Investigation of hot electron behaviors in plasmonic AgAu@TiO₂ nanostructures

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**NANYANG
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UNIVERSITY**

SINGAPORE

**INVESTIGATION OF HOT ELECTRON BEHAVIORS IN
PLASMONIC AgAu@TiO₂ NANOSTRUCTURES**

YU SIJIA

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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PLASMONIC AgAu@TiO₂ NANOSTRUCTURES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Abstract

Exploiting plasmonic metal nanostructure is of great importance to achieve highly efficient light-matter interactions. Anisotropic plasmonic metal nanoparticles display excellent optical characteristics from UV, throughout the visible light region to the NIR region of the solar spectrum, which allows high-efficiency conversion of solar energy into chemical energy. Under surface plasmon resonance (SPR) excitation, energetic hot carriers can be generated via dephasing of free electrons oscillation. However, efforts are still needed for better understanding the plasmonic induced hot electrons. In this thesis, several metal/semiconductor hybrid nanostructures based on AgAu core-shell nanoprisms and titanium dioxide were successfully synthesized, photocatalysis efficiencies based on hydrogen generation under visible light were evaluated aim to discover the generation and transfer process of plasmon generated hot electrons. To achieve this goal, the following works have been done.

First, for the first time, a Janus nanostructure composed of AgAu nanoprism and titanium dioxide nanosphere was reported. The hybrid nanostructure experience enhanced photocatalytic activity for hydrogen evolution reaction (HER) compare with the conventional metal@semiconductor core-shell nanostructure. The three-phase interphase connecting AgAu nanoprisms, TiO_2 nanosphere and environment close the gap between hot electron generation location and photocatalytic reaction site. Moreover, the interface experience largely enhanced electric field along the plasmonic AgAu nanoprisms edges. The site-selective Au nanoparticles photodeposition further confirmed the photocatalysis reaction site on the AgAu/ TiO_2 Janus nanostructure.

Second, facet-selective gold nanoparticles deposition onto AgAu@ TiO_2 nanoprisms was achieved. Plasmonic metal nanostructures can enhance the local electric field around the nanoparticles under plasmon excitation, the distribution of electric field is closely related to the morphology of the anisotropic nanostructure. To evaluate the relationship between electric field enhancement and hot electron generation distribution, photodeposition of gold nanoparticles on AgAu@ TiO_2 nanoprisms were performed under irradiation of visible

light covering their localized surface plasmon resonance wavelength. Gold nanoparticles were preferentially loaded at the tips and started growing along the side of AgAu@TiO₂ nanoprisms with the increasing amount of gold precursor. The deposition site of gold nanoparticles intuitively represent the hot carriers' distribution and corresponding the electric field enhancement of an anisotropic nanostructure.

Third, silver nanoprisms were synthesized and coated by a thin layer of gold; the Ag@Au core-shell nanoprisms were employed as plasmonic templates. Titanium dioxide shell with different thickness was further coated onto the AgAu nanoprisms, the direct contact of TiO₂ and AgAu nanoprisms improved the hot electron lifetime by plasmon-mediated electron transfer process. TiO₂ shell works as an electron filter, and the photocatalytic efficiency decrease as TiO₂ shell become thicker, which is caused by the increased travel distance of hot electrons. Photocatalytic efficiencies of the hybrid nanostructures under visible light can be enhanced by loading platinum nanoparticles as co-catalyst to reduce the charge carrier recombination. However the photocatalytic efficiency increase then decrease with increase TiO₂ shell thickness, the close gap between plasmonic AgAu core and Pt nanoparticles is conducive to hot electron transfer, but the plasmon coupling between AgAu nanoprisms and Pt nanoparticles lead to damping of local E-field and further affect the hot carrier generation and recombination.

Lay Summary

Energy crisis is one of the most concerned topics nowadays. Fossil fuels are the primary energy source to support the daily lives of the growing population. However, fossil fuels are unsustainable energy sources and cause more environmental problems including acid rain, global warming, air and water pollutions in the meantime. Therefore discovering and developing alternative clean energy supplies have become the problems that brook no delay. In this case, solar energy is a promising clean, free, unlimited energy source. Photocatalysts which can turn solar energy into chemical energy have been studied over the last century. Among them, specific kinds of metal including silver and gold are drawing more attention on account of their unique properties to interact with full spectrum irradiation. This phenomenon of specific plasmonic materials is referred to as localized surface plasmon resonance. When the nanoparticles made of plasