Design of metallic nanostructures for plasmonics based applications : chemo/biosensing, solar evaporation, and photocatalysis

Zhang, Lulu

2018

Zhang, L. (2018). Design of metallic nanostructures for plasmonics based applications : chemo/biosensing, solar evaporation, and photocatalysis. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/75422>

<https://doi.org/10.32657/10356/75422>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**Design of Metallic Nanostructures for Plasmonics
Based Applications: Chemo/Biosensing, Solar
Evaporation, and Photocatalysis**

Lulu Zhang

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2018

Design of Metallic Nanostructures for Plasmonics Based Applications: Chemo/Biosensing, Solar Evaporation, and Photocatalysis

Lulu Zhang

Division of Physics and Applied Physics

School of Physical and Mathematical Sciences

A thesis submitted to the Nanyang Technological University

in fulfilment of the requirement for the degree of

Doctor of Philosophy

2018

For my parents
and
my wife Houjuan Zhu.

ACKNOWLEDGEMENTS

As my Ph.D. study in NTU is approaching the end, herein, I would like to convey my sincere gratitude to my supervisor Prof. Xiong Qihua, for his generous support and continual guidance throughout my doctoral research. With the patient help and the systematic academic training offered by Prof. Xiong, I have learned how to be a professional researcher in doing research, which I believe it will also benefit me a lot in my future academic career. He has set me an example of a professional researcher, whose diligent, aggressive, rigorous attitude and enthusiasm in research has motivated me to pursue higher academic achievement.

Thanks to Dr. Cao Cuong at Queen's University Belfast for the precious advice and patient discussions on my first manuscript revision and submission. Appreciations to Dr. Xing Jun for his constant willingness in sharing exciting research ideas and useful material synthesis skills. Thanks to Dr. Zhang Jun, Dr. Xu Weigao, Dr. Wen Xinglin, Dr. Zhao Yanyuan for the meticulous instrument training.

I would also like to take this chance to acknowledge other group members and all of my friends for their kind help in the past few years, especially Dr. Yu Huakang, Dr. Zhang Qing, Dr. Yuan Yanwen, Dr. Lu Xin, Dr. Wang Xingzhi, Dr. Ye Huanqing, Dr. Peng Bo, Dr. Zhao Weijie, Dr. Zhang Chaohua, Su Rui, Bao Di, Zhao Jiaxin, Liu Sheng. I really appreciate that they can share with me good ideas and provide useful suggestions when I am suffering from the bottleneck in my research.

Last but not least, I would like to express my deepest gratitude to my beloved family for their wholehearted dedication and unconditional love. Thanks to my wife Dr. Zhu Houjuan for her unwavering understanding and support, which inspires me to overcome the hardship and be a better man.

List of Publications

Journal Papers

1. **Lulu Zhang**, Jun Xing, Xinglin Wen, Jianwei Chai, Shijie Wang and Qihua Xiong, Plasmonic heating from indium nanoparticles on a floating microporous membrane for enhanced solar seawater desalination”, *Nanoscale*, 2017, 9, 12843-12849.
2. Yuyan Jiang, Paul Kumar Upputuri, Chen Xie, Yan Lyu, **Lulu Zhang**, Qihua Xiong, Manojit Pramanik, and Kanyi Pu, Broadband absorbing semiconducting polymer nanoparticles for photoacoustic imaging in second near-Infrared window, *Nano Lett.*, 2017, 17, 4964-4969.
3. Hsin-Yi Wang, Sung-Fu Hung, Ying-Ya Hsu, **Lulu Zhang**, Jianwei Miao, Ting-Shan Chan, Qihua Xiong and Bin Liu, In situ spectroscopic identification of μ -OO bridging on spinel Co_3O_4 water oxidation electrocatalyst, *J. Phys. Chem. Lett.*, 2016, 7, 4847-4853.
4. **Lulu Zhang**, Yanwen Yuan, Xinglin Wen, Yue Li, Cuong Cao and Qihua Xiong, A coordination and ligand replacement based three-input colorimetric logic gate sensing platform for melamine, mercury ions, and cysteine, *RSC Adv.*, 2015, 5, 59106-59113.
5. Yanwen Yuan, **Lulu Zhang**, Jun Xing, M. Iqbal Bakti Utama, Xin Lu, Kezhao Du, Yongmei Li, Xiao Hu, Shijie Wang, Aziz Genç, Rafal Dunin-Borkowski, Jordi Arbiol and Qihua Xiong, High-yield synthesis and optical properties of g- C_3N_4 , *Nanoscale*, 2015, 7, 12343-12350.
6. **Lulu Zhang**, Xinglin Wen, Jun Xing, and Qihua Xiong, Tuning surface plasmon of indium nanoparticles for plasmon enhanced photocatalysis, *in preparation*.

Conference Presentations and Posters

1. **Lulu Zhang**, Xinglin Wen, Cuong Cao and Qihua Xiong, Coordination and ligand replacement based colorimetric logic gates of melamine, Hg^{2+} , and cysteine, *Nanoscience and Nanomedicine Workshop*, 2014, MSE, ER@N, NITHM, IGS and Chulalongkorn University.

2. Andres Granados del Águila, Thi Thu Ha Do, Jun Xing, Wen Jie Jee, **Lulu Zhang**, and Qihua Xiong, Efficient up-conversion photoluminescence in all-inorganic perovskite colloidal semiconductor nanocrystals, 2017, *International Conference on Materials for Advanced Technologies (ICMAT)*, Singapore.

Table of Contents

List of Tables.....	VII
List of Figures	VIII
Abstract	XVII
Chapter 1	1
Introduction.....	1
1.1 Basics of plasmonics	2
1.1.1 The origin of plasmonics	2
1.1.2 Surface plasmon polaritons and localized surface plasmon resonance	4
1.1.3 The Mie theory.....	6
1.2 Plasmonics based applications	10
1.2.1 Plasmonic colorimetric sensing based on colloid metal nanoparticles	10
1.2.2 Plasmonic passive solar desalination	16
1.2.3 Plasmonic photocatalysis	20
1.2.4 Surface-enhanced Raman scattering (SERS).....	23
1.3 Thesis Scope and Structure	26
Chapter 2.....	30
Fabrication and characterization of gold and indium nanostructures	30
2.1 Fabrication of gold and indium nanostructures.....	30
2.1.1 Synthesis and surface chemistry of Au NPs	30
2.1.2 Fabrication of indium nanostructures on different substrates	36
2.2 Characterizations of Au and In nanostructures	42
2.2.1 Transmission electron microscopy.....	42
2.2.2 Scanning electron microscopy	43
2.2.3 UV/Vis/NIR optical absorption spectroscopy.....	44

2.2.4 X-ray photoelectron spectroscopy	45
2.2.5 X-ray diffraction	47
Chapter 3	49
Controllable plasmon coupling of Au NPs induced color changes for plasmonic colorimetric logic gate sensing.....	49
3.1 Introduction	49
3.1.1 Background	49
3.1.2 Plasmonic colorimetric logic gate.....	49
3.1.3 Design of a three-input colorimetric logic gate sensing system	50
3.2 Experimental section	51
3.2.1 Plasmonic colorimetric logic gate operations by using Au NPs solutions.....	51
3.2.2 Melamine sensing	51
3.2.3 Cysteine sensing.....	52
3.2.4 Hg ²⁺ sensing.....	52
3.3 Results and discussion.....	53
3.3.1 Construction of a three-input (cysteine, melamine, and Hg ²⁺) plasmonic colorimetric logic gate based on colloid Au NPs	53
3.3.2 Logic operations in the plasmonic colorimetric sensing system	55
3.3.3 Investigation of the mechanism through UV/Vis absorption spectra evolutions induced by competing coordination reactions	59
3.3.4 Application in sensing of different analytes.....	64
3.4 Conclusion.....	70
Chapter 4.....	71
Plasmonic heating effect of In NPs and its application for enhanced solar evaporation	71
4.1 Introduction	71
4.1.1 Background	71

4.1.2 Plasmonic nanoparticles for light to heat conversion	71
4.1.3 Fabrication of a floating solar desalination device based on In NPs	72
4.2 Experimental setup	73
4.3 Results and discussion.....	74
4.3.1 Theoretical calculation of plasmonic heating ability of In NPs.....	74
4.3.2 Morphology and optical properties of In NPs on MPM	77
4.3.3 In NPs on MPM for plasmon enhanced solar evaporation	79
4.3.4 In NP/MPM for solar desalination of a real seawater sample	82
4.3.5 Stability of In NP/MPM in solar evaporation	84
4.4 Conclusion.....	87
Chapter 5	88
Near-field enhancement and LSPR induced hot carrier injection of In NPs for enhanced photocatalysis of TiO ₂ NPs	88
5.1 Introduction	88
5.1.1 Creation and transfer of charge carriers in photocatalysis	88
5.1.2 TiO ₂ in photocatalysis	89
5.1.3 In NPs for plasmonic photocatalysis.....	90
5.2 Experimental section	91
5.3 Results and discussion.....	92
5.3.1 Preparation of In NPs with different sizes on quartz substrate	92
5.3.2 Fabrication of In NPs@TiO ₂ nanostructures	93
5.3.3 Optical properties of In NPs@TiO ₂ nanostructures.....	95
5.3.4 Enhanced photodegradation of MB on In NPs@TiO ₂	97
5.3.5 Effect of In NPs sizes on In NPs@TiO ₂ on photocatalysis performance	99
5.3.6 Dependence of photocatalysis performance on excitation wavelength	100

5.3.7 Effect of a SiO ₂ dielectric layer between In NPs and TiO ₂ on photocatalysis performance	102
5.4 Conclusion.....	105
Chapter 6.....	107
Near-field enhancement of In NPs and its application for UV SERS using 325 and 355 nm Laser	107
6.1 Background	107
6.1.1 Introduction.....	107
6.1.2 UV SERS using different metals	108
6.1.3 In NPs for UV SERS.....	108
6.2 Experimental setup.....	110
6.3 Results and discussions	111
6.3.1 Comparison of near field enhancement ability of Al and In NPs	111
6.3.2 Preparation of In NPs with different sizes on ITO glass.....	113
6.3.3 Optical properties of In NPs on ITO glass	115
6.3.4 In NPs for UV SERS using 325 nm laser	116
6.3.5 Effect of In NPs sizes on UV SERS performances with 325 nm laser	118
6.3.6 Comparison between 325 and 355 nm laser excitation	120
6.3.7 Effect of a SiO ₂ dielectric layer coating on In NPs on UV SERS performance	120
6.4 Conclusions	122
Chapter 7	124
Summary and Future work.....	124
7.1 Original contribution of this thesis.....	124
7.2 Future work	126
References.....	129

List of Tables

Table 2.1 Syntheses of different Au nanostructures using different methods.	35
Table 2.2 Preparation of different In nanostructures using different methods.	39
Table 3.1 Truth table of INH, OR and AND gates based on Boolean logic operations.	57
Table 3.2 Stability constants of the complexes formed through coordination with Hg^{2+}	64

List of Figures

Figure 1.1 Schematic illustrations of SPPs and LSPR. (A) Propagating surface plasmon polaritons along the metal/dielectric interface. (B) Localized surface plasmon on a subwavelength metal nanosphere.	4
Figure 1.2 Sketch of a metal nanosphere immersed in an electrostatic field.	8
Figure 1.3 (A) Optical image of Au NPs colloid solutions upon the addition of melamine from 0 to 1.5 μM . (B) The evolution of the absorption spectra as a result of the introduced melamine. TEM images of Au NPs colloid solutions with (C) 0, (D) 1.1, and (E) 1.5 μM melamine. (F) Schematic depiction of the formation of Au NP aggregates the cross-linked by the melamine molecules.	11
Figure 1.4 Electrodynamic modeling of the evolutions of extinction spectra of Au NPs with (A) fixed particle size and different particle distances, (B) fixed particle distance and different particle sizes, and (C) fixed particle distance and different aggregate sizes.....	13
Figure 1.5 (A) Scheme of DTT, Cys, and GSH modified gold nanoparticles for arsenic detection. Photograph of Au NPs in aqueous solution modified with GSH/DTT/Cys upon addition of (B) different metal ions (5 ppb) and (C) As^{III} with different concentrations..	14
Figure 1.6 (A) Scheme of a competition format colorimetric Assay for detection of cysteine by using DNA modified Au NPs. (B) Colorimetric responses of the assay to different amino acids (1 μM) at room temperature and 50 $^{\circ}\text{C}$	15
Figure 1.7 (A) Scheme of the efficient solar steam generation with highly localized plasmonic heating effect. (B) Visible-Near-Infrared (Vis-NIR) absorption spectrum of plasmonic Au NSs. Inset is the SEM images of Au NSs.....	18
Figure 1.8 Schematic illustration of solar steam generation using floating plasmonic device to enable the evaporation at water-air interface.	19
Figure 1.9 (A) Cross-section TEM image of the Ag NPs/ SiO_2 / TiO_2 structure. (B) UV/Vis absorption spectra of bare TiO_2 film (curve a), Ag NPs/ TiO_2 (curve b), and the Ag	

NPs/SiO₂/TiO₂ structure (curve c). (C) Time dependent photo degradation of MB using bare TiO₂ film (curve a), the Ag NPs/SiO₂ (20 nm)/TiO₂ structure (curve b), and the Ag NPs/SiO₂ (5 nm)/TiO₂ structure (curve c). 21

Figure 1.10 Charge carrier generations in different systems. (A) Charge carrier in a conventional semiconducting photocatalyst. (B) Electron trapping by a metal nanoparticle (without plasmonic effect). (C) A direct electron transfer (DET) process in a plasmonic photocatalyst. (D) Plasmonic photocatalyst with local electromagnetic field (LEMF). (E) A dipole-dipole resonant energy transfer (RET) mechanism in a plasmonic photocatalyst. 23

Figure 1.11 Schematics of Stokes and anti-Stokes Raman scattering processes. 24

Figure 2.1 Cartoon showing the growth process of Au NPs in aqueous using classic Turkevich method..... 31

Figure 2.2 Schematic depiction of the Au-S bonding interaction. 33

Figure 2.3 Schematics of the intrinsic surface chemistry of solution processed Au nanostructures. 34

Figure 2.4 Diagram of components and processes involved in a thermal evaporation system. .. 40

Figure 2.5 TEM images of (A) well dispersed and (B) aggregated state Au NPs. 43

Figure 2.6 SEM images of In NPs prepared on different substrates. (A) Quartz. (B) ITO glass. (C) TiO₂ nanorod array. (D) MPM. 44

Figure 2.7 UV/Vis absorption spectra of Au NPs in solution with ~13 (A) and ~30 (B) nm sizes, and (C) In NPs prepared with different thicknesses of thermal evaporated indium. 45

Figure 2.8 (A) SEM image of In NPs prepared on MPM. (B) XPS spectrum of indium on In NP/MPM. (C) XPS spectrum of oxygen on In NP/MPM. (D) XPS spectrum of oxygen on bare MPM. 47

Figure 2.9 XRD pattern of In NPs prepared on MPM. 48

Figure 3.1 Illustration of the design principles of the three-input colorimetric logic gate. 55

Figure 3.2 TEM images of the states of ~13 nm Au NPs after the analytes (60 μM melamine, 360 μM cysteine, and 180 μM Hg^{2+}) were added with different logic combinations. All scale bars in the images are 50 nm. 55

Figure 3.3 Logic operations performed by using Au NPs solutions with different analyte combinations. (A) UV/Vis absorption spectra of Au NPs solutions with analytes (60 μM melamine, 360 μM cysteine, and 180 μM Hg^{2+}) in different logic combinations. (B) Their corresponding $A_{650\text{nm}}/A_{520\text{nm}}$ values. (C) Network map of the logic gate sensing system with logic operations. (D) The inputted and their corresponding outputted signals in this logic system. Inset displays the outputted color readouts..... 57

Figure 3.4 An illustration to show how different combinations of analytes can be discriminated. (A) Discrimination of a single kind of analyte. (B) Discrimination of the combination of two kinds of analytes. The analytes can be discriminated step by step with the help of an additional solution of Hg^{2+} when it is known that how many kinds of targeted species are in the sample solution. There will be only one case when the number of species is three, namely, the coexistence of Hg^{2+} , melamine, and cysteine. The output of this combination will always be 1, namely the formation of Au NPs aggregates, so the discrimination of this case is not needed.... 58

Figure 3.5 Competing coordination reactions induced UV/Vis absorption spectra evolutions of the analytes. (A) Hg^{2+} induced changes of UV-vis absorption spectra of 20 μM melamine. Concentration of Hg^{2+} was increased from 0 to 80 μM , (B) cysteine induced changes of UV/Vis absorption spectra of Hg^{2+} -melamine complex (60 μM Hg^{2+} + 20 μM melamine) solution. Concentration of cysteine was increased from 0 to 160 μM , (C) UV/Vis absorption spectra of cysteine alone in aqueous solution. The concentration of cysteine was increased from 40 to 160 μM , and (D) cysteine induced changes of UV/Vis absorption spectra of 60 μM Hg^{2+} . Concentration of cysteine was increased from 0 to 160 μM 60

Figure 3.6 (A) UV/Vis absorption spectra of Au NPs solution upon the addition of cysteine at the concentrations ranging from 0 to 404 μM , (B) Au NPs solution upon the addition of melamine at the concentrations ranging from 0 to 200 μM in the presence of 6 μM cysteine, (C) Au NPs

solution upon the addition of Hg^{2+} at the concentrations ranging from 0 to 60 μM in the presence of 6 μM cysteine, Au NPs solution upon the addition of (D) HCl and (E) NaOH at the concentrations ranging from 0 to 120 μM in the presence of 6 μM cysteine. These results imply that cysteine can be served as a stabilizing agent against melamine induced aggregation of Au NPs. However, this stabilizing effect will be broken when Hg^{2+} is introduced into the system at the same time. 61

Figure 3.7 Control experiments to verify the role of $-\text{SH}$ group in the logic gates. (A) Color readouts induced by melamine (60 μM) and Hg^{2+} (180 μM) with 360 μM alanine (top) and cysteine (bottom) in different combinations. (B) Alanine induced changes of UV/Vis absorption spectra of Hg^{2+} -melamine complex (60 μM Hg^{2+} + 20 μM melamine) solution. Concentration of alanine was increased from 0 to 160 μM , (C) alanine induced changes of UV/Vis absorption spectra of 60 μM Hg^{2+} . Concentration of alanine was increased from 0 to 160 μM , (D) UV/Vis absorption spectra of alanine alone in aqueous solution. The concentration of alanine was increased from 40 to 160 μM . Melamine (20 μM) solutions upon the addition of alanine (E) and cysteine (F) from 40 to 160 μM 63

Figure 3.8 Selectivity to melamine like compounds. (A) UV/Vis absorption spectra of Au NPs solutions with the addition of six nitrogen containing compounds with the concentration of 1.5 μM , (B) their corresponding $A_{650\text{nm}}/A_{520\text{nm}}$ values, (C) the photos of color readouts of the above samples, and (D) molecular structures of the six compounds. 65

Figure 3.9 Comparison between Au NPs with ~ 13 and ~ 30 nm sizes. (A) SEM image of ~ 30 nm Au NPs. UV/Vis absorption spectra responses of ~ 30 nm (B) and ~ 13 nm (C) Au NPs solutions after the addition of 1.5 μM melamine, (D) the corresponding $A_{676\text{nm}}/A_{519\text{nm}}$ (13 nm Au NPs) and $A_{820\text{nm}}/A_{527\text{nm}}$ (30 nm Au NPs) values, (E) the color readouts of the Au NPs solutions. 66

Figure 3.10 (A) 0.6 μM melamine induced evolutions of UV/Vis absorption spectra of Au NPs in 30 minutes. (B) Time dependent visual detections of Hg^{2+} by using 0.6 μM melamine as a reference. 67

Figure 3.11 Cysteine sensing. (A) UV/Vis absorption spectra of Au NPs in solution after 60 μM different amino acids are added together with 60 μM melamine, (B) the corresponding

$A_{650\text{nm}}/A_{520\text{nm}}$ values of the samples, (C) the photos of the color readouts of the samples, and (D) the 13 kinds of amino acids used in this study. (E) $A_{650\text{nm}}/A_{520\text{nm}}$ values of the samples obtained by adding different concentrations of cysteine together with 1.4 μM melamine, (F) the visualized color readouts of the samples, and (G) the linear relationship between the $A_{650\text{nm}}/A_{520\text{nm}}$ values and the concentration of cysteine..... 68

Figure 3.12 Hg^{2+} sensing. (A) Absorption spectra responses of Au NPs solutions after 50 μM different amino acids are added together with 1.5 μM melamine, (B) the corresponding signal readouts in the form of $A_{650\text{nm}}/A_{520\text{nm}}$, and (C) the photos of the corresponding color readouts of the samples (after 2 min). (D) $A_{650\text{nm}}/A_{520\text{nm}}$ values of the samples obtained by adding different concentrations of Hg^{2+} together with 0.6 μM melamine, (E) the photos of their corresponding visualized color readouts of the samples (E) the linear relationship between the $A_{650\text{nm}}/A_{520\text{nm}}$ values and the concentration of Hg^{2+} 69

Figure 4.1 (A) Calculated Joule heat generation ability curves of different metal nanoparticles. (B) Calculated Joule heat generation ability curves of irregular shaped In NPs based on the ellipsoid model..... 76

Figure 4.2 SEM images of In NPs with different deposition thicknesses (A) 10 nm, (B) 20 nm, (C) 40 nm, and (D) 80 nm on MPM. The scale bars here are 500 nm. (E) Visible and (F) NIR light absorption spectra of In NPs on MPM. (G) Optical images of MPM substrates with different deposition thicknesses of indium. 78

Figure 4.3 SEM images of bare MPM substrates at different scales, displaying a porous nature. 78

Figure 4.4 Measurements of contact angle of water drop on In NP/MPM device. Water droplets on the surface of the device can rapidly disperse, demonstrating the hydrophilic surface of the device. 79

Figure 4.5 (A) A schematic diagram of the device we designed for enhancing steam generation. The In NP/MPM was floating on the upper surface of water. (B) The weight change curves of water with different In NP/MPM devices under 3 sun solar irradiation. The inset illustration shows the device was floating on the surface of water. (C) The IR images of water before solar

irradiation (I), without (II) and with (III) In NP/MPM after irradiation under 3 sun for 30 minutes. The irradiation time is 30 minutes. IV is the side view of III at the same irradiation intensity. (D) The weight changes of water without and with the device as a function of irradiation time under 1 and 3 sun irradiations. (E) The weight change of water at different irradiation intensities (1 sun, 2 sun, and 3 sun) in 30 minutes with and without In NP / MPM devices..... 81

Figure 4.6 Cycle solar evaporation performances of a seawater sample using In NP/MPM device at fixed irradiation intensities in 30 min (1 and 3 sun). 82

Figure 4.7 Optical photographs of the water condensation on the quartz cover after 30 minutes in the absence (A) and presence (B) of the In NP/MPM device..... 83

Figure 4.8 The concentrations of five main ions (Na^+ , K^+ , Mg^{2+} , B^{3+} and Ca^{2+}) before and after desalination measured by ICP-OES. It was noted that the concentration of Mg^{2+} was lower than the detection limit (N.D.) of ICP-OES after desalination. For the shaded areas, the light blue portion and light green portions refer to the overall common salinity achieved by conventional membrane and distillation-based desalination techniques, respectively. The dashed lines represent the drinkable water salinity standards regulated by WHO and EPA..... 83

Figure 4.9 Cycle solar evaporation performances (15 rounds) of In NP/MPM plasmonic device at 3 sun solar illumination intensity. 84

Figure 4.10 (A) XPS spectra of In 3d of In NP/MPM before and after solar evaporation. (B) XPS spectra of O 1s of In NP/MPM before and after solar evaporation. (C) XPS spectrum of O 1s from bare MPM substrate..... 85

Figure 4.11 XRD characterizations of In NPs on MPM before and after 15 cycles solar evaporation processes. 86

Figure 4.12 SEM images of In NP/MPM (A) before and (B) after 15 cycles solar evaporation processes. The scale bars here are 500 nm..... 87

Figure 5.1 Generation of electron-hole pair and their corresponding transfer pathways in a semiconductor in a typical photocatalysis process. 89

Figure 5.2 SEM images of In NPs on quartz prepared by thermal evaporation of indium with different thicknesses. (A) 5 nm. (B) 10 nm. (C) 20 nm. (D) 30 nm. (E) 40 nm. (F) 50 nm. The scale bars are 100 nm. 92

Figure 5.3 SEM images of TiO₂ film on quartz prepared by spin coating TiO₂ NPs (4.5 N.V. % in water) with different magnifications. (A) 1500×. (B) 3000×. (C) 5000×. (D) 10000×. The scale bars are 10 μm, 1 μm, 1 μm, and 1 μm, respectively. 94

Figure 5.4 SEM images of In NPs prepared on quartz before (A) and after (B) TiO₂ coating.... 95

Figure 5.5 Absorption spectra of the prepared In NPs@TiO₂ nanostructures. 97

Figure 5.6 Evolutions of absorption spectra of MB on different structures in 36 minutes. (A) TiO₂. (B) In NPs@TiO₂. (C) Bare In NPs. 98

Figure 5.7 Degradation of MB on In NPs@TiO₂ with different indium deposition thickness ranging from 5 to 50 nm. 99

Figure 5.8 Degradation of MB on In NPs@TiO₂ with different indium thicknesses under sunlight and visible light. (A) 5 nm. (B) 10 nm. (C) 20 nm. (D) 30 nm. (E) 40 nm. (F) 50 nm. 101

Figure 5.9 SEM images of In NPs prepared by thermal evaporation of indium with 10 nm (A) and 20 nm (C) thickness before (A and C) and after (B and D) the sputtering of 10 nm SiO₂. . 102

Figure 5.10 (A) Absorption spectra of In NPs prepared by deposition of 5, 10, 20, and 30 nm indium before and after coating a layer of SiO₂ with 10 nm thickness. (B) Absorption spectra evolutions of In NPs prepared by deposition of 20 nm indium with increasing coating thickness of SiO₂..... 103

Figure 5.11 SEM images of In NPs@10 nm SiO₂ prepared on quartz before (A) and after (B) TiO₂ coating. 104

Figure 5.12 Photodegradation of MB on In NPs@SiO₂@TiO₂ with different SiO₂ thickness ranging from 10 to 50 nm. 105

Figure 6.1 Real and imaginary part of the dielectric constants of aluminum and indium as a

function of wavelength in the UV region.....	110
Figure 6.2 Schematics of the components and setup for the UV SERS measurements.....	111
Figure 6.3 Calculated Fa values for aluminum and indium at different wavelengths in the UV region.	113
Figure 6.4 SEM images of In NPs on ITO prepared by thermal evaporation of indium with different thicknesses. (A) 10 nm. (B) 20 nm. (C) 30 nm. (D) 50 nm.	114
Figure 6.5 Absorption spectra of the prepared In NPs with deposition of 10 to 50 nm thickness of indium on ITO glass.	116
Figure 6.6 Raman signals of 10^{-2} and 10^{-3} M PATP on (A) ITO and (B) In NPs coated ITO. Acquisition time is set as 10 s.....	117
Figure 6.7 Raman signals of 10^{-2} and 10^{-3} M PATP on (A) ITO and (B) In NPs coated ITO. Acquisition time is set as 100 s.....	118
Figure 6.8 Raman signals of 10^{-2} M PATP on In NPs prepared with different indium deposition thickness ranging from 10 to 50 nm on ITO. Acquisition time is set as 100 s with 325 nm laser excitation.....	119
Figure 6.9 (A) Raman signals of 10^{-2} M PATP on In NPs prepared with different indium deposition thickness ranging from 10 to 50 nm on ITO. Acquisition time is set as 100 s with 355 nm laser excitation. (B) Comparison of the UV SERS performances between 325 and 355 nm laser excitations on different sizes of In NPs prepared with different indium deposition thickness ranging from 10 to 50 nm on ITO.....	120
Figure 6.10 SEM images of In NPs prepared by thermal evaporation of indium with 25 nm thickness before (A) and after (B) the sputtering of 10 nm SiO ₂	121
Figure 6.11 Absorption spectra of In NPs prepared by thermal evaporation of indium with 25 nm thickness before and after the sputtering of 10 nm SiO ₂	121
Figure 6.12 UV SERS of PATP on In NPs@SiO ₂ with different SiO ₂ thickness ranging from 10	

to 50 nm. Acquisition time is set as 100 s with 325 nm laser excitation.	122
Figure 7.1 (A) SEM image and (B) absorption spectra of solution synthesized In NPs. (C) SEM and TEM image of In@SiO ₂ core-shelled nanoparticles.	126
Figure 7.2 SEM image of In NPs on TiO ₂ nanorods.	128

Abstract

Metallic nanostructures based plasmonics have been widely studied and proven as powerful platforms in biosensing, photocatalysis, surface enhanced Raman spectroscopy (SERS) and solar energy harvesting related studies. The broad application potentials of plasmonics make people find more and more interesting phenomena and propose even more novel and useful applications based on this fascinating technology.

