RGC Ref.: M-CUHK410/12
(please insert ref. above)

The Research Grants Council of Hong Kong
SRFDP & RGC ERG Joint Research Scheme
Completion Report

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

Part A: The Project and Investigator(s)

1. Project Title

A Gold Nanoplate-Based Plasmonic Platform for Sensing and Photoswitching Applications

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/The Chinese University of Hong Kong	College of Chemistry and Molecular Engineering/Peking University
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Co-investigator(s) *(with title and Institution)*		
PhD student(s) (with period of involvement)	Name: Mr. TAO Yuting (changed from PhD to MPhil study)/Mr. QIN Feng (PhD student, later added) Institution: CUHK/CUHK Period from March 1, 2013 / Aug. 1, 2013 to Nov. 15, 2014 / Feb. 29, 2016	Name: Mr. XIAO Jia-Wen (PhD student) Institution: PKU Period from March 1, 2013 to June 30, 2015

Note: The Hong Kong project team must involve at least one research postgraduate student pursuing a Doctor of Philosophy degree at the UGC-funded university (PhD student) at any time throughout the project period.

3. Project Duration

	Original	Revised	Date of RGC/ Institution Approval *(must be quoted)*
Project Start date	March 1, 2013		
Project Completion date	Feb. 29, 2016		
Duration *(in month)*	36		
Deadline for Submission of Completion Report	Feb. 28, 2017		

Part B: The Completion Report

5. Project Objectives

5.1 Objectives as per original application

1. Grow Au nanoplates with varying sizes and shapes in high yields;
2. Develop methods for depositing Au nanoplates on substrates in large areas at varying surface densities reproducibly;
3. Study the configuration-dependent plasmon coupling behaviors in Au nanoplate/nanosphere and Au nanoplate/nanorod heterodimers;
4. Demonstrate biological sensing with Au nanoplate/nanosphere structures;
5. Fabricate photoswitches with Au nanoplate/azobenzene/Au nanosphere (or Au nanorod) hybrid structures.

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)

There are 5 major findings out of this project.

First, we developed a method for the synthesis of Au nanoplates with different shapes, lateral sizes and thicknesses (*Advanced Optical Materials* **2016**, *4*, 76). The thickness can be varied in the range of 10–50 nm. The plasmon wavelength can be tailored from the near-infrared region to the visible region. In most previous related studies, the thickness of Au nanoplates is uncontrollable, the lateral size is very large, and the plasmon resonance is in the near-infrared region. Due to their particular geometrical structure, Au nanoplates possess unusual optical properties. Their sharp corners and straight edges offer large electric field enhancements. Their crystalline nature, which enables low plasmon damping, and large-area atomically flat surfaces make them attractive for constructing plasmon-based optical devices as well as creating meta-surfaces with controllable light transmission and reflection. Our synthetic method therefore opens a way to the use of Au nanoplates in developing ultrasensitive plasmonic sensors and other plasmon-based devices that work in the visible and near-infrared regions.

Second, we developed a method for the purification of Au nanobipyramids, with the number yields reaching 100% (*Advanced Optical Materials* **2013**, *3*, 81). Au nanobipyramids have several attractive plasmonic features. Their sizes are extremely uniform. They have two very sharp tips with extremely large electric field enhancements. Their refractive index sensitivities are very high. Moreover, similar to Au nanorods, the longitudinal plasmon resonance of Au nanobipyramids can be controlled from the visible to near-infrared region. We are the first in producing such highly pure Au nanobipyramids. Our method relies on a stepwise combination of seed-mediated growth, Ag overgrowth, depletion force-induced self-separation, and final chemical etching of Ag. Systematic experimental comparison showed that Au nanobipyramids are superior to Au nanorods in terms of the plasmon peak width, refractive index sensitivity, figure of merit, two-photon photoluminescence, and surface-enhanced Raman scattering.

Third, we developed a method for coating polyaniline on Au nanocrystals and realized active plasmon switching (*Advanced Materials* **2014**, *26*, 3282). Polyaniline is a conducting polymer. Its dielectric function can be varied dramatically by proton doping or electrochemical potential. By proton-doping and dedoping the polyaniline shell, we demonstrated the switching of the localized plasmon of Au nanorods and nanospheres with reversible plasmon shifts over 100 nm and modulation depths over 10 dB. Our polyaniline-coated Au nanocrystals will find intriguing applications in areas such as smart windows/mirrors, information displays, anti-counterfeiting inks, and pH-responsive photothermal systems for cancer therapy.

Fourth, we synthesized bimetallic Au/Pd nanostructures on the basis of Au nanorods and demonstrated ultrasensitive hydrogen sensing by depositing the bimetallic nanostructures on transparent glass slides (*Advanced Functional Materials* **2014**, *24*, 7328). Palladium can interact reversibly with hydrogen in a unique way through the formation of palladium hydride, leading to large changes in the dielectric function. As a result, the plasmon peak of the bimetallic nanostructure red-shifts in the presence of hydrogen and shifts back when hydrogen is removed. The plasmon shift is strongly dependent on the concentration of hydrogen in the gaseous environment.

Fifth, in collaboration with a team from Sun Yat-sen University, we fabricated arrays of submicrometer gold mushrooms with a sensing figure of merit reaching 108, which is the theoretically predicted upper limit for standard propagating surface plasmon resonance sensors (*Nature Communications* **2013**, *4*, 2381). The high figure of merit was understood to arise from the interference between Wood's anomaly and localized plasmon resonance modes. Our plasmonic array sensors are a promising candidate for label-free biomedical sensing.

