

Synthesis of wastewater sludge-derived TiO₂ and its composites for NO_x removal

by Sayed Mukit Hossain

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the degree of

Doctor of Philosophy

under the supervision of Prof. Hokyoung Shon and Dr.
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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.

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DEDICATION

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LIST OF PUBLICATIONS

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- ****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 NO_x. *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 NO_x 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**).
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- ***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**).
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- ***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 TiCl_4 based coagulation/flocculation aided with $\text{Ca}(\text{OH})_2$. *J Environ Manage* **2019**, 250, 109521, doi:10.1016/j.jenvman.2019.109521 (**Chapter 4**).

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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.

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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 $\text{TiO}_2/\text{g-CN}$ 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 $\text{TiO}_2/\text{g-CN}$ 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.