The phenomena of analytes induced shift of surface plasmon resonance (SPR) of gold nanoparticles (Au NPs) and the color changes of Au NP solutions offers a simple and effective strategy of constructing colorimetric sensing systems. However, most of the Au NPs colorimetric sensing systems developed in previous studies were designed and aiming at the sensing/detection of one certain target/analyte, and unable to be employed for multiple analytes sensing/discrimination. In this thesis, by introducing the concept of logic gate in constructing plasmonic colorimetric sensing system and taking advantage of the highly specific competing coordination reactions between the targeted analytes, we designed for the first time an integrated Au NPs colorimetric sensing platform which can achieve the sensing of Hg^{2+} , melamine, and cysteine.

In the field of plasmonics, application-based studies were mostly relying on the limited candidate metals such as Au and Ag which are noble metals, which hampers the design of novel LSPR based systems to be employed in a broad range of practical applications. In this thesis, we have designed different plasmonic nanostructures by using indium which is a kind of poor metal for different applications: (1) Taking advantage of the superior plasmonic heating ability of In NPs and the simple device fabrication process when compared to other metals/materials, we prepared In NPs on a paper like microporous membrane (MPM) to achieve a portable device

with broad light absorbing ability, which showed enhanced solar evaporation performance. As a proof of concept, its application was demonstrated in the solar desalination of the real seawater sample with high stability; (2) In NPs with UV and Visible LSPRs prepared on quartz substrates were coated with layer of TiO_2 NPs, the substrate showed an enhanced photocatalysis performance for the degradation of methylene blue when compared with substrate which only had TiO_2 coating. The UV and Visible LSPRs can benefit the enhancement through both the hot carrier injection and near-field enhancement mechanisms, while for previous studies using Au, Ag, and Al, only one of the two mechanisms can be observed; (3) In NPs were prepared on ITO with 300 to 400 nm LSPR can be used for UV SERS using 325 and 355 nm laser, which can achieve comparable enhancement when compared to Al, and better enhancement when compared to previous study using In NPs with 266 nm excitation.

Our strategy on the Au NPs colorimetric logic gate may be extended to the design of logic gate sensing systems by using other techniques such as SERS and fluorescent sensing, or other analytes with specific coordination interactions. Our findings in In NPs based systems can help others gain further insight of the plasmonic properties of In NPs, which may on other hand inspire the design of other novel applications and broaden their capabilities in different fields.

In the future, I will try to improve the synthesis of In NPs to obtain In NPs with good size and shape control. Then we can have an in-depth fundamental study of the size and shape induced LSPR property of In NPs, such as single particle UV plasmonics of In NPs both theoretically and experimentally. I will also try to design other novel applications based on the superior plasmonic heating ability of In NPs and its UV LSPR feature, for example, to combine the plasmonic heating effect of In NPs with the photocatalysis of TiO_2 together, to achieve simultaneously water treatment and evaporation.

Chapter 1

Introduction

Design of unique metallic nanostructures for light-matter interactions has become a research interest across the world for a few decades. With the rapid growth of studies in this field, “plasmonics” has been emerging as a new subject which has drawn tremendous research attentions.¹ The plasmonic effect is mainly the result of the collective oscillations of free conduction electrons when shining the metallic nanostructures with light, in which if the light is in resonant with the oscillation, there will be the formation of surface plasmon resonance (SPR). This resonance can create various unique optical and electromagnetic effects, such as light absorption and scattering, as well as the strong near field enhancement around the surface.²

In recent years, the rapid evolutions and innovations in material processing and synthesis have enabled the controllable fabrication of metallic structures in nanoscale, which on the other hand have provided the reliable means to tune the SPR to meet the specific requirements for different applications, such as surface enhanced Raman scattering,³ SPR sensors,⁴ plasmonic lasers,⁵ photothermal conversion,⁶ and solar energy harvesting.⁷ Meanwhile, since plasmonic nanostructure is capable of confining the light in a subwavelength volume, it can break the diffraction limit of light and propagate in the plasmonic nanowaveguide. This feature is highly desirable and will play an important role in super resolution imaging and high density integrated optical information processing related technologies.

Based on the above features, plasmonics based techniques have shown broad application prospects and are increasingly of crucial importance in the fields of physics, chemistry, material

science, biological science, energy, and environment monitoring. Therefore, both plasmonics related fundamental mechanism and practical application based studies will help us in comprehensively understanding the features of plasmonics, which is also significant in inspiring the development of novel applications of plasmonics in other fields.

1.1 Basics of plasmonics

1.1.1 The origin of plasmonics

The history of plasmonics started with gold which is a noble metal and was discovered in Bulgaria around 5000 years ago.⁸ With the shining golden color, bulk gold was originally used for decorative purpose, or severed as commodities and currency. Unlike the shining bulk gold, gold in nanoscale can display vivid colors, which had been principally used as colorants and dye in enamel pottery, ceramics, clothes, and stained glass windows and artworks, among which the most famous one was the Lycurgus cup (British Museum, London, UK) which could be dated back to the 4th century Roman times.⁸ At that time, people had no understanding of the underlying reasons for this fantastic phenomenon that this Roman chalice can appear green under ambient lighting, while the shimmered transmission light was bright red when there was illumination from the inside. Nowadays, we have known the reason for this striking phenomenon is that a trace amount of gold and silver nanoparticles are embedded in the glass and the surface plasmons generated near the nanoparticle surfaces. As surface plasmon is the electromagnetic oscillations of free electrons that occur at the surface of a metal nanoparticle, when it is in resonance with the frequency of the incoming light, the light absorption at a particular wavelength will be amplified to display a certain color which highly depends on the size and the shape of the nanoparticle, the nature of the metal, and the surrounding medium.⁸ Of course the glassmakers in 4th century were not likely to have a comprehensive understanding of the tunable

optical properties of metal nanoparticles and the relevant knowledge of plasmonics. In fact, in ancient Roman, the elemental antimony was often added by glassmakers during heating process of sand to prepare glass. On a serendipitous occasion, the added antimony could react with the gold and silver impurities to form nanoparticles which could show specific light absorption and scattering. Until 1857, it was then reported by Faraday in a scientific article that describing the production of colloid Au NPs through the reduction of chloroaurate by phosphorus in CS₂, showing a beautiful ruby color of the colloid solution.⁸ 50 years later in 1908, a systematic explanation of the red color of Au NPs colloid solution was proposed by Gustav Mie by solving the classic Maxwell's equations, which became a well-known and commonly used theory in plasmonics, namely, the Mie theory.⁹ However, it was until 1957 the concept of surface plasmon was first proposed by Ritchie who thought that there will be collective oscillations of the free electrons at metal surface upon the excitation under external electromagnetic field.¹⁰ This oscillatory motion of free electrons induced by the time-dependent electromagnetic field of incident light was first experimentally proven by Powell *et al.* in 1959.¹¹ As the surface plasmon is essentially an electromagnetic mode, and its wavenumber is often higher than the wavenumber of the photon in vacuum or the surrounding medium, it can only propagate along the surface and will decrease exponentially with the depth in the metal.⁴ However, the creation of this collective oscillation often requires the metal to have negative real part with high absolute value and a small positive imaginary part of the permittivity of the material at the considered excitation wavelength. Therefore, plasmonic phenomena were usually observed on metals, such as Au, Ag, Cu, Al, and In. Recently, graphene was also found can show plasmonic effect, which further promoted the development of this discipline.¹²

1.1.2 Surface plasmon polaritons and localized surface plasmon resonance

Generally, there are two distinct forms of SPR which are defined as localized SPR (LSPR) and propagating surface plasmon polaritons (SPPs). LSPR refers to collective but non-propagating oscillations of surface electrons in the metallic nanostructure when the wavelength of incident light is longer than the size of the metal nanostructure, while SPPs usually appear as the propagating charge oscillations along the surface of thin metal films. Both SPPs and LSPR are capable of enhancing the electromagnetic field in the near-field. Figure 1.1 shows the difference between SPPs and LSPR.³

Figure 1.1 Schematic illustrations of SPPs and LSPR.³ (a) Propagating surface plasmon polaritons along the metal/dielectric interface. (b) Localized surface plasmon on a subwavelength

metal nanosphere.

For SPPs, they are propagating charge waves along the metal/dielectric interface, and the corresponding electric field is given by:¹³

$$E_{SP}(x, z) = E_0 e^{ik_{sp} \cdot k_z |z|} \quad (1-1)$$

For instance, in a metal thin film, the propagation distance of the chare waves in the x and y directions can reach as long as tens of micrometers, while the propagation depth in the z direction will decrease exponentially and will decay to $1/e$ around 200 nm. This process can be described by using a Fabry-Pérot resonant cavity model with $L = n\lambda_{SP}$, in which L is the length of the metal film and λ_{SP} is the wavelength of the SPPs mode.¹⁴ SPPs mode is then can be tuned by changing the geometry parameters of the metal film. For a continuous metal film with perfect surface smoothness, the dispersion curve of SPPs is given by:¹³

$$k_{SP}^2 = \left(\frac{\omega}{c}\right)^2 \frac{\varepsilon_m \varepsilon}{\varepsilon_m + \varepsilon} \quad (1-2)$$

where ε and ε_m are the dielectric constant of the metal and the medium, respectively, while ω and c are the frequency and the velocity in vacuum of the incident light. In the commonly investigated wavelength range of the light, $\varepsilon < 0$ and $|\varepsilon| \gg 1$, and $|\varepsilon + \varepsilon_m| < \varepsilon$, therefore, the wave vector or momentum of the SPPs is always higher than that of the incident massless photon and cannot match with each other, in this case, a Kretschmann geometry prism or a grating are often required to provide the extra momentum to excite the SPPs. Another unique feature of SPPs is that it can enhance the electric field in the near-field of the metal film, and this effect is correlated with the dielectric constant of the metal, the surface roughness and the thickness of the metal film, which can give the near-field enhancement around the metal film surface as high as:¹³

$$\left| \frac{E_{SP}^{Z=0}}{E_0} \right|^2 = \frac{2}{\varepsilon_{air}} \frac{|\varepsilon_1|^2}{\varepsilon_2} \frac{\alpha}{1 + |\varepsilon_1|} \quad (1-3)$$

where

$$\alpha^2 = |\varepsilon_1|(\varepsilon_0 - 1) - \varepsilon_0 \quad (1-4)$$

where E_0 is the electric field of the incident light, ε_{air} is the dielectric constant of the air, and ε_0 is the dielectric constant of prism used to couple with the metal film, while ε_1 and ε_2 are the real and imaginary part of the dielectric constant of the metal, respectively.

Apart from the smooth metal thin film, in reality, there are also metallic structures such as metal film with rough surface or metallic nanoparticles in which there exists the LSPR modes with strong surface confinement. When there is light shining on the metal nanoparticle, there will be collective oscillations of the electron cloud against the nanoparticle core with a restoring Coulomb force which will lead to a characteristic frequency like a harmonic oscillator, which is known as LSPR. Since the geometry of the metal nanoparticle can provide the additional momentum to overcome the mismatch, LSPR can be directly excited by the incident light, benefiting the detection of LSPR using a simple UV-visible absorption spectrometer without the use of a specific prism or a grating. The highly localized feature of LSPR endows the metal nanoparticle the ability to enhance the electromagnetic field in the near-field with even higher order than that of SPPs.⁴

1.1.3 The Mie theory

The optical response of a single metal nanosphere under external fields was first given by Mie in 1908 by solving the Maxwell's equations within the framework of classic electrodynamics, which described theoretically the extinction (scattering + absorption) of spherical particles with arbitrary sizes.⁹ Meanwhile, as most of the standard preparations for colloidal metal particles can

produce the nanoparticles with approximately spherical morphology, and the commonly employed techniques for optically characterizing nanoparticle spectra were usually collecting the signal from the ensemble of many particles, enabling reasonably modeled results when using Mie theory.

As metallic nanostructures that can support LSPRs often with the dimensions in subwavelength scale, they will experience a uniform externally applied electric field $\mathbf{E}_0$ when excited by the incident light. Under the excitation of this electrostatic field $\mathbf{E}_0$, it can create an electric field $\mathbf{E}_i$ inside the nanosphere, which is given by

$$\mathbf{E}_i = \mathbf{E}_0 \frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m} \quad (1-5)$$

where ε_m and ε are the dielectric function of the surrounding medium and the metallic nanoparticle, respectively.

The surrounding electromagnetic field around the nanosphere can be obtained by solving fundamental Laplace's equation of electrostatics, $\nabla^2\varphi = 0$, where φ is the electric potential. Note that φ and the field $\mathbf{E}_0$ satisfy the relation $\mathbf{E}_0 = -\nabla\varphi$, when considering the two boundary conditions that both φ at the metallic nanosphere surface and the normal component of the electric displacement D are continuous, where $D = \varepsilon_m\mathbf{E}_0$. This introduced electromagnetic field on the spherical metal nanoparticle surface leads to the polarization of the density of free conduction electrons on the nanosphere. By applying the boundary conditions, the resulting polarization of the sphere can be calculated as a whole. The resulting dipole moment, $p = \varepsilon_m\alpha\mathbf{E}_0$, and the corresponding static polarizability of the particle, α , is given by

$$\alpha = 4\pi a^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \quad (1-6)$$

in which a is the radius of the sphere (Figure 1.2).

Taking into consideration the combinational contribution of the real and imaginary parts, the expression of ε for the metal nanosphere is given by

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 = (n + i\kappa)^2 \quad (1-7)$$

in which n is the refractive index and κ is associated with light absorption. Since ε_m is usually taken as a real constant throughout the visible light wavelength range, making it is possible to allow the polarization to achieve a resonance state at a certain wavelength. At this resonance state, the modified relationship in eq 1-6 will be

$$(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^2 = \text{minimum} \quad (1-8)$$

It is apparent that the plasma resonance wavelength of this nanosphere is mainly determined by ε_1 when ε_2 is small or slowly-varied with wavelength around the resonance condition in which the relation $\varepsilon_1 = -2\varepsilon_m$ is fulfilled and the local field at the particle will be dramatically enhanced. In addition, the ε_2 value of the metal at this resonance wavelength could determine the height and width of the resonance.

Figure 1.2 Sketch of a metal nanosphere immersed in an electrostatic field.

In particular, the dependence of optical properties of individual metal nanoparticle on its size effect has also been intensively modeled in the framework of Mie theory which mathematically and physically described the scattering of electromagnetic wave by subwavelength metal particle placed in a continuous and isotropic medium, in which the solution starts with macroscopic Maxwell equations in the electrostatic approach in the following form

$$\nabla \cdot \mathbf{E} = 0 \quad (1-9)$$

$$\nabla \cdot \mathbf{H} = 0 \quad (1-10)$$

$$\nabla \times \mathbf{E} = i\omega\mu\mathbf{H} \quad (1-12)$$

$$\nabla \times \mathbf{H} = -i\omega\varepsilon\mathbf{E} \quad (1-13)$$

By using the Helmholtz's equation, the two components (the electric field $\mathbf{E}$ and the magnetic field $\mathbf{H}$) of the incident electromagnetic field can be written as

$$\nabla^2 \mathbf{E} + k^2 \mathbf{E} = 0 \quad (1-13)$$

$$\nabla^2 \mathbf{H} + k^2 \mathbf{H} = 0 \quad (1-14)$$

where k is the wavenumber defined as

$$k^2 \equiv \omega^2 \varepsilon \mu \quad (1-15)$$

By inserting the series for $\mathbf{E}$ and $\mathbf{H}$ for the scattering amplitude functions into the appropriate integrals, and carrying out the integration term by term, the extinction and scattering cross-sections can be obtained as

$$\sigma_{ext} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) [\text{Re}(a_n + b_n)] \quad (1-16)$$

$$\sigma_{sca} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) (|a_n|^2 + |b_n|^2) \quad (1-17)$$

$$\sigma_{abs} = \sigma_{ext} - \sigma_{sca} \quad (1-18)$$

where the size parameter x is given by

$$x = \frac{2\pi R n_m}{\omega} \quad (1-19)$$

where n_m is the refractive index of the surrounding medium, ω is the wavelength of the incident light in vacuum, R is the radius of the particle, and a_n and b_n are the coefficients expressed using the Ricatti-Bessel expressions:

$$a_n = \frac{m\psi_n(mx)\psi'_n(x) - \psi_n(y)\psi'_n(mx)}{m\psi_n(mx)\xi'_n(x) - \xi_n(x)\psi'_n(mx)} \quad (1-20)$$

$$b_n = \frac{\psi_n(mx)\psi'_n(x) - m\psi_n(y)\psi'_n(mx)}{\psi_n(mx)\xi'_n(x) - m\xi_n(x)\psi'_n(mx)} \quad (1-21)$$

where $m = n_p/n_m$, in which n_m and n_p denote the real refractive index of the surrounding medium and the complex refractive index of the particle, respectively, and $\psi_n(x)$ and $\xi_n(x)$ are Ricatti-Bessel cylindrical functions. In the above expressions, n is the summation index of the partial waves, for example, $n = 1$ and $n = 2$ are correspondingly representing the dipole and quadruple oscillation mode. To have a better understanding of the LSPR phenomenon, the expression can be reduced to a simpler form with the assumption that R of the particle is much smaller than the wavelength of the incident light, in which the dipole oscillation will be the dominate mode and it gives the relationship

$$\sigma_{ext} = 9 \frac{\omega}{c} \varepsilon_m^{3/2} V \frac{\varepsilon_2}{(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^2} \quad (1-22)$$

where $V = 4\pi R^3/3$ is the volume of the metal sphere, while ω and c are the angular frequency and the velocity of the incident light. Through a similar treatment, it also be obtained that

$$\sigma_{sca} = 2 \left(\frac{\omega}{c}\right)^4 \varepsilon_m^2 V^2 \frac{(\varepsilon_1 - \varepsilon_m)^2 + \varepsilon_2^2}{(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^2} \quad (1-23)$$

The above equations have been widely employed to explain the optical properties of subwavelength metallic nanoparticles as a both qualitative and quantitative approach.

1.2 Plasmonics based applications

1.2.1 Plasmonic colorimetric sensing based on colloid metal nanoparticles

The well dispersed Au NPs colloid could show a vivid wine-red color in aqueous solution, which was systematically studied by Michael Faraday in 1850s, whose works also inspired Mie to

propose the famous theory in plasmonics, namely, the Mie theory. According to Mie theory, when the surrounding medium for Au NPs is water with the $\epsilon_m \approx 1.7$, the resonant condition ($\epsilon_1 = -2\epsilon_m$) can be satisfied at a wavelength around 520 nm, which is consistent with the experimental absorption spectrum that Au NPs colloid solution has a strong LSPR peak as a result of the extinction maximum of the incident light around that wavelength. However, the aggregated Au NPs in solution will show a purple or dark blue color depending on the aggregation degree. This aggregation effect can be easily observed by simply introducing certain chemicals into the colloid solution of Au NPs. Figure 1.3A shows the color change (from wine red to dark blue) of colloid Au NPs solution by adding different amount of melamine, correspondingly a new peak around 650 nm is emerging clearly in the absorption spectra in Figure 1.3B. The aggregation degree of Au NPs caused by the addition of different amount of melamine can be further confirmed by using Transmission Electron Microscopy (TEM) as shown in Figure 1.3C, D and E. Figure 1.3F is the schematic depiction of the formation of the cross linked Au NP aggregates induced by melamine molecules.¹⁵

Figure 1.3 (A) Optical image of Au NPs colloid solutions upon the addition of melamine from 0 to 1.5 μM . (B) The evolution of the absorption spectra as a result of the introduced melamine. TEM images of Au NPs colloid solutions with (C) 0, (D) 1.1, and (E) 1.5 μM melamine. (F) Schematic depiction of the formation of Au NP aggregates the cross-linked by the melamine

molecules.¹⁵

This phenomenon shows great perspective in controllable manipulation of the LSPR of metallic nanoparticles, which is highly desirable in designing specific systems in practical applications such as plasmonic biosensing and SERS in which unique aggregated plasmonic structures are often required. To gain a comprehensive insight of the aggregation induced evolutionary LSPR property of metallic nanoparticles, tremendous efforts have been devoted both theoretically and experimentally. As shown in Figure 1.4, it has been revealed that the distance between the metal nanoparticles, the size of the metal nanoparticles as well as the size of the as formed aggregates could significantly influence the resulting extinction spectra through theoretical calculations. One can see from the results that the formation of the aggregate accompanies a red shift of the LSPR peak, which could be ascribed to the plasmon hybridization of multiple metal nanoparticles.⁸

Figure 1.4 Electrodynamic modeling of the evolutions of extinction spectra of Au NPs with (A) fixed particle size and different particle distances, (B) fixed particle distance and different particle sizes, and (C) fixed particle distance and different aggregate sizes.⁸

The inter-particle plasmon coupling induced shift of the SPR of metal nanoparticles as well as the clear visual color change of the colloid solution provide the exciting basis for developing novel plasmonic sensing assays based on this colorimetric effect. Plasmonic colorimetric detection using colloid metallic nanoparticles is thereby a simple, rapid, and cost-effective approach, in which the sensing can be completed using just naked eye observation. However, colloid metal nanoparticles in aqueous suffer from the vulnerability to introduced species to form aggregates, which may cause interference issues when applied in complex matrices.⁴ One typical way for the construction of robust sensing system is the implementation of an effective surface-modification strategy which introduces the ligands at the surface of the metal nanoparticles. On the one hand, the ligands can expand the colloidal stability of the metal nanoparticles at harsh sensing environment. On the other hand, only the target analyte which has highly specific affinity to the ligands could induce the aggregation of the modified metal nanoparticles, thus the aggregation can be well controlled, which will endow the assay with good sensitivity and selectivity to the analyte.

The typical design of this kind of chemical coordination-based Au NPs colorimetric sensor is as reported by Ray et al. (Figure 1.5).¹⁶ In this assay, Au NPs were modified with glutathione (GSH), dithiothreitol (DTT), and cysteine (Cys), all of which have strong affinity to As^{III} ions as ligands and the stability constants ($\log K$) of the as formed complexes through coordination are as high as 32.0 (GSH), 37.8 (DTT), and 29.84 (Cys). As a result, upon the addition of As^{III} ions to the modified Au NPs solution, the coordination between As^{III} ions and the ligands on Au NPs will induce the strong aggregation of Au NPs. In addition, since the coordinations between the

surface ligands and other metal ions are much weaker and their stability constants are only 11.06 (Zn), 13.89 (Pb), 14.6 (Cd), 10.7 (Ni), 15.3 (Cu), 17.6 (Hg), the colorimetric responses of Au NPs to these metal ions are much lower, which enables selective detection of As^{III} ions. Based on the colorimetric responses of the modified Au NPs upon the addition of As^{III} ions, the limit of detection of this assay can reach as low as 1 ppb. Besides the commonly reported Au NPs based sensing assays, Ag NPs based colorimetric sensing systems were also developed through the rational surface modification of Ag NPs. By using 1-(2-mercaptoethyl)-1, 3, 5-triazine-2, 4, 6-trione (MTT) and thiomalic acid (TMA) as ligands, Pb^{2+} and Cu^{2+} can be detected, respectively.^{17, 18}

Figure 1.5 (A) Scheme of DTT, Cys, and GSH modified gold nanoparticles for arsenic detection. Photograph of Au NPs in aqueous solution modified with GSH/DTT/Cys upon addition of (B) different metal ions (5 ppb) and (C) As^{III} ions with different concentrations.¹⁶

All of the systems discussed above were designed to detect the target based on the analyte induced aggregation of the metal nanoparticles. Meanwhile, if the aggregation of metal

nanoparticles induced by a chemical could be inhibited by a certain target, this could be another way of colorimetric sensing, namely the anti-aggregation of metal nanoparticles based colorimetric sensing. Mirkin group designed a typical assay based on this kind of strategy through the competing coordination between DNA modified Au NPs and cysteine with Hg^{2+} , which can be used for the detection of cysteine (Figure 1.6).¹⁹ In their design, Au NPs were first modified with DNA with T bases, upon the addition of Hg^{2+} , there will be strong coordination between Hg^{2+} and the T base pair of DNA. As a result, this coordination effect could help the DNA modified Au NPs remain the aggregation state at certain temperature. However, when cysteine was introduced to the system, there will be even stronger coordination between cysteine and Hg^{2+} , which will remove Hg^{2+} from the network structure of the T base pairs and thereby cause Au NPs to lose their aggregation state. Therefore, cysteine can be detected through this competing coordination mechanism in a colorimetric format. Because of the strong coordination between Hg^{2+} and the T base pair of DNA, the amino acids except cysteine are not capable of removing Hg^{2+} from the network. Thus, the assay shows high selectivity to cysteine and the limit of detection of this assay can reach as low as 100 nM.

Figure 1.6 (A) Scheme of a competition format colorimetric Assay for detection of cysteine by

using DNA modified Au NPs. (B) Colorimetric responses of the assay to different amino acids (1 μ M) at room temperature and 50 °C.¹⁹

1.2.2 Plasmonic passive solar desalination

Water scarcity has become an increasing issue of our time around the world and the situation may be even worse due to population and economy growth, climate change induced by greenhouse gases, contamination of freshwater resources, and expansion in industrial and agricultural activities when looking into the future. Currently the most successful commercialized technology for seawater desalination is the reverse osmosis (RO) processes. However, the RO processes consume a great amount of electric energy, and thus lead to the release of a large quantity of greenhouse gases. Moreover, a large number of marine organisms, especially juvenile-stage fish, are killed during the seawater intake process, which indicates that developing green and sustainable methods for seawater desalination is still of crucial importance.²⁰

Metal nanostructures have the capability to confine light into subwavelength volumes, which is known as surface plasmon that is generated through the interaction between light and the free electrons of the metal. This phenomenon has been extensively investigated in the area of solar energy conversion due to their strong visible and infrared (IR) plasmonic responses. Since surface plasmon is the result of the collective oscillation of the electron cloud around the metal surface, the damping of this oscillation can efficiently generate heat in this process, which is known as plasmonic heating.⁶ As there is almost no radiative damping from surface, the efficiency of plasmonic heating could be very high, which makes metal nanostructures become ideal candidates for light to heat conversion for solar seawater desalination. Solar seawater desalination based on plasmonic heating from metal nanoparticles thereby can offer a simple,

efficient, green and environmental friendly strategy, which is sustainable in the future.

