Synthesis of wastewater sludge-derived TiO_2 and its composites for NO_x removal

by Sayed Mukit Hossain

Thesis submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

under the supervision of Prof. Hokyong Shon and Dr. Leonard Demegilio Tijing

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January 2022

CERTIFICATE OF ORIGINAL AUTHORSHIP

I, *Sayed Mukit Hossain* declare that this thesis, is submitted in fulfilment of the requirements for the award of *Doctor of Philosophy*, in the *School of Civil and Environmental Engineering/Faculty of Engineering and IT* at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

This research is supported by the Australian Government Research Training Program.

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Date: 15/07/2022

DEDICATION

The thesis is wholeheartedly dedicated to my beloved parents, Sayed Md. Mostaque Hossain, and Kamrun Naher, who have been my source of inspiration and gave me strength when I thought of giving up, who continuously provided their moral, spiritual, emotional, and financial support.

To my brother and sisters who have encouraged me to finish this study.

Lastly, to my wife, Israt Zahan, for having my back, motivating me, and sharing the path with me.

ACKNOWLEDGEMENT

I would like to offer my heartfelt appreciation to everyone who has helped me along the way to finishing my Ph.D. thesis, which has been a long but rewarding journey.

First and foremost, I want to express my gratefulness to Prof. Hokyong Shon, my principal supervisor, for his excellent mentoring, professional guidance, encouragement, and unwavering support. I am thankful for bringing out the best in me during my Ph.D. studies. I would also like to express my appreciation to my co-supervisor, Dr. Leonard Demegilio Tijing, for his insightful remarks and constructive criticism during my research. Their constant supervision and support during my Ph.D. studies inspired me to develop as a researcher and do my best to accomplish this thesis.

Apart from my supervisors, I would like to express my gratitude to external collaborators Prof. Jong-Ho Kim and Dr. Young-Si Jun, for allowing me to use their labs and research facilities at Chonnam National University (CNU) in South Korea. I would like to express my gratitude to Hui-Ju Kang and Jong Seok Mun for their invaluable assistance throughout my study at CNU. I want to thank Prof. Akira Fujishima of Tokyo University of Science in Japan for his input on this study.
I would like to express my heartfelt appreciation to Dr. Md. Johir and Dr. Nirenkumar Pathak for their assistance in the laboratory. I would like to express my gratitude to my good colleagues Van Huy Tran, Syed Muztuza Ali, Nawshad Akther, Ralph Rolly Gonzales, Myongjun Park, Ugyen Dorji, Pema Dorji, Jiawei Ren, and Idris Ibrahim for their contributions.

I want to acknowledge the full financial support that I received from the UTS International Research Scholarship (UTS IRS) and the Higher Degree by Research Industry Scholarship to complete my Ph.D. study. Finally, I would like to express my gratitude to my parents and uncle Humayun Kabir for teaching me the value of education and hard work, ensuring the success of my academic journey, and inspiring me to achieve my aspirations and be self-sufficient. I am thankful to my wife, Israt Zahan, for her unwavering faith in my ability to accomplish my goals and her steadfast optimism despite the hardships we faced throughout my Ph.D. journey. It would not have been possible to achieve my research objectives without her help, collaboration, and drive.

LIST OF PUBLICATIONS

This list includes journal articles that have been prepared during the PhD candidature, which are either *part of or **not part of the thesis.