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

Among the results out of this project, there are three aspects that are worthy of further development. **The first** is the successful synthesis of circular Au nanoplates with controllable diameters and thicknesses. Three-dimensional Au nanospheres have played a central role in the development of the field of nanoplasmonics, because of their spherical symmetry, easy assembly into superstructures at different size scales, and the existence of analytical solutions to Maxwell's equations for spherical particles. Circular Au nanoplates can be treated as the pseudo-two-dimensional counterparts to three-dimensional Au nanospheres. The availability of high-quality circular Au nanoplates is expected to stimulate the study of their physical and chemical properties as well as the exploration of their technological applications. **The second** is the rich Fano resonance behaviors exhibited by Au nanoplate-based heterostructures. The Fano resonance is highly dependent on the geometry, size, relative position, the polarization of the excitation light, and the dielectric function of the supporting substrate. Fano resonance is nearly a universal phenomenon in many sub-fields of physics. It also has important scientific and technological applications, such as electromagnetically induced transparency for slowing or even stopping light. Our results on the Fano resonance in Au nanoplate-based heterostructures will greatly stimulate the exploration of Fano resonance for ultrasensitive sensing, surface-enhanced spectroscopy, nonlinear optics and active plasmon switching. **The third** is the coating of a conducting polymer, polyaniline, on colloidal Au nanocrystals for the realization of active plasmon switching. Compared with those demonstrated in previous works, our plasmonic switches exhibit a superior switching performance in both the modulation depth and plasmon shift. We expect that out method can also be applied to many other plasmonic nanostructures to achieve even better switching performances. We are currently working actively on all of these aspects.

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)

In this project, we have successfully made gold nanoplates, which can be triangular, hexagonal or circular. The lateral size can be varied from ~100 nm to several micrometers, and the thickness can be adjusted from ~10 nm to ~50 nm. These nanoplates exhibit intense plasmon resonance, which is collective oscillation of conduction-band electrons. At the plasmon resonance energy, these nanoplates possess many interesting optical properties. They can absorb or scatter light strongly; they can focus light into nanoscale spatial volumes; their plasmon resonance peak is extremely sensitive to the surrounding environment. Therefore, these nanoplates can have many applications in optics, spectroscopy, sensing, imaging, medical diagnostics and therapy. The unique plate geometry of Au nanoplates can greatly facilitate their deposition on flat substrates and assembly with other molecular species. Therefore, Au nanoplates are particularly appealing for various plasmonic applications. Because different applications often work at different light wavelengths, Au nanoplates having different plasmon resonance wavelengths will be strongly desirable. By synthetically controlling their sizes, we can tailor the plasmon resonance wavelength of Au nanoplates. This is the key motivation for and the greatest achievement from our project.

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)*						
2013				Yang Shen, Jianhua Zhou, Tianran Liu, **Yuting Tao**, Ruibin Jiang, Mingxuan Liu, Guohui Xiao, Jinhao Zhu, Zhang-Kai Zhou, Xuehua Wang, Chongjun Jin*, **Jianfang Wang***	Plasmonic gold mushroom arrays with refractive index sensing figures of merit approaching the theoretical limit, Nature Communications, 2013, 4, 2381 (1 - 9)	2014	Yes	Yes	No
2014				Nina Jiang, Lei Shao, **Jianfang Wang***	(Gold nanorod core)/(polyaniline shell) plasmonic switches with large plasmon shifts and modulation depths, Advanced Materials, 2014, 26, 3282 - 3289	2014	Yes	Yes	No

2014				Ruibin Jiang, **Feng Qin**, Qifeng Ruan, **Jianfang Wang***, Chongjun Jin*	Ultrasensitive plasmonic response of bimetallic Au/Pd nanostructures to hydrogen, Advanced Functional Materials, 2014, 24, 7328 - 7337	2016	Yes	Yes	No
2015				Qian Li, Xiaolu Zhuo, Shuang Li, Qifeng Ruan, Qing-Hua Xu, **Jianfang Wang***	Production of monodisperse gold nanobipyramids with number percentages approaching 100% and evaluation of their plasmonic properties, Advanced Optical Materials, 2015, 3, 801 - 812	2016	Yes	Yes	No
2015				Nina Jiang, Qifeng Ruan, **Feng Qin**, **Jianfang Wang***, Hai-Qing Lin	Switching plasmon coupling through the formation of dimers from polyaniline-coated gold nanospheres, Nanoscale, 2015, 7, 12516 - 12526	2016	Yes	Yes	No

2015				Yang Shen, Tianran Liu, Qiangzhong Zhu, **Jianfang Wang**, Chongjun Jin	Dislocated double-layered metal gratings: refractive index sensors with high figure of merit, Plasmonics, 2015, 10, 1489 - 1497	2016	Yes	Yes	No
2016				**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, 2016, 4, 76 - 85	2016	Yes	Yes	No

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)*
3/2014/Dallas	Effect of surface coatings on the cytotoxicity and cellular uptake of gold nanorods	247th ACS National Meeting & Exhibition, Website: https://www.acs.org/content/acs/en/meetings/nationalmeetings/programarchive.html	2016	Yes	Yes	No

12/2014/Boston	Bimetallic nanostructures and their plasmonic properties	2014 MRS Fall Meeting & Exhibit, Website: https://www.mrs.org/Fall2014	2016	Yes	Yes	No
12/2015/Honolulu	Colloidal plasmonic metal nanocrystals	2015 International Chemical Congress of Pacific Basin Societies (2015 PacifiChem), website: http://www.pacifichem.org/	2016	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
Mr. TAO Yuting	PhD (transformed into MPhil in 2014)	August 2012	April 2015
Mr. QIN Feng	PhD	August 2013	July 2016

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

None