The heat generation process in plasmonic nanostructures is very simple, in which the incident light electric field strongly drives the collective oscillation of the free electrons at the surface, and the energy gained by the electrons turns into heat through the damping of this oscillation. The generated heat will diffuse away from the nanoparticle surface and lead to an increase of the temperature of the surrounding medium. As surface plasmon is a collective motion of a large number of electrons, heat generation becomes especially strong in the case of metal NPs in the regime of plasmon resonance. In the case of semiconductor NPs, the heat generation rate is much weaker since heat dissipation occurs through an interband absorption process with the creation of a single mobile electron and hole (exciton). The heat generation Q from metal nanoparticles can be calculated analytically when assuming that the wavelength of the incident light is much longer than the size of the nanoparticles, which is given by⁶

$$Q = \frac{\omega}{8\pi} E_0^2 \left| \frac{3\varepsilon_m}{2\varepsilon_m + \varepsilon} \right|^2 \varepsilon_2 \quad (1-24)$$

where E_0 is the amplitude of the incident radiation, ε is the complex dielectric constant of the metal, and ε_2 is its imaginary part, while ε_m is the dielectric constant of the surrounding medium. Based on this equation, a recent study did some approximations and using a simpler equation to quantitatively evaluate the heating abilities (Jo) of different metals, which gives the expression²¹

$$Jo = 9 \frac{e\varepsilon_2}{n_m} \left| \frac{\varepsilon_m}{2\varepsilon_m + \varepsilon} \right|^2 \quad (1-25)$$

where n_m is the refractive index of the surrounding medium, e is photon energy in eV. The plasmonic heating ability of the commonly used plasmonic metals such as gold, silver, and aluminum are thus can be reasonably evaluated using the above equation.

Taking advantage of the superior plasmonic heating effects from metal nanostructures when

exposed to light radiation, Halas group previously reported that aqueous solution containing light-absorbing Au NPs exposed to sunlight can induce plasmonic heating, resulting in relatively efficient evaporation.²² In their design, Au nanoshells (Au NSs) were synthesized and dispersed in water with broad and strong LSPR peak to sufficiently overlap with the solar spectrum (Figure 1.7B), which can accelerate the steam generation under sunlight illumination. The unique feature of plasmonic heating is that the heat generation is highly localized at the surface of plasmonic nanoparticles, which could avoid the bulk heating of the entire solution volume to efficiently produce bubbles to achieve rapid vaporization of water (Figure 1.7A). The findings open up a broad range of solar energy conversion related applications such as desalination, distillation, and waste water treatment.

Figure 1.7 (A) Scheme of the efficient solar steam generation with highly localized plasmonic heating effect. (B) Visible-Near-Infrared (Vis-NIR) absorption spectrum of plasmonic Au NSs. Inset is the SEM images of Au NSs.²²

It is worth noting that for the above design, the metal nanoparticles served as localized light-to-heat converters and were dispersed throughout the solution. However, the vapor bubbles were generated inside the solution and travelled to the water-air interface to release the steam trapped inside the bubbles. The heat transfer from the traveling vapor bubbles to the bulk water still intrinsically and substantially limited the efficiency of evaporation applications where the

heating loss is inevitable. An emerging approach is to fabricate floating thin-film to focus the intense plasmonic heating effect on the water-air interface, vapor bubbles thus can be generated in proximity to the evaporative surface (Figure 1.8). Therefore, the as-formed bubbles can directly release the vapor to the air without travelling through the bulk liquid volume to reduce the heat loss and improve the evaporation efficiency.⁷

Figure 1.8 Schematic illustration of solar steam generation using floating plasmonic device to enable the evaporation at water-air interface.⁷

Noble metal-based plasmonic nanostructures with strong visible and infrared SPR responses have been the most extensively studied candidates for the application in solar energy conversion, because of their SPR can significantly overlap with the solar spectrum. To enable efficient and cost effective solar desalination, finding low-cost alternative candidates with broadband and efficient light absorption is the critical first step. However, for the poor metal with good plasmonic properties like aluminum, the plasmon frequency is in the ultraviolet (UV) regime.²³ Therefore, tuning the structure of poor metals to achieve the plasmonic resonances in visible and IR regime is highly desirable and will be of crucial importance in the practical application. Recently, Zhu's group reported efficient solar desalination using aluminum nanostructure fabricated through the 3D assembly of Al NPs, showing great perspective in exploring poor

metals for this application in this field.²⁴

1.2.3 Plasmonic photocatalysis

TiO₂ is well known for its superior photocatalysis performance in the degradation of some organic compounds, which is important for environment protection.²⁵ However, the band gap of commonly used anatase TiO₂ in photocatalysis is 3.26 eV, which implies that only light with the wavelength in the UV region can effectively excite it. Introducing plasmonic nanoparticles to TiO₂ photocatalysis system has been proven an effective method to improve the photocatalysis performance. On the one hand, the loading of metal nanoparticles on TiO₂ could enhance the absorption of the incident light, thus leading to higher excitation efficiency. On the other hand, the metal nanoparticles will also generate an intense localized electromagnetic field to boost the excitation of TiO₂.^{23, 25, 26}

Awazu *et al.* innovatively designed the Ag NPs/SiO₂/TiO₂ structure with strong light absorption ability in the near UV region (Figure 1.9A and B) in the year of 2008.²⁶ With the strong plasmonic effect caused by the LSPR of the embedded Ag NPs in the structure, the photo-degradation performance towards methylene blue (MB) can be dramatically enhanced, in which the concept of plasmonic photocatalysis was proposed for the first time. Since Ag NPs can be easily oxidized in the air, coating a layer of SiO₂ on Ag NPs can effectively protect them from oxidation. Through a theoretical calculation based on Mie theory, they can also obtain the optimal size of Ag NPs and the thickness of the SiO₂ protection layer. In an optimized condition, the photocatalysis performance of TiO₂ can be enhanced by 7 times by using the Ag NPs/SiO₂/TiO₂ structure with 5 nm SiO₂ thickness (Figure 1.9C). Unlike Ag NPs, the stability of Au NPs is excellent, so the protection layer is often not required for Au NPs based plasmonic photocatalysis system. Mubeen *et al.* fabricated the multi-layered Au NPs/TiO₂ structure by

using e-beam evaporation.²⁷ When excited by the light with a wavelength of 600 nm, the multi-layered Au NPs/TiO₂ structure can generate a photocurrent which is about 3 orders higher than the bare TiO₂ film. As it is well-known that the band gap for TiO₂ is more than 3 eV, it is with little possibility that the electrons on the valence band can be excited by using 600 nm light. And the photocurrent intensity is related the optical absorption spectra of Au NPs, which manifests that the enhanced photo current is due to the plasmonic effect from the Au NPs in the structure.

Figure 1.9 (A) Cross-section TEM image of the Ag NPs/SiO₂/TiO₂ structure. (B) UV-Visible absorption spectra of bare TiO₂ film (curve a), Ag NPs/TiO₂ (curve b), and the Ag NPs/SiO₂/TiO₂ structure (curve c). (C) Time dependent photo degradation of MB using bare TiO₂ film (curve a), the Ag NPs/SiO₂ (20 nm)/TiO₂ structure (curve b), and the Ag NPs/SiO₂ (5 nm)/TiO₂ structure (curve c).²⁶

Although numerous studies have been reported regarding the construction of novel plasmonic photocatalysts through the combination of different plasmonic nanoparticles and the semiconducting photocatalysts, the mechanism involved in the plasmonic photocatalysis process

can vary with different designs in which the excitation wavelength, the configuration of the structure as well as the materials employed are all important factors. Figure 1.10 summarizes the commonly proposed mechanisms in previous reports:²⁸ (A) the conventional semiconducting photocatalyst receives the energy from the photons with energy are higher than the band gap of the photocatalyst and creates electron and hole pairs. If the carriers can migrate to the surface and the band levels can fit with certain species, the oxidation/reduction reactions will take place; (B) the loading of plasmonic nanoparticles can create a Schottky barrier which can effectively inhibit the recombination of electron and hole by trapping of the as formed electrons, and provide additional reaction sites at the metal nanoparticle surface; (C) if the excitation is made on the metal nanoparticles to generate strong LSPR, the LSPR induced hot electrons can be directly injected to the conduction band of the photocatalyst and thereby leaves the holes at the metal surface. This process occurs when the metal and the semiconductor are in contact with each other, enabling a direct electron transfer (DET) process; (D) apart from the DET process, if the metal and semiconductor are not in direct contact, for instance, Ag NPs/SiO₂/TiO₂ structure reported by Awazu *et al.*, the excitation of LSPR of metal nanoparticles induced local electromagnetic field (LEMF) can also contributed to the local generation of carriers; (E) it has also been reported that generation of carriers in the photocatalyst can happen through a dipole-dipole resonant energy transfer (RET) mechanism in which the relaxation of LSPR can directly excites electron-hole pairs in a nonradiative manner.

Figure 1.10 Charge carrier generations in different systems. (A) Charge carrier in a conventional semiconducting photocatalyst. (B) Electron trapping by a metal nanoparticle (without plasmonic effect). (C) A direct electron transfer (DET) process in a plasmonic photocatalyst. (D) Plasmonic photocatalyst with local electromagnetic field (LEMF). (E) A dipole-dipole resonant energy transfer (RET) mechanism in a plasmonic photocatalyst.²⁸

1.2.4 Surface-enhanced Raman scattering (SERS)

When a photon is scattered by a molecule, the scattering can be either elastic or inelastic. In the first case, the photon just changes its propagation direction without losing any energy, and this phenomenon is known as Rayleigh scattering. While the incoming photon could also gain/lose part of its energy from/to the molecule, resulting in anti-Stokes and Stokes scattering lines appear symmetrically at the two sides of Rayleigh scattering line, respectively. This unique interaction between light and molecule was discovered by Raman in 1928, and was named Raman scattering from then on.²⁹ At that time, with the lack of strong light source, the Raman effect was often observed with very weak intensity. Until it was after 1961, the emergence of laser drove the development of this technique rapidly. Figure 1.11 briefly depicts the diagrams of Stokes and anti-Stokes Raman process. The incident photons ($h\nu_L$) can interact with the molecules in a

vibrational ground state, in which the photons lose their energy to excite the molecule to a virtual state, followed by a relaxation process to a vibrational excited state in which the scattered photons are with lower frequency ($h\nu_S$), namely, the Stokes Raman scattering. In a similar process, if the molecules are excited when they are already in the vibrational excited state and then relax to the vibrational ground state with higher frequency scattering photons ($h\nu_{aS}$), the anti-Stokes Raman scattering will be obtained. Since most of the molecules are in the ground state at room temperature, the intensity of Stokes Raman scattering is often much higher than that of the anti-Stokes Raman scattering. As the Raman shift is the result of the relaxations in the vibrational states, it can probe the structure and group information of molecules as IR spectroscopy. However, the Raman scattering is a weak process, and the intensity is only 10^{-6} to 10^{-9} of the incident light, which has largely hampered the practical application of this technique.

Figure 1.11 Schematics of Stokes and anti-Stokes Raman scattering processes.²⁹

The breakthrough in this field was made by Fleischmann et al. in 1974, who observed a dramatically enhanced Raman signal from pyridine on a electrochemically etched silver electrode with rough surface.³⁰ The Raman signal can be enhanced by 10^6 times, while the surface area of the rough surface is not more than 10 times of the electrode with smooth surface, which gave evidence the evidence that this huge enhancement must be a true effect. In the

following few years, Van Duyne, and Creighton et al. reported similar observations by using different molecule on different rough metal surfaces, which further confirmed this effect and produced the new term “surface-enhanced Raman scattering (SERS)” in this field.^{31, 32} After that SERS have drawn intensive research attention both theoretically and experimentally. The number of published papers was increasing exponentially year by year, leading to deepened insight towards the enhancement mechanism, and useful applications in different research areas. In recent years, with the development of nanofabrication technology and the increasing comprehensive theory in plasmonics, SERS has become a powerful in chemo/biosensing, which possesses the capability of ultrasensitive and nondestructive detection that can be down to a single molecule level with fingerprint information.²⁹ Therefore, different molecules in complex sensing matrixes can be distinguished through the Raman shift, which is hard to achieve by using other techniques.

Although the SERS phenomenon has been discovered for more than 40 years, the debates still exist regarding the mechanism of the enhancement, which is the result of the complicated factors that may be involved in the process such as the surface roughness, the configuration of the nanoparticles and the molecules, and the possible chemical interaction between the nanoparticles and the molecules. So far, it is widely acknowledged that the enhancement mechanism can be classified into two categories: electromagnetic field enhancement and chemical enhancement. The electromagnetic field enhancement is often considered as the dominate mechanism which could contribute to the enhancement factor on the order that can reach as high as 10^6 to 10^{14} , whereas the chemical enhancement is commonly observed in the range of 10 to 10^2 .²⁹ As the electromagnetic field enhancement mainly originates from the LSPR induced near-field enhancement at the metal nanoparticle surface, it is not directly related to the chemical nature of

the molecule and chemical bonding between the metal and the molecule. Typically, for the spontaneous Raman scattering, for a molecule in the electric field E , the intensity of Raman signal can be given as

$$I_{Raman} \propto |\mu_{ind}|^2 = |\alpha E|^2 \quad (1-26)$$

where μ_{ind} is the induced dipole moment in the molecule, and α is the molecular polarizability.

When the incident laser light frequency is in resonance with the LSPR of the metal nanoparticles, the energy sucked by the nanoparticles will be re-emitted through Mie scattering and generate an intense scattered field E_{surf} which can be given as

$$E_{surf}^2 = 4E_0^2 g^2 \quad (1-27)$$

where E_0 is the incoming electric field, and g can be expressed as

$$g = \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \quad (1-28)$$

in which ε is the complex dielectric constant of the metal, while ε_m is the dielectric constant of the surrounding medium.

As the Raman shift is usually very small, leading to the closed wavelengths of the incident and scattering radiations. Thus, an approximation can be made, resulting in the famous fourth-power relationship of SERS intensity I_{SERS} with the incoming electric field E_0

$$I_{SERS} = 16E_0^4 g^4 \quad (1-29)$$

1.3 Thesis Scope and Structure

The research on SPR based nanostructure systems has become one of the most fascinating research fields that experiences rapid growth, namely, plasmonics. Plasmonic colorimetric sensing based on Au NPs has been widely used in chemo/biosensors for the detection of various analytes owing to its integration of simplicity and rapidness. Up to now, most of the colorimetric

platforms based on Au NPs are designed to detect one certain target and cannot be employed for the discrimination of different species in various target scopes within a single sensing platform. By designing molecular logic gates using Au NPs to construct chemo/biosensors, we have demonstrated a possible way of solving the above problem.

The development of novel LSPR based systems to be employed in a broad range of practical applications is still constrained by the limited candidate metals. Previous studies were mostly relying on Au and Ag which are noble metals, and the cost of using them is still a concern if a large amount of the metals is required in some practical applications. In this thesis, we have designed different plasmonic nanostructures by using indium which is a kind of poor metal for different applications, such as plasmonic solar desalination, plasmonic photocatalysis, and UV SERS. Our findings can help others gain further insight of the plasmonic properties of In NPs, which may on other hand inspire the design of other novel applications and broaden their capabilities in different fields.

The motivation of this thesis is presented as the above discussions. After giving the introduction of some basics and background information in **Chapter 1**, the organization of the rest thesis will follow the sequence listed below:

In **Chapter 2**, we will discuss explicitly the synthesis procedure of colloid Au NPs via a solution chemistry method. The reaction mechanism, the experimental setup as well as the control of the particle size will be introduced in detail. We will also present the versatile fabrication of indium nanostructures on different substrates through a simple thermal evaporation method. Different characterization methods including UV/Vis/NIR absorption spectrometer, scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction meter (XRD), and X-ray photoelectron spectroscopy (XPS) were employed, in which

the optical property, the morphology information, the crystal structure, and the chemical state of the as fabricated plasmonic nanostructures can be well understood.

In the following **Chapter 3**, we will introduce the design of a plasmonic logic gate sensing platform based on Au NPs, which achieved the sensing of different analytes among various scopes of targets on one sensing platform. The competing coordination-based mechanism, the formulation of the logic gate system, the detection of different analytes (Hg^{2+} , melamine, and cysteine), and the discrimination strategy of different species will be discussed in detail.

Chapter 4 will be the discussion of fabricating a paper like floating plasmonic device for plasmon enhanced solar desalination, which was motivated by a theoretical calculation of the superior plasmonic heating ability of In NPs and the simple preparation of the indium nanostructure. We have investigated the size effect of In NPs on the solar evaporation performance, the stability of the plasmonic device fabricated after multi-cycles usage, and the desalination of a real seawater sample followed by the check of the salinity using inductively coupled plasma optical emission spectrometry (ICP-OES).

It will be presented in **Chapter 5** that the tuning of LPSR of In NPs on quartz for plasmon enhanced photocatalysis performance of TiO_2 NPs, in which the photo-degradation of MB under sunlight and visible light will be systematically discussed. The SPR shift induced by the coating of TiO_2 and a thickness dependent photocatalysis performance of a dielectric SiO_2 layer between In NPs and TiO_2 NPs were observed in the experiment, which will help us in understanding the enhancement mechanism.

For **Chapter 6**, it will be the presentation of UV SERS observed on In NPs on indium-tin oxide (ITO) substrate using 325 and 355 nm laser. The theoretical calculation of the near-field enhancement ability and its comparison with aluminum, and size effect of In NPs and a dielectric

SiO₂ layer on In NPs on UV SERS will be introduced in detail.

In the final **Chapter 7**, we will give the summary of the major contribution of this work, and then give the proposal for future research plans based on some preliminary results.

Chapter 2

Fabrication and characterization of gold and indium nanostructures

2.1 Fabrication of gold and indium nanostructures

2.1.1 Synthesis and surface chemistry of Au NPs

Gold appears in the nature as one of the most stable elements, while Au NPs can exhibit unique physical and chemical properties distinct from bulk gold, including the generation of LSPR and its corresponding optical effects, and the multifunctional surface chemistry. The Lycurgus cup and church windows with stained glass in ancient times represent a few examples of the original applications of manmade Au NPs. However, the preparations at that time were mostly relying on personal skill and experience due to the lack of scientific understanding for the underlying mechanism, hampering the development of a controllable and reproducible synthesis procedure. The revolution of this situation occurred in 1857, which was reported by Michael Faraday for the first time in a scientific journal the preparation of colloid Au NPs through reducing (hydrogen tetrachloroaurate) HAuCl_4 in aqueous solution with phosphorus dissolved in CS_2 , which produced Au NPs dispersed in solution with a beautiful ruby color.⁸ In 1951, Turkevich and coworkers improved the synthesis strategy of Au NPs by using sodium citrate as an alternative reducing agent for HAuCl_4 .³³ Later in 1973, Frens refined the synthesis by changing the molar ratio of sodium citrate to AuCl_4^- to a serial of values, and obtained Au NPs with controllable size ranging from 16 to 147 nm.³⁴ From then on, this method became a routinely followed method in Au NPs synthesis and is still the most popular method among the plasmonics community due to its simplicity.³⁵

In a typical process for preparing colloidal Au NPs using the classic Turkevich method, it

involves combining hydrogen HAuCl_4 and sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) in a boiling aqueous solution. Upon dissociation, the citrate ions ($\text{C}_6\text{H}_5\text{O}_7^{3-}$) reduce Au^{3+} resulting in the formation of Au particles in tens of nanometer size. The net ionic equation for the reaction is³⁶

The corresponding schematic illustration of the formation of the Au NPs is sketched in Figure 2.1. As is shown in the cartoon, after dissolving the water-soluble gold salt HAuCl_4 in an aqueous solution, followed by heating it up to boiling under continuous stirring, a solution of sodium citrate which is a reducing agent is then rapidly added to reduce AuCl_4^- ions to form Au^0 atoms. As Au^0 atoms are increasingly generated, they will become supersaturated in the solution, leading to the crystallization of Au^0 atoms to form subnanometer Au seeds. The crystallized Au seeds keep growing up and eventually become Au NPs.

Figure 2.1 Cartoon showing the growth process of Au NPs in aqueous using classic Turkevich method.

The kinetics of growth in terms of the size evolution of Au NPs using this method was systematically investigated by Peng and co-workers.³⁷ The formation of Au NPs is highly dependent on the pH value of the solution, which shows two distinct pathways with a critical pH value around 6.2. When the pH of the growth solution is below this value, the growth of Au NPs can be formulated into mainly three steps: nucleation of small Au seeds; formation of wavy Au

nanowire intermediates attributed to the random attachment of Au⁰; intraparticle ripening and smoothing of the as formed Au nanowires to result in Au NPs. Another pathway will dominate the growth when the pH is higher than the critical value, following the well-known LaMer model which was proposed for the explanation of crystallization of colloidal particles. By optimizing the reaction condition with appropriate pH value, they can achieve the controllable synthesis of Au NPs in the range of 20 to 40 nm with relatively narrower size distribution.

The side reaction which is caused by the thermal decomposition of sodium citrate can create various species in the growth process of Au NPs, including acetoacetate, acetone or dicarboxyacetone. Puentes *et al.* demonstrated these species could have influenced the final morphology of Au NPs.³⁸ The sequence for adding the reagents (HAuCl₄ and sodium citrate) in synthesis process using the Turkevich method was also reported can lead to better size uniformity of the Au NPs synthesized. Conventionally, HAuCl₄ aqueous solution was heated to boiling prior to the rapid addition of sodium citrate to initialize to reaction. By altering the sequence, namely, introducing HAuCl₄ to a boiling aqueous solution of sodium citrate, after which Au NPs can be obtained with better monodispersity in size distribution. Based on this simple innovation in the experimental operation, Santhanam *et al.* prepared more uniform 5 to 10 nm Au NPs when compared to the unmodified Turkevich approach.³⁹ In an in-depth study, Puentes *et al.* further explored the isotopic effect in Au NPs preparation. The size evolution of Au NPs was recorded by using D₂O instead of H₂O as the reaction solvent.⁴⁰ The replacement of the reaction medium from H₂O to D₂O will lead to formation of smaller Au NPs, which could be ascribed to the faster reaction kinetics in the D₂O solvent system. Essentially, they claimed that the coordination between HAuCl₄ and sodium citrate will result in a complex of [AuCl₃(C₆H₅O₇)]⁻, which can disproportionate into the Au NPs in the rate-limiting step in the

reaction.

Figure 2.2 Schematic depiction of the Au-S bonding interaction.³⁵

As a noble metal, Au is found to display extraordinary resistance against oxidation and is commonly impressing people by its chemical inertness. When exposed to ambient condition, even a single oxidation layer can hardly be detected on Au surface, which makes Au become the only colored metal which can retain its luster feature almost permanently. The inert nature of Au NPs thus endows it to have superior biocompatibility for a broad range of *in vitro* and *in vivo* biological systems. Another amazing feature of Au NPs is its versatile capability to form the strong gold-thiolate (Au-S) bond (about 184 kJ/mol) with molecules which have the disulfide group (S-S) or thiol (-SH) in their molecular structure. This kind of chemical bonding has been extensively built to introduce different surface chemistry on Au NPs with various self-assembled monolayers (SAMs) (Figure 2.2).³⁵ The functionality of Au surface can be simply realized by using compounds with specific functional group in the configuration of the thiol or disulfide containing molecule. For instance, Au surfaces are often functionalized with poly(ethylene glycol) (PEG) which can serve as a biocompatible layer to protect the surface from interference binding of proteins and therefore improve the targeted binding performance.³⁵ Au NPs can also be modified with molecules with specific targeting capability, such that the Au NPs can selectively assemble at some targeted surface such as cancer cells or antigens, or serve as probes

in chemo/biosensing which we have discussed in last chapter.

Apart from the employment of the Au-S linkage in Au surface modification, for Au NPs synthesized through wet chemistry method, the intrinsic capping ligands bonded to Au surface which serve as stabilizer could also be a type of functionality which could be with different surface charges, solvent compatibility, and functional chemical groups.³⁵ As illustrated in Figure 2.3, for Au NPs prepared using the Turkevich method, there are capped citrate ions at Au surface, which is the reason for the negatively charged Au surface, and thus their electrostatic interactions with some positively charged surface, benefiting the self-assembly of novel hybrid nanostructures.⁴ Moreover, many surfactants were demonstrate can induce the growth of well-defined Au nanoparticles, the explanation for this phenomenon is that the surfactants could bind to certain Au crystal faces, leading to the growth along selected directions and thus the well-defined morphology (Figure 2.3). The surfactant could also act as stabilizers or surface ligands, which endow Au NPs with plentiful surface charges or chemistry, which is favorable in assembling well-ordered nanoarrays or nanostructures.³⁵ In Table 2.1, we summarized the syntheses of different Au nanostructures using different methods and their corresponding LSPR features.

Figure 2.3 Schematics of the intrinsic surface chemistry of solution processed Au nanostructures.

Table 2.1 Syntheses of different Au nanostructures using different methods.

Au nanostructures	LSPR wavelength (nm)	Synthesis method	Size (nm)
Conventional particles ^{15, 34}	520-650	Turkevich method	13-160
Spheres ^{41, 42}	520-650	Seed mediated growth	5-200
Rods ⁴³	600-1300	Seed mediated growth	30-500
Prisms ⁴⁴	1200-1500	Seed mediated growth	150-220
Shells ^{22, 45}	520-900	Templated growth	60-400
Hollow structures ^{46, 47}	400-1200	Galvanic replacement	20-200
Polyhedra NPs ^{48, 49}	560-1000	Polylo process, seed mediated growth	20-250
Branched NPs ^{50, 51}	550-800	One-pot synthesis, seed mediated growth	50-300

In this thesis, we synthesized of ~13 nm colloidal Au NPs using the above discussed Turkevich method for the application of plasmonic colorimetric sensing, namely, reduction of HAuCl₄ in aqueous solution, in which trisodium citrate was the reducing agent. Therefore, the as obtained Au NPs were capped with citrate ions as the ligands, and correspondingly the surface charge will be negative. In a detailed synthesis procedure, HAuCl₄ (100 mL, 1 mM) aqueous solution was heated to boiling under stirring, then trisodium citrate (10 mL, 38.8 mM) aqueous solution was injected rapidly. After refluxing the mixture for 15 min, a wine-red of the solution could be observed. After its gradual natural cooling at room temperature, UV-vis spectrometry measure was conducted to confirm the concentration of the Au NPs was ~10 nM. Then 50 mL of ultrapure water was added to 10 mL of the above Au NPs solution to make a total volume of 60 mL solution, which will be used as a stock liquid in the following sensing experiments. By changing the molar ratio of HAuCl₄ to sodium citrate, we were also able to synthesize ~30 nm colloidal Au NPs, in which a similar procedure was adopted. Briefly, HAuCl₄ (100 mL, 1 mM) aqueous solution was heated to boiling under stirring, then trisodium citrate (1.5 mL, 1%) aqueous solution was injected rapidly. After refluxing the mixture for 30 min, the ~30 nm Au NPs were obtained. Then 10 mL of ultrapure water was added to 10 mL of the above Au NPs

solution to make a total volume of 20 mL solution for use.