- ***Hossain, S.M.**; Tijing, L.; Suzuki, N.; Fujishima, A.; Kim, J.-H.; Shon, H.K. Visible light activation of photocatalysts formed from the heterojunction of sludge-generated TiO2 and g-CN towards NO removal. *Journal of Hazardous Materials* **2022**, *422*, doi:10.1016/j.jhazmat.2021.126919 **(Chapter 6)**.
- **Kim, J.-H.; **Hossain, S.M.**; Kang, H.-J.; Park, H.; Tijing, L.; Park, G.W.; Suzuki, N.; Fujishima, A.; Jun, Y.-S.; Shon, H.K., et al. Hydrophilic/Hydrophobic Silane Grafting on TiO2 Nanoparticles: Photocatalytic Paint for Atmospheric Cleaning. *Catalysts* **2021**, *11*, doi:10.3390/catal11020193.
- **Khan, T.; Bari, G.; Kang, H.-J.; Lee, T.-G.; Park, J.-W.; Hwang, H.; **Hossain, S.**; Mun, J.; Suzuki, N.; Fujishima, A., et al. Synthesis of N-Doped TiO2 for Efficient Photocatalytic Degradation of Atmospheric NOx. *Catalysts* **2021**, *11*, doi:10.3390/catal11010109.
- ***Hossain, S.M.**; Park, H.; Kang, H.J.; Mun, J.S.; Tijing, L.; Rhee, I.; Kim, J.H.; Jun, Y.S.; Shon, H.K. Synthesis and NOx removal performance of anatase S-TiO2/g-CN heterojunction formed from dye wastewater sludge. *Chemosphere* **2021**, *275*, 130020, doi:10.1016/j.chemosphere.2021.130020 **(Chapter 7)**.
- ****Hossain, S.M.**; Park, H.; Kang, H.J.; Mun, J.S.; Tijing, L.; Rhee, I.; Kim, J.H.; Jun, Y.S.; Shon, H.K. Facile synthesis and characterization of anatase TiO2/g-CN composites for enhanced photoactivity under UV-visible spectrum. *Chemosphere* **2021**, *262*, 128004, doi:10.1016/j.chemosphere.2020.128004.
- ***Hossain, S.M.**; Park, H.; Kang, H.-J.; Mun, J.S.; Tijing, L.; Rhee, I.; Kim, J.-H.; Jun, Y.-S.; Shon, H.K. Modified Hydrothermal Route for Synthesis of Photoactive Anatase TiO2/g-CN Nanotubes from Sludge Generated TiO2. *Catalysts* **2020**, *10*, doi:10.3390/catal10111350 **(Chapter 8)**.
- ***Hossain, S.M.**; Park, H.; Kang, H.-J.; Kim, J.B.; Tijing, L.; Rhee, I.; Jun, Y.-S.; Shon, H.K.; Kim, J.-H. Preparation and Characterization of Photoactive Anatase TiO2 from Algae Bloomed Surface Water. *Catalysts* **2020**, *10*, doi:10.3390/catal10040452 **(Chapter 5)**.
- ***Hossain, S.M.**; Park, M.J.; Park, H.J.; Tijing, L.; Kim, J.H.; Shon, H.K. Preparation and characterization of TiO2 generated from synthetic wastewater

using TiCl4 based coagulation/flocculation aided with Ca(OH)2. *J Environ Manage* **2019**, *250*, 109521, doi:10.1016/j.jenvman.2019.109521 **(Chapter 4)**.

- ***Hossain, S.M.**; Jun, Y.-S.; Kim, J.-H.; Shon, H.K. Photocatalytically enhanced TiO2/g-CN composites preparation and environmental applications. *Journal of the Research Institute for Catalysis* **2019**, *40*, 25 – 40 **(Chapter 2)**.

PREFACE

This doctoral thesis is prepared in a "Thesis by compilation" format according to the "Graduate Research Candidature Management, Thesis Preparation, and Submission Procedures, 2021" of the University of Technology Sydney. It comprises the articles that have been published or submitted for publication.

This thesis contains one published review paper in Chapter 2 and five original research articles in Chapters 4 through 8, all of which are published. The authorship of these works has been decided after discussion with the supervisory team.

Chapter 2 comprises the following article:

Hossain, S.M.; Jun, Y.-S.; Kim, J.-H.; Shon, H.K. Photocatalytically enhanced TiO2/g-CN composites preparation and environmental applications. *Journal of the Research Institute for Catalysis* **2019**, *40*, 25 - 40.

Chapter 4 is published in the Journal of Environmental Management:

Hossain, S.M.; Park, M.J.; Park, H.J.; Tijing, L.; Kim, J.H.; Shon, H.K. Preparation and characterization of TiO2 generated from synthetic wastewater using TiCl4 based coagulation/flocculation aided with Ca(OH)2. *J Environ Manage* **2019**, *250*, 109521, doi:10.1016/j.jenvman.2019.109521.

Chapter 5 is published in Catalysts:

Hossain, S.M.; Park, H.; Kang, H.-J.; Kim, J.B.; Tijing, L.; Rhee, I.; Jun, Y.-S.; Shon, H.K.; Kim, J.-H. Preparation and Characterization of Photoactive Anatase TiO2 from Algae Bloomed Surface Water. *Catalysts* **2020**, *10*, doi:10.3390/catal10040452.

Chapter 6 is published in the Journal of Hazardous Materials:

Hossain, S.M.; Tijing, L.; Suzuki, N.; Fujishima, A.; Kim, J.-H.; Shon, H.K. Visible light activation of photocatalysts formed from the heterojunction of sludge-generated TiO2 and g-CN towards NO removal. *Journal of Hazardous Materials* **2022**, *422*, doi:10.1016/j.jhazmat.2021.126919.

Chapter 7 is published in Chemosphere:

Hossain, S.M.; Park, H.; Kang, H.J.; Mun, J.S.; Tijing, L.; Rhee, I.; Kim, J.H.; Jun, Y.S.; Shon, H.K. Synthesis and NOx removal performance of anatase S-TiO2/g-CN heterojunction formed from dye wastewater sludge. *Chemosphere* **2021**, *275*, 130020, doi:10.1016/j.chemosphere.2021.130020.

Chapter 8 is published in Catalysts:

Hossain, S.M.; Park, H.; Kang, H.-J.; Mun, J.S.; Tijing, L.; Rhee, I.; Kim, J.-H.; Jun, Y.-S.; Shon, H.K. Modified Hydrothermal Route for Synthesis of Photoactive Anatase TiO2/g-CN Nanotubes from Sludge Generated TiO2. *Catalysts* 2020, *10*, doi:10.3390/catal10111350.

