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The Research Grants Council of Hong Kong
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

Metal/Oxide Nanostructures as Plasmonic Catalysts for the Synthesis of Organic Molecules
金屬/氧化物納米結構作為合成有機分子的表面等離子體共振催化劑的研究

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

	Hong Kong Team	Mainland Team
Name of Principal Investigator *(with title)*	Prof. WANG Jianfang	Prof. YAN Chun-Hua
Post	Professor	Professor
Unit / Department / Institution	Physics/CUHK	Chemistry/PKU
Contact Information	Room G9, Science Center North Block Department of Physics The Chinese University of Hong Kong Shatin, Hong Kong SAR	292 Cheng Fu Road College of Chemistry and Molecular Engineering Peking University Hai Dian District, Beijing 100871, Beijing
Co-investigator(s) *(with title and institution)*		Prof. SUN Ling-Dong Chemistry/PKU

3. Project Duration

	Original	Revised	Date of RGC/ Institution Approval *(must be quoted)*
Project Start date	1 Jan. 2015		
Project Completion date	31 Dec. 2018		

Duration *(in month)*	48		
Deadline for Submission of Completion Report	31 Dec. 2019		

Part B: The Completion Report

5. Project Objectives

5.1 Objectives as per original application

1. Synthesize colloidal (metal nanocrystal core)/(oxide semiconductor shell) nanostructures.
2. Understand the plasmon-induced hot-electron injection behavior in the core/shell nanostructures.
3. Understand the plasmonic photocatalytic activity of the core/shell nanostructures in organic transformation.

4. Find out the correlation between the plasmon-induced hot-electron injection behavior and the plasmon-enhanced photocatalytic activity in the core/shell nanostructures.
5. Explore the plasmon-induced hot-hole injection and its role for plasmon-enhanced catalytic reactions by coating p-type semiconductor shell.
6. Design colloidal (metal core)/(semiconductor shell)nanostructures as high-performance versatile plasmonic photocatalysts for different chemical reactions.

5.2 Revised Objectives

Date of approval from the RGC: ____________________

Reasons for the change: ____
____

1.
2.
3. ....

6. Research Outcome

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

The major findings and research outcome for this project are summarized below. (i) We developed chemical methods for the synthesis of a variety of colloidal plasmonic metal nanocrystals, including (metal core)@(semiconductor shell) nanostructures, porous Au nanoparticles (Output No. 6: *Nanoscale* **2018**, *10*, 18473), Au nanocrystals site-selectively deposited with Pd, Pt (Output No. 2: *Adv. Funct. Mater.* **2017**, *27*, 1700016; Output No. 3: *J. Am. Chem. Soc.* **2017**, *139*, 13837) and

CeO_2 (Output No. 9: *J. Am. Chem. Soc.* **2019**, *141*, 5083). These nanocrystals and nanostructures enable us to study and understand the role of localized plasmons in driving chemical transformations for both solar-to-fuel production and organic synthesis.
(ii) We found that plasmonic hot holes require to be neutralized so that plasmonic hot electrons can drive chemical reactions in a sustainable way (Output No. 1: *ACS Appl. Mater. Interfaces* **2017**, *9*, 2560). Otherwise hot electrons will be pulled back by hot holes and get recombined in the metal nanocrystal, without injecting into the semiconductor or participating in any reaction. In this regard, care must be taken when (metal core)@(semiconductor shell) nanostructures are designed for the use of plasmons to drive chemical reactions. When one type of plasmonic charge carriers is consumed in the reaction, the other type must be consumed to allow for the reaction to continue.
(iii) An all-inorganic catalyst, mimicking the functions of the two major proteins in nitrogenases, was designed by depositing Au nanocrystals on ultrathin TiO_2 nanosheets with oxygen vacancies (Output No. 4: *J. Am. Chem. Soc.* **2018**, *140*, 8497). The catalyst accomplishes high-efficiency photodriven N_2 fixation in a "working-in-tandem" manner at room temperature and atmospheric pressure under visible light. The oxygen vacancies on the TiO_2 nanosheets act as activation sites to adsorb N_2 molecules and reduce the activation barrier, while the Au nanocrystals provide electrons through plasmon excitation. A similar structure was also designed by depositing Au nanocrystals on graphitic carbon nitride nanosheets for photocatalytic H_2 generation (Output No. 5: *Phys. Chem. Chem. Phys.* **2018**, *20*, 22296). Moreover, we further realized N_2 photofixation under near-infrared light by depositing site-selectively CeO_2 on Au nanorods (Output No. 9: *J. Am. Chem. Soc.* **2019**, *141*, 5083).
(iv) We showed that the deposition of catalytic materials at the hot spot sites on Au nanocrystals can lead to higher photocatalytic activities. This was realized by selectively depositing Pd at the ends of Au nanobipyramids for Suzuki coupling reactions (Output No. 2: *Adv. Funct. Mater.* **2017**, *27*, 1700016) and CeO_2 at the ends of Au nanorods for N_2 photofixation (Output No. 9: *J. Am. Chem. Soc.* **2019**, *141*, 5083). We reasoned that the local electromagnetic field enhancement at the hot spots is larger, which causes the generation of more hot electrons and therefore higher photocatalytic activities. More experimental and theoretical investigations will be required to further confirm this point.
(v) We contributed an invited progress report on the use of localized plasmons to drive chemical transformations (Output No. 7: *Adv. Mater.* **2018**, *30*, 1802227).

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

We have shown in this project that localized plasmons can be used to drive various chemical reactions. Plasmon excitation can generate hot charge carriers, which can enable and accelerate reactions under proper conditions. In traditional semiconductor photocatalysts, hot charge carriers are generated through the excitation of photons with energies larger than the bandgap of the semiconductor.

The bandgap is fixed for a given semiconductor. Plasmon excitation offers a new means for the generation of hot charge carriers. An extremely attractive feature of plasmon-driven generation of hot charge carriers is that the plasmon energy of noble metal nanocrystals can be synthetically controlled over the entire solar spectral range. The control of the plasmon energy is much facile than the variation of the bandgap energy of a semiconductor. We think that there are two major future developments along the direction of this project. One is the deep understanding of the rich involved processes, including plasmon excitation, plasmon decay, charge carrier generation and separation, charge carrier transfer, and redox reactions. This is not an easy task because it requires the knowledge from inorganic chemistry, electromagnetism, optics, solid state physics, semiconductor physics, physical chemistry and organic chemistry. The other is the dramatic improvement of the catalytic activities of plasmonic photocatalysts for different reactions towards the practically useful level through the careful systematic design and development based on the fundamental understanding. Although much understanding on the separate aspects of this topic has been achieved, a tremendous amount of effort is still required to gain an integrated, complete picture.

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)

Localized plasmons are associated with noble metal nanoparticles. They refer to the collective oscillations of nearly free electrons in noble metal nanoparticles. The plasmon energy can be synthetically varied over a wide range from the ultraviolet to the infrared region by changing the composition, shape, size, and environment. Plasmonic nanoparticles can interact extremely strongly with light. Upon excitation, they can cause enormous electromagnetic field enhancement in the nanoscale region around them. They can generate hot charge carriers, including electrons and holes, which possess energies above their equilibrium values. Plasmon excitation offers a new means for the photogeneration of hot charge carriers for driving a variety of chemical reactions for solar-to-fuel conversion and green organic synthesis. In contrast, the photogeneration of hot charge carriers in semiconductors requires photons with energies larger than the bandgap. In this project, we synthesized different types of metal and metal-semiconductor nanostructures and realized the plasmonic driving of chemical reactions. The studied reactions include Suzuki coupling, selective aerobic oxidation of alcohols, N_2 phtofixation, and water splitting. Decent photocatalytic activities and the understanding of the mechanisms to a certain degree are achieved for these reactions under ultraviolet and visible light.

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 Journal/ 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)	Acknowledged the support of this Joint Research Scheme (Yes or No)	Accessible from the institutional repository (Yes or No)
Year of publication	Year of Acceptance (For paper accepted but not yet published)	Under Review	Under Preparation (optional)						
2016 (No. 1)				Feng Qin, Tian Zhao, Ruibin Jiang, Nina Jiang, Qifeng Ruan, **Jianfang Wang***, **Ling-Dong Sun***, **Chun-Hua Yan***, Hai-Qing Lin	Thickness Control Produces Gold Nanoplates with Their Plasmon in the Visible and Near-Infrared Regions, Advanced Optical Materials, vol 4, pp 76-85.	No	Yes	No	Yes
2017 (No. 2)				Henglei Jia, Xiao-Ming Zhu, Ruibin Jiang, **Jianfang Wang***	Aerosol-Sprayed Gold/Ceria Photocatalyst with Superior Plasmonic Hot Electron-Enabled Visible-Light Activity, ACS Applied Materials & Interfaces, vol 9, pp 2560-2571.	Yes, 2016	Yes	Yes	Yes

