## **Springer Theses** Recognizing Outstanding Ph.D. Research

# Nailiang Yang

# The Preparation of Nano Composites and Their Applications in Solar Energy Conversion



### **Springer Theses**

Recognizing Outstanding Ph.D. Research

#### Aims and Scope

The series "Springer Theses" brings together a selection of the very best Ph.D. theses from around the world and across the physical sciences. Nominated and endorsed by two recognized specialists, each published volume has been selected for its scientific excellence and the high impact of its contents for the pertinent field of research. For greater accessibility to non-specialists, the published versions include an extended introduction, as well as a foreword by the student's supervisor explaining the special relevance of the work for the field. As a whole, the series will provide a valuable resource both for newcomers to the research fields described, and for other scientists seeking detailed background information on special questions. Finally, it provides an accredited documentation of the valuable contributions made by today's younger generation of scientists.

#### Theses are accepted into the series by invited nomination only and must fulfill all of the following criteria

- They must be written in good English.
- The topic should fall within the confines of Chemistry, Physics, Earth Sciences, Engineering and related interdisciplinary fields such as Materials, Nanoscience, Chemical Engineering, Complex Systems and Biophysics.
- The work reported in the thesis must represent a significant scientific advance.
- If the thesis includes previously published material, permission to reproduce this must be gained from the respective copyright holder.
- They must have been examined and passed during the 12 months prior to nomination.
- Each thesis should include a foreword by the supervisor outlining the significance of its content.
- The theses should have a clearly defined structure including an introduction accessible to scientists not expert in that particular field.

More information about this series at http://www.springer.com/series/8790

Nailiang Yang

# The Preparation of Nano Composites and Their Applications in Solar Energy Conversion

Doctoral thesis accepted by University of Chinese Academy of Sciences, China



Author Dr. Nailiang Yang Institute of Process Engineering Chinese Academy of Sciences Beijing China Supervisor Prof. Dan Wang Institute of Process Engineering Chinese Academy of Sciences Beijing China

ISSN 2190-5053 ISSN 2190-5061 (electronic) Springer Theses ISBN 978-3-662-53483-0 ISBN 978-3-662-53485-4 (eBook) DOI 10.1007/978-3-662-53485-4

Library of Congress Control Number: 2016952907

#### © Springer-Verlag GmbH Germany 2017

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made.

Printed on acid-free paper

This Springer imprint is published by Springer Nature The registered company is Springer-Verlag GmbH Germany The registered company address is: Heidelberger Platz 3, 14197 Berlin, Germany

### **Supervisor's Foreword**

I first met Nailiang in 2006 when he was still a bachelor's candidate in Sun-Yet-Sen University. At that time, he interviewed in our institute for doctorate degree. I was very glad to see a young student who was so obsessed with science and had such solid knowledge in chemistry; hence, I introduced him to our group. After five years of research, I am very happy to see a rising young scientist coming from our group. This book not only comprises a summary of scientific thesis but also serves a review of his life in those years.

His main works are based on the novel two-dimensional (2D) carbon materials, specifically on graphene and graphdiyne, which are considered as the rising star in materials science. In this topic, he also focused on the applications of their nanocomposites forms with solar cells and photocatalysis as specialties. These works can be considered as the pioneer of graphene-related research, started two years before the announcement of graphene works in the Nobel Prize. The basis of these works was also the first few papers which reported and proved the charge transport between graphene and other semiconductors, and hence received many citations. Beyond them, in this thesis, he pointed out the potential applications and designation for graphene composite referring the structure and function of granum, which may be beneficial for designing new integrated circuit and chips. Importantly, he also honestly listed the defects of recent research in this field to give a thorough guide for further improvement. In the booming age of two-dimensional nanomaterials, I am confident that the ideas from this thesis can also be referred and extended to other materials.

I hope the publication of this thesis will be smooth, to allow more readers grasp new ideas from his discussions. As I know from him, Nailiang is still working on the synthesis and assembly of novel nanomaterials after his graduation. A broad and kind discussion with the author in the future will be very beneficial for both the readers and him.

