO

Layer-by-layer approach to (2+1)D photonic crystal superlattice with Stopband tuning of TiO

Fabrication of TiO

Fabrication of high-quality planar titania inverse opals.

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158
K42–K46.

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Global warming brings unprecedented challenges on the life of society. The CO$_2$ level is growing constantly that induces a rise of the temperature in planet scale. Hence, urgent actions are needed to reduce CO$_2$ level in the atmosphere. Photocatalysis is a promising solution for this problem.

In this work photocatalytic activity of TiO$_2$ based inverse opal nanostructures was studied. The results indicated that the photocatalytic activity of such nanostructures can be increased by deposition of metal nanoparticles providing potential solutions both for atmospheric CO$_2$ reduction and emerging energy crisis.