UTS UNIVERSITY OF TECHNOLOGY SYDNEY

Novel nanomaterials for efficient photocatalytic ammonia synthesis

by Qiang Hao

Thesis submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

under the supervision of Prof. Bruce Ni and Dr. Yiwen Liu

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Certification of original authorship

I, Qiang Hao 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 Information Technology 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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Table of contents

Table list

Figure list

pseudocubic-C_3N_4 view from the [001] axis.

Figure. 2.7 Triazine-(a) and tri-s-triazine-based connection patterns (b) of potential g-C_3N_4 allotropes.

Figure 2.8 (a) The crystal structure of metal Bi from standard orientation, (b) Scheme of the defective Bi nanoplates for the N_2 fixation reaction, (c) The free-energy charts for the N2 fixation response on Bi(110) and Bi(110) features through a response pathway, and (d) Limiting potentials for nitrogen reduction on different metals vs. the binding energy of N_2H^*; (e) Volcano plot for the HER on representative transition metals; (f) activation energy of the rate-determining step. (b-f) Reproduced with permission (Wang, Shi, et al. 2019). Copyright 2019, Wiley-VCH.

Figure 2.9 (a) The crystal structure of δ-Bi_2O_3 from standard orientation. (b) EPR spectra of δ-Bi_2O_3 and 3% AgCl/δ-Bi_2O_3. (c) The crystal structure of BiO from standard orientation. The calculated charge density at the VB of BiO (010) surfaces by (d) top view and (e) side view. (f) A probable route for the nitrogen molecule activation and the hydrogenation on the surface of the bismuth oxide catalyst. (b) Reproduced with permission (Gao, Shang, et al. 2019a). Copyright 2019, Elsevier. (d-f) Reproduced with permission (Sun et al. 2017). Copyright 2017, Royal Society of Chemistry.

Figure 2.10 (a) The crystal structure of BiOBr from standard orientation; (b) schematic illustration of the probable photocatalytic nitrogen fixation over defect-rich Bi_3O_4Br. (b) Reproduced with permission (Di et al. 2019). Copyright 2019, Wiley-VCH.

5 to 80 degrees. (b) The FTIR spectra of BiOBr and BiOBr-TCNQ between 2300 to 500 cm^{-1}. The narrow XPS spectra of O1*s* (c) and Bi 4*f* (d). The EPR spectra of BiOBr (e) and BiOBr-TCNQ samples (f). Inserted image in Figure 2f: The proposed possible structure of BiOBi-TCNQ sample.

Figure 5.3 The zoom-in part of FTIR spectra of prepared samples.

Figure 5.4 (a) The ammonia concentration changes over time. (b) The NH_3 yield by prepared samples. (c) The NMR spectra of $^{15}NH_4Cl$ standard solution and the final photoreduction production of $15N_2$ by BiOBi-TCNQ-2. (d) The NH_3 yield of BiOBi-TCNQ-2 in cycle uses.

Figure 5.5 The UV-vis spectra of the solution to detect hydrazine with color reagent.

Figure 5.6 (a) The UV-vis DRS spectra of BiOBr, TCNQ and BiOBr-TCNQ samples. (b) The photoluminescence spectra, (c) photocurrent response and (d) electrochemical impedance spectroscopy of BiOBr and BiOBr-TCNQ-2. (e) The mechanisms of the separation and transfer of photogenerated electron-hole pairs for the remarkable photocatalytic N_2 fixation performance.

Figure 6.1 HRTEM image of g-C_3N_4 nanosheets (a), CN-Ru-1 (b) and the zoom-in part of the lattice (c), high-angle annular dark-field image (d), energy dispersive spectroscopy for Ru element mapping (e), and SEM image of CN-Ru-1 (f).

Figure 6.2 The XRD patterns of bulk CN, 2D-CN and CN-Ru samples.

Figure 6.3 Narrow C 1*s* XPS spectra of 2D-CN (a) and CN-Ru-1 (b). Narrow N 1*s* XPS spectra of 2D-CN (c) and CN-Ru-1 (d).

mapping of C (g), O (h) and Bi (i) of BiO-160.