2017 (No. 3)				Xingzhong Zhu, Henglei Jia, Xiao-Ming Zhu, Si Cheng, Xiaolu Zhuo, Feng Qin, Zhi Yang,* **Jianfang Wang***	Selective Pd Deposition on Au Nanobipyramids and Pd Site-Dependent Plasmonic Photocatalytic Activity, Advanced Functional Materials, vol 27, 1700016, 15 pages.	No	Yes	Yes	Yes
2017 (No. 4)				Xingzhong Zhu, Hang Kuen Yip, Xiaolu Zhuo, Ruibin Jiang, Jianli Chen, Xiao-Ming Zhu, Zhi Yang,* **Jianfang Wang***	Realization of Red Plasmon Shifts up to ~900 nm by AgPd-Tipping Elongated Au Nanocrystals, Journal of the American Chemical Society, vol 139, pp 13837-13846.	No	Yes	Yes	Yes

2018 (No. 5)				Jianhua Yang, Yanzhen Guo, Ruibin Jiang, Feng Qin, Han Zhang, Wenzheng Lu, **Jianfang Wang***, Jimmy C. Yu	High-Efficiency "Working-in-Tandem" Nitrogen Photofixation Achieved by Assembling Plasmonic Gold Nanocrystals on Ultrathin Titania Nanosheets, Journal of the American Chemical Society, vol 140, pp 8497-8508.	No	Yes	Yes	Yes
2018 (No. 6)				Yanzhen Guo, Henglei Jia, Jianhua Yang, Hang Yin, Zhi Yang,* **Jianfang Wang***, Baocheng Yang	Understanding the Roles of Plasmonic Au Nanocrystal Size, Shape, Aspect Ratio and Loading Amount in Au/g-C_3N_4 Hybrid Nanostructures for Photocatalytic Hydrogen Generation, Physical Chemistry Chemical Physics, vol 20, pp 22296-22307.	No	Yes	Yes	Yes

2018 (No. 7)				Jinhui Hu, Ruibin Jiang,* Han Zhang, Yanzhen Guo, Jing Wang, **Jianfang Wang***	Colloidal Porous Gold Nanoparticles, Nanoscale, vol 10, pp 18473-18481.	No	Yes	Yes	Yes
2018 (No. 8)				Jianhua Yang, Yanzhen Guo, Wenzheng Lu, Ruibin Jiang,* **Jianfang Wang***	Emerging Applications of Plasmons in Driving CO_2 Reduction and N_2 Fixation, Advanced Materials, vol 30, 1802227, 21 pages.	No	Yes	Yes	Yes
2019 (No. 9)				Yanzhen Guo, Xingzhong Zhu, Nannan Li, Jianhua Yang, Zhi Yang,* **Jianfang Wang***, Baocheng Yang	Molecular Sensitivities of Substrate-Supported Gold Nanocrystals, The Journal of Physical Chemistry C, vol 123, pp 7336-7346.	No	Yes	Yes	Yes

2019 (No. 10)				Henglei Jia, Aoxuan Du, Han Zhang, Jianhua Yang, Ruibin Jiang,* **Jianfang Wang***, Chun-yang Zhang*	Site-Selective Growth of Crystalline Ceria with Oxygen Vacancies on Gold Nanocrystals for Near-Infrared Nitrogen Photofixation, Journal of the American Chemical Society, vol 141, pp 5083-5086.	No	Yes	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. All listed papers must acknowledge RGC's funding support by quoting the specific grant reference.)*

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)*	Accessible from the institutional repository *(Yes or No)*
December/2015/Honolulu, Hawaii, USA (No. 11)	Colloidal Plasmonic Metal Nanocrystals	The International Chemical Congress of Pacific Basin Societies (PacifiChem 2015)	Yes, 2016	Yes	Yes	No
August/2016/Philadelphia, Pennsylvania, USA (No. 12)	Colloidal Plasmonic Nanocrystals	252nd American Chemical Society National Meeting & Exhibition	Yes, 2016	Yes	Yes	No

October/2017/Washington, DC/National Harbor, Maryland, USA (No. 13)	Plasmonic Driving of Chemical Reactions	232th Electrochemical Society (ECS) Meeting	No	Yes	Yes	No
August/2018/Boston, Massachusetts, USA (No. 14)	Anisotropic Plasmonic Light Scattering	256th ACS National Meeting & Exhibition	No	Yes	Yes	No

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
YANG Jianhua (No. 15)	PhD	August 2015	September 2018
YIP Hang Kuen (No. 16)	PhD	August 2014	July 2018

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

The collaborations with three research groups from the mainland have been established. They are listed below.
(i) Prof. YANG Zhi from the Department of Micro/Nano Electronics of Shanghai Jiao Tong University.
(ii) Prof. JIANG Ruibin from the School of Materials Science and Engineering of Shaanxi Normal University.
(iii) Prof. ZHANG Chun-yang from the College of Chemistry, Chemical Engineering and Materials Science of Shandong Normal University.