2.1.2 Fabrication of indium nanostructures on different substrates

With the remarkable LSPR effect which shows the great application potentials in catalysis,²⁵ energy conversion,⁶ sensing,⁴ and clinical imaging/diagnostics/therapeutics,³⁵ developing controllable and effective synthesis approaches to obtain specific metal nanoparticles have attracted enormous research efforts in the field of plasmonics. To date, amongst the studies of the investigated metals, gold and silver have taken an overwhelming majority, which could be ascribed to their compelling plasmon responses to the visible light radiation, the versatile and well-established chemistry, as well as their chemical inertness towards oxidation or in biological systems. Unfortunately, the high ohmic losses and the poor LSPR responses when using UV excitations strongly hamper their applications that involve a variety of photophysical/chemical processes that can take place only in the UV light range. Moreover, as silver and gold are typically scarce nature resource, they often appear as expensive commodities or are stashed as currency. Taking into account the above limitations, there are increasing efforts in looking for other alternative materials including poor metals or alloys,^{52, 53} carbon based material such as graphene,¹² semiconducting material like indium-tin oxide (ITO),⁵⁴ and other broad kinds of materials.⁵⁵

By far, the most promising results come from the reports using the poor metals such as aluminum and indium, both of which can be tuned to achieve LSPR from UV to visible and even NIR region experimentally.^{24, 56} However, although both of the approaches of preparing In and Al nanostructures have been reported, the number and diversity of the methodologies in the literatures are only taking a tiny fraction, and the quality are often far from expectation when compared to those developed for noble metals. In particular, the situation for Al based

nanostructures is even worse and it is still a big challenge until now. The existing methods are limited in a narrow range such as vapor/electrochemical deposition with nanopatterns or nanotemplates,^{57, 58} pulsed laser irradiation of Al film,⁵⁹ and chemical aerosol flow.⁶⁰

As a group III element, indium metal in its bulk form has been found to show some unique and important characteristics, it can exhibit the superconducting phenomenon with a critical temperature at 3.4 K, and serve as a soldering material, as well as a solid state lubricant.⁶¹ In NPs have been previously reported can be a catalyst in promoting anisotropic growth of semiconducting III-V and II-IV compounds into high aspect ratio nanorods or nanowires.⁶¹ More importantly, it has been demonstrated that In NPs could lead to comparable or even better LSPR responses as Al NPs.^{62, 63} Considering also the relative ease of preparation of In NPs when compared to Al NPs, In NPs could be a better choice in designing some plasmonics based applications.

Taking advantage of the unique property of indium metal and the promising LSPR effect as well as the catalysis ability of In NPs, synthesis of In NPs have been demonstrated from different chemical and physical approaches. In 2008, indium nanowires (In NWs) and nanooctahedras (In NOs) with well-defined shapes were prepared through reduction of InCl_3 by sodium borohydride (NaBH_4) in the presence of polyvinylpyrrolidone (PVP), resulting in In NPs size can be down to 80 nm by controlling the dropping rate of the reducing solution (NaBH_4 in tetraethylene glycol).⁶⁴ Later on, Hammarberg *et al.* developed a two-step procedure to prepare In NPs with 10 to 15 nm sizes in diethylene glycol (DEG), in which the reducing agent was also NaBH_4 .⁶⁵ By carrying out the phase transfer using oleylamine, the resultant In NPs in DEG can be easily transferred to the nonpolar solvents such as pentane and dodecane. This report represents an innovative and important improvement; however, as there are the two steps involving in the

synthesis route, it may on the other hand induce more difficulties in achieving scale-up production. Particularly, the phase transfer step often spends a large volume of the two immiscible solvents, which may in the end lead to low yield of In NPs. To improve the synthesis yield of In NPs, Yu *et al.* reported a system using decomposition of cyclopenta-dienyl-indium assisted by methanol for the production of In NPs, in which the particle size can be controlled through a seed growth process mediated by poly(styrene_{0.86}-*co*-vinylpyrrolidinone_{0.14}) which plays the role as a surfactant.⁶⁶ The seeds are small gold clusters [Au₁₀₁(PPh₃)₂₁C₁₅] of 3 nm in size, which can serve as the cores for the growth of In NPs, and the as obtained monodispersed In NPs were smaller than 10 nm. However, concerns still exist if there is a demand for large scale production, because all the reagents including the indium precursor cyclopenta-dienyl-indium, the Au clusters seeds, and the polymeric surfactant, whose availabilities are mostly relying on in-house synthesis. Moreover, it should also be noted that the yield of In NPs was determined by the amount of gold clusters introduced. However, since the fact is that the yield for Au clusters is often very low (26%), the large-scale production of In NPs using this method would be not cost-effective. In this context, the development of a simple, controllable, and cost-effective method for preparing In NPs is still highly desirable and of crucial importance. In 2014, Kumamoto *et al.* reported the preparation of In NPs on quartz substrates through a simple one step thermal evaporation method, in which the only source used is indium metal, and the size of In NPs can be simply controlled by changing the deposition thickness of indium on the substrate, showing a great potential in promoting the practical application of In NPs.⁶³ We summarize here the preparation of different In nanostructures using different methods and their corresponding LSPR features in Table 2.2.

Table 2.2 Preparation of different In nanostructures using different methods.

In nanostructures	LSPR wavelength (nm)	Synthesis method	Size
In NWs and In NOs ⁶⁴	380 nm for In NOs	Reducing In salt by NaBH ₄ in TEG	50 nm-4 μ m
Spheres ⁶⁵	ND	Two-step method in DEG	10-15 nm
Spheres ⁶⁶	ND	Seed mediated growth	7-16 nm
Spheres ⁶⁷	350	Laser ablation	43 nm
Spheres ⁶⁸	ND	Ultrasonication	50 nm-2 μ m
Spheres ⁶⁹	240-280	One-pot synthesis	10-100 nm
Spheres and irregular shapes ⁶³	200-600	Thermal evaporation	10-300 nm
In NWs ⁷⁰	ND	Decomposition of In complex	200 nm in diameter

As an extension of the thermal evaporation approach, we demonstrate that well defined In NPs could also be prepared on different substrates, which inspires us to design different In NPs plasmonic systems for a broad range of applications. The configuration of a typical thermal evaporation system usually contains two main parts: a chamber and a high vacuum generation system. The high vacuum of the system is achieved through a two-level pumping process. In the first roughing pumping process, a mechanical pump can pump the chamber to reach the vacuum around 10^{-2} Torr. Then the Cryo pump will further pump the chamber after the vacuum of the roughing process have reached a critical value, in which the vacuum can achieve 10^{-7} to 10^{-8} Torr, providing superior safe condition for the evaporation of some metal sources which are not stable in the air at high temperature. The general configuration of the commonly used thermal evaporation system is illustrated in Figure 2.4 (Semicore Equipment, Inc).

Figure 2.4 Diagram of components and processes involved in a thermal evaporation system.

The source material with high purity is placed on the thermal filament, upon applying power through the electrode to thermal filament, the heat generation from the thermal filament will quickly melt the source material to result in the evaporation of the source. The real-time evaporation rate of the source and vacuum value in the chamber are monitored by corresponding sensors. The substrate is fixed and face down on the substrate holder with appropriate distance to the source. The as formed vapor of the source material will then condense at the substrate surface.

The evaporation process can be divided into two processes: 1) the vaporization of the source material, in which thermodynamics is given by Hertz-Knudsen equation⁷¹

$$\frac{dN}{Adt} = \alpha(2\pi mkT)^{-1/2}(p^* - p) \quad (2-1)$$

where dN/dt is the evaporation rate in which N is the number of vaporized molecules and t is the

corresponding time. A denotes the surface area of the source, α is the sticking coefficient of the molecule, k is the Boltzmann constant, m is the mass of a molecule, T is the temperature, p and p^* refer to the hydrostatic pressure on the source surface and the equilibrium vapor pressure of the evaporant, respectively. From the above equation, we can see that the evaporation rate is dependent on temperature, and the sticking coefficient which is determined by the material used, as well as the vacuum of the system; 2) the vapor transport between the source and the substrate, in which high vacuum is required to avoid the collisions of the vapor molecules before they condense at the substrate surface. The transport length can be obtained through the calculation of the average free path λ for every two consecutive collisions using the following equation

$$\lambda = kT/\sqrt{2}\pi Pd^2 \quad (2-2)$$

in which P denotes the pressure, while d is the diameter of the molecule. For instance, if gold whose atom diameter is 0.2 nm is used as the source material under a normal pressure of the thermal evaporation system around 10^{-5} Pa, the calculated λ is around 1200 m which is much longer than the distance between the source and the substrate, which implies that the collision between molecules can be effectively inhibit by using the thermal evaporation system with good vacuum condition.

In our thermal evaporation system (Elite Engineering, Singapore), the equipped Cryo pump can maintain a temperature around 10 K through the helium gas compressing and create the vacuum in the chamber to reach down to 10^{-8} Torr which is monitored by a Pirani gauge. The evaporation rate can be known by using a SQM-160 film thickness monitor, whose working mechanism is that the resonant frequency shift of the quartz crystal sensor is proportional to the deposition thickness of the material on it, whose attainable accuracy can reach as high as 1 Å/sec. To achieve the best accuracy, different materials will be set with different parameters in the

controlling program such as the material density and the Z factor. In the thesis, we performed the evaporation of indium on different substrates such as quartz, microporous membrane (MPM) and ITO at a base pressure of 3×10^{-7} Torr, in which we can obtain high quality In NPs on all of the substrates. And the sizes of In NPs can be easily controlled by simply changing the deposition thickness of the indium source, which have inspired us to design a serial of applications based on the as obtained In NPs plasmonic nanostructures.

2.2 Characterizations of Au and In nanostructures

2.2.1 Transmission electron microscopy

In 1931, the first TEM instrument was invented by a group at the Technical University of Berlin. From then on, TEM has experienced rapid innovations and quickly become a powerful tool for scientists in performing material characterizations.^{72, 73} In this thesis, JEOL JEM 1400 TEM system was employed for the characterization of the prepared Au NPs. The acceleration voltage was 100 kV for our characterizations. In our experiments, we dropped 10 μ L of the Au NPs solution on a copper TEM grid with a filter paper under it to absorb the redundant water and make it dry quickly, Au NPs could remain their dispersion state on TEM grid as in solution, for this reason, TEM has been widely used in confirming the dispersion state of Au NPs in solution. Figure 2.5 shows the TEM images of Au NPs with well dispersed and aggregated state in aqueous solution we have intentionally prepared, from which we can confirm Au NPs we prepared is homogeneous and the size is ~ 13 nm.

Figure 2.5 TEM images of (A) well dispersed and (B) aggregated state Au NPs.

2.2.2 Scanning electron microscopy

SEM is a useful technique which can provide information for investigating the surface structures of materials. We performed our SEM characterization of In NPs nanostructures using a field emission JEOL 7001F model SEM. The acceleration voltage in our characterizations was 10 kV with a working distance of 10 mm. Figure 2.6 shows the SEM images of In NPs on different substrates such as quartz, ITO, TiO₂ and MPM. We took advantage of the poor wettability of indium for solid surface, through which well-separated grains will form when indium vapor meets a cold surface, thus we can prepare In NPs on different substrate through a thermal evaporation method.

Figure 2.6 SEM images of In NPs prepared on different substrates. (A) Quartz. (B) ITO glass. (C) TiO₂ nanorod array. (D) MPM.

2.2.3 UV/Vis/NIR optical absorption spectroscopy

Optical absorption spectroscopy has been routinely used in characterizing the optical properties of different materials, for instance, the excitonic states of semiconductors, the energy states of organic molecules, the transparency of thin films, as well as the LSPR of plasmonic nanoparticles. In this study, we use a Lambda 950 UV/Vis/NIR absorption spectrometer to characterize the LSPR properties of colloid Au NPs in aqueous solution (Figure 2.7 A and B) and In NPs prepared on a specific substrate (Figure 2.7 C). By measuring the absorption data of Au NPs in aqueous solution, we can see their LSPR features. For ~13 and ~30 nm size Au NPs with well dispersed state in solution, both they can show a wine-red color, corresponding to their LSPR peaks at 519 and 527 nm, respectively. It also can be observed in their aggregation states that strong peaks appear at 676 nm for ~13 nm size Au NPs and 820 nm for ~30 nm Au NPs,

which is due to the aggregation induced plasmon coupling of Au NPs. We can measure the In NPs prepared on a quartz substrate. By controlling the deposition thickness of indium on quartz, we can prepare In NPs with different sizes on the substrate. Due to the increasing size and the formation of irregular shape of In NPs prepared with larger thickness of indium, the LSPR of In NPs becomes broader because of the appearance of higher order plasmon modes, which can be monitored in the UV/Vis absorption spectra.

Figure 2.7 UV/Vis absorption spectra of Au NPs in solution with ~ 13 (A) and ~ 30 (B) nm sizes, and (C) In NPs prepared with different thicknesses of thermal evaporated indium.

2.2.4 X-ray photoelectron spectroscopy

With the increasing importance of developing high performance materials for different applications, accurate characterization technique for materialist in confirming the surface chemical and elemental state of the material is highly desirable to provide the basis for achieving

effective surface engineering. The surface can provide the point where different interactions can take place, and many problems encountered in modern material researches are related to the surface chemical or physical properties, which will affect many factors of a material such as wettability, adhesive properties, catalytic activity, corrosion rates. X-ray photoelectron spectroscopy (XPS) is a technique which is capable of analyzing the surface chemistry of a material such as electronic state and chemical state of the elements, empirical formula, as well as elemental composition within a material.⁷⁴ In this thesis, we use a VG ESCALAB 220i-XL XPS system equipped with a monochromatic Al K α X-ray source to characterize the chemical state of the In NPs we prepared on MPM (Figure 2.8 A), which is then used as a plasmonic device for solar evaporation. The XPS spectrum of indium (Figure 2.8 B) shows two distinct peaks at ~443 and ~451 eV with asymmetric shapes, and a weak peak around 454 eV, which are well agreed with the feature of indium metal. For the O1s spectra, the In NP/MPM structure shows a peak around 528.5 eV (Figure 2.8 C) which is absent in the bare MPM structure (Figure 2.8 D). This is due to the formation of an intrinsic oxidation layer on In NPs, in this case, the chemical environment of O changed due to the formation of In-O bond. Therefore, we can observe the appearance of a new peak.

Figure 2.8 (A) SEM image of In NPs prepared on MPM. The scale bar is 500 nm. (B) XPS spectrum of indium on In NP/MPM. (C) XPS spectrum of oxygen on In NP/MPM. (D) XPS spectrum of oxygen on bare MPM.

2.2.5 X-ray diffraction

The properties of a material can experience a dramatic change with the different arrangements of the building block atoms in its crystal structure. Therefore, figuring out the crystal structure of a material is helpful in understanding its physical and chemical properties. In the past few decades, X-ray diffraction has contributed powerful support in providing non-destructive characterizations of materials by yielding the unique fingerprint diffraction peaks of X-ray which is highly dependent on the crystal structure. In our study, we conduct the XRD characterizations of In NPs prepared on MPM using a high-resolution Phillips PANalytical X'Pert Pro diffractometer, and the X-Ray source is Cu K α radiation (1.5406 Å). The as obtained XRD

pattern of In NPs on MPM is consistent with a standard reference of indium (ICSD collection code: 064794) (Figure 2.9), showing a body-centered tetragonal crystal structure.

Figure 2.9 XRD pattern of In NPs prepared on MPM.

Chapter 3

Controllable plasmon coupling of Au NPs induced color changes for plasmonic colorimetric logic gate sensing

3.1 Introduction

3.1.1 Background

With the rapid growth of public concerns on environmental issues, food safety, and human healthcare, topics of keeping healthier lifestyles have also drawn greater attentions across the world in the past few decades. Particularly, melamine was found in infant formula in 2008, which quickly became a shocking scandal, and warned human society that there is still a long-lasting battle to solve the issues on food safety.¹⁵ Heavy metal contaminations caused by hazardous metal such as mercury, on the other hand, gives rise to severe threats to both human health and the environment.⁷⁵ Cysteine is generally known as a sulphur-containing amino acid, however, its biological function in human body is also irreplaceable.⁷⁶ Therefore, it is demanding for the general public to explore a simple and cost-effective sensing system for detecting these targets, which will also benefit the public in food and environment safety, medical diagnostics, and even for fundamental researches. However, conventional sensing methods for Hg^{2+} , melamine and cysteine were often time-consuming, costly, procedure-complicated, and non-portable. For this reason, it is highly desirable to develop rapid, inexpensive, simple, and portable methods.

3.1.2 Plasmonic colorimetric logic gate

Plasmonics based colorimetric sensing which aims at designing controllable aggregation or anti-aggregation system of Au NPs has been proven a powerful tool in chemo/biosensors. Hence, the

detection systems for various analytes were widely developed based on this simple, rapid and cost effective technique.⁴ More importantly, accompanied with the aggregation or anti-aggregation process of Au NPs, there is always a shift of the SPR peak of Au NPs, which can be explained by the inter-particle plasmon coupling. At the same time, it will also cause a distinct color switch between blue and red, which only simple UV-vis spectroscopy measurement or even naked eye observation is needed to perform the sensing process. However, colorimetric sensing has its own weaknesses because of its own limitations. Until now, the majority of the colorimetric systems were using Au NPs to fabricate the assays to detect one certain target. Therefore, most of them were not capable of discriminating different analytes in different target scopes in one sensing system. Constructing molecular logic gate in chemo/biosensors that employs the concept of logic gate which is commonly used in semiconductor industry offers an effective way of overcoming the above weakness of plasmonic colorimetric biosensing.⁷⁷ As is well known, a variety of logic operations including AND, NOT, YES, NAND, INH, OR, NOR, and XOR are existing based on the number as well as the logic relationship between the inputs in a logic gate.⁷⁸ By changing the inputs to a logic gate sensing assay, different targets can be discriminated by using outputted signals as references. For this reason, all kinds of molecular logic gate sensors were constructed for different sensing purposes.^{77, 79, 80}

3.1.3 Design of a three-input colorimetric logic gate sensing system

Up to now, most of the formulated plasmonic colorimetric sensing systems based on Au NPs were two-input systems because of the poorly specific interactions among multiple analytes and Au NPs, therefore, developments of logic gate sensing systems that includes more inputs were seldom reported.⁸¹⁻⁸³ Moreover, if interactions between analytes that serve as inputs are poorly specific, aggregation and dispersion of Au NPs may not be controllable. Therefore, making sure

inputted analytes have high specific interactions between each other is the key to successfully design a multiple-input logic gate sensor. Herein, we have developed a three-input colorimetric logic gate sensing system which can achieve the detection of cysteine, melamine and Hg^{2+} , in which the mechanism is target-induced controllable aggregation and anti-aggregation of Au NPs which can be ascribe to the highly specific competing coordination reactions between the analytes and Au NPs. Hence, a series of logic operations which includes OR, INH, and AND as well as an inter-connected logic gate was built based on these highly specific interactions, which endows the as constructed logic gate system the ability in performing highly sensitive and selective detections to the analytes. Moreover, Au NPs are intrinsically sensitive to melamine in plasmonic colorimetric sensing,¹⁵ which makes the logic sensing system also have good performance in the detection of cysteine, and Hg^{2+} .

3.2 Experimental section

3.2.1 Plasmonic colorimetric logic gate operations by using Au NPs solutions

Combinational mixtures of melamine, cysteine and Hg^{2+} were first prepared and then added into 1 mL of the above ~13 nm Au NPs solutions. The final effective concentrations of the analytes were fixed at 1.8×10^{-4} M (Hg^{2+}), 3.6×10^{-4} M (cysteine), and 6×10^{-5} M (melamine). The effect of dilution was eliminated by fixing the volume of the combinational mixtures of the targets not more than 30 μL . Absorption spectra of the above Au NPs solutions were measured with UV/Vis absorption spectrometer after 2 minutes. Their corresponding digital photos were also taken by a digital camera at the same time.

3.2.2 Melamine sensing

For melamine sensing, the aggregation degree of 1 mL Au NPs solutions upon the addition of 10 μL melamine with certain concentrations were investigated. For selectivity analysis, different

nitrogen containing compounds in aqueous solutions were added into 1 mL of Au NPs solutions and mixed thoroughly, all the final effective concentration of these samples was 1.5×10^{-6} M. The incubation time was all 2 minutes, UV/Vis absorption spectra and photos of Au NPs solutions were recorded with spectrometer and the digital camera, respectively.

3.2.3 Cysteine sensing

In the selectivity experiments, different amino acids in aqueous solutions were mixed with melamine thoroughly one by one first, and then the mixture were added into 1 mL of Au NPs solutions. The final concentrations of melamine and the amino acids in all samples were fixed at 60 μ M. After incubating for 2 minutes, their corresponding digital photos and absorption spectra were taken by a digital camera and UV/Vis absorption spectrometer, respectively. To investigate the sensitivity of the assay, the sample of 1 mL of Au NPs solution caused by the addition of 1.4 μ M melamine was chosen as a control sample. Then 10 μ L of cysteine with a serial of concentrations were mixed with 10 μ L of melamine thoroughly, after which the mixtures were injected into 1 mL of Au NPs stock sensing solutions. Absorption spectra of the above Au NPs solutions were measured with UV-vis spectrometer after 2 minutes. Their corresponding digital photos were also taken in the meantime by a camera.

3.2.4 Hg²⁺ sensing

To perform the selectivity experiments, different metal ions in aqueous solutions were mixed with melamine thoroughly one by one first, and then the mixture were added into 1 mL of Au NPs solutions. The final effective concentrations of the metal ions and melamine were all fixed at 50 and 1.5 μ M, respectively. After incubating for 2 minutes, their corresponding digital photos and absorption spectra were taken by a digital camera and UV/Vis absorption spectrometer, respectively. To conduct the sensitivity experiments, the sample of 1 mL of Au NPs solution

caused by the addition of 0.6 μM melamine with 15 mM NaCl was chosen as the control sample. Then 10 μL of Hg^{2+} with a serial of concentrations were mixed with 10 μL of melamine thoroughly, after which the mixtures were injected into 1 mL of Au NPs stock sensing solutions. Absorption spectra of the above Au NPs solutions were measured with UV/Vis absorption spectrometer after 2 minutes. Their corresponding digital photos were also taken in the meantime by a camera.

3.3 Results and discussion

3.3.1 Construction of a three-input (Hg^{2+} , melamine, and cysteine) plasmonic colorimetric logic gate based on colloid Au NPs

Figure 3.1 is an illustration of the working principles of our as designed colorimetric logic gate. In our design, the inputs are the analytes and the outputs will be the induced colors of Au NPs. To be more specific, since we are aiming at the combinational detections of three kinds of analytes (Hg^{2+} , melamine, and cysteine), if there is only one analyte presenting in the sensing matrix, the inputs can be expressed as 100, or 001, or 010. In the case of the co-existence of two analytes, the inputs will be 110, 101, or 011. Along this way, the inputs without and with the presence of all the three analytes will be 000 and 111, respectively. The outputs 0 and 1 of the logic gate correspond to the dispersed (red color) and aggregated (dark blue color) state of Au NPs in solution, respectively. Melamine molecule in aqueous solution often carries positive charges, this is due to its amine groups can be protonated by H^+ in an aqueous solution. On the contrary, Au NPs prepared by reduction of HAuCl_4 with sodium citrate in aqueous solution are negatively charged because of the deprotonated citrate ligands on Au surface. Since there will be strong counter charge interactions, once melamine is added to Au NPs solution, Au NPs will form aggregates quickly, in which the color of the Au NPs solution will change from red to blue

(input 001, output 1). This aggregation process of Au NPs caused by melamine will be easily inhibited when Hg^{2+} is added with melamine together. It has been reported that strong coordination reaction exists between the nitrogen atoms of melamine and Hg^{2+} ,⁸² which on the other hand could explain the inhibition effect from Hg^{2+} to melamine induced aggregation of Au NPs. It is anticipated that melamine which is bound by Hg^{2+} cannot lead to the formation of Au NPs aggregates, thus red color of Au NPs solution remains (input 101, output 0). Sulfhydryl group (-SH) has been well known for its excellent affinity for Au surface and a kind of Au-S bond can form between them, which makes it become a widely used method for surface modification of different molecules on Au surface.³⁵ Cysteine is a well-known amino acid as it contains sulfhydryl group which can lead to the formation of a cysteine molecule layer on Au NPs when it is added to the Au NPs solution (input 010, output 0). Since the Au-S bond can form in this process, compared with the electrostatic reaction between melamine and Au NPs, Au-S bond is much stronger, which could protect Au NPs to stay in a well dispersed state even when melamine is introduced (input 011, output 0). A unique feature of the as formed Au-S bond is that it can be destroyed by Hg^{2+} through the formation of a stable cysteine- Hg^{2+} complex, which will result in the removal of the thiolates that have been chemisorbed on the Au surface.⁸⁴ As a result, Au NPs without surface ligands that help stabilize them in solution will quickly aggregate (input 110, output 1). It is worth noting that Hg^{2+} ions themselves will not have any effects on the well dispersed state of Au NPs in solution (input 100, output 0). However, if all the three analytes are introduced to Au NPs solution together, dramatic aggregation of Au NPs will be observed (input 111, output 1), which is due to the competing coordination reactions between the analytes, in which only the cysteine- Hg^{2+} complex can form. The competing formation of different complexes when different analytes are introduced is the key in designing this logic gate sensing

system.

Figure 3.1 Illustration of the design principles of the three-input colorimetric logic gate.

3.3.2 Logic operations in the plasmonic colorimetric sensing system

The size of the as prepared Au NPs was confirmed by TEM, displaying a size of ~13 nm (Figure 3.2).

Figure 3.2 TEM images of the states of ~13 nm Au NPs after the analytes (60 μM melamine, 360 μM cysteine, and 180 μM Hg^{2+}) were added with different logic combinations. All scale bars in the images are 50 nm.

Figure 3.3A is the UV/Vis absorbance of Au NPs solutions with the addition of analytes (60 μM melamine, 360 μM cysteine, and 180 μM Hg^{2+}) in different logic combinations. The spectra with analyte combinations in 001, 111, and 110 can show obvious changes when compared with those in the conditions of 000, 100, 010, 101, and 011. The strong absorption bands around 600 to 700 nm are the result of the appearance of aggregates of Au NPs in these samples, which are induced by the analytes, demonstrating that aggregation of Au NPs occurred in these solutions. It is consistent with TEM result (Figure 3.2) that aggregates appear only under the combination conditions 001, 111, and 110. Their aggregation degrees can be evaluated by calculating the corresponding $A_{650\text{nm}}/A_{520\text{nm}}$ values (Figure 3.3B). Figure 3.3C shows the network map of the logic gate sensing system in which different logic operations are incorporated. Both Hg^{2+} and cysteine cannot make Au NPs become aggregates alone unless they are added to the Au NPs solution together. Therefore, this phenomenon agrees well with the function of AND gate. On the other hand, melamine alone is enough to cause the aggregation effect of Au NPs, thus an OR operation could convey the inter-relationship between AND gate of cysteine/ Hg^{2+} and melamine. Moreover, either cysteine or Hg^{2+} can inhibit the formation of melamine induced Au NPs aggregates when they were separately added together with melamine. Hence, two INH gate functions are required in the network map of the logic gate. To illustrate in detail how the AND, OR, and INH functions in the as designed logic gate system, Table 3.1 is presented as a reference. In Figure 3.3D one can read the inputs and their corresponding outputs by using our logic gate sensing system in which the readouts from the color (only red or blue) can be clearly distinguished.