Beijing, China July 2016 Prof. Dan Wang

### Acknowledgments

After graduation of 3 years, it is time to reread the original acknowledgment, and I can still feel my mixed feelings at that moment. Nine years ago, I walked through the gate of Graduate University of Chinese Academy of Sciences (now named as University of Chinese Academy of Sciences), and started my scientific research. Since then, I have witnessed lots of graduate defences, and every time I asked myself what it would be like for mine. I thought about what I should write and say in the acknowledgment. Now I understand that one can never know where to start how to write until that very moment. In this more than five years' period, I have too many things to say, with all the memories flashing in my mind. With the time prolonged, there are more and more people to whom I need to express my thanks. Because of them, I have this opportunity to write this acknowledgment. Because of them, I could overcome the difficult barriers and because of them, I could enjoy the fantastic research life.

First, with no doubt, I would like to express my great thanks to my supervisor, Prof. Dan Wang. I first met him in the summer of 2006, and he led me to the palace of science. In these years, he gave me lot of opportunities to exercise, so that I can access to the most advanced technology area, which made me grow up rapidly in science. In academy, his open and active mind, accompanied with his hard working deeply impressed me; in life, he is a model as a man in family and concerns about our happiness and health. To us students, he is more than a teacher, a friend.

Since 2008, I had the chance to attend the academician Lei Jiang's group and started a five-year research as a joint doctoral candidate. What I have to say is, the most impressive thing about Prof. Jiang is his strong "aura", which is full of confidence and energy, and I always felt nervous when talking with him. But with time passing by, I started to know he is very humorous and easy-going. He is always glad to help and encourage students to immerse in science. In those years, I admired on his broad knowledge and smart ideas very much. He taught us to stay curious about everything happening around us, and to explore the scientific reason behind it. He taught us the evolution of nature is a good teacher for scientists, and nature can tell you why it should be like this. He taught us to follow the traditional ideas in Chinese

culture, such as the philosophy of "Dao" and "Yin-Yang". He taught us the synergistic effects in nature and applying them in science. He supplied the best equipment for research and supported our ideas positively. Moreover, he encouraged us to go abroad, to know more about the scientific frontier. Thank you, Sir.

Also, I would like to thank for Prof. Jin Zhai in Beihang University. She guided me thoroughly in the experiment and paper writing. I admire her very much for her solid chemistry knowledge and sensitive sense to the hottest topics in science. Thanks to her that I was supported to attend lots of academic conferences and meet many top scientists in the world, and know the culture of other countries.

I would also like to thank other staffs in our group, namely Dan Mao, Xiaoyong Lai, Jianxi Yao, Chaojian Xing, Nan Xu, Mei Yang, Luoxin Yi, Zhudong Hu, Jiajia Wu, and Quan Jin. You provided a kind environment in my daily life and studies. Also many thanks to the labmates, Jun Li, Zhenmin Li, Ronghai Zhu, Shengdong Wang, Rongguo Xu, Xiaoqing Jiang, Li Li, Jiang Du, Ying Cui, Yuanyuan Liu, Shuo Wang, Zhenghong Dong, Gongling Wang, Hongjie Tang, Jiangyan Wang, Yu Yang, Hao Ren, Simeng Xu, Dong Guo, Wei Xu, and others; because of you, we formed an active group, which brought us lot of happiness beyond the experiments. I also want to express my thanks to Dr. Yuanyuan Liu and Mr. Yibo Zhao for their kind help, which helped the conclusion of Chap. 5, and to Yu Zhang and Qi Yuan, who accompanied me to finish the LBL work through many nights. In addition, I would like to express my thanks for Jingtao Wang and Jiwei Li's help in the Au-DSSC work, and also to the teachers, Ms. Lijuan Guo, Ms. Jing Wang, and Mr. Jianghua Ma in IPE, who provided good life and experiment experiences for all the graduated students.

Furthermore, dear Academician Daoben Zhu, thanks for guiding me in the synthesis and characterization of graphene. Dear Prof. Zhiyong Tang, Prof. Zhixiang Wei and Prof. Dong Han in Nanocenter, thanks for helping me in the material characterization. Dear Prof. Meixiang Wan, thanks for helping me in organic synthesis. Dear Prof. Dongsheng Liu in Tsinghua University, thanks for helping me in the gold synthesis. Dear Prof. Tianxin Wei in Beijing Institute of Technology, thanks for helping me in in the preparing the gold film and SPR testing. Dear Prof. Jingxia Wang, Dr. Yu Huang and Dr. Libin Wang, thanks for helping me in PS synthesis and assembly. Dear Mrs. Guilan Wang and Dr. Ye Tian, thanks for helping me in the thesis guiding and writing. Dear Dr. Luoxin Yi and Dr. Hao Ren, thanks for helping me in the help of thesis translation.