LIST OF ABBREVIATIONS

AOM	Algal organic matter
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BTSE	Biologically treated secondary effluent
CB	Conduction band
CPAM	Cationic polyacrylamide
DAF	Dissolved air floatation
DBP	Disinfection by-products
DOC	Dissolved organic carbon
DRA	Diffuse reflectance
DRS	Diffuse reflection spectroscopy
DW	Drinking water
DWW	Dye wastewater
EDX	Energy-dispersive X-ray spectroscopy
EOM	Extracellular organic matters
FTIR	Fourier-transform infrared spectroscopy
FWHM	Full width at half maximum
IOM	Intercellular organic matters
LMW	Low molecular weight
MB	Methylene blue
MO	Methyl orange
MW	Molecular weight
NF	Nanofiber
NHE	Normal hydrogen electrode
NOM	Natural organic matter
NP	Nanoparticle
NTU	Nephelometric Turbidity unit
PAC	Poly aluminium chloride
PAFS	Polymeric aluminium ferric sulfate
PATC	Polyaluminium titanium silicate chloride
PFC	Polyferric chloride
PFS	Polyferric sulfate

PFZS	Polymeric ferric zinc sulfate
PL	Photoluminescence
PPAC	Polymeric phosphate aluminium chloride
PPW	Printing paper wastewater
PTC	Polytitanium chloride
PVP	Poly vinylpyrrolidone
RhB	Rhodamine B
SEM	Scanning electron microscope
SWW	Synthetic wastewater
TBA	Tert butyl alcohol
TBT	Tetrabutyl titanate
TEM	Transmission electron microscopy
TNBT	Titanium (IV) n-butoxide
TNT	Titania nanotube
TP	Total phosphate
TXC	Titanium xerogel
UV	Ultraviolet
VB	Valency band
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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ABSTRACT

This research focuses on wastewater flocculation, sludge recycling, and degrading air pollutants using recovered sludge by-products. Resource recovery from coagulation and flocculation is a holistic environmental and economic sustainability approach. Reusing treated wastewater, by-products, and residues created after treatment helps wastewater treatment protect the environment and essential resources. By calcining Ti^{4+} flocculated wastewater sludge, TiO_2 could be synthesized. However, Ti-salt-based coagulation produces acidic effluent, and the photoactivity of sludge-generated TiO_2 (S-TiO_2) is confined to UV spectra only. So, this study's broad goals are to (a) investigate the possibility of generating metal-doped and undoped photocatalyst grade titania while solving Ti-salt-based flocculation's low pH challenge, along with (b) visible light activation of S-TiO_2 for photodegradation of NO_x.

Initially, $TiCl_4$ and $Ca(OH)_2$ were employed to flocculate synthetic wastewater, and an optimum coagulant dose was determined by measuring the treated water's turbidity, DOC, and zeta potential. As a coagulant aid, $Ca(OH)_2$ attained a neutral pH, at 32.40 mg Ca/L and 14.54 mg Ti/L coagulant dose. Both Ca-doped and S-TiO_2 were produced from flocculated sludge for morphological and photocatalytic assessment. The doped Ca atoms prevented the production of anatase TiO_2, and no CaO was observed. At the optimum $Ca(OH)_2$ dose, Ca-doped TiO_2 was inferior to S-TiO_2 in acetaldehyde photodegradation. Subsequently, for the viability of A-TiO_2 production from algae blooming surface water, $TiCl_4$ was found to be better than commercially available polyaluminum chloride. In a microcosm jar test, 0.3 g Ti/L removed 99.8% of turbidity, 67% COD, and 96% TP. Under a 10 W/m^2 UV-A lamp, A-TiO_2 nanoparticles and coated mortar blocks successfully eliminated gaseous CH_3CHO and NO_x.

In addition, this study investigates the feasibility of producing TiO_2/g-CN heterojunction using Ti-incorporated dried dye wastewater sludge to enhance S-TiO_2's photoactivity. Primarily, only the dried sludge and melamine mixture were calcined, and the one-step calcination technique did not produce heterojunction, only N-doped anatase TiO_2. However, a successful TiO_2/g-CN composite was formed by calcining S-TiO_2 and melamine, and the optimum mixing ratio was evaluated as 1:3. Lastly, titanium nanotubes (S-TNT) were produced from S-TiO_2 and coupled with g-CN. The composite tripled the effective surface area (153.61 m^2/g) and reduced the energy bandgap to 3.0 eV. The as-

prepared composite's extended light absorption facilitated 19.62% and 32.44% of NO removal under 1 h of visible and UV light, respectively. In conclusion, it is feasible to make water and air safer and cleaner when considering Ti coagulants' exceptional coagulation performance.