(Revised 07/09)

RGC Ref.: N_HKU 705/10 NSFC Ref. : 51061160500
(please insert ref. above)

NSFC/RGC Joint Research Scheme
Joint Completion Report

(Please attach a copy of the completion report submitted to the NSFC by the Mainland researcher)

Part A: The Project and Investigator(s)

1. Project Title

Development of Functional Transition Metal Supramolecules For the Fabrication of Dye-Sensitized Photovoltaic Cells by Self-Assembly Method

2. Investigator(s) and Academic Department/Units Involved

	Hong Kong Team	Mainland Team
Name of Principal Investigator *(with title)*	Prof. Wai Kin Chan	Prof. Yuping Dong
Post	Professor	Professor
Unit / Department / Institution	Department of Chemistry The University of Hong Kong	College of Materials Science and Engineering Beijing Institute of Technology
Co-investigator(s) *(with title)*	Dr. Aleksandra B. Djurišić	Dr. Bin Tong Dr. Junge Zhi

3. Project Duration

	Original	Revised	Date of RGC/ Institution Approval *(must be quoted)*
Project Start date	Jan 1, 2011		
Project Completion date	Dec 31, 2013		
Duration *(in month)*	36		

recorded

Part B: The Completion Report

5. Project Objectives

5.1 Objectives as per original application

1. To synthesize different functional conjugated molecules with diazonium groups. The functional molecules include mono and polyfunctional pyridyl complexes, charge transport units, and other organic/organometallic photosensitizing molecules.
2. To functionalize the surface of various inorganic semiconductors nanostructures by the diazonium salts synthesized, and to construct organic-inorganic hybrid multilayers with direct connection between the π-system of the dye molecules synthesized and metal oxide surface by using layer-by-layer deposition techniques. The electrochemical, photophysical, and other physical properties of the multilayers will be investigated.
3. To fabricate dye sensitized solar cells using the functional multilayers prepared, and to optimize the device fabrication conditions.
4. To characterize the performance of the devices fabricated. The device performances will be optimized by varying the deposition conditions and investigating the fundamental photophysical properties of the materials prepared.

5.2 Revised Objectives

N/A.

6. Research Outcome

Major findings and research outcome
(maximum 1 page; please make reference to Part C where necessary)

The functionalization of the surface of inorganic metal oxides has been a very interesting area because it is possible to modify the electronic or photophysical properties of the metal oxides, which can be either semiconducting or conducting materials. The operation of dye-sensitized solar cells is based on this principle, in which a layer of photosensitizing molecules was anchored on the surface of a semiconducting metal oxide. Due to the fact that only one single layer of molecules is introduced on the substrate surface, the materials are also ideal model systems for the investigation of the photophysical or other electronic processes occurred at the organic-inorganic interfaces. We have synthesized different diazo-substituted compounds for the surface functionalization of various metal oxides. They include bis(diazonium) substituted biphenyl and phenylpyridine derivatives. These compounds served as the linker between the metal oxide surface or as the surface modifying reagents.

These molecules were adopted in the fabrication of self-assembled multilayered on ITO substrate surface. The generation of photocurrent upon light irradiation was monitored. The bis(diazonium) biphenyl was used as a linker that connected a substrate surface with horizontally aligned zinc oxide nanorods. The molecules developed were then used in the functionalization of ZnO surface, which is another interesting semiconductor. However, ZnO is not stable in a strongly acidic or basic environment. We developed a new approach by which the functionalization of the diazonium substituted molecules were incorporated in organic medium. This is quite different from the reported procedure for the functionalization of TiO_2 or ITO surfaces [unpublished results].

The functionalized of TiO_2 was also achieved by using metal containing polymers. The conjugated polymers consisted of heteroleptic ruthenium complexes. The ligands on the ruthenium center were modified in order to tune the optical absorption properties of the resulting polymers. The absorption energy of the polymer can be tuned by changing the ancillary ligands so that photos in the near IR region could be harvested more efficiently [Ref 1].

In order to have a better understanding in the performance of different dyes in DSSCs, we have studied the dynamics of the photo-induced electron transfer process by ultrafast spectroscopy. The work was done in collaboration with Prof. D. L. Phillips of the University of Hong Kong. A series of donor-acceptor organic dyes was synthesized [Ref 2]. These dye molecules are introduced onto different

semiconductor surface (ZnO, TiO_2) and the lifetimes of the excited states after photoexcitation were monitored by transient fluorescence and absorption spectroscopies. The experimental data obtained will be very important for us to study the ultrafast spectroscopic properties of dyes introduced through diazo linkage in this project. Based on the experimental setup developed, we also attempted to investigate the electronic interactions between organic dye and carbon nanotube. It was found that the carbon nanotube surface could strongly influence the excited state properties of the organic molecules, even though they were anchored by non-covalent interaction [Ref 3].

Four postgraduate students have been involved in this project. Two of them (one M.Phil. and one Ph.D) have already graduated, and the other two students (both are Ph.D. candidates) are expected to graduate later this year.