I also want to express my thanks to all the group members in Prof. Lei Jiang, Prof. Yanlin Song and Prof. Qinghua Fan's group in ICCAS, the group members in Prof. Jin Zhai and Prof. Ying Zhu's group in BUAA and all the group members in Prof. Dongsheng Liu's group in Tsinghua University. Thanks you for the supporting and discussion in experiment.

We also thank the National Natural Science Foundation of China, National Basic Research Program, 863 Program, State Key Laboratory of Multiphase Complex Systems, Ph.D. Programs Foundation of the Ministry of Education of China and Beijing Municipal Natural Science Foundation for the continuing financial support.

Here, I would like to appreciate my wife, Dr. Liying Wang. Because of the simple words "I do" 12 years ago, we decided to move forward together. No matter what kind of trouble we faced these years, I can always get the support from her. In the past 12 years' life of study and work, I felt so blessed to have her always staying with me, encouraging me, comforting my sadness, and sharing my happiness. Because of her, I gained confidence to finish my doctor career; because of her, I overcame the difficulties one by one; because of her, I received so much joy which could never happen without her. It is fortunate to be with her.

Lastly, I need to say that the source of my happiness is also from my beloved parents. They always take care of my business as priority, bless me safe and happy, and support my choices. Although our distance became farther geographically, their concern was getting closer. Since 2003, I spent lesser time with them. I know they want me to be around, but they also hope that I would fight for my own career for a brighter future, so they even encouraged me to go overseas. This is the priceless love I will forever appreciate.

Yunnan Garden, Singapore May 2016

### Contents

1	Introduction			1
	1.1	Dye-S	ensitized Solar Cell (DSSC)	2
		1.1.1	Development of Solar Cells	2
		1.1.2	Basic Principle of DSSC	5
		1.1.3	Introduction of the Constitution of DSSC	10
	1.2	Photo	catalysis	15
		1.2.1	Principle	15
		1.2.2	Modification of Catalyst	17
	1.3	Carbo	n Materials in Photoelectric Conversion System	20
		1.3.1	Donor-Acceptor Photovoltaic Material Based	
			on Zero-Dimensional Fullerenes	20
		1.3.2	Application of One-Dimensional Carbon Nanotubes	
			in Photoelectric Conversion System	22
		1.3.3	Applications of Two-Dimensional Carbon Materials	
			in Photoelectric Conversion System	24
	1.4	Novel	ty and Significance of This Thesis	33
	Refe	erences.		35
2	Two	-Dimer	nsional Graphene Bridges Enhanced Photoinduced	
			ansport in Dye-Sensitized Solar Cells	41
	2.1	Introd	uction	41
	2.2			40
	2.2	Result	s and Discussion	42
	2.2	Result 2.2.1		42 42
	2.2		The Characterization of GO and Graphene Photocurrent–Voltage ( <i>I–V</i> ) Characteristics of Different	
	2.2	2.2.1	The Characterization of GO and Graphene	
	2.2	2.2.1	The Characterization of GO and Graphene Photocurrent–Voltage ( <i>I–V</i> ) Characteristics of Different	42
	2.2	2.2.1 2.2.2	The Characterization of GO and Graphene Photocurrent–Voltage ( <i>I–V</i> ) Characteristics of Different Electrodes	42
	2.2	2.2.1 2.2.2	The Characterization of GO and Graphene    Photocurrent–Voltage ( <i>I–V</i> ) Characteristics of Different    Electrodes  Incident Monochromatic Photo-to-Current Conversion	42 43
	2.2	2.2.1 2.2.2 2.2.3	The Characterization of GO and Graphene    Photocurrent–Voltage ( <i>I–V</i> ) Characteristics of Different    Electrodes    Incident Monochromatic Photo-to-Current Conversion    Efficiency (IPCE) Performance of Different Electrodes	42 43