Figure 3.3 Logic operations performed by using Au NPs solutions with different analyte combinations. (A) UV/Vis absorption spectra of Au NPs solutions with analytes (60 μ M melamine, 360 μ M cysteine, and 180 μ M Hg^{2+}) in different logic combinations. (B) Their corresponding A_{650nm}/A_{520nm} values. (C) Network map of the logic gate sensing system with logic operations. (D) The inputted and their corresponding outputted signals in this logic system. Inset displays the outputted color readouts.

Table 3.1 Truth table of INH, OR and AND gates based on Boolean logic operations.

Input		Output		
(A)	(B)	AND	OR	INH
0	0	0	0	0
0	1	0	1	1
1	0	0	1	0
1	1	1	1	0

Therefore, different analytes can be distinguished by using their inter-connected reactions step by step. An illustration to show how different combinations of analytes can be discriminated is presented in Figure 3.4. In addition, for an unknown solution that may contain 0, 1, 2 or 3

components of the analytes (melamine, cysteine and Hg^{2+}), we cannot determine how many components are in the solution. However, we can discriminate the analytes or their combinations when the number of components in the unknown solution is fixed. For instance, the discrimination of one kind of analyte (melamine, cysteine and Hg^{2+}) or the combination of two kinds of analytes (melamine/cysteine, melamine/ Hg^{2+} and cysteine/ Hg^{2+}).

Figure 3.4 An illustration to show how different combinations of analytes can be discriminated. (A) Discrimination of a single kind of analyte. (B) Discrimination of the combination of two kinds of analytes. The analytes can be discriminated step by step with the help of an additional solution of Hg^{2+} when it is known that how many kinds of targeted species are in the sample solution. There will be only one case when the number of species is three, namely, the coexistence of Hg^{2+} , melamine, and cysteine. The output of this combination will always be 1, namely the formation of Au NPs aggregates, so the discrimination of this case is not needed.

3.3.3 Investigation of the mechanism through UV/Vis absorption spectra evolutions induced by competing coordination reactions

To have a better understanding of the competing coordination reactions between the three targets, we first performed a titration experiment to investigate the coordination reaction between melamine and Hg^{2+} (Figure 3.5A). Melamine in aqueous solution shows two typical peaks at 204 and 234 nm, which is consistent with previous report.⁸² It can be observed that the strong absorption peak of melamine located at 204 nm decreases when more amount of Hg^{2+} is added, whereas its weak absorption peak around 234 nm at the same time shows dramatic enhancements, which is an indication of the formation of complex through coordination. One can still see this change when the concentration of Hg^{2+} is increased from 60 to 80 μM , from which we can make sure 60 μM Hg^{2+} can be totally coordinated to 20 μM melamine. Then the Hg^{2+} -melamine complex (60 μM Hg^{2+} + 20 μM melamine) solution was chosen for ligand replacement study for this reason. It can be seen in Figure 3.5B that the absorbance of the bands with wavelength ranging from 200 to ~230 nm increases dramatically with the increasing amount of the added cysteine, and the maxima appears when 120 μM cysteine is added. To confirm whether this increment is caused by the effect of cysteine's addition, the effect induced by a same amount of cysteine was studied for comparison (Figure 3.5C). The result shows that cysteine induced increments in the absorbance without the formation of complex is almost 8 times lower, which demonstrates that ligand replacement reaction indeed has occurred in the case of Figure 3.5B. In this process, the Hg^{2+} -melamine complex is transformed into the Hg^{2+} -cysteine complex. Similar phenomenon is also observed when Hg^{2+} is added in cysteine solution, in which the maxima of absorption bands in 200 to ~230 nm also appear when 120 μM cysteine is added, suggesting the complete transition between the two forms of complex of Hg^{2+} . It agrees well with many

published works that cysteine and Hg^{2+} can form a kind of $\text{Hg}^{2+}(\text{cysteine})_2$ complex whose stability constant could reach as high as 2×10^{40} .^{85, 86}

Figure 3.5 Competing coordination reactions induced UV/Vis absorption spectra evolutions of the analytes. (A) Hg^{2+} induced changes of UV-vis absorption spectra of 20 μM melamine. Concentration of Hg^{2+} was increased from 0 to 80 μM , (B) cysteine induced changes of UV/Vis absorption spectra of Hg^{2+} -melamine complex (60 μM Hg^{2+} + 20 μM melamine) solution. Concentration of cysteine was increased from 0 to 160 μM , (C) UV/Vis absorption spectra of cysteine alone in aqueous solution. The concentration of cysteine was increased from 40 to 160 μM , and (D) cysteine induced changes of UV/Vis absorption spectra of 60 μM Hg^{2+} . Concentration of cysteine was increased from 0 to 160 μM .

Figure 3.6 (A) UV/Vis absorption spectra of Au NPs solution upon the addition of cysteine at the concentrations ranging from 0 to 404 μM , (B) Au NPs solution upon the addition of melamine at the concentrations ranging from 0 to 200 μM in the presence of 6 μM cysteine, (C) Au NPs solution upon the addition of Hg^{2+} at the concentrations ranging from 0 to 60 μM in the presence of 6 μM cysteine, Au NPs solution upon the addition of (D) HCl and (E) NaOH at the concentrations ranging from 0 to 120 μM in the presence of 6 μM cysteine. These results imply

that cysteine can be served as a stabilizing agent against melamine induced aggregation of Au NPs. However, this stabilizing effect will be broken when Hg^{2+} is introduced into the system at the same time.

To further study the interactions between Hg^{2+} , melamine, cysteine, and Au NPs, detailed experiments were conducted. Only minimal changes in absorption spectra of Au NPs are observed upon the additions of cysteine ranging from 0 to 404 μM (Figure 3.6A). The additions of melamine with concentrations from 0 to 200 μM to Au NPs solution in the presence of 6 μM cysteine almost have no effect on the absorption spectra of Au NPs (Figure 3.6B). These results imply that cysteine can be served as a stabilizing agent against melamine induced aggregation of Au NPs. However, this stabilizing effect will be broken when Hg^{2+} is introduced into the system at the same time. The absorption band of Au NPs around 650 nm increases remarkably with the addition of Hg^{2+} in the presence of cysteine (Figure 3.6C). The effects of strong acid and base on the absorption spectra of Au NPs in the presence of cysteine were also investigated by using HCl and NaOH (Figure 3.6D, E). These results indicate that Hg^{2+} can strongly destabilize the well-dispersed solution of Au NPs in the presence of cysteine.

To verify the important role of the sulfhydryl group of cysteine in our as-designed colorimetric logic gate, alanine, an amino acid which has the same structure as cysteine except the absence of sulfhydryl group was used for comparison. It can be seen from Figure 3.7A that completely different results were obtained when alanine and cysteine is added to the Hg^{2+} -melamine complex solution. Alanine with chelating ligands has also been reported can bind with Hg^{2+} to form a stable complex and the stability constant is about 10^{20} , however, this value is much lower than that of $\text{Hg}^{2+}(\text{cysteine})_2$ due to the high affinity of Hg^{2+} for the sulfhydryl group of cysteine (Table 3.2). Absorption spectra the Hg^{2+} -melamine complex (60 μM Hg^{2+} + 20 μM melamine) in aqueous solution shows minimal response upon the addition of alanine, which demonstrates that

Hg^{2+} -melamine complex is very stable and cannot be damaged upon the addition of alanine without sulfhydryl group (Figure 3.7B). Furthermore, adding alanine alone to Hg^{2+} aqueous solution almost has no effect on the absorption spectra of Hg^{2+} aqueous solution (Figure 3.7C), which suggests that the increment of the absorption band of Hg^{2+} aqueous solution upon the addition of cysteine in Figure 3.5D should be ascribed to the coordination between Hg^{2+} and sulfhydryl group of cysteine. Absorption spectra of alanine, alanine/melamine and cysteine/melamine aqueous solutions suggest that the presence of alanine or cysteine also has no effect on the absorption spectra of melamine (Figure 3.7D, E and F).

Figure 3.7 Control experiments to verify the role of –SH group in the logic gates. (A) Color readouts induced by melamine (60 μM) and Hg^{2+} (180 μM) with 360 μM alanine (top) and cysteine (bottom) in different combinations. (B) Alanine induced changes of UV/Vis absorption spectra of Hg^{2+} -melamine complex (60 μM Hg^{2+} + 20 μM melamine) solution. Concentration of alanine was increased from 0 to 160 μM , (C) alanine induced changes of UV/Vis absorption spectra of 60 μM Hg^{2+} . Concentration of alanine was increased from 0 to 160 μM , (D) UV/Vis absorption spectra of alanine alone in aqueous solution. The concentration of alanine was increased from 40 to 160 μM . Melamine (20 μM) solutions upon the addition of alanine (E) and cysteine (F) from 40 to 160 μM .

Table 3.2 Stability constants of the complexes formed through coordination with Hg^{2+} .⁸⁶

Amino acid	Stability constant- $\beta(\text{ML}_2)$
Alanine	19.6
Cysteine	39.4

3.3.4 Application in sensing of different analytes

To study the melamine-induced aggregation mechanism of Au NPs, different nitrogen containing compounds were employed to compare the colorimetric selectivity of the 13 nm citrate-stabilized Au NPs. Figure 3.8A shows the UV-vis absorption of Au NPs colloidal solutions upon the addition of these compounds at the concentration of 1.5 μM . It can be seen that only melamine and an analog of melamine (cyromazine) can induce the aggregation of Au NPs, while the other types of compounds do not show obvious influences on Au NPs at the same concentration. The very small $A_{650\text{nm}}/A_{520\text{nm}}$ ratios of Au NPs solutions with cyanuric acid, dicyandiamide, butylamine and acetonitrile are almost show no difference to the stock Au NPs sensing solution, suggesting no obvious aggregation of Au NPs formed in these solutions (Figure 3.8B). Meanwhile, clear color change of the solution with such a low concentration of melamine or cyromazine can be directly observed by naked eye (Figure 3.8C), indicating the high selectivity

of the assay to melamine like molecules among various nitrogen containing compounds (Figure 3.8D).

Figure 3.8 Selectivity to melamine like compounds. (A) UV/Vis absorption spectra of Au NPs solutions with the addition of six nitrogen containing compounds with the concentration of 1.5 μ M, (B) their corresponding A_{650nm}/A_{520nm} values, (C) the photos of color readouts of the above samples, and (D) molecular structures of the six compounds.

To study the effect of Au NPs size on their sensitivity to melamine, Au NPs with the size of ~30 nm were also investigated. Compare to ~13 nm Au NPs, ~30 nm Au NPs show lower sensitivity to melamine both by instrument measurements and naked eye observation under the same condition (Figure 3.9). Under optimized condition, even 6×10^{-7} M melamine could induce the severe aggregation of ~13 nm Au NPs, demonstrating the high sensitivity of ~13 nm Au NPs to melamine (Figure 3.10).

Figure 3.9 Comparison between Au NPs with ~13 and ~30 nm sizes. (A) SEM image of ~30 nm Au NPs. UV/Vis absorption spectra responses of ~30 nm (B) and ~13 nm (C) Au NPs solutions after the addition of 1.5 μ M melamine, (D) the corresponding A_{676nm}/A_{519nm} (13 nm Au NPs) and A_{820nm}/A_{527nm} (30 nm Au NPs) values, (E) the color readouts of the Au NPs solutions.

Figure 3.10 (A) 0.6 μM melamine induced evolutions of UV/Vis absorption spectra of Au NPs in 30 minutes. (B) Time dependent visual detections of Hg^{2+} by using 0.6 μM melamine as a reference.

Cysteine is widely used in Au NPs community for different applications due to its well-known ability to cause Au NPs to form aggregates when its concentration is high, or it is used at low pH condition, by forming the zwitterionic networks. The deprotonated carboxylate ($-\text{COO}^-$) and protonated amine ($-\text{NH}_3^+$) groups of cysteine will have head-to-head interaction between adjacent particles, thus aggregation of Au NPs will happen.⁸⁷ Besides this well-known phenomenon, we found that cysteine could serve as a surface ligand to protect Au NPs to stay in a well dispersed state by inhibiting the melamine induced aggregation effect. Therefore, in our unusual design, the INH relationship between melamine and cysteine was applied in cysteine sensing. Figure 3.11A shows the UV-vis absorption spectra of Au NPs in solution after different amino acids are added with 60 μM melamine together. We can see the selectivity for cysteine is very high based on the $A_{650\text{nm}}/A_{520\text{nm}}$ values and the corresponding color readouts of the samples (Figure 3.11B and C). It can be explained by the molecular structure differences between cysteine and other amino acids. Only cysteine with sulfhydryl group could inhibit the formation of Au NPs aggregates when melamine is added to Au NPs solution (Figure 3.11D). In Figure 3.11E, one can see that the $A_{650\text{nm}}/A_{520\text{nm}}$ values decreases when more amount of cysteine is

added. Even when the concentration of cysteine is as low as 0.6 μM , the decreased $A_{650\text{nm}}/A_{520\text{nm}}$ value can still be detected on the UV-vis spectrometer, indicating the sensitivity of this assay to cysteine. The corresponding visualized color readouts of the samples from dark blue to wine red can be easily observed (Figure 3.11F). It can be seen in Figure 3.11G that the $A_{650\text{nm}}/A_{520\text{nm}}$ value and the amount of cysteine almost shows a linear relationship, which is important for the quantification of cysteine.

Figure 3.11 Cysteine sensing. (A) UV/Vis absorption spectra of Au NPs in solution after 60 μM different amino acids are added together with 60 μM melamine, (B) the corresponding

$A_{650\text{nm}}/A_{520\text{nm}}$ values of the samples, (C) the photos of the color readouts of the samples, and (D) the 13 kinds of amino acids used in this study. (E) $A_{650\text{nm}}/A_{520\text{nm}}$ values of the samples obtained by adding different concentrations of cysteine together with 1.4 μM melamine, (F) the visualized color readouts of the samples, and (G) the linear relationship between the $A_{650\text{nm}}/A_{520\text{nm}}$ values and the concentration of cysteine.

By using a similar idea, the INH relationship between melamine and Hg^{2+} can be applied in Hg^{2+} sensing (Figure 3.12).

Figure 3.12 Hg^{2+} sensing. (A) Absorption spectra responses of Au NPs solutions after 50 μM different amino acids are added together with 1.5 μM melamine, (B) the corresponding signal readouts in the form of $A_{650\text{nm}}/A_{520\text{nm}}$, and (C) the photos of the corresponding color readouts of the samples (after 2 min). (D) $A_{650\text{nm}}/A_{520\text{nm}}$ values of the samples obtained by adding different concentrations of Hg^{2+} together with 0.6 μM melamine, (E) the photos of their corresponding visualized color readouts of the samples (E) the linear relationship between the $A_{650\text{nm}}/A_{520\text{nm}}$ values and the concentration of Hg^{2+} .

3.4 Conclusion

In summary, a logic gate sensing system is devised by employing the competing coordination reactions between the targets (melamine, Hg^{2+} , and cysteine) in this system, and it can be used for the sensing of either one of the targets all of which are health related species selectively and sensitively. We have also done careful study of the mechanism of the logic gate which is due to competing coordination and ligand replacement interaction between the targets. The study of the competing reactions between melamine, cysteine and Hg^{2+} in our work was not only qualitative but also quantitative, which was never fully investigated before. It will also benefit the readers in designing sensing systems of melamine, cysteine and Hg^{2+} by using other methods such as fluorescence, surface-enhanced Raman etc.

Chapter 4

Plasmonic heating effect of In NPs and its application for enhanced solar evaporation

4.1 Introduction

4.1.1 Background

Solar energy has been greatly concerned because of its sustainability as a green and clean energy supply, which does not depend on the potential of fossil fuels that can lead to sustainable development and environmental issues.⁸⁸⁻⁹⁰ Converting solar energy into heat is one of the most important aspects of solar energy harvesting, which has been widely applied in solar power generation,⁹¹ enhanced hydrogen production,⁸⁹ chemical separation/purification,²² wastewater treatment,⁹² and steam sterilization.⁹³ At present, the water shortage is an urgent problem that is world widely suffering for human beings. Considering the demand for water will be much higher with the social and industrial development in the future, seawater desalination/evaporation using sunlight to evaporate seawater to produce clean water has been studied extensively.^{7, 20, 24, 94-96} In order to effectively perform solar seawater desalination using solar energy, good light-absorbing materials are particularly important for increasing the absorption efficiency of solar energy.

4.1.2 Plasmonic nanoparticles for light to heat conversion

Due to their excellent LSPR characteristics, the sub-wavelength metal particles were widely made into good photothermal conversion materials.⁶ When illuminated with an external light radiation, the resonance between the incident light and the particles can lead to strong light absorption and heat generation. Because of their Vis/NIR LSPR features, gold and silver-based nanostructures can have enough spectral overlap with sunlight, making them become the most

widely used plasmonic structures for the conversion of solar energy to heat.^{97, 98} Although silver and gold have such advantages, they are rare and costly as goods and commodities, whose sophisticated preparations in making them into plasmonic nanostructures are also concerns in the practical applications. It is therefore important to find alternative metal materials with excellent performance that can be used for low-cost technologies for light to heat conversion, which requires in-depth explorations to further study the properties and LSPRS of other metal materials. A recent study has shown a refreshed understanding of other potential metals as light to heat conversion materials by numerical analysis, and quantified their photothermal conversion efficiencies with plasmonic properties.²¹ In line with this study, Zhu's team in 2016 succeeded in designing a desalination plant for the first time using Al NPs.²⁴ The device was designed by three-dimensional assembly of plasmonic Al NPs on a floating porous substrate which can enhance solar desalination through the plasmonic heating effect. And the significance of their research is that it provides an experimental basis for exploring the use of plasmonic heating of metals other than silver and gold for seawater evaporation.

4.1.3 Fabrication of a floating solar desalination device based on In NPs

In this thesis, we have utilized for the first time a new kind of metallic material, In NPs, to design a portable device for desalination of seawater using solar energy, which is inspired by theoretically the superior plasmonic heating ability of In NPs when compare to Au and Ag NPs. Another advantage of the device we designed is that the simple preparation by only one step of thermal evaporation. For silver, aluminum, gold and other materials which have been employed in solar evaporation, complex steps in device fabrication, chemical synthesis or treatment, and specifically designed substrates were often required.^{92, 94-102} In addition, the paper-like device we designed can float on the surface of water to avoid the overall heating of the whole water volume

based on the concept of "solar heating water air interface",⁷ which on the other hand can reduce the heat loss of from the device, thus improving the efficiency of evaporation. Besides, the MPM's special porous nature can lead to enhanced internal light scattering and reduced surface reflection,^{24, 96, 103} benefiting the light absorption in a sunlight harvesting process. In addition, when the deposition thickness of indium on MPM is increasing, the In NPs on MPM tend to merge into larger and irregular particles, resulting in broad and strong plasmonic absorption, which is beneficial to the applications based on solar energy. The characteristics of notable plasmonic heating effect, simple device fabrication and expandable production process show that the portable type paper-like device has vast prospects in the actual solar evaporation related applications.

4.2 Experimental setup

The In NP/MPM devices were fabricated by depositing indium sources on MPM substrates by thermal evaporation with different thicknesses at a base pressure of 3×10^{-7} Torr. The thermal evaporation rate was 0.5 Å/s. The MPM substrate was purchased from Sigma-Aldrich. The water evaporation experiment was carried out in the 100 mL breaker filled with 100 g water. In order to monitor the in-situ weight change of water during evaporation, a piece of In NP/MPM was placed on the water surface and then transferred with the breaker to a Sartorius 4-decimal electronic precision balance under a Sun 2000 solar simulator (ABET technologies) which can provide 280 to 2500 nm range light radiation. The electronic precision balance was equipped with a 2-door glass chamber, which could prevent the vibrations caused by strong airflow from the cooling fan of the solar simulator. We replaced the top glass cover of the chamber with quartz to maximize the transmittance of sunlight. In the cycle experiments, the illumination time for the device was 30 minutes per cycle. The weight of water in the container is recorded every 5

minutes during this process. After each cycle, the In NP/MPM needs to be removed from the breaker, cleaned with deionized water, finally dried under natural conditions. The surrounding humidity and temperature in our lab were 55.4% and 23.2 °C, respectively. An ICP-OES spectrometer (PerkinElmer Optima2000) was used to measure the ion concentrations before and after seawater desalination.

4.3 Results and discussion

4.3.1 Theoretical calculation of plasmonic heating ability of In NPs

There are a lot of free electrons in metal nanoparticles, which can generate LSPR under light illumination, resulting in enhanced near field and plasmonic heating effect. For semiconductor nanoparticles, their performance in photothermal conversion is poorer and the rate of heat generation is much lower because of the heat dissipation through the process of interband absorption, in which producing pairs of hole and electron (excitons).⁶ It should also be noted that, unlike other photothermal materials or semiconductors, the plasmonic absorber can confine light into volumes in deep sub-wavelength scale, which will result in extremely localized light excitation at very high near-field intensities. It can thus achieve the local heating for plasmon-enhanced vapor-liquid phase change.²² Therefore, research efforts were dedicated to the design of various kinds of metal nanostructures for photothermal conversion.^{24, 96} Although the researches on the plasmonic heating effects of the noble metals have made some exciting progresses, in the cases of poor metals, attention paid to them is lacking, so the related experimental research results are still very few. Interestingly, based on a recent research of numerical analysis on the efficiency of photothermal conversion, the heat generated by many metal nanoparticles, including silver, gold, and aluminum, have been calculated theoretically.²¹ The results show that plasmonic metals other than commonly used ones might be used as

effective photothermal conversion materials. According to this study, a simple proposed equation can be used to calculate joule heat generation ability (Jo) of different plasmonic nanoparticles, which is given by

$$Jo = 9 \frac{e\epsilon_2}{n_m} \left| \frac{\epsilon_m}{2\epsilon_m + \epsilon} \right|^2 \quad (4-1)$$

where e is the energy of the photons radiated by the incident light, n_m and ϵ_s denote the refractive index and dielectric constant of the surrounding medium, respectively, and ϵ denotes the dielectric constant of the material and ϵ_2 refers to its the imaginary part. In line with the calculated result of aluminum using this theory, in the following year, it was reported the use of Al NPs for solar seawater desalination,²⁴ which provided an experimental support for exploring other materials for sunlight harvesting.

In addition to aluminum, indium is one of the most studied poor metals which can be used as plasmonic materials, and experimental results in previous studies have shown that LSPR feature of indium can be activated by using light ranging from deep ultraviolet region to visible region.^{63, 104, 105} On the basis of previous theoretical calculation, indium can be comparable or even more effective in supporting near-field enhancement than aluminum.^{62, 63} We have also used the above equation to calculate Jo of In NPs. The result was compared with Al NPs, Au NPs and Ag NPs (Figure 4.1A). From the obtained curves, it can be seen that In NPs have the highest value of Jo when compared to Ag, Al and Au NPs at their plasmon resonance wavelengths. As solar spectrum contains broad radiations which can span from UV to Vis/NIR, further tuning the LSPR of In NPs to achieve broad band light absorption is still required to maximize the plasmonic heating effect. A common and effective way to tune the LSPR of a metal nanoparticle is to adjust the shape of it.¹⁰⁶ Through this method, the depolarization factor can be reduced in a certain direction to achieve the red shift of LSPR. Considering this shape induced effect, it is possible to

calculate (Figure. 4.1B) Jo of irregularly shaped NPs with different LSPR wavelengths based on an ellipsoid model:²¹

$$Jo = \frac{e\epsilon_2}{n_m} \left| \frac{\epsilon_m}{\epsilon + L_j(\epsilon - \epsilon_m)} \right|^2 \quad (4-2)$$

where

$$L_j = \frac{R_1 R_2 R_3}{2} \int_0^\infty \frac{du}{(u + R_j^2) \sqrt{(u + R_1^2)(u + R_2^2)(u + R_3^2)}} \quad (4-3)$$

among which, R_1 , R_2 and R_3 represent the radius of the ellipsoid along the major axis $J = 1, 2$, and 3. It is noted that the depolarization factor L_j satisfies the relation $L_1 + L_2 + L_3 = 1$. L_j usually describes the deviation extent of the shape of the metal NP from the sphere in that direction. As depolarization factors decrease, the plasmon bands of In NPs with different shapes undergo red shift and broadening. Notably, it can be seen that when In NPs LSPRs are tuned to the near-infrared and visible regions, the Jo values still remain high, which indicates that plasmonic devices using such In NPs can be used as excellent light to heat converters for the applications of sunlight harvesting.

Figure 4.1 (A) Calculated Joule heat generation ability curves of different metal nanoparticles. (B) Calculated Joule heat generation ability curves of irregular shaped In NPs based on the ellipsoid model.

4.3.2 Morphology and optical properties of In NPs on MPM

Because aluminum, gold and silver tend to form flat films on the substrate during evaporation,^{5, 26, 107} additional processing is typically required to obtain a well-defined nanostructure, such as using substrate annealing or patterned substrates. On the contrary, indium vapor condenses on the widely used substrates such as quartz and glass will result in the formation of separated particles due to inherently unique poor wettability of indium to the surfaces of them.^{63, 108} By utilizing such special property of indium, a convenient one-step thermal evaporation approach was used to prepare In NPs on MPM. This method does not require any other treatments or modifications for MPM surface. The SEM images of MPM with 10 to 80 nm indium evaporation thicknesses are correspondingly presented in Figure 4.2A, B, C, and D. From these SEM images one can see that it is clear that the In NPs are densely distributed on the MPM substrate. In addition, when increasing the deposition thickness, it also can be observed that larger particles with irregular morphologies will form. Due to their strong plasmonic effects, and the inhomogeneities of the size and shape of dense In NPs on the MPM, our device could show strong and broad LSPRs, on which only tens of nanometers thick indium are deposited. This light absorption can achieve light absorption in visible (Figure 4.2E) and NIR (Figure 4.2F) spectral region. At the same time, we can see obvious changes that the original white color of the MPM is significantly darken with indium deposited on it, directly indicating the broadband and efficient light absorption of the plasmonic devices (Figure 4.2G).

Figure 4.2 SEM images of In NPs with different deposition thicknesses (A) 10 nm, (B) 20 nm, (C) 40 nm, and (D) 80 nm on MPM. The scale bars here are 500 nm. (E) Visible and (F) NIR light absorption spectra of In NPs on MPM. (G) Optical images of MPM substrates with different deposition thicknesses of indium.

The MPM microporous structure has two functions (Figure 4.3): first, to endow the floating nature of the device; and second, to rapidly replenish water after evaporation of surface water by capillary effect. The floating nature will also enable vapor-liquid phase change to occur near the water-air interface.

Figure 4.3 SEM images of bare MPM substrates at different scales, displaying a porous nature.

In addition, after indium was deposited on it, the hydrophilic nature of the MPM can retain, making the device to have the ability to induce water attachment, and accelerating moisture

transfer to the surface (Figure 4.4).

Figure 4.4 Measurements of contact angle of water drop on In NP/MPM device. Water droplets on the surface of the device can rapidly disperse, demonstrating the hydrophilic surface of the device.