Figure 7.3 (a) The ammonia concentration in the photocatalytic reaction system with time went by. (b) The ammonia yield of prepared samples. (c) The cycle stability of BiO-160 used for 4-time nitrate reduction. (d) The NMR spectra of $^{15}NH_4^+$ standard solution and the final photoreduction production of $^{15}NO_3^-$ by BiO-160. The proportions of productions and NO_3^- after photocatalytic reaction by (e) BiO-120 and (f) BiO-160. The selectivity of photocatalytic reduction of NO_3^- by (g) BiO-120 and (h) BiO-160.

Figure 7.4 (a) The DFT calculated band structure of Bi_2O_3. (b) The UV-vis DRS spectra of prepared bismuth/bismuth oxide samples. (c) The photocurrent response of prepared samples with the light on and off. (d) The EIS Nyquist plots of prepared-sample electrodes in the dark.

Figure 7.5 The band structure and possible separation pathways of photogenerated charge carriers for enhanced photocatalytic activity.

List of abbreviations

Symbol	Description
$BaSO_4$	Barium sulfate
BET	Brunauer-Emmett-Teller
Bi	Bismuth
$Bi(NO_3)_3 \cdot 5H_2O$	Bismuth nitrate pentahydrate
BiOBr	Bismuth bromide oxide
Bi_2MoO_6	Bismuth molybdate
$BiVO_4$	Bismuth vanadate
C	Carbon
CB	Conduction band
CN	Carbon nitride
CO_2	Carbon dioxide
Cu	Copper
DFT	Density functional theory
D-CN	Defective g-C_3N_4
DRS	Diffuse reflectance spectra
DMF	*N*,*N*-dimethylformamide
DMSO	Dimethyl sulfoxide
EIS	Electrochemical impedance spectroscopy
ESR	Electron spin resonance
EDS	Energy dispersive spectroscopy
EDTA	Ethylenediaminetetraacetic acid
Fe	Iron
FT-IR	Fourier transform infrared

$g\text{-}C_3N_4$	Graphitic carbon nitride
H_2	Hydrogen
HER	Hydrogen evolution reaction
H_2O	Water
HAADF-STEM	High-angle annular dark-field scanning transmission electron microscopy
HI	Hydriodic acid
HCl	Hydrochloric acid
H_2SO_4	Sulfuric acid
HNO_3	Nitric acid
IC	Ion chromatography
ITO	Indium-tin oxide
K	Potassium
K_2SO_4	Potassium sulphate
KBr	Potassium bromide
La	Lanthanum
Li	Lithium
LiOH	Lithium hydroxide
Mo	Molybdenum
Mg	Manganese
N	Nitrogen
N_2	Nitrogen gas
NH_3	Ammonia
NO_2^-	Nitrite
NO_3^-	Nitrate

NH_4^+	Ammonium
N_2O	Nitrous oxide
NO	Nitric oxide
NO_2	Nitrogen dioxide
N_2O_5	Dinitrogen pentoxide
N_2H_4	Hydrazine
NH_4Cl	Ammonium chloride
NaClO	Sodium hypochlorite
NaOH	Sodium hydroxide
Ni	Nickle
NRR	Nitrogen reduction reaction
NMR	Nuclear Magnetic Resonance
$NaNO_3$	Sodium nitrate
Na_2SO_4	Sodium sulfate
Pt	Platinum
Pd	Palladium
PL	Photoluminescence
Ru	Ruthenium
$RuCl_3$	Ruthenium trichloride
rGO	reduced graphene oxide
RHE	Reversible hydrogen electrode
SCE	Saturated calomel electrode
Sn	Selenium
SPR	Surface plasmon resonance
SEM	Scanning electron microscope

TCNQ	Tetracyanoquinodimethane
TEM	Transmission electron microscope
TiO_2	Titanium dioxide
THF	Tetrahydrofuran
V	Vanadium
VB	Valence band
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
XRF	X-ray fluorescence
ZnO	Zinc oxide
ZIF	Zeolitic imidazolate framework

List of publications

Note: The candidate prefers to use his preferred name "Derek" in publications as the given name start with "q" is difficult to pronounce for English speakers.