	2.3	Conclusions	52		
	2.4	Postscript	52		
	2.5	Detailed Methods	53		
	Refe	erences	55		
3	Bioi	nspired Stacking Structures for Photoelectric Conversion	57		
	3.1	Granum-Like Stacking Structures with TiO <sub>2</sub> –Graphene			
		Nanosheet for Improving Photoelectric Conversion	57		
		3.1.1 Introduction.	57		
		3.1.2 Results and Discussion	59		
		3.1.3 Conclusions.	67		
		3.1.4 Detailed Methods	68		
	3.2	Stacking Nanostructures of Polyaniline with Graphene			
		Oxide as the Dopant and Template	69		
		3.2.1 Introduction	69		
		3.2.2 Results and Discussion	70		
		3.2.3 Conclusion	75		
		3.2.4 Detailed Methods	75		
	3.3	Postscript	76		
		3.3.1 Discussion About Experiment Details	76		
		3.3.2 Perspective	77		
	Refe	erences	77		
4	Enhanced Light Harvesting in Plasmonic Dye-Sensitized Solar				
		s Using Gold Topological Light Trapping Layer	81		
	4.1				
		Introduction	81		
	4.2				
	4.2	Introduction	81		
	4.2	Introduction	81 83		
	4.2	Introduction  Results and Discussion    4.2.1  Characterization of the Topological Ordered Au Film	81 83 83		
	4.2	IntroductionResults and Discussion4.2.1Characterization of the Topological Ordered Au Film4.2.2Photovoltaic Behavior of DSSCs4.2.3Light Harvesting Properties of Two Electrodes	81 83 83 84		
	4.2	IntroductionResults and Discussion4.2.1Characterization of the Topological Ordered Au Film4.2.2Photovoltaic Behavior of DSSCs4.2.3Light Harvesting Properties of Two Electrodes	81 83 83 84		
	4.2	IntroductionResults and Discussion4.2.1Characterization of the Topological Ordered Au Film4.2.2Photovoltaic Behavior of DSSCs4.2.3Light Harvesting Properties of Two Electrodes4.2.4Incident Monochromatic Photo-to-Current Conversion	81 83 83 84 86		
	<ul><li>4.2</li><li>4.3</li></ul>	Introduction  Results and Discussion    4.2.1  Characterization of the Topological Ordered Au Film.    4.2.2  Photovoltaic Behavior of DSSCs    4.2.3  Light Harvesting Properties of Two Electrodes    4.2.4  Incident Monochromatic Photo-to-Current Conversion Efficiency (IPCE) Performance of Different Electrodes    4.2.5  Photovoltaic Behavior Under Different Light Intensity    Conclusion	81 83 83 84 86 86		
		Introduction  Results and Discussion    4.2.1  Characterization of the Topological Ordered Au Film.    4.2.2  Photovoltaic Behavior of DSSCs    4.2.3  Light Harvesting Properties of Two Electrodes.    4.2.4  Incident Monochromatic Photo-to-Current Conversion Efficiency (IPCE) Performance of Different Electrodes.    4.2.5  Photovoltaic Behavior Under Different Light Intensity	81 83 83 84 86 86 87		
	4.3	Introduction  Results and Discussion    4.2.1  Characterization of the Topological Ordered Au Film.    4.2.2  Photovoltaic Behavior of DSSCs    4.2.3  Light Harvesting Properties of Two Electrodes    4.2.4  Incident Monochromatic Photo-to-Current Conversion Efficiency (IPCE) Performance of Different Electrodes    4.2.5  Photovoltaic Behavior Under Different Light Intensity    Conclusion	81 83 83 84 86 86 87 88		
	4.3 4.4 4.5	Introduction  Results and Discussion    4.2.1  Characterization of the Topological Ordered Au Film.    4.2.2  Photovoltaic Behavior of DSSCs    4.2.3  Light Harvesting Properties of Two Electrodes    4.2.4  Incident Monochromatic Photo-to-Current Conversion Efficiency (IPCE) Performance of Different Electrodes    4.2.5  Photovoltaic Behavior Under Different Light Intensity    Conclusion  Detailed Methods	81 83 84 86 86 87 88 88		
5	4.3 4.4 4.5 Refe	Introduction    Results and Discussion    4.2.1  Characterization of the Topological Ordered Au Film.    4.2.2  Photovoltaic Behavior of DSSCs    4.2.3  Light Harvesting Properties of Two Electrodes    4.2.4  Incident Monochromatic Photo-to-Current Conversion Efficiency (IPCE) Performance of Different Electrodes    4.2.5  Photovoltaic Behavior Under Different Light Intensity    Conclusion  Detailed Methods    Postscript  Encode State	81 83 84 86 86 86 87 88 88 88		