4.3.3 In NPs on MPM for plasmon enhanced solar evaporation

The excellent light absorption features of In NP/MPM provide a great opportunity to develop efficient sunlight to heat conversion systems. To realize this concept, we showed the solar water evaporation by using the devices we designed. Figure 4.5A is a schematic diagram of the device we designed in a solar evaporation system. We systematically evaluated the influence of indium deposition thickness on the performance of water evaporation under a solar light intensity of 3 kW/m^2 (3 sun), and the results are shown in Figure 4.5B. For reference, we also conducted experiments of water evaporation in the presence and absence of bare MPM. We plotted the water weight variation curves of different indium deposition thicknesses resultant devices under solar illumination for 30 minutes. In accordance with expectation, as indium deposition thickness increases, the weight changes of water appear more dramatically, which also generally agrees with the evolution of the absorption spectra of the device with different indium thicknesses. When the thickness of the indium deposition is increased, the absorption spectra will become broader and stronger, resulting in better performance of solar evaporation. Meanwhile, the effect of bare MPM itself on water evaporation is not obvious, which indicates that the improvement of the performance of water evaporation of the devices we designed should be attributed to the

plasmonic heating effect of In NPs on MPM. In particular, we have found that in the indium deposition thickness range of 20 to 80 nm, the evaporation performance of water only increased slightly with increasing thickness of indium. However, for the device with deposition of 20 nm thickness of indium on two sides of the MPM (40 nm in total), its water evaporation performance is better than the devices which have only one side indium deposition. The possible explanations for this phenomenon can be the increased light absorption in the visible range and the calculated stronger Joule heating abilities at shorter wavelengths. Therefore, we chose the In NP/MPM with 20 nm thickness indium on two sides in the following studies. After exposed to sunlight radiation (3 sun) for 30 minutes, the surface temperatures of the devices were confirmed by the IR images. As can be seen from Figure 4.5C, the device surface temperature can rise from about 24 °C to about 50 °C (III and IV) in 30 minutes. In contrast, the blank water without the plasmonic device used in the control experiment can only achieve about 38 °C (I and II). Owing to the capability of floating at water surface, the heat generation is highly confined at In NP/MPM surface, it shows an obvious temperature evolution from the top to bottom regions (IV) in the IR image. We also investigated the influence of the intensity of solar radiation on water evaporation rate by monitoring the changes of water weight at different optical concentrations over time by using the device we designed (Figure 4.5D). The results demonstrate that under all of the 1, 2 and 3 sun optical concentrations, the efficiencies of using In NP/MPM device to generate steam are higher than that of pure water (Figure 4.5E), in which 2.4, 2.9 and 3.1 times enhancement can be achieved respectively, which is even better than the recently reported results using specially-synthesized black TiO_x NPs (at 1 sun, 1.5-fold enhancement)²⁰ and Al NPs (optimal at 4 sun, 2.4-fold enhancement).²⁴ The solar steam efficiencies can be calculated through the expression^{7, 24}

$$\eta = \frac{\dot{m}h_{LV}}{I} \quad (4-4)$$

in which, $\dot{m}$ refers to the mass flux, I donates solar illumination power density, and h_{LV} represents the total vapor-liquid phase change enthalpy (including phase-change enthalpy and sensible heat). Through this calculation, solar steam efficiencies can be obtained with 71.6% (1 sun), 79.2% (2 sun), and 84.2% (3 sun).

Figure 4.5 (A) A schematic diagram of the device we designed for enhancing steam generation. The In NP/MPM was floating on the upper surface of water. (B) The weight change curves of water with different In NP/MPM devices under 3 sun solar irradiation. The inset illustration shows the device was floating on the surface of water. (C) The IR images of water before solar irradiation (I), without (II) and with (III) In NP/MPM after irradiation under 3 sun for 30 minutes. The irradiation time is 30 minutes. IV is the side view of III at the same irradiation intensity. (D) The weight changes of water without and with the device as a function of irradiation time under

1 and 3 sun irradiations. (E) The weight change of water at different irradiation intensities (1 sun, 2 sun, and 3 sun) in 30 minutes with and without In NP/MPM devices.

4.3.4 In NP/MPM for solar desalination of a real seawater sample

In order to evaluate the performance of the device we designed in practical solar desalination, we used real seawater samples which were collected from the east coast of Singapore. Subsequently, we investigated the performances of this device at fixed intensities (1 sun and 3 sun) of irradiation light. As can be seen from Figure 4.6, the performance of steam generation is steady when the illumination intensity is switched from 1 to 3 sun. The performances are similar to the previous data obtained using pure water (Figure 4.3E).

Figure 4.6 Cycle solar evaporation performances of a seawater sample using In NP/MPM device at fixed irradiation intensities in 30 min (1 and 3 sun).

As can be directly observed, condensate water forms quickly on the quartz cover of the setup when using In NP/MPM plasmonic device. In contrast, only minimal amount of water can be evaporated without this In NP/MPM device (Figure 4.7), showing the improved solar evaporation performance using In NP/MPM device. It is easy to collect the condensed water on the quartz cover produced by In NP/MPM heating by using a pipette.

Figure 4.7 Optical photographs of the water condensation on the quartz cover after 30 minutes in the absence (A) and presence (B) of the In NP/MPM device.

The collected water from the quartz cover was then carefully measured by ICP-OES to confirm the concentration of different elements therein (Figure 4.8). From the results one can see that the concentrations of the main ions (Na^+ , K^+ , Mg^{2+} , B^{3+} , and Ca^{2+}) naturally appeared in seawater are significantly decreased, which is much lower than those obtained by commonly used membrane (10 to 500 ppm) and distillation (1 to 50 ppm) based seawater desalination techniques. It is also well below the reference standards regulated by the World Health Organization (WHO) and United States Environmental Protection Agency (EPA).^{24, 109}

Figure 4.8 The concentrations of five main ions (Na^+ , K^+ , Mg^{2+} , B^{3+} and Ca^{2+}) before and after

desalination measured by ICP-OES. It was noted that the concentration of Mg^{2+} was lower than the detection limit (N.D.) of ICP-OES after desalination. For the shaded areas, the light blue portion and light green portions refer to the overall common salinity achieved by conventional membrane and distillation-based desalination techniques, respectively. The dashed lines represent the drinkable water salinity standards regulated by WHO and EPA.

4.3.5 Stability of In NP/MPM in solar evaporation

In order to assess the stability of the device we designed during solar desalination, we recorded its cycle performance at fixed irradiation intensity at 3 sun. As is shown in Figure 4.9, the performance of the device remains relatively stable for 15 cycles with 30 min per cycle.

Figure 4.9 Cycle solar evaporation performances (15 rounds) of In NP/MPM plasmonic device at 3 sun solar illumination intensity.

In order to further verify the robustness of this device, we studied the chemical state of indium on the MPM before and after seawater desalination using XPS. From XPS data (Figure 4.10A), it is observed that there is no significant change in asymmetric peak shapes and loss characteristics that were commonly found in the XPS of indium metal, demonstrating stable indium chemical state during solar desalination. In previous report, it was found that the transformation of indium

metal to indium compounds can lead to the broadening of In 3d peaks.¹¹⁰ In our experiment, after the desalination process, we didn't observe any obvious change of In 3s peaks, which provides further proof for the stability of the device we designed. In addition, Figure 4.10B displays the high-resolution O 1s XPS spectra, in which the generation of these two peaks may be attributed to the inherent thin oxides on In NPs after the fabrication, and the physical adsorption or chemical containment of oxygen on the MPM, respectively. Meanwhile, as there are only insignificant differences between the indium oxide peaks before and after solar desalination, suggesting that no further oxidation of indium occurs. This stable feature of In NPs may be due to the protective effect from the formed indium oxides on the surface of In NP, which is also in accordance with the previous study that indium metal can form natural oxides with little or no more than 4 to 5 nm thickness in the air below 145 °C.¹¹¹

Figure 4.10 (A) XPS spectra of In 3d of In NP/MPM before and after solar evaporation. (B)

XPS spectra of O 1s of In NP/MPM before and after solar evaporation. (C) XPS spectrum of O 1s from bare MPM substrate.

To confirm the steadiness of the crystal structure of In NPs on MPM, we also performed X-ray diffraction (XRD) (Figure 4.11). From the XRD data, we can see that the diffraction peaks are well matched to the body centered tetragonal crystal structure of indium (ICSD code: 064794) and the crystal structure remains unchanged after the 15 cycles solar evaporation processes.

Figure 4.11 XRD characterizations of In NPs on MPM before and after 15 cycles solar evaporation processes.

The SEM images are also shown in Figure 4.12 to further check that the size and shape of In NPs on the MPM have not changed significantly after desalination. The proposed In NP/MPM device is thus expected to be applied in practical solar evaporation desalination because of its high stability and stable performance.

Figure 4.12 SEM images of In NP/MPM (A) before and (B) after 15 cycles solar evaporation processes. The scale bars here are 500 nm.

4.4 Conclusion

In this chapter, we have demonstrated the preparation of dense In NPs with broad size and morphology distribution on MPM. The In NPs on MPM exhibit broadband and strong light absorption which could span from NIR to visible spectral region due to the dense distribution and irregular morphologies on the substrate. Combining the floating nature of the MPM matrix and the theoretically excellent photothermal conversion performance of In NPs, for the first time we designed an In NP/MPM solar thermal device for solar evaporation. It is demonstrated the probability of making an efficient and portable device for enhancing desalination. And this device can maintain good stability and evaporation performance after many desalination cycles. Considering the increasing efforts to explore the use of clean and renewable solar energy, the device we designed and the results we found using In NPs may be applied to many other potential applications using solar energy, such as photocatalysis and thermal-optics.

Chapter 5

Near-field enhancement and LSPR induced hot carrier injection of In NPs for enhanced photocatalysis of TiO₂ NPs

5.1 Introduction

5.1.1 Creation and transfer of charge carriers in photocatalysis

In a photocatalysis process, when a photocatalyst which is often a semiconductor material is excited by the light with higher energy than its absorption threshold ($h\nu \geq E_{CB} - E_{VB}$), there will be electron transitions from valence band to conduction band, in which electrons and holes are created (Figure 5.1).²⁵ Herein, h is the Planck constant, ν is the frequency of the excitation light, and E_{CB} and E_{VB} are the conduction and valence band energy level of the semiconductor photocatalyst, respectively. As soon as the active charge carriers are generated, they could transfer to the intermediate levels with lower energies E'_{CB} (electron) and E'_{VB} (hole), after which the active electron can react with an acceptor molecule A through a reduction reaction $A + e^- \rightarrow A^-$, while the similar oxidation reaction $D + h^+ \rightarrow D^+$ can also occur between an active hole and an electron donor molecule. For example, the as generated electrons can be captured by the dissolved oxygen on the catalyst surface and superoxide anions will form. The adsorbed hydroxide ion and water on the surface of the catalyst can be oxidized by the holes to produce hydroxyl free radicals. Both the superoxide anions and hydroxyl free radicals are very reactive species which can react with most of the organic compounds to result in their photodegradations, in which the organic compounds were degraded into CO₂ and H₂O.¹¹² By exploring appropriate photocatalysts, other novel and useful applications such as self-cleaning and disinfection surfaces,¹¹³ CO₂ reduction,¹¹⁴ water splitting,¹¹⁵ air purification,¹¹⁶ and wastewater treatment¹¹⁷

were also developed. To achieve the spontaneous electron and hole transfer to initiate the redox reactions, the corresponding layout of energy levels should in the order of $E_{CB} \geq E'_{CB} \geq E_{red}$ (electron) and $E_{VB} \geq E'_{VB} \geq E_{ox}$ (hole) to enable efficient electron-hole separation. The creation and transfer of electrons and holes in a photocatalysis process is therefore a crucial first process in initiating photocatalytic reactions.

Figure 5.1 Generation of electron-hole pair and their corresponding transfer pathways in a semiconductor in a typical photocatalysis process.²⁵

5.1.2 TiO₂ in photocatalysis

Many different materials such as TiO₂,²⁵ ZnO,¹¹⁸ WO₃¹¹⁹ and CdS¹²⁰ have been proven can act as photocatalysts, among which TiO₂ is the one which has attracted the most attention all over the world due to its strong oxidation ability, chemical stability and non-toxicity. TiO₂ has different phases and anatase phase TiO₂ with the band gap of 3.26 eV was proven the best one that can be used in photocatalysis, which on the other hand determines that only light with the wavelength in the UV region can be absorbed and contribute to photocatalysis process.²⁵ However, as UV light contribute only 5% to sunlight, hampering the good performance of TiO₂ in sunlight or visible

light source based practical applications. Moreover, the photocatalysis efficiency of TiO_2 can be also constrained by the recombination of the photogenerated carriers before they migrate to the surface to participate in the redox reactions. The migration of the charge carriers in a semiconductor is a random process, resulting plenty of chances for them to recombine and thus the low photocatalysis efficiency.

5.1.3 In NPs for plasmonic photocatalysis

Plasmonics photocatalysis by using metal nanoparticles to enhance the photocatalysis performance has been proven a possible way.^{23, 25, 26} To maximize photocatalysis performance, a high overlap between plasmonic band of metal nanoparticles and absorption band of TiO_2 is preferred, either because plasmonic band can enhance the absorption of the incoming light or boost the excitation of TiO_2 by creating an intense electromagnetic field in the near field. Since TiO_2 can only absorb light in the UV region, along this line, metal nanoparticles with plasmons in the UV region are highly desirable. Up to now, only silver and aluminum nanoparticles for UV plasmon enhanced photocatalysis were designed based on this strategy.^{23, 26} Recently, In NPs were reported to show good performance for UV plasmonics because of their UV plasmon.^{62, 63} Also, we have shown that the LSPR of In NPs can be tuned to visible and NIR range, providing the opportunity of fabrication of In NPs/ TiO_2 based plasmonic nanostructures to act as visible light photocatalyst.⁵⁶ It is anticipated that In NP will be a good candidate for enhancing the photocatalysis performance of TiO_2 .

Herein, dense In NPs on quartz substrates over a large area ($> \text{cm}^2$) were prepared by a thermal evaporation method in vacuum and the size of In NPs can be easily tuned by controlling the deposition thickness of indium on the substrate. After coating the as obtained In NPs with another layer of TiO_2 , the substrate shows an enhanced photocatalysis performance for the

degradation of methylene blue (MB) when compared with substrate which only has TiO₂ coating. The coating of TiO₂ on In NPs will also lead the red shift of the LSPR of In NPs and produce strong LSPR in the visible range. Consequently, the In NP/TiO₂ structure also can show dramatically enhanced photocatalysis performance when only visible light excitation is provided. We have also investigated the effect of the In NP sizes and the thickness of a SiO₂ dielectric layer between In NPs and TiO₂. Our present data shows that In NPs prepared through the deposition of 40 nm thickness indium on quartz substrate can most efficiently enhance the photocatalysis performance of TiO₂.

5.2 Experimental section

In NPs were prepared by thermal evaporation of indium source with different thicknesses (5 to 50 nm) on quartz substrates at a base pressure of 3×10^{-7} Torr. The evaporation rate was 0.5 Å/s. After completing the thermal deposition process, it is better to wait several minutes for the evaporated indium on the substrate to cool down to room temperature, which can protect In NPs from strong oxidation when exposed to the air at temperature higher than 145 °C. At room temperatures, indium is very stable with the protection effect from the intrinsic oxidation layer (~4 to 5 nm in thickness) at the surface according to previous reports. Then anatase TiO₂ nanocrystals with a diameter of 6 nm (Titania Coating, Tayca Corporation, suspended in water) were coated on the substrates by spin-coating at 7000 rpm for 1 minute. A solar simulator (Sun 2000, ABET technologies, 280 to 2500 nm light source) was employed in providing the solar or visible irradiations. A 400 nm long pass filter was used to cut the UV light from the solar simulator to result in the visible light irradiation. Photocatalysis performances of the above samples were evaluated by monitoring the degradation of methylene blue (spin coating, 0.1 M in aqueous solution) on the samples on a Lambda 950 UV/Vis absorption spectrometer, in which

absorbance at ~575 nm is recorded within certain time intervals. All of the measurements were repeated for more than 3 times to collect the average values.

5.3 Results and discussion

5.3.1 Preparation of In NPs with different sizes on quartz substrate

Figure 5.2 SEM images of In NPs on quartz prepared by thermal evaporation of indium with different thicknesses. (A) 5 nm. (B) 10 nm. (C) 20 nm. (D) 30 nm. (E) 40 nm. (F) 50 nm. The scale bars are 100 nm.

Taking advantage of the unique feature that well-separated grains will form when indium vapor meets a cold solid surface, dense In NP can be prepared on different substrates through thermal evaporation, which we have also discussed in chapter 2 and chapter 4. Moreover, as the size of In NPs formed on a substrate is dependent on the deposition thickness of indium, it is anticipated that the size can be easily tuned by simply controlling the thickness of the evaporated indium on the substrate. It can be seen from Figure 5.2 that multiple nanograins of indium form under all conditions, and the size of the obtained In NPs is increasing with the evaporated indium thicknesses ranging from 5 to 50 nm. It is noted that small grains of indium always appear in all

of the obtained In NPs on the substrate and they will be in the gaps between larger particles when the deposition thickness is more than 10 nm. This phenomenon can be ascribed to the merging of the preformed small In NPs when the deposition thickness is increasing. As there are always unmerged or freshly formed small In NPs when the indium vapor keeps condensing at the substrate, small In NPs will be always there when the deposition thickness of indium has reached a certain value, which also implies that the formation of small In NPs on the substrate can be independent on the evaporation thickness.

5.3.2 Fabrication of In NPs@TiO₂ nanostructures

In our study, we employed the widely used commercial anatase TiO₂ nanocrystals dispersed in water (Titania Coating, Tayca Corporation, suspended in water) to prepare the TiO₂ film by spin coating for the photocatalysis study. As the size of the used TiO₂ is only ~6 nm (information provided by vendor), it can be easily deposited in the nanoscale gap areas between In NPs to result in sufficient contact with In NPs and enable efficient TiO₂-In NPs coupling. On the one hand, it has been well proven that the strong nearfield enhancement which is highly favorable in plasmonic photocatalysis, only occurs at the vicinity and gap areas of plasmonic nanoparticles, which is usually in tens of nanometers distance from the surface of plasmonic nanoparticle. On the other hand, a sufficient contact between TiO₂ NPs and In NPs will also benefit the plasmonic photocatalysis process in achieving effective carrier transfer, providing additional reaction sites on the metal nanoparticles, and resulting in strong hot carrier injections through the LSPR effect. Therefore, preparation of high quality thin film based on small TiO₂ NPs which can have sufficient contact with plasmonic nanoparticles plays an important role in construction of efficient plasmonic photocatalysis system. In order to prepare a continuous and thin film on a substrate, we gradually increase the concentration of the TiO₂ coating solution from 0.9% to 4.5%

(N.V.), and at a concentration of 4.5%, we can first obtain the continuous TiO_2 film with good uniformity. Although further increase the concentration may also result in continuous and uniform film, their thickness might be relatively higher, which is not favorable in plasmonic photocatalysis system which requires efficient coupling between TiO_2 and metal nanoparticles. Figure 5.3 shows the SEM images of TiO_2 film on quartz prepared by spin coating TiO_2 NPs (4.5 N.V.% in water) with different magnifications. It can be observed that TiO_2 NPs can form a continuous and uniform film over a very large scale at this concentration. At high magnification as shown in Figure 5.3D, we can see but not very clearly the TiO_2 NPs, which is due to the very small size of the TiO_2 NPs that can hardly be observed under SEM.

Figure 5.3 SEM images of TiO_2 film on quartz prepared by spin coating TiO_2 NPs (4.5 N.V.% in water) with different magnifications. (A) 1500 $\times$. (B) 3000 $\times$. (C) 5000 $\times$. (D) 10000 $\times$. The scale bars are 10 μm , 1 μm , 1 μm , and 1 μm , respectively.

By using the same parameters, TiO_2 can be coated on the dense In NPs loaded quartz substrate to form the In NPs@ TiO_2 structure. It can be seen from the SEM images that the contrast is getting poorer and the well define shapes of the as formed In NPs is also blurring after TiO_2 coating in which the In NPs are still distinguishable, which demonstrates the successful coating of TiO_2 with very thin thickness (Figure 5.4). Both the surface and gap areas can be observed with the filling/coating of TiO_2 NPs, which is expected to result in sufficient coupling for plasmon enhanced photocatalysis of TiO_2 .

Figure 5.4 SEM images of In NPs prepared on quartz before (A) and after (B) TiO_2 coating.

5.3.3 Optical properties of In NPs@ TiO_2 nanostructures

To investigate the optical properties of the as fabricated nanostructures, we measured the absorption spectra of In NPs with and without SiO_2 coating (Figure 5.5). Before TiO_2 coating, all the absorption spectra of In NPs on quartz prepared with indium evaporation thicknesses ranging from 5 to 50 nm show strong LSPR peaks in the UV region. For indium deposited with 5 and 10 nm thickness, only a single peak is observed in the spectra, while for the 20, 30, 40, and 50 nm indium-evaporated quartz substrates much weaker peaks at longer wavelength beyond the UV region are also observed. This can be explained by the increasing size of In NPs and formation of

irregular shapes. Both of these effects have been well proven in plasmonics theory that can induce the red shift of the LSPR of metal nanoparticles due to the appearance of higher order LSPR modes. After TiO_2 coating, one can see that the main LSPR peaks of In NPs are still in the UV region. However, for the 20, 30, 40, and 50 nm indium-evaporated quartz substrates, their absorption spectra show dramatic increases in the visible range, which could be ascribed to the change of refractive index after the coating of TiO_2 and hence red shift of LSPRs. For smaller In NPs prepared by depositing with 5 and 10 nm thickness of indium, the red shift is not obvious, which may be due to the weak coupling efficiency between TiO_2 NPs and In NPs, in which most of the TiO_2 NPs are not in direct contact with In NPs because of the small size of In NPs which have relatively small surface and gap areas. For reference, absorption spectra of bare TiO_2 NPs on quartz and bare quartz substrate are also presented.

Figure 5.5 Absorption spectra of the prepared In NPs@TiO₂ nanostructures.

5.3.4 Enhanced photodegradation of MB on In NPs@TiO₂

To get a better understanding of the LSPR effects from In NPs on TiO₂ photocatalysis performance, we monitored the photodegradation evolution of MB on TiO₂ in 36 minutes, In

NPs@TiO₂, and bare In NPs, in which the absorption peaks of MB at 580 nm serve as the reference. In NPs prepared by deposition of 20 nm indium were used to fabricate the plasmonic system with TiO₂ for the comparison study. Figures 5.6A displays the result obtained with bare TiO₂, in which a minor decreasing trend of MB peak is observed with increasing irradiation time. In contrast, when the In NPs@TiO₂ is used, a dramatic enhancement of the degradation performance can be achieved (Figures 5.6B). To exclude any possible contributions from the In NPs themselves, bare In NPs on quartz were also investigated (Figures 5.6C), in which a negligible degradation of MB indicates that In NPs themselves do not contribute to the photocatalysis in the plasmonic photocatalyst system.

Figure 5.6 Evolutions of absorption spectra of MB on different structures in 36 minutes. (A) TiO₂. (B) In NPs@TiO₂. (C) Bare In NPs.

5.3.5 Effect of In NPs sizes on In NPs@TiO₂ on photocatalysis performance

To gain insight of In NPs sizes effect in the plasmonic photocatalyst system, we systematically studied the In NPs prepared by deposition of 5 to 50 nm of indium in combination with TiO₂ for the photodegradation of MB. For purpose of assessing the photocatalytic performances of all samples with different In NPs sizes, the absorption spectra were collected at same time intervals and the degradation performance was evaluated by recording the change of peak intensity at the wavelength of 580 nm versus irradiation time (Figure 5.7). From the plotted curves, one can see that after In NPs are combined with TiO₂, all the samples show enhanced performance, demonstrating the strong LSPR effect from In NPs. In a plasmonic system, the absorption and scattering efficiency are two important factors for the LSPR effect. For plasmonic nanoparticles, their absorption and scattering efficiency follow the Mie theory. For small nanoparticles, the absorption will be the dominant factor in determine the LSPR effect, while for large particle the scattering contributes more. Therefore, there should be an optimal size of In NPs in the plasmonic In NPs@TiO₂ structures for enhancing the photocatalysis performance. In our case, it is found that the In NPs prepared by 40 nm indium deposition can lead to the best performance.

Figure 5.7 Degradation of MB on In NPs@TiO₂ with different indium deposition thickness

ranging from 5 to 50 nm.

5.3.6 Dependence of photocatalysis performance on excitation wavelength

We have observed in the UV-Vis spectra that the coating of TiO_2 on In NPs will induce the red shifts of LSPRs of In NPs to visible range in which we can clearly observe the shifted LSPR peaks, which offers the opportunity of conducting the photocatalysis using visible light. The visible light driven plasmonic photocatalysis process often involves a hot electron injection mechanism from plasmonic nanoparticle to TiO_2 , in which hot electrons are created through the strong LSPR effect from the metal nanoparticle. To achieve this goal, we then use a 400 nm long pass filter to cut the UV light from the white light source and provide the visible light for photocatalysis using In NPs@ TiO_2 nanostructures with different In NPs sizes (Figure 5.8). As expected, our results show that In NPs with larger sizes can contribute more to the photodegradation performance of MB, which is consistent with the UV/Vis spectra that In NPs with larger particle sizes can have strong LSPR in the visible range after TiO_2 coating. As can be seen in the obtained curves, MB on bare TiO_2 can hardly be degraded without the LSPR effect from In NPs using visible light, because of the fact that band gap of TiO_2 determines that photo generated charge carriers will only be available by using UV light excitation. As TiO_2 cannot be excited by visible light, the enhanced photocatalysis by using In NPs@ TiO_2 could be ascribed to the LSPR induced hot carrier injection from In NPs to TiO_2 . Moreover, although the photocatalysis can be achieved using visible light excitation, their contribution to the whole photocatalysis performance using sunlight is only a small part. As shown in the data, photocatalysis using visible light is less than 20% when compared to the sunlight driven photocatalysis, which further confirms that the UV LSPR effects from In NPs play the dominant role in enhancing the photocatalysis performance of TiO_2 . This is also one of the reasons that

why a lot of efforts have been devoted to develop Al or Ag nanostructures which have strong LSPR in the UV/NUV region to enhance the photocatalysis performance of TiO_2 .

Figure 5.8 Degradation of MB on In NPs@TiO_2 with different indium thicknesses under sunlight and visible light. (A) 5 nm. (B) 10 nm. (C) 20 nm. (D) 30 nm. (E) 40 nm. (F) 50 nm.

5.3.7 Effect of a SiO₂ dielectric layer between In NPs and TiO₂ on photocatalysis performance

Another important mechanism in a plasmonic photocatalysis system is the strong near field enhancement near the metal nanoparticle surface, which could boost the excitation of TiO₂ even when they are not in direct contact. To probe this near field enhancement effect, we coat the In NPs with a layer of SiO₂ before the coating of TiO₂ by using sputtering. Based on previous study, a layer of SiO₂ of 5 nm thickness prepared by sputtering could provide enough protection and separation for the metal nanoparticles,²⁶ before the additional coating of other species. A layer of 10 nm thickness SiO₂ was then coated on the as obtained substrates with In NPs coating. From the SEM images one can see that the In NPs are still uniformly distributed on the quartz without any obvious change in morphology and size on substrate after the coating of SiO₂, which also confirms that the sputtering process will not damage the as formed In NPs (Figure 5.9).

Figure 5.9 SEM images of In NPs prepared by thermal evaporation of indium with 10 nm (A)

and 20 nm (C) thickness before (A and C) and after (B and D) the sputtering of 10 nm SiO₂.