Potential for further development of the research and the proposed course of action *(maximum half a page)*

We would like to investigate the feasibility of using this process to functionalize more variety of metal complexes and organic dyes on different kind of inorganic semiconductors. For example, group III-V semiconductors based on nitrides, phosphides, and arsenides will be very interesting materials for further studies. Some of them are known to be very robust and resistant to surface modification. In addition, the detailed photophysical processes at the organic-inorganic interfaces can be studied in more detail by using ultrafast spectroscopic techniques.

7. The Layman's Summary

(describe in layman's language the nature, significance and value of the research project, in no more than 200 words)

The introduction of organic molecules to the surface of inorganic materials has been a very interesting topic both from scientific and practically perspectives. It is possible to modify the electronic and optical properties of the inorganic substrate by depositing functional organic molecules on the surface, even though the thickness is only one layer of molecule. In this work, we have developed a new approach to deposit different functional metal complexes/molecules on the surface of semiconducting/conducting metal oxide surfaces, including TiO_2, ZnO, and ITO. The molecules are linked to the surface by strong covalent bonds, resulting in a strong electronic interaction between the organic and inorganic species. State-of-the-art spectroscopic techniques were employed to investigate the fundamental photophysical processes occurred in these materials. Photovoltaic cells based on the materials developed were fabricated. The results obtained in this project help us to understand the details of some basic electronic processes, and are useful for the design of new materials for energy conversion.

Part C: Research Output

8. Peer-reviewed journal publication(s) arising directly from this research project

(Please attach a copy of each publication and/or the letter of acceptance if not yet submitted in the previous progress report(s). All listed publications must acknowledge RGC's funding support by quoting the specific grant reference.))

The Latest Status of Publications				Author(s) *(**bold** the authors belonging to the project teams and denote the corresponding author with an asterisk*)*	Title and rnal/Book *(with the volume, pages and other necessary publishing details specified)*	Submitted to RGC *(indicate the year ending of the relevant progress report)*	Attached to this report *(Yes or No)*	Acknowled ged the support of this Joint Research Scheme *(Yes or No)*
Year of publication	Year of Acceptance *(For paper accepted but not yet published)*	Under Review	Under Preparation *(optional)*					
2012				W. K. Cheung, C. S. K. Mak, W. K. Chan*	"Heteroleptic Ruthenium(II) Complex Containing Polymers and Their Bandgap Tuning and Photosensitizing Properties" –*Macromol. Rapid Commun.* **2012**, *33*, 585	2012	Yes	Yes
2013				L.H. Yu, J. Y. Xi, H. T. Chan, T. Su, L. J. Antrobus, B. Tong, Y.P. Dong, W.K. Chan, D.L. Phillips	"Novel organic D–π-2A sensitizers for dye sensitized solar cells and its electron-transfer kinetics on TiO_2 surface" *J. Phys. Chem. C* **2013**, *117*, 2041.	2014	Yes	Yes
2013				L. H. Yu, K. C. Lo, J. Y. Xi, D. L. Phillips, W. K. Chan	"Photo-induced electron transfer in a pyrenylcarbazole containing polymer-multiwalled carbon nanotube composite" *New J. Chem.* **2013**, *37*, 1833.	2014	Yes	Yes

9. Recognized International conference(s) in which paper(s) related to this research project was/were delivered *(Please attach a copy of each delivered paper)*

Month/Year/ Place	Title	Conference Name	Submitted to RGC *(indicate the year ending of the relevant progress report)*	Attached to this report *(Yes or No)*	Acknowledged the support of this Joint Research Scheme *(Yes or No)*
September 2011 Dublin, Ireland	Metal Containing Block Copolymer-Carbon Nanotube Composites For Photovoltaic Applications (Invited Talk)	12th International Conference-Organic Nonlinear Optics and Organic Photonics and Electronics	2011	Yes	Yes
April 2013 New Orleans, USA	Synthesis of block copolymer-carbon nanotube composites and study of photo-induced electron transfer processes	245th American Chemical Society National Meeting	2014	Yes	Yes
June 2013 Pisa, Italy	Carbon Nanotubes Functionalized With Metal Containing Block Copolymers and Their Applications in Optoelectronics	European Polymer Congress 2013	2014	Yes	Yes

10. Student(s) trained *(Please attach a copy of the title page of the thesis.)*

Name	Degree registered for	Date of registration	Date of thesis submission/ graduation
Mr. Wai Kei Cheung	M.Phil.	September 1, 2009	August 2011
Mr. Hung Tat Chan	Ph.D.	September 1, 2007	August 2011
Miss Lihong Yu	Ph.D.	September 1, 2010	Thesis to be submitted in April 2014
Mr. Kin Cheung Lo	Ph.D.	September 1, 2010	Thesis to be submitted in August 2014

11. Other impact *(e.g. award of patents or prizes, collaboration with other research institutions, technology transfer, etc.)*

N. A.