A. First-author Peer-Reviewed Journal Articles

1) **Q. Hao**, Y. Liu, T. Chen, Q. Guo, W. Wei, B. J. Ni. Bi_2O_3@Carbon Nanocomposites for Solar-Driven Photocatalytic Degradation of Chlorophenols. ACS Applied Nano Materials. 2019, 2 (4), 2308-2316. (JCR: Q2)

2) R. Wang, **Q. Hao**, J. Feng, G.C. Wang, H. Ding, D. Chen, B. Ni. Enhanced separation of photogenerated charge carriers and catalytic properties of ZnO-MnO_2 composites by microwave and photothermal effect. Journal of Alloys and Compounds. 2019, 786, 418-427. (Equal contribution) (JCR: Q1)

3) **Q. Hao**, C. Liu, G. Jia, Y. Wang, H. Arandiyan, W. Wei, B.J. Ni. Catalytic reduction of nitrogen to produce ammonia by bismuth-based catalysts: state of the art and future prospects. Materials Horizons. 2020, 7 (4), 1014-1029. (JCR: Q1, ESI highly cited paper)

4) **Q. Hao**, G. Jia, W. Wei, A. Vinu, Y. Wang, H. Arandiyan, B.J. Ni. Graphitic carbon nitride with different dimensionalities for energy and environmental applications. Nano Research. 2020. 13, 18-37. (JCR: Q1, ESI highly cited paper)

5) **Q. Hao**, C. Xie, Y. Huang, D. Chen, Y. Liu, W. Wei, B.J. Ni. Accelerated separation of photogenerated charge carriers and enhanced photocatalytic performance of g-C_3N_4 by Bi_2S_3 nanoparticles. Chinese Journal of Catalysis. 2020. 41 (2), 249-258. (JCR: Q1,

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6) **D. Hao**, C. Liu, X. Xu, M. Kianinia, I. Aharonovich, X. Bai, X. Liu, Z. Chen, W. Wei, G. Jia, B.J. Ni. Surface defect-abundant one-dimensional graphitic carbon nitride nanorods boost photocatalytic nitrogen fixation. New Journal of Chemistry. 2020, 44, 20651-20658. (JCR: Q2)

7) **D. Hao**, Z. Chen, M. Figiela, I. Stepniak, W. Wei, B.J. Ni. Emerging alternative for artificial ammonia synthesis through catalytic nitrate reduction. Journal of Materials Science & Technology. 2021, 77, 163-168. (JCR: Q1)

8) **D. Hao**, Y. Liu, S. Gao, H. Arandiyan, X. Bai, Q. Kong, W. Wei, P.K. Shen, B.J. Ni. Emerging artificial nitrogen cycle processes through novel electrochemical and photochemical synthesis. Materials Today. 2021, 46, 212-233. (JCR: Q1, Inner cover)

9) **D. Hao**, Q. Huang, W. Wei, X. Bai, B.J. Ni. A reusable, separation-free and biodegradable calcium alginate/g-C_3N_4 microsphere for sustainable photocatalytic wastewater treatment. Journal of Cleaner Production. 2021, 128033. (JCR: Q1)

10) **D. Hao**, J. Ren, H. Arandiyan, M. Garbrecht, X. Bai, H. K. Shon, W. Wei, Y. Wang, B. J. Ni. A green synthesis of Ru modified g-C_3N_4 nanosheets for enhanced photocatalytic ammonia synthesis. Energy Materials Advances. 2021, 2021, 9761263.

11) **D. Hao**, T. Ma, B. Jia, Y. Wei, X. Bai, W. Wei. B. J. Ni. Small molecule π-conjugated electron acceptor for highly enhanced photocatalytic nitrogen reduction of BiOBr. Journal of Materials Science ＆ Technology. (Accepted) (JCR: Q1)

B: First-author Articles Under Consideration

12) **D. Hao**, Y. Wei, L. M, X. Bai, W. Wei. B. J. Ni. Boosted selective catalytic nitrate reduction to ammonia on carbon/bismuth/bismuth oxide photocatalysts. Journal of Cleaner Production. (Major revision) (JCR: Q1)

C: Co-author Peer-Reviewed Journal Articles

13) M. Ma, Y. Liu, Y. Wei, **D. Hao**, W. Wei. B.J. Ni. A facile oxygen vacancy and bandgap control of $Bi(OH)SO_4H_2O$ for achieving enhanced photocatalytic remediation. Journal of Environmental Management, 2021, 294, 113046. (JCR: Q1)

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16) A. Wang, W. Wang, J. Chen, R. Mao, Y. Pang, Y. Li, W. Chen, D. Chen, **D. Hao**, B.J. Ni, M. Saunders, G. Jia. Dominant Polar Surfaces of Colloidal II–VI Wurtzite Semiconductor Nanocrystals Enabled by Cation Exchange. Journal of Physical Chemistry Letters. 2020, 11 (13), 4990-4997. (JCR: Q1)

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19) X. Bai, X. Wang, X. Lu, Y. Liang, J. Li, L. Wu, H. Li, **Q. Hao**, B.J. Ni, C Wang. Surface defective g-$C_3N_{4-x}Cl_x$ with unique spongy structure by polarization effect for enhanced photocatalytic removal of organic pollutants. Journal of Hazardous Materials, 2020, 398, 122897. (JCR: Q1)

20) X. Liu, B. Xu, X. Duan, **D. Hao**, W. Wei, S. Wang, B.J. Ni. Facile preparation of hydrophilic In_2O_3 nanospheres and rods with improved performances for photocatalytic degradation of PFOA. Environmental Science: Nano. 2021, 8，1010−1018．(JCR: Q1)

Abstract

Ammonia is a key industrial raw material for fertilizers, chemicals and energy. The annual artificial ammonia synthesis via the Haber-Bosch process causes about 2% of global energy consumption and can lead to 1.6% CO_2 emission. Therefore, it is urgent to develop low-cost and environmentally friendly approaches for artificial ammonia synthesis under ambient conditions. In this thesis, we summarized the current research status. Besides, a new concept of "artificial nitrogen cycle process based on photochemical and electrochemical reactions" was proposed. Through nanostructure control, metal modification, small π-conjugated molecule modification, plasma modification, several kinds of novel nanomaterials were developed and achieved highly efficient artificial ammonia synthesis under ambient conditions.

A facile approach was used to prepare defective g-C_3N_4 nanorods with a narrower bandgap and a sub-gap, which can significantly enhance the light utilization ratio. More importantly, the defects of g-C_3N_4 nanorods can also enhance light absorption and boost the cleavage of N_2 molecules, which is the rate-determining step of nitrogen fixation. Compared with bulk g-C_3N_4, the photocatalytic N_2 reduction rate of defective g-C_3N_4 nanorods as the catalysts was increased by 3.66 times.

We also report a novel bismuth bromide oxide (BiOBr)-Tetracyanoquinodimethane (TCNQ) photocatalyst prepared via a facile self-assembly method. Due to the well-match band structure of TCNQ and BiOBr, the separation and transfer of photogenerated electron-hole pairs were significantly boosted. The highest ammonia yield of the optimized sample reached 2.617 mg/h/g_{cat}, which was 5.6-fold as that of

pristine BiOBr and higher than the reported BiOBr-based photocatalysts.

Nitrate is a crucial environmental pollutant and its risk on the ecosystem keeps increasing. In this thesis, we reported a green and facile synthesis of novel metallic ruthenium particle modified graphitic carbon nitride photocatalysts. Compare with bulk graphitic carbon nitride, the optimal sample had 2.93-fold photocatalytic nitrate reduction to ammonia activity.

We also report a facile synthesis of carbon/bismuth/bismuth oxide photocatalyst via a one-pot hydrothermal reaction without using reducing reagent. Compared with bismuth oxide (α-Bi_2O_3), the photocatalytic ammonia yield of the optimum sample increased 3.65 times. In addition, the ammonia selectivity increased from 65.21% to 95.00%. The highly enhanced photocatalytic performance was attributed to the surface plasmon resonance of metallic bismuth. Meanwhile, the formation of carbon enables to boost the transfer of electrons significantly. The results and research findings of these works will contribute to the green artificial ammonia synthesis under ambient conditions.

Keywords: graphitic carbon nitride; bismuth; tetracyanoquinodimethane; bismuth bromide oxide; nitrogen reduction, nitrate reduction, photocatalysis; ammonia synthesis