After 10 nm SiO₂ sputtering, the absorption spectra of In NPs prepared with different indium thickness show red shifts (Figure 5.10A), which are different from the phenomenon of TiO₂ coating that obvious red shift of the LSPRs can only be observed on In NPs with larger particle sizes (Figure 5.5). This difference may be caused by the fine control of the deposition thickness of sputtering, in which sufficient coating can be achieved even the surface and gap areas are small for small In NPs. Taking the In NPs prepared by deposition of 20 nm indium as an example, further increase the sputtered SiO₂ thickness to 50 nm will keep inducing the red shift of the LSPRs of In NPs. As we have discussed in chapter 1, the LSPR of a metal nanoparticle can appear at a wavelength when the condition $\varepsilon_1 = -2\varepsilon_m$ is satisfied according to Mie theory. Therefore, the change of the refractive index of the surrounding medium will affect the position of the LSPR peak.

Figure 5.10 (A) Absorption spectra of In NPs prepared by deposition of 5, 10, 20, and 30 nm indium before and after coating a layer of SiO₂ with 10 nm thickness. (B) Absorption spectra evolutions of In NPs prepared by deposition of 20 nm indium with increasing coating thickness of SiO₂.

To examine the effect caused by the coating of a SiO₂ layer on the plasmonic photocatalysis, TiO₂ is spin coated on the In NPs@SiO₂ nanostructures on the quartz substrate using the same

parameters as In NPs without SiO₂ coating. From the SEM images one can see that TiO₂ can also be well coated on the In NPs@SiO₂ nanostructure, showing a similar result when compared to In NPs without SiO₂ coating (Figure 5.11).

Figure 5.11 SEM images of In NPs@10 nm SiO₂ prepared on quartz before (A) and after (B) TiO₂ coating.

We then systematically studied the photocatalysis performances of the as obtained In NPs@SiO₂@TiO₂ nanostructures with different SiO₂ thicknesses ranging from 10 to 50 nm (Figure 5.12). It can be seen from the resultant plots that increasing the thickness of SiO₂ between In NPs and TiO₂ will lead to a decreased photocatalysis performance. In the cases of 10 and 30 nm thickness of SiO₂, although the performances are weaker when compared to In NPs@TiO₂ without SiO₂, they are still better than the performance of bare TiO₂. For 50 nm thickness, the photocatalysis performance is even weaker when compared to bare TiO₂, which arises potentially from the rough surface structures of In NPs@SiO₂ which will hamper the formation of a flat and continuous TiO₂ film by spin coating, which will on the other hand lead to a poorer photocatalysis performance when compared to the flat TiO₂ film on the quartz substrate. In addition, as TiO₂ and In NPs are isolated by a layer of SiO₂, the electron transfer mechanism can be excluded here, which implies that the enhancement photocatalysis performance in the cases 10 and 30 nm SiO₂ should be ascribed to the strong near field enhancement of In NPs.

Moreover, the phenomenon of decreased photocatalysis performances induced by increasing the thickness of the SiO_2 agree well with many plasmonic systems that the near field enhancement will decrease dramatically in the range of tens of nanometers from the metal nanoparticle surface.

Figure 5.12 Photodegradation of MB on In NPs@ SiO_2 @ TiO_2 with different SiO_2 thickness ranging from 10 to 50 nm.

5.4 Conclusion

In conclusion, In NPs on quartz substrates were prepared by a thermal evaporation method in vacuum and the size of In NPs can be easily tuned by controlling the deposition thickness of indium on the substrate. After that TiO_2 NPs was spin coated on In NPs, the resultant In NPs@ TiO_2 nanostructures can show enhanced photocatalysis performances using both sunlight and visible light excitations for the degradation of methylene blue when compared with substrate which only has TiO_2 coating. We also investigated the effect of the In NP sizes. Our present data shows that In NPs prepared through the deposition of 40 nm thickness indium on quartz substrate can most efficiently enhance the photocatalysis performance of TiO_2 . Through systematic studies using visible light excitation and introducing a SiO_2 layer between In NPs and TiO_2 , both the electron transfer and near field enhancement mechanisms were proposed in the In NPs@ TiO_2

plasmonic photocatalysis system. Taking into consideration of the simple preparation of In NPs when compared to Al NPs, and the strong UV LSPR feature, In NPs can show great potentials in coupling with other photocatalyst in achieving other novel applications.

Chapter 6

Near-field enhancement of In NPs and its application for UV SERS using 325 and 355 nm Laser

6.1 Background

6.1.1 Introduction

Owing to the capabilities in providing fingerprint information of different species, nondestructive and ultrasensitive sensing which could down to a single molecule, and NIR excitations for sensing and imaging in complicated biological system, SERS has resulted in the publication of more than 11000 papers in different research areas after it was discovered 40 years ago.²⁹ Traditionally, SERS related applications were mostly relying on visible or NIR light excitations, which are determined by the fact that commonly used plasmonic metals such as Ag, Au, and Cu can only have LSPR in the visible and NIR region. Recently, SERS based applications have been extending to UV region with significant efforts, in which the UV excitation has been proven can provide even higher signal to noise ratios in collecting the signal from the targeted molecules.⁶³ Moreover, this superiority of UV SERS can be shown better in the detection of some essential aromatic species in biological systems such as DNA/RNA bases and amino acids with aromatic groups.^{121, 122} The UV SERS of these molecules are often accompanied with the resonance Raman effects, which make them to have higher scattering efficiency which can reach as high as up to 10^6 when compared to visible/NIR excitations.¹²³ In addition, the fingerprint feature make UV SERS signals can be discriminated from the intrinsic fluorescence background of an analyte in the spectra. Furthermore, as the Raman scattering efficiency and the excitation wavelength follow an inverse fourth power dependence relationship, UV excitation of a molecule even at off-

resonance can also result in a Raman signal which is 10 to 100 times stronger than visible/NIR excitation.⁶³

6.1.2 UV SERS using different metals

To achieve the UV SERS on a metal nanoparticle, it requires the metal nanoparticle to have LSPR in the UV region, which is impossible for the commonly used plasmonic metals such as silver, gold, and copper. Therefore, it is essential to search other plasmonic metals which can support UV LSPR to enable the UV SERS. To date, aluminum has been the mostly investigated plasmonic metal for UV SERS, its LSPR in the UV region was first measured and demonstrated with optical transmission in 2007.¹²⁴ In the same year, UV SERS using Al NPs was also demonstrate at an excitation wavelength of 244 nm.¹²⁵ From then on, Al NPs were fabricated with different methods and structures for UV SERS for various applications.^{126, 127} Inspired by these findings, the UV plasmonics of Al NPs was also employed in other applications such as UV fluorescence enhancement¹²⁸ and UV plasmonic photocatalysis in combination with TiO₂.²³ In 2013, other kinds of poor metals such as Bi, Pb, Tl, Sn, In, and Ga were systematically studied through theoretical calculations, in which plasmonic responses in the near or deep UV region were predicted.⁵² However, experimental results on other metals besides aluminum for UV SERS or UV plasmonics are still seldom reported until now.

6.1.3 In NPs for UV SERS

In the history of indium plasmonics, it has been first reported can enhance the Raman scattering and photoluminescence of some molecules by using visible light excitation more than 30 years ago.¹⁰⁴ In 1987, theoretical result showed that it can be a potential candidate plasmonic material for UV SERS.¹²⁹ However, there were no experimental results regarding this prediction of In NPs for UV SERS in the following more than 20 years. Until recently, In NPs for UV SERS

using 266 nm laser was reported⁶³, demonstrating refreshed understanding of In NPs for UV SERS. According to Mie theory, the plasmonic effect of a metal nanoparticle is highly dependent on its complex dielectric constant ε which has a real part ε_1 and an imaginary part ε_2 .⁸ When compared to the dielectric constant of aluminum, its real part is larger in the UV region, which will result a relatively red shifted LSPR in the UV region when compared to aluminum (Figure 6.1).⁶³ As Al NPs have been well proven as deep UV SERS candidate, In NPs can show better potentials to be employed in near UV SERS. Moreover, as the imaginary part of the dielectric constant of a metal is often associated with absorption losses, the smaller values of indium in the UV region when compared to aluminum imply that indium will be a lower loss plasmonic metal for UV SERS, which is also ensured by an interband transition that will happen in the NIR region at 1.3 eV. Another important factor that has constrained the broad applications of Al NPs is that the preparations of Al NPs is rather challenging, which is due to the high reactivity of aluminum. The fabrications of Al nanostructures were mostly relying on physical processes which were hard to achieve high crystalline nanostructures. On the contrary, the preparation of indium nanostructures can be done more easily, and both physical and chemical methods have been reported.^{63, 64} In 2014, a theoretical study based on the dimmers model of In NPs, in which it was demonstrated that a SERS enhancement factor can reach as high as 1.2×10^9 can be achieved at a wavelength of 359 nm, showing great perspectives of exploring experimentally the UV SERS of In NPs using near UV excitations.⁶² Based on the above discussions, in this thesis, we explore the potentials of In NPs on ITO prepared by a simple one step thermal evaporation method for UV SERS using both 325 and 355 nm lasers.

Figure 6.1 Real and imaginary part of the dielectric constants of aluminum and indium as a function of wavelength in the UV region.⁶³

6.2 Experimental setup

The optical setup of the UV SERS measurement is schematically presented in Figure 6.2. A 325/355 nm laser was guided into the HR 800 Raman Evolution spectrometer by using optical mirrors. The intensity of the incident laser can be tuned by the ND filter from 0.01 to 100% of the incident intensity. The incident laser will be partly reflected by a UV beam splitter and then go to the objective lens which can focus the incident light on the sample. The Raman signal will then go back and pass through the UV beam splitter. A 325/355 nm long pass filter was used to filter out the laser line in the Raman signal from the sample. The purified Raman signal will be sent to a liquid nitrogen cooled detector, after which the Raman spectrum can be obtained. The laser power at the objective was measured ~ 0.3 mW by a power meter. The Acquisition time was ranging from 10 to 100 s. A 1800 g/mm grating and a UV objective (40 $\times$) were used in the measurements. A standard molecule p-aminothiophenol (PATP) in ethanol with different concentrations was drop casted on the samples for providing the Raman signals.

Figure 6.2 Schematics of the components and setup for the UV SERS measurements.

6.3 Results and discussions

6.3.1 Comparison of near field enhancement ability of Al and In NPs

Conventionally, the expression of $-\epsilon_1/\epsilon_2$ was widely used in the plasmonics community in briefly understand the plasmonic properties at a certain wavelength.¹³⁰ However, it cannot enable the quantitative comparison between different metals, and the influence of the surrounding medium is also not taken into consideration. To achieve more liable upstanding of the plasmonic property of metal nanostructures, numerical simulations based on different models and theories were also

developed. In 2015, Lalisse *et al.* reported a theoretical work in which a figures of merit parameter Fa was defined to quantitatively compare the near field enhancement abilities of different metals using a simple close form expression without complicated numerical simulations. The expression of Fa is given by²¹

$$Fa = |E_{max}/E_0|^2 = 9 \left| \frac{\varepsilon}{\varepsilon + 2\varepsilon_m} \right|^2 \quad (6-1)$$

where E_{max} and E_0 denote the maximum electric field that can be enhanced by a metal nanoparticle and the incident electric field, respectively. ε refers to the complex dielectric constant of the metal, while ε_m is the dielectric constant of the surrounding medium. The superiorities of this parameter when compared to the conventional numerical studies or expressions can be in the following two aspects: 1) the simple close-form expression can be calculated with just the inputs of the dielectric functions of the metal without numerical simulations; 2) it can quantitatively estimate the performances of different metals within different surrounding mediums. By using the dielectric functions of aluminum and indium displayed in Figure 6.1, the Fa values of aluminum of indium can be calculated and plotted in curves which can be found in Figure 6.3. According to the calculated Fa values of indium and aluminum, In NP can result in near field enhancement in the UV region, which could be even better than Al NP in the near UV region. Therefore, using In NPs for UV SERS is theoretically sound based on the famous fourth-power relationship of SERS intensity I_{SERS} with the incoming electric field E_0

$$I_{SERS} = 16E_0^4 g^4 \quad (6-2)$$

Figure 6.3 Calculated Fa values for aluminum and indium at different wavelengths in the UV region.

6.3.2 Preparation of In NPs with different sizes on ITO glass

The In NPs on ITO for UV SERS studies were also prepared by thermal evaporation of indium source, in which the parameters (base pressure was 3×10^{-7} Torr, and the evaporation rate was $0.5 \text{ \AA/s}$) were the same as we have discussed for MPM and quartz substrates. Similar to the observations in previous chapters, taking advantage of the unique feature that well-separated grains will form when indium vapor meets a cold solid surface, dense In NP can also be prepared on ITO glass through thermal evaporation, which implies that the thermal evaporation method for In NPs preparation can be a versatile approach for preparing In NPs on different substrate. Moreover, as the size of In NPs formed on a substrate is dependent on the deposition thickness of indium, it is also anticipated that the size can be easily tuned by simply controlling the thickness of the evaporated indium on ITO glass. Figure 6.4 shows the typical SEM images of In NPs we prepared on ITO glass, it can be seen from that multiple nanograins of indium also form under all conditions, and the size of the obtained In NPs is also increasing with the evaporated indium

thicknesses ranging from 10 to 50 nm. It is noted that there are also small grains of indium in all of the obtained In NPs on the substrate and they will be in the gaps between larger particles, which is due to the merging of the preformed even smaller In NPs when the deposition thickness is increasing. When compared with In NPs prepared on quartz using the same parameters, it can be observed the morphologies of In NPs on ITO are more uniform, and the densities of In NPs formed on ITO are higher. The uniform morphology of metal nanoparticles is often preferred in SERS as it can result in uniform and reproducible SERS signal. Moreover, the high density of In NPs on ITO will endow the indium nanostructures with plenty of “hot spots” which were proven can result in dramatic enhancement of the Raman signal.⁶²

Figure 6.4 SEM images of In NPs on ITO prepared by thermal evaporation of indium with different thicknesses. (A) 10 nm. (B) 20 nm. (C) 30 nm. (D) 50 nm.

6.3.3 Optical properties of In NPs on ITO glass

To investigate the LSPR of the as prepared In NPs on ITO glass, the absorption spectra were measured by using a Lambda 950 UV/Vis/NIR spectrometer. Figure 6.5 displays the absorption spectra of the as prepared In NPs prepared with deposition of 10 to 50 nm thickness of indium on ITO glass. As shown in the figure, all the spectra can show strong light absorption peaks in the range from 300 to 400 nm, which are the results of the strong UV LSPRs of In NPs. It is noted that the LSPR peaks are sharper and different modes can be distinguished clearly when compared to the results obtained on quartz, which could be ascribed to the more uniform morphologies of In NPs formed on ITO. In addition, for In NPs prepared on quartz, their LSPRs mainly appear in the range of 200 to 300 nm, while for In NPs prepared on ITO glass, the observed LSPRs of In NPs are in the region of 300 to 400 nm, which can be explained by the different dielectric constants of quartz and ITO glass. According to Mie theory, the LSPR of a metal nanoparticle can appear at a wavelength when the condition $\varepsilon_1 = -2\varepsilon_m$ is satisfied. Therefore, the change of the refractive index of the surrounding medium will affect the position of the LSPR peak of In NPs. With the increasing deposition thickness of indium on ITO, the absorption spectra become broader, which is due to the formation of larger and irregular In NPs. There are always LSPRs in the range of 300 to 400 nm, potentially arises from small grains of indium in the gaps between larger particles when the deposition thickness is more than 10 nm. This phenomenon can be ascribed to the merging of the preformed small In NPs when the deposition thickness is increasing. As there are always unmerged or freshly formed small In NPs when the indium vapor is keep condense at the substrate, small In NPs will be always there when the deposition thickness of indium has reached a certain value, which also implies that the formation of small In NPs on the ITO can be independent on the evaporation thickness, and

therefore the appearance of the LSPRs in the 300 to 400 nm region. The LSPRs in this region show great potentials in resonance with the commonly used 325 or 355 nm lasers, which is promising for UV SERS based applications.

Figure 6.5 Absorption spectra of the prepared In NPs with deposition of 10 to 50 nm thickness of indium on ITO glass.

6.3.4 In NPs for UV SERS using 325 nm laser

In the UV SERS measurements, 10 μL of the Raman dye PATP in ethanol was drop casted onto the In NPs (prepared with 20 nm indium deposition) coated ITO substrate (SERS) or bare ITO substrate (reference). As shown in Figure 6.6, when the acquisition time is set as 10 s, PATP at a concentration as high as 10^{-2} M still cannot be detected on the bare ITO glass substrate. However, when 10^{-2} M is drop casted on ITO with In NPs, Raman peak of PATP at 1600 cm^{-1} (C-C stretch) can be observed, which could be ascribed to the a_1 type in-plane mode. If we further decrease the concentration of PATP by 10 times to 10^{-3} M, a weaker Raman signal could also be obtained. For reference, we have also measured the signal from the In NPs on ITO substrate, in which we cannot obtain any Raman peaks. Therefore, it is clear that the Raman signal of PATP can be

enhanced by using In NPs coated ITO substrate.

Figure 6.6 Raman signals of 10^{-2} and 10^{-3} M PATP on (A) ITO and (B) In NPs coated ITO. Acquisition time is set as 10 s.

To gain further insight of the enhancement of Raman signal of PATP, a Raman signal of PATP should be obtained on ITO for quantitative comparison. To achieve this goal, we extend the acquisition time to 100 s, through which a clear Raman peak of PATP is observed at the concentration of 10^{-2} M on bare ITO, which is consistent with the Raman spectrum obtained on PATP powder. Accordingly, an even strong Raman signal of 10^{-2} M PATP can be observed on the In NPs coated ITO substrate (Figure 6.7). To quantitatively evaluate the enhancement of PATP Raman signal by In NPs, the Raman peaks at 1600 cm^{-1} are fitted into Lorentz peaks, whose areas therefore can be calculated for comparison of the Raman signal of PATP on bare ITO and In NPs coated ITO. By using this method, In NPs (prepared with 20 nm indium deposition) can be calculated can result in a 11.8 times enhancement of the Raman signal from 10^{-2} M PATP. For 10^{-3} M PATP, even we have increased the acquisition time to 100 s, we still cannot obtain the Raman signal on bare ITO, therefore, in our following studies, PATP at the concentration of 10^{-2} M is chosen for systematic studies.

Figure 6.7 Raman signals of 10^{-2} and 10^{-3} M PATP on (A) ITO and (B) In NPs coated ITO. Acquisition time is set as 100 s.

6.3.5 Effect of In NPs sizes on UV SERS performances with 325 nm laser

To have a better understanding of the influence of In NPs sizes on UV SERS performance, we systematically investigated 10^{-2} M PATP on different sizes of In NPs prepared by deposition of 10 to 50 nm of indium. For purpose of assessing the UV SERS performances of all samples with different sizes, the acquisition time are all set as 100 s and the enhancement was evaluated by calculating the fitted Lorentz peak areas at the Raman shift of 1600 cm^{-1} (Figure 6.8). From the obtained results, one can see that once In NPs are used, all the samples show enhanced performance, demonstrating the strong SERS effect from In NPs. In our UV SERS measurements, we can observe the strongest enhancement on the In NPs prepared by deposition of 25 nm indium on ITO. According to the results of absorption spectra of In NPs on ITO, higher enhancements are not obtained on the ITO substrates with 30 or 50 nm deposition thickness of indium, on which the LSPRs of In NPs are more resonant with the 325 nm excitation laser. According to previous studies, SERS excitation efficiency often cannot match very well with the measured LSPR features of the investigated plasmonic nanostructures with complex properties such as densely distributed metal nanoparticles on a substrate, on which the In NPs will not

behave like an isolated nanoparticle. The explanation for this phenomenon could be the formation of plenty of “hot spots” on the substrate.¹³¹ As not all the In NPs can be involved in the “hot spots”, the absorption spectra are still displaying the LSPR features of entire contributions of the In NPs. For In NPs on ITO, In NPs with large sizes can act as antenna, while smaller ones can result in strong near field enhancement.^{132, 133} As the gaps between large In NPs are too large to form hot spots, the hot spots will be mainly induced by the coupling between large In NPs and the smaller In NPs in their gaps. Therefore, in our case, strong enhancements can be obtained on In NPs prepared with indium thickness more than 10 nm, in which we can observe smaller In NPs are formed in the gap of large In NPs. The enhancement of PATP Raman signal is around 16.7 times on In NPs prepared with 25 nm indium deposition, which is in similar order when compared to previous report using Al nanostructures,¹²⁶ and is better than the 11 times enhancement in previous report using 266 nm laser.⁶³

Figure 6.8 Raman signals of 10^{-2} M PATP on In NPs prepared with different indium deposition thickness ranging from 10 to 50 nm on ITO. Acquisition time is set as 100 s with 325 nm laser excitation.

6.3.6 Comparison between 325 and 355 nm laser excitation

By using 355 nm laser excitations, the best UV SERS enhancement can be achieved is around 5 times on In NPs prepared with 50 nm indium deposition on ITO (Figure 6.9A). In both studies using 325 and 355 nm laser excitations, it is found that In NPs prepared with 10 nm indium depositions on ITO are always showing weaker enhancements, which implies that smaller In NPs themselves only contribute a small part to the UV SERS enhancement, and the hot spots are created through the coupling between small and larger In NPs. Figure 6.9B summarizes the systematic studies using 325 and 355 nm lasers. For In NPs with different sizes, 325 nm laser excitations can give higher UV SERS enhancements, and the best performance is found on the 25 nm indium deposition ITO substrate on which a 16.7 times enhancement can be obtained.

Figure 6.9 (A) Raman signals of 10^{-2} M PATP on In NPs prepared with different indium deposition thickness ranging from 10 to 50 nm on ITO. Acquisition time is set as 100 s with 355 nm laser excitation. (B) Comparison of the UV SERS performances between 325 and 355 nm laser excitations on different sizes of In NPs prepared with different indium deposition thickness ranging from 10 to 50 nm on ITO.

6.3.7 Effect of a SiO₂ dielectric layer coating on In NPs on UV SERS performance

SERS is highly dependent on the near field enhancement effect at the metal nanoparticle surface.

To probe this effect, we coated the In NPs with a layer of SiO_2 to see the evolution of SERS signal at different distances from the In NPs surfaces. Figure 6.10 shows the SEM images of In NPs (prepared with 25 nm indium deposition) on ITO before and after a layer of 10 nm thickness SiO_2 coating. From the SEM images one can see that the In NPs are still uniformly distributed on the quartz without any obvious change in morphology and size substrate after the coating of SiO_2 , which also confirms that the sputtering process will not damage the as formed In NPs.

Figure 6.10 SEM images of In NPs prepared by thermal evaporation of indium with 25 nm thickness before (A) and after (B) the sputtering of 10 nm SiO_2 .

After 10 nm SiO_2 sputtering, the absorption spectra of In NPs will show a red shift (Figure 6.11), which is similar to the phenomenon we have observed on quartz.

Figure 6.11 Absorption spectra of In NPs prepared by thermal evaporation of indium with 25 nm thickness before and after the sputtering of 10 nm SiO₂.

We then systematically studied the UV SERS performances of the as obtained In NPs@SiO₂ with different SiO₂ thicknesses ranging from 10 to 50 nm (Figure 6.12). It can be seen from the resultant SERS signal that increasing the thickness of SiO₂ between In NPs and PATP will lead to a decreased UV SERS enhancement, which agrees well with many plasmonic systems that the near field enhancement will decrease dramatically in the range of tens of nanometers from the metal nanoparticle surface.

Figure 6.12 UV SERS of PATP on In NPs@SiO₂ with different SiO₂ thickness ranging from 10 to 50 nm. Acquisition time is set as 100 s with 325 nm laser excitation.

6.4 Conclusions

In summary, we have demonstrated the preparation of densely distributed In NPs on ITO glass through a one-step vacuum evaporation method, in which the sizes of In NPs can be easily controlled by tuning the deposition thickness of indium. The as obtained In NPs can show strong LSPR in 300 to 400 nm spectral region, and can form many hot spots on the substrates, which

make them suitable for UV SERS based applications. The Raman signal of a widely used Raman reporter PATP can be enhanced by ~17 times by using the prepared In NPs. Our results show that indium is an efficient and easy-to-use metal for exciting UV-SERS and will accelerate the development of research applications in UV-SERS by extending the choice of metal that can be used. Taking into consideration of the simple preparation of In NPs when compared to Al NPs, and the strong UV LSPR feature, In NPs can show great potentials in UV SERS based applications.

Chapter 7

Summary and Future work

7.1 Original contribution of this thesis

In this dissertation, through careful and reasonable designs, we developed different metallic nanostructures based on Au and In NPs for plasmonics based applications including plasmonic colorimetric sensing, plasmonic solar desalination, plasmon enhanced photocatalysis of TiO₂, and UV SERS. We started with the basics and fundamentals of plasmonics, which provided the theoretical supports for our studies. We then discussed in detail the principles, controls, influence factors, relevant surface chemistry/physics in the synthesis/fabrication processes of the metal nanostructures. Various characterization techniques such as TEM, SEM, UV/Vis/NIR absorption spectroscopy, and XRD were employed to help us gain insight of the morphologies and chemical/physical/optical properties of the obtained plasmonic nanostructures. By utilizing the unique features of the as obtained different plasmonic nanostructures, novel designs thus can be achieved for different applications.

Plasmonic colorimetric sensing based on colloid Au NPs has been proven a simple, visual, and cost-effective detection technique in chemo/biosensing. Traditionally, a colorimetric sensing strategy based on Au NPs was often designed to detect one certain kind of analyte. To extend the capability of plasmonic colorimetric sensing based on colloid Au NPs for multiplex analytes sensing, we introduced the concept of logic gate to construct a single platform for sensing and discrimination of different species. In our study, we designed a three-input logic gate sensing system which can be used for the sensing and discrimination of Hg²⁺, cysteine, and melamine based on colloid Au NPs. This is the first demonstrated colorimetric logic gate sensing system

for these three kinds of analytes.

Plasmonic nanoparticles have proven to be an effective way to enhance the generation of solar steam by plasmonic heating effects. Its efficiency in conventionally designed systems is often constrained by unavoidable bulk heating and energy loss to the entire water volume, and the typically used plasmonic metal nanoparticles such as Au and Ag NPs whose availability and complexity in their preparation are not cost-effective. Inspired by theoretically the superior plasmonic heating effects of In NPs, in this thesis, we developed for the first time a paper-like plasmonic device through combination of In NPs and a microporous film for solar desalination of a real seawater sample with stable and excellent performances, in which bulk heating issue can also avoided due to its floating nature.

Using metal nanoparticles to enhance the photocatalysis performance of TiO_2 have been proven possible. In the construction of plasmonic photocatalysis system based on TiO_2 , metal nanoparticles with LSPR in the UV region which can have spectral overlap with absorption band of TiO_2 is preferred, either because plasmonic band can enhance the absorption of the incoming light or boost the excitation of TiO_2 by creating an intense electromagnetic field in the near field. Up to now, only silver and aluminum nanoparticles for UV plasmon enhanced photocatalysis were designed based on this strategy. In our study, we prepared In NPs with LSPR feature in the UV region and showed for the first time using In NPs to enhance the photocatalysis performance of TiO_2 .

UV SERS have shown great potentials in the detection of some essential aromatic species in biological systems such as DNA/RNA bases and amino acids with aromatic groups. Up to now, most of the UV SERS systems were developed using Al NPs. Motivated by our theoretical calculation result that In NPs can show even stronger near field enhancement ability than Al NPs

in the UV region, we investigated for the first time of In NPs on ITO, which can show strong LSPR in spectral region from 300 to 400 nm, for UV SERS using both 325 and 355 nm laser.

7.2 Future work

Although we have demonstrated some novel plasmonics based applications based on different designs of metallic nanostructures, further improvement of the designs or exploring new designs are still important for broadening their application potentials. In the future, I will continue to explore in the following aspects based on some preliminary results:

1. Using solution synthesized In NPs for UV plasmonics based applications

Figure 7.1 (A) SEM image and (B) absorption spectra of solution synthesized In NPs. (C) SEM

and TEM image of In@SiO₂ core-shelled nanoparticles.

By using solution method, we can synthesize In NPs with very uniform sizes and morphologies. The as obtained In NPs can show the LSPR peak at a wavelength of 269 nm, implying the potentials in UV plasmonics (Figure 7.1). Moreover, the as obtained In NPs can also be coated with a layer of SiO₂ to form In@SiO₂ core-shelled nanoparticles. The solution method can enable synthesis of In NPs in large scale, which will be useful in solution based practical photocatalysis in which a large amount of the photocatalyst is required. The uniform size and morphology will benefit a fundamental study in which highly defined shapes and sizes are required. The SiO₂ shell will provide protection to In NPs in complex systems. It can also introduce new surface chemistry to In NPs, which may extend the application range of In NPs. In the future, we will keep on exploring the synthesis condition to try to control the size and shape of In NPs.

2. Combination of the photocatalysis of TiO₂ and plasmonic heating effect from In NPs

According to previous report, core-shelled SiO₂/Ag@TiO₂ NPs were synthesized to be employed as thermal collector and photocatalyst, and the heat generation in this design was demonstrated can synergistically benefit for both desalination and catalysis processes.⁹⁷ As we have presented in chapter 2, In NPs were found can also be prepare on TiO₂ nanorods (Figure 7.2). Based on this hybrid and novel nanostructure, we expect to combine the photocatalysis feature and the plasmonic heating effect from In NPs together, to construct plasmonic nanostructures for water treatment and at the same time for water desalination. Further efforts will be devoted on finding suitable substrates for TiO₂, to achieve a floating device as we have discussed in chapter 4. In an optimized condition, we may need to use a more finely controlled dielectric layer (SiO₂ by e-beam evaporation or Al₂O₃ by atomic layer deposition) to control the

charge transfer and nearfield enhancement effect, to see which one is dominated in the process, and then try to do further optimization.

Figure 7.2 SEM image of In NPs on TiO₂ nanorods.

References

1. Halas, N.J. "Plasmonics: An Emerging Field Fostered by Nano Letters". *Nano Letters* **10**, 3816-3822, (2010).
2. Olson, J. et al. "Optical Characterization of Single Plasmonic Nanoparticles". *Chemical Society Reviews* **44**, 40-57, (2015).
3. Willets, K.A. et al. "Localized Surface Plasmon Resonance Spectroscopy and Sensing". *Annual Review of Physical Chemistry* **58**, 267-297, (2007).
4. Li, M. et al. "Plasmon-enhanced Optical Sensors: A Review". *Analyst* **140**, 386-406, (2015).
5. Zhang, Q. et al. "A Room Temperature Low-threshold Ultraviolet Plasmonic Nanolaser". *Nature Communications* **5**, 4953, (2014).
6. Govorov, A.O. et al. "Generating Heat with Metal Nanoparticles". *Nano Today* **2**, 30-38, (2007).
7. Liu, Y. et al. "A Bioinspired, Reusable, Paper-Based System for High-Performance Large-Scale Evaporation". *Advanced Materials* **27**, 2768-2774, (2015).
8. Ghosh, S.K. et al. "Interparticle Coupling Effect on the Surface Plasmon Resonance of Gold Nanoparticles: From Theory to Applications". *Chemical Reviews* **107**, 4797-4862, (2007).
9. Mayer, K.M. et al. "Localized Surface Plasmon Resonance Sensors". *Chemical Reviews* **111**, 3828-3857, (2011).
10. Ritchie, R.H. "Plasma Losses by Fast Electrons in Thin Films". *Physical Review* **106**, 874-881, (1957).
11. Powell, C.J. et al. "Origin of the Characteristic Electron Energy Losses in Aluminum". *Physical Review* **115**, 869-875, (1959).
12. Grigorenko, A.N. et al. "Graphene Plasmonics". *Nature Photonics* **6**, 749, (2012).
13. Raether, H. "Surface Plasmons on Smooth and Rough Surfaces and on Gratings". Ed. Hohler G. Springer, Berlin (1988).
14. Yan, R. et al. "Nanowire Photonics". *Nature Photonics* **3**, 569, (2009).
15. Chi, H. et al. "A Simple, Reliable and Sensitive Colorimetric Visualization of Melamine in Milk by Unmodified Gold Nanoparticles". *Analyst* **135**, 1070-1075, (2010).
16. Kalluri, J.R. et al. "Use of Gold Nanoparticles in a Simple Colorimetric and Ultrasensitive Dynamic Light Scattering Assay: Selective Detection of Arsenic in Groundwater". *Angewandte Chemie International Edition* **48**, 9668-9671, (2009).
17. Noh, K.C. et al. "A Colorimetric Probe to Determine Pb²⁺ Using Functionalized Silver Nanoparticles". *Analyst* **140**, 8209-8216, (2015).
18. Tharmaraj, V. et al. "Sensitive and Selective Colorimetric Detection of Cu²⁺ in Aqueous Medium via Aggregation of Thiomalic Acid Functionalized Ag Nanoparticles". *Analyst* **139**, 6304-6309, (2014).
19. Lee, J.S. et al. "A DNA-gold Nanoparticle-based Colorimetric Competition Assay for the Detection of Cysteine". *Nano Letters* **8**, 529-533, (2008).
20. Ye, M. et al. "Synthesis of Black TiO_x Nanoparticles by Mg Reduction of TiO₂ Nanocrystals and their Application for Solar Water Evaporation". *Advanced Energy Materials* **7**, 1601811, (2017).
21. Lalis, A. et al. "Quantifying the Efficiency of Plasmonic Materials for Near-Field Enhancement and Photothermal Conversion". *The Journal of Physical Chemistry C* **119**,

- 25518-25528, (2015).
22. Neumann, O. et al. "Solar Vapor Generation Enabled by Nanoparticles". *ACS Nano* **7**, 42-49, (2013).
23. Hao, Q. et al. "Aluminum Plasmonic Photocatalysis". *Scientific Reports* **5**, 15288, (2015).
24. Zhou, L. et al. "3D Self-assembly of Aluminium Nanoparticles for Plasmon-enhanced Solar Desalination". *Nature Photonics* **10**, 393-398, (2016).
25. Xuming, Z. et al. "Plasmonic Photocatalysis". *Reports on Progress in Physics* **76**, 046401, (2013).
26. Awazu, K. et al. "A Plasmonic Photocatalyst Consisting of Silver Nanoparticles Embedded in Titanium Dioxide". *Journal of the American Chemical Society* **130**, 1676-1680, (2008).
27. Mubeen, S. et al. "Plasmonic Photosensitization of a Wide Band Gap Semiconductor: Converting Plasmons to Charge Carriers". *Nano Letters* **11**, 5548-5552, (2011).
28. Cushing, S.K. et al. "Photocatalytic Activity Enhanced by Plasmonic Resonant Energy Transfer from Metal to Semiconductor". *Journal of the American Chemical Society* **134**, 15033-15041, (2012).
29. Katrin, K. et al. "Surface-enhanced Raman Scattering and Biophysics". *Journal of Physics: Condensed Matter* **14**, R597, (2002).
30. Fleischmann, M. et al. "Raman Spectra of Pyridine Adsorbed at a Silver Electrode". *Chemical Physics Letters* **26**, 163-166, (1974).
31. Jeanmaire, D.L. et al. "Surface Raman Spectroelectrochemistry: Part I. Heterocyclic, Aromatic, and Aliphatic Amines Adsorbed on the Anodized Silver Electrode". *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **84**, 1-20, (1977).
32. Albrecht, M.G. et al. "Anomalously Intense Raman Spectra of Pyridine at a Silver Electrode". *Journal of the American Chemical Society* **99**, 5215-5217, (1977).
33. Turkevich, J. et al. "A Study of the Nucleation and Growth Processes in the Synthesis of Colloidal Gold". *Discussions of the Faraday Society* **11**, 55-75, (1951).
34. Frens, G. "Controlled Nucleation for the Regulation of the Particle Size in Monodisperse Gold Suspensions". *Nature Physical Science* **241**, 20, (1973).
35. Yang, X. et al. "Gold Nanomaterials at Work in Biomedicine". *Chemical Reviews* **115**, 10410-10488, (2015).
36. Blair, A.C. et al. "Discovering Nanoscience". *Science* **337**, 1056, (2012).
37. Ji, X. et al. "Size Control of Gold Nanocrystals in Citrate Reduction: The Third Role of Citrate". *Journal of the American Chemical Society* **129**, 13939-13948, (2007).
38. Ojea-Jiménez, I. et al. "Influence of the Sequence of the Reagents Addition in the Citrate-Mediated Synthesis of Gold Nanoparticles". *The Journal of Physical Chemistry C* **115**, 15752-15757, (2011).
39. Sivaraman, S.K. et al. "Monodisperse Sub-10nm Gold Nanoparticles by Reversing the Order of Addition in Turkevich Method - The Role of Chloroauric Acid". *Journal of Colloid and Interface Science* **361**, 543-547, (2011).
40. Ojea-Jiménez, I. et al. "Small Gold Nanoparticles Synthesized with Sodium Citrate and Heavy Water: Insights into the Reaction Mechanism". *The Journal of Physical Chemistry C* **114**, 1800-1804, (2010).
41. Zheng, Y. et al. "Seed Mediated Synthesis of Single Crystal Gold Nanospheres with Controlled Diameters in the Range 5-30 nm and their Self-Assembly upon Dilution". *Chemistry - An Asian Journal* **8**, 792-799, (2013).

42. Lee, Y.-J. et al. "Ultrasoft, Highly Spherical Monocrystalline Gold Particles for Precision Plasmonics". *ACS Nano* **7**, 11064-11070, (2013).
43. Ye, X. et al. "Improved Size-Tunable Synthesis of Monodisperse Gold Nanorods through the Use of Aromatic Additives". *ACS Nano* **6**, 2804-2817, (2012).
44. Millstone, J.E. et al. "Controlling the Edge Length of Gold Nanoprisms via a Seed-Mediated Approach". *Advanced Functional Materials* **16**, 1209-1214, (2006).
45. Wang, H. et al. "Plasmonic Nanostructures: Artificial Molecules". *Accounts of Chemical Research* **40**, 53-62, (2007).
46. Lu, X. et al. "Fabrication of Cubic Nanocages and Nanoframes by Dealloying Au/Ag Alloy Nanoboxes with an Aqueous Etchant Based on $\text{Fe}(\text{NO}_3)_3$ or NH_4OH ". *Nano Letters* **7**, 1764-1769, (2007).
47. Cobley, C.M. et al. "Engineering the Properties of Metal Nanostructures via Galvanic Replacement Reactions". *Materials Science and Engineering: R: Reports* **70**, 44-62, (2010).
48. Zheng, Y. et al. "Seed-Mediated Synthesis of Gold Tetrahedra in High Purity and with Tunable, Well-Controlled Sizes". *Chemistry - An Asian Journal* **9**, 2635-2640, (2014).
49. Kim, F. et al. "Platonic Gold Nanocrystals". *Angewandte Chemie International Edition* **43**, 3673-3677, (2004).
50. Chen, S. et al. "Monopod, Bipod, Tripod, and Tetrapod Gold Nanocrystals". *Journal of the American Chemical Society* **125**, 16186-16187, (2003).
51. Burt, J.L. et al. "Beyond Archimedean Solids: Star Polyhedral Gold Nanocrystals". *Journal of Crystal Growth* **285**, 681-691, (2005).
52. McMahon, J.M. et al. "Plasmonics in the Ultraviolet with the Poor metals Al, Ga, In, Sn, Tl, Pb, and Bi". *Physical Chemistry Chemical Physics* **15**, 5415-5423, (2013).
53. Gong, C. et al. "Noble Metal Alloys for Plasmonics". *ACS Photonics* **3**, 507-513, (2016).
54. Li, S.Q. et al. "Infrared Plasmonics with Indium-Tin-Oxide Nanorod Arrays". *ACS Nano* **5**, 9161-9170, (2011).
55. Naik, G.V. et al. "Alternative Plasmonic Materials: Beyond Gold and Silver". *Advanced Materials* **25**, 3264-3294, (2013).
56. Zhang, L. et al. "Plasmonic Heating from Indium Nanoparticles on a Floating Microporous Membrane for Enhanced Solar Seawater Desalination". *Nanoscale* **9**, 12843-12849, (2017).
57. Chan, G.H. et al. "Localized Surface Plasmon Resonance Spectroscopy of Triangular Aluminum Nanoparticles". *The Journal of Physical Chemistry C* **112**, 13958-13963, (2008).
58. Pomfret, M.B. et al. "Electrochemical Template Deposition of Aluminum Nanorods Using Ionic Liquids". *Chemistry of Materials* **20**, 5945-5947, (2008).
59. Eliezer, S. et al. "Synthesis of Nanoparticles with Femtosecond Laser Pulses". *Physical Review B* **69**, 144119, (2004).
60. Helmich, R.J. et al. "Chemical Aerosol Flow Synthesis of Hollow Metallic Aluminum Particles". *Chemistry of Materials* **22**, 4835-4837, (2010).
61. Lim, T.H. et al. "Solution Synthesis of Monodisperse Indium Nanoparticles and Highly Faceted Indium Polyhedra". *Crystal Growth & Design* **10**, 3854-3858, (2010).
62. Ross, M.B. et al. "Aluminum and Indium Plasmonic Nanoantennas in the Ultraviolet". *The Journal of Physical Chemistry C* **118**, 12506-12514, (2014).
63. Kumamoto, Y. et al. "Indium for Deep-Ultraviolet Surface-Enhanced Resonance Raman

- Scattering". *ACS Photonics* **1**, 598-603, (2014).
64. Chou, N.H. et al. "Room-Temperature Chemical Synthesis of Shape-Controlled Indium Nanoparticles". *Journal of the American Chemical Society* **130**, 8140-8141, (2008).
 65. Hammarberg, E. et al. "In⁰ Nanoparticle Synthesis Assisted by Phase-Transfer Reaction". *Chemistry of Materials* **21**, 771-774, (2009).
 66. Yu, H. et al. "Heterogeneous Seeded Growth: A Potentially General Synthesis of Monodisperse Metallic Nanoparticles". *Journal of the American Chemical Society* **123**, 9198-9199, (2001).
 67. Ganeev, R.A. et al. "Structural, Optical, and Nonlinear Optical Properties of Indium Nanoparticles Prepared by Laser Ablation". *Applied Physics B* **86**, 337-341, (2007).
 68. Li, Z. et al. "A Simple and Rapid Method for Preparing Indium Nanoparticles from Bulk Indium via Ultrasound Irradiation". *Materials Science and Engineering: A* **407**, 7-10, (2005).
 69. Kind, C. et al. "One-Pot Synthesis of In⁰ Nanoparticles with Tuned Particle Size and High Oxidation Stability". *Chemistry of Materials* **23**, 4982-4987, (2011).
 70. Soulantica, K. et al. "Selective Synthesis of Novel In and In₃Sn Nanowires by an Organometallic Route at Room Temperature". *Angewandte Chemie International Edition* **40**, 2983-2986, (2001).
 71. Holyst, R. et al. "A Molecular Dynamics Test of the Hertz-Knudsen Equation for Evaporating Liquids". *Soft Matter* **11**, 7201-7206, (2015).
 72. Brent, F. "Transmission Electron Microscopy and Diffractometry of Materials". Springer. (2007).
 73. Champness, P.E. "Electron Diffraction in the Transmission Electron Microscope". Garland Science (2001).
 74. Dalton, J.S. et al. "Photocatalytic Oxidation of NO_x Gases Using TiO₂: A Surface Spectroscopic Approach". *Environmental Pollution* **120**, 415-422, (2002).
 75. Selid, P. et al. "Sensing Mercury for Biomedical and Environmental Monitoring". *Sensors* **9**, 5446, (2009).
 76. Jung, H.S. et al. "Recent Progress in Luminescent and Colorimetric Chemosensors for Detection of Thiols". *Chemical Society Reviews* **42**, 6019-6031, (2013).
 77. Freeman, R. et al. "Multiplexed Analysis of Hg²⁺ and Ag⁺ Ions by Nucleic Acid Functionalized CdSe/ZnS Quantum Dots and Their Use for Logic Gate Operations". *Angewandte Chemie International Edition* **48**, 7818-7821, (2009).
 78. de Silva, A.P. et al. "Molecular Logic and Computing". *Nature Nanotechnology* **2**, 399, (2007).
 79. Hettie, K.S. et al. "Three-Input Logic Gates with Potential Applications for Neuronal Imaging". *Journal of the American Chemical Society* **136**, 4877-4880, (2014).
 80. Cao, C. et al. "Intelligent and Ultrasensitive Analysis of Mercury Trace Contaminants via Plasmonic Metamaterial-Based Surface-Enhanced Raman Spectroscopy". *Small* **10**, 3252-3256, (2014).
 81. Huang, Z. et al. "Glutathione-facilitated Design and Fabrication of Gold Nanoparticle-Based Logic Gates and Keypad Lock". *Nanoscale* **6**, 8300-8305, (2014).
 82. Du, J. et al. "A Colorimetric Logic Gate based on Free Gold Nanoparticles and the Coordination Strategy between Melamine and Mercury ions". *Chemical Communications* **49**, 4196-4198, (2013).
 83. Liu, D. et al. "Resettable, Multi-Readout Logic Gates Based on Controllably Reversible

- Aggregation of Gold Nanoparticles". *Angewandte Chemie International Edition* **50**, 4103-4107, (2011).
84. Liu, D. et al. "Highly Sensitive, Colorimetric Detection of Mercury(II) in Aqueous Media by Quaternary Ammonium Group-Capped Gold Nanoparticles at Room Temperature". *Analytical Chemistry* **82**, 9606-9610, (2010).
 85. Cheesman, B.V. et al. "Nuclear Magnetic Resonance Studies of the Solution Chemistry of Metal Complexes. 25. Hg(thiol)₃ Complexes and HG(II)-thiol Ligand Exchange Kinetics". *Journal of the American Chemical Society* **110**, 6359-6364, (1988).
 86. Van Der Linden, W.E. et al. "Determination of the Composition and the Stability Constants of Complexes of Mercury(II) with Amino Acids". *Analytica Chimica Acta* **68**, 143-154, (1974).
 87. Mocanu, A. et al. "Self-assembly Characteristics of Gold Nanoparticles in the Presence of Cysteine". *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **338**, 93-101, (2009).
 88. Calvin, M. "Solar Energy by Photosynthesis". *Science* **184**, 375-381, (1974).
 89. Kim, J. et al. "Hydrogen Producing Water Treatment Through Solar Photocatalysis". *Energy & Environmental Science* **3**, 1042-1045, (2010).
 90. Lewis, N.S. "Research Opportunities to Advance Solar Energy Utilization". *Science* **351**, (2016).
 91. Coelho, B. et al. "Concentrated Solar Power for Renewable Electricity and Hydrogen Production from Water-A Review". *Energy & Environmental Science* **3**, 1398-1405, (2010).
 92. Li, X. et al. "Three-dimensional Artificial Transpiration for Efficient Solar Waste-water Treatment". *National Science Review* **5**, 70-77, (2017).
 93. Neumann, O. et al. "Compact Solar Autoclave based on Steam Generation Using Broadband Light-Harvesting Nanoparticles". *Proceedings of the National Academy of Sciences* **110**, 11677-11681, (2013).
 94. Li, X. et al. "Graphene Oxide-based Efficient and Scalable Solar Desalination under One Sun With a Confined 2D Water Path". *Proceedings of the National Academy of Sciences* **113**, 13953-13958, (2016).
 95. Hu, X. et al. "Tailoring Graphene Oxide-Based Aerogels for Efficient Solar Steam Generation under One Sun". *Advanced Materials* **29**, 1604031, (2017).
 96. Zhou, L. et al. "Self-assembly of Highly Efficient, Broadband Plasmonic Absorbers for Solar Steam Generation". *Science Advances* **2**, (2016).
 97. Gao, M. et al. "Plasmonic Photothermal Directed Broadband Sunlight Harnessing for Seawater Catalysis and Desalination". *Energy & Environmental Science* **9**, 3151-3160, (2016).
 98. Wang, Z. et al. "Bio-Inspired Evaporation Through Plasmonic Film of Nanoparticles at the Air-Water Interface". *Small* **10**, 3234-3239, (2014).
 99. Wang, J. et al. "High-Performance Photothermal Conversion of Narrow-Bandgap Ti₂O₃ Nanoparticles". *Advanced Materials* **29**, 1603730, (2017).
 100. Zhang, C. et al. "Shape-Controlled Synthesis of High-Quality Cu₇S₄ Nanocrystals for Efficient Light-Induced Water Evaporation". *Small* **12**, 5320-5328, (2016).
 101. Zhang, L. et al. "Hydrophobic Light-to-Heat Conversion Membranes with Self-Healing Ability for Interfacial Solar Heating". *Advanced Materials* **27**, 4889-4894, (2015).
 102. Zeng, Y. et al. "Solar Evaporation Enhancement Using Floating Light-absorbing

- Magnetic Particles". *Energy & Environmental Science* **4**, 4074-4078, (2011).
103. Vynck, K. et al. "Photon Management in Two-dimensional Disordered Media". *Nature Materials* **11**, 1017-1022, (2012).
 104. Loutfy, R.O. et al. "Interaction of Indium Metal with Phthalocyanine Molecules: Luminescence Enhancement". *Journal of Luminescence* **26**, 359-366, (1982).
 105. Magnan, F. et al. "Indium@silica Core-shell Nanoparticles as Plasmonic Enhancers of Molecular Luminescence in the UV Region". *Chemical Communications* **49**, 9299-9301, (2013).
 106. Myroshnychenko, V. et al. "Modelling the Optical Response of Gold Nanoparticles". *Chemical Society Reviews* **37**, 1792-1805, (2008).
 107. Zhang, J. et al. "Tailoring Alphabetical Metamaterials in Optical Frequency: Plasmonic Coupling, Dispersion, and Sensing". *ACS Nano* **8**, 3796-3806, (2014).
 108. Dragan, A.I. et al. "Indium Nanodeposits: A Substrate for Metal-enhanced Fluorescence in the Ultraviolet Spectral Region". *Journal of Applied Physics* **108**, 094701, (2010).
 109. Surwade, S.P. et al. "Water Desalination Using Nanoporous Single-layer Graphene". *Nature Nanotechnology* **10**, 459-464, (2015).
 110. Hewitt, R.W. et al. "Oxidation of Polycrystalline Indium Studied by X-ray Photoelectron Spectroscopy and Static Secondary Ion Mass Spectroscopy". *Journal of Applied Physics* **51**, 2620-2624, (1980).
 111. Schoeller, H. et al. "Oxidation and Reduction Behavior of Pure Indium". *Journal of Materials Research* **24**, 386-393, (2009).
 112. Chen, X. et al. "Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications". *Chemical Reviews* **107**, 2891-2959, (2007).
 113. Hu, C. et al. "Ag/AgBr/TiO₂ Visible Light Photocatalyst for Destruction of Azodyes and Bacteria". *The Journal of Physical Chemistry B* **110**, 4066-4072, (2006).
 114. Hou, W. et al. "Photocatalytic Conversion of CO₂ to Hydrocarbon Fuels via Plasmon-Enhanced Absorption and Metallic Interband Transitions". *ACS Catalysis* **1**, 929-936, (2011).
 115. Liu, Z. et al. "Plasmon Resonant Enhancement of Photocatalytic Water Splitting Under Visible Illumination". *Nano Letters* **11**, 1111-1116, (2011).
 116. Ao, C.H. et al. "Indoor Air Purification by Photocatalyst TiO₂ immobilized on an Activated Carbon Filter Installed in An Air Cleaner". *Chemical Engineering Science* **60**, 103-109, (2005).
 117. Hamdy, M.S. et al. "A Novel TiO₂ Composite for Photocatalytic Wastewater Treatment". *Journal of Catalysis* **310**, 75-83, (2014).
 118. Lee, K.M. et al. "Recent Developments of Zinc Oxide Based Photocatalyst in Water Treatment Technology: A Review". *Water Research* **88**, 428-448, (2016).
 119. Szilágyi, I.M. et al. "WO₃ Photocatalysts: Influence of Structure and Composition". *Journal of Catalysis* **294**, 119-127, (2012).
 120. Fang, Y. et al. "Intermittent Photocatalytic Activity of Single CdS Nanoparticles". *Proceedings of the National Academy of Sciences* **114**, 10566-10571, (2017).
 121. Fodor, S.P.A. et al. "Ultraviolet Resonance Raman Spectroscopy of the Nucleotides with 266-, 240-, 218-, and 200-nm Pulsed Laser Excitation". *Journal of the American Chemical Society* **107**, 1520-1529, (1985).
 122. Johnson, C.R. et al. "UV Resonance Raman Spectroscopy of the Aromatic Amino Acids and Myoglobin". *Journal of the American Chemical Society* **106**, 5008-5010, (1984).

123. Wen, Z.Q. et al. "UV Resonance Raman spectroscopy of DNA and Protein Constituents of Viruses: Assignments and Cross Sections for Excitations at 257, 244, 238, and 229 nm". *Biopolymers* **45**, 247-256, (1998).
124. Ekinci, Y. et al. "Extraordinary Optical Transmission in the Ultraviolet Region Through Aluminum Hole Arrays". *Optics Letters* **32**, 172-174, (2007).
125. Dörfer, T. et al. "Deep-UV Surface-enhanced Raman Scattering". *Journal of Raman Spectroscopy* **38**, 1379-1382, (2007).
126. Jha, S.K. et al. "Deep-UV Surface-Enhanced Resonance Raman Scattering of Adenine on Aluminum Nanoparticle Arrays". *Journal of the American Chemical Society* **134**, 1966-1969, (2012).
127. Sigle, D.O. et al. "Reproducible Deep-UV SERRS on Aluminum Nanovoids". *The Journal of Physical Chemistry Letters* **4**, 1449-1452, (2013).
128. Ray, K. et al. "Aluminum Nanostructured Films as Substrates for Enhanced Fluorescence in the Ultraviolet-Blue Spectral Region". *Analytical Chemistry* **79**, 6480-6487, (2007).
129. Zeman, E.J. et al. "An Accurate Electromagnetic Theory Study of Surface Enhancement Factors for Silver, Gold, Copper, Lithium, Sodium, Aluminum, Gallium, Indium, Zinc, and Cadmium". *The Journal of Physical Chemistry* **91**, 634-643, (1987).
130. West, P.R. et al. "Searching for Better Plasmonic Materials". *Laser & Photonics Reviews* **4**, 795-808, (2010).
131. Moskovits, M. "Persistent Misconceptions Regarding SERS". *Physical Chemistry Chemical Physics* **15**, 5301-5311, (2013).
132. Yang, Y. et al. "Ultraviolet Nanoplasmonics: A Demonstration of Surface-Enhanced Raman Spectroscopy, Fluorescence, and Photodegradation Using Gallium Nanoparticles". *Nano Letters* **13**, 2837-2841, (2013).
133. Sun, G. et al. "Optimization of the Nanolens Consisting of Coupled Metal Nanoparticles: An Analytical Approach". *Applied Physics Letters* **98**, 153115, (2011).