5	4.3 4.4 4.5 Refe Pho	Introduction  Results and Discussion    4.2.1  Characterization of the Topological Ordered Au Film.    4.2.2  Photovoltaic Behavior of DSSCs    4.2.3  Light Harvesting Properties of Two Electrodes    4.2.4  Incident Monochromatic Photo-to-Current Conversion Efficiency (IPCE) Performance of Different Electrodes    4.2.5  Photovoltaic Behavior Under Different Light Intensity    Conclusion  Detailed Methods    Postscript	81 83 84 86 86 86 87 88 88 88		
5	4.3 4.4 4.5 Refe Pho	Introduction  Results and Discussion    4.2.1  Characterization of the Topological Ordered Au Film.    4.2.2  Photovoltaic Behavior of DSSCs    4.2.3  Light Harvesting Properties of Two Electrodes    4.2.4  Incident Monochromatic Photo-to-Current Conversion Efficiency (IPCE) Performance of Different Electrodes    4.2.5  Photovoltaic Behavior Under Different Light Intensity    Conclusion  Detailed Methods    Postscript  Postscript    trences  the	81 83 84 86 86 87 88 88 88 89 90		
5	4.3 4.4 4.5 Refe Pho Mod	Introduction  Results and Discussion    4.2.1  Characterization of the Topological Ordered Au Film.    4.2.2  Photovoltaic Behavior of DSSCs    4.2.3  Light Harvesting Properties of Two Electrodes    4.2.4  Incident Monochromatic Photo-to-Current Conversion Efficiency (IPCE) Performance of Different Electrodes    4.2.5  Photovoltaic Behavior Under Different Light Intensity    Conclusion  Detailed Methods    Postscript  Erences    tocatalytic Properties of Graphdiyne and Graphene    lifed TiO2: From Theory to Experiment	81 83 83 84 86 87 88 88 88 89 90		
5	4.3 4.4 4.5 Refe <b>Pho</b> 5.1	Introduction  Results and Discussion    4.2.1  Characterization of the Topological Ordered Au Film.    4.2.2  Photovoltaic Behavior of DSSCs    4.2.3  Light Harvesting Properties of Two Electrodes    4.2.4  Incident Monochromatic Photo-to-Current Conversion Efficiency (IPCE) Performance of Different Electrodes    4.2.5  Photovoltaic Behavior Under Different Light Intensity    4.2.5  Photovoltaic Behavior Under Different Light Intensity    Conclusion  Detailed Methods    Postscript  Properties of Graphdiyne and Graphene    Ified TiO2: From Theory to Experiment  Introduction	81 83 83 84 86 87 88 88 89 90 93 93		
5	4.3 4.4 4.5 Refe <b>Pho</b> 5.1	Introduction  Results and Discussion    4.2.1  Characterization of the Topological Ordered Au Film.    4.2.2  Photovoltaic Behavior of DSSCs    4.2.3  Light Harvesting Properties of Two Electrodes    4.2.4  Incident Monochromatic Photo-to-Current Conversion Efficiency (IPCE) Performance of Different Electrodes    4.2.5  Photovoltaic Behavior Under Different Light Intensity    Conclusion  Detailed Methods    Postscript  Postscript    tocatalytic Properties of Graphdiyne and Graphene    lified TiO2: From Theory to Experiment    Introduction    Results and Discussion	81 83 83 84 86 87 88 88 88 89 90 93 93 94		

6	Con	clusions and Perspectives	111	
	References			
		Postscript		
	5.4	Detailed Methods	106	
	5.3	Conclusion	105	

### Abbreviations

AFM	Atomic Force Microscopy
CBM	Conduction Band Minimum
CNT	Carbon Nanotube
DSSC	Dye-Sensitized Solar Cell
EIS	Electrochemical Impedance Spectroscopy
FT-IR	Fourier Transform Infrared
FTO	Fluorine-doped Tin Oxide
GD	Graphdiyne
GO	Graphene Oxide
GR	Graphene
HOMO	Highest Occupied Molecular Orbital
IPCE	Monochromatic Incident Photon-to-Electron Conversion Efficiency
LUMO	Lowest Unoccupied Molecular Orbital
PANI	Polyaniline
SEM	Scanning Electron Microscope
SPR	Surface Plasmon Resonance
TEM	Transmission Electron Microscopy
UV–Vis	Ultraviolet–Visible
VBM	Valence Band Maximum
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction