Graphitic Carbon Nitride and Its Derivative Toward Energy Conversion

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This thesis is presented as part of the requirement for the conferral of the degree:

DOCTOR OF PHILOSOPHY

University of Technology Sydney

Faculty of Science

School of Mathematical and Physical Sciences

Centre for Clean Energy Technology

July 2020

Abstract

This Ph.D. project focus on graphitic carbon nitride (g-C_3N_4) and its derivatives toward energy conversion applications, including the photocatalytic hydrogen evolution and lithium sulfur (Li-S) batteries. Bulk g-C_3N_4 materials suffer from the insufficient supply of valid photocarriers due to the low surface area, poor visible light absorption, and fast photocarrier recombination. While Li-S batteries have been severely impeded by fast capacity fading and severe electrochemical polarization. Therefore, a rational morphology, defect, or hybrid modification on g-C_3N_4 and its derivatives is designed to boost the photocatalytic H_2 evolution or battery performance.

A facile structure and doping engineering strategy is proposed to obtain the atomic-thin mesoporous C/O-doped g-C_3N_4 nanosheets via an acid-assisted exfoliation route without any hard templates. The theoretical calculations reveal that C/O atoms would boost the charge transfer rate and charge separation efficiency due to the enhanced electronic polarization effect and shortened bond lengths. Additionally, the electronic conductivity is enhanced due to the formation of delocalized π-bonding. The synergic contribution of textural and electronic features renders an excellent photoelectrochemical (PEC) performance and superior H_2 evolution rates.

A broadband photocatalyst composed of defect engineered g-C_3N_4 (DCN) and upconversion $NaYF_4$: Yb^{3+}, Tm^{3+} (NYF) nanocrystals is proposed to boost

the utilization of solar energy. The simultaneous introduction of S dopants and C vacancies renders DCN with defect states to effectively extend its visible light absorption to 590 nm and provide a moderate electron-trapping ability, thus facilitating the re-absorption of upconverted photons and boosting photocarrier separation efficiency. Through the defect engineering, a promoted interfacial charge polarization between DCN and NYF is achieved, which favors the upconverted excited energy transfer from NYF onto DCN as verified both theoretically and experimentally. With the optimization of a 3D framework architecture, the NYF@DCN catalyst exhibits a superior solar H_2 evolution rate.

We report a strategy to trap polysulfides and boost Li-S redox kinetics by embedding, the g-C_3N_4 derivative, surface oxidized quantum-dot-size TiN (TiN-O) into the highly ordered mesoporous carbon matrix. While the carbon scaffold offers sufficient electrical contact to the insulate sulfur, benefiting the full usage of sulfur and physical confinement of polysulfides. The surface oxygen defects render TiN-O with a stronger charge polarization effect for polysulfides via the S-O-Ti bond as verified experimentally and theoretically. Remarkably, TiN-O based coin cells and prototype soft-package cells exhibit excellent cycling stability with great flexibility, demonstrating their potential for practical applications.

Acknowledgments

Time flies, and my three and a half year's Ph.D. study will finish soon. I would like to express my sincere gratitude to my principal supervisor Prof. Guoxiu Wang, who offers me a Ph.D. position with a full scholarship in UTS. It is his professional guidance, critical thinking, and warm encouragement that help me move forward. I would also like to thank my co-supervisor, Dr. Dawei Su, for his constructive suggestions, skillful experience to help address my research problems. He is very knowledgeable in both physics and chemistry, and I always learn a lot when discussing with him. Besides, I would also like to thank Dr. Jane Yao, who mangers everything well in our team. Without her support, the research work cannot be completed smoothly. Thanks for her insistence on journal club where I improve my academic presentation skills significantly.

I want to thank my colleagues at UTS, Dr. Bing Sun, Dr. Hao Liu, Dr. Dong Zhou, Dr. Pan Xiong, Dr. Liubin Dong, Dr. Huajun Tian, Dr. Xin Guo, Dr. Jinqiang Zhang, Dr. Yufei Zhao, Dr. Jing Xu, Dr. Weizhai Bao, Dr. Lin Liu, Shaoqi Hou, Xingxing Yu, Jiayan Liao, Yi Chen, Shijian Wang, Xiao Tang, Kang Yan, Fan Zhang, Javad Safaei, Shuoqin Zhao, Tianyi Wang, Wang Yang, Wu Yang, Min Luo, Ziqi Guo, Anastasia Tkacheva, Tuhin Subhra Sahu, Pauline Jaumaux, and Yuhan Xie for all your kind assistance and collaboration during my Ph.D. study and life.

I am also grateful for the kind help from Prof. Jintao Zhang at Shandong University, who always gives me useful suggestions on planning my research. Thanks to A/Prof. Dr. Jin Feng for her help with the theoretical calculations.

I appreciate the excellent technical support from Dr. Ronald Shimmon, Dr. Linda Xiao, Alexander Angeloski, Katie McBean, Herbert Yuan, Mark Berkahn, Mark Lockrey, and Geoff McCredie.

The financial support from UTS and Australian Research Council (ARC) through the Discovery Project (DP170100436), ARENA 2014/RND106 are gratefully acknowledged.

Last, I would like to express my sincerest thanks to my four parents, my brother, my sister, my grandparents, who always support me selflessly. Endless thanks and apologies to my beloved, Shaoqi, thanks for giving up all but understanding, encouraging, and supporting me. Without you, my Ph.D. study cannot be so smooth, happy, and enjoyable.

CERTIFICATE OF AUTHORSHIP

I, Xiaochun Gao, certify that the work presented in this thesis has not previously been submitted for a degree nor has been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work, and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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

Xiaochun Gao

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Sydney, Australia

8 July 2020

Lists of Nomenclature

Abbreviations

g-C_3N_4	graphitic carbon nitride
Li-S batteries	lithium sulfur batteries
PEC	photoelectrochemical
DCN	defect engineered g-C_3N_4
NYF	$NaYF_4$: Yb^{3+}, Tm^{3+}
TiN-O	surface oxidized TiN (TiN-O)
CB	conductive band
VB	valence band
SHE	standard hydrogen electrode
NIR	near-infrared
UV	ultraviolet
2D	two dimensional
IPA	isopropanol
NMP	N-methy-pyrrolidone
AAO	anodic aluminum oxide
AQE	apparent quantum efficiency
DOSs	density of states
DFT	density functional theory

SEM	scanning electron microscopy
STEM	scanning transmission electron microscopy
TEM	transmission electron microscopy
AFM	atomic force microscopy
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
FT-IR	Fourier-transform infrared spectroscopy
EPR	electron paramagnetic resonance
UV-vis DRS	UV-vis diffusion-reflectance spectra
PL	photoluminescence
TGA	Thermal Gravimetric analysis
CV	cycling voltammogram
EIS	electrochemical impedance spectra
XANES	X-ray absorption near-edge structure

List of Symbols

θ	Angle of incidence with the lattice plane	degree
d	Lattice spacing	nm
λ	Wavelength	nm
τ	Decay time	s
I	Current density	mA cm^{-2}
E	Voltage	V
η	Overpotential	V
γ	Stretch constant	a.u.
C	Concentration	a.u.

List of Organisations

ISEM	Institute for Superconducting and Electronic Materials
NSW	The New South Wales
ARENA	Australian Renewable Energy Agency
UTS	University of Teehnology Sydney
ARC	Australian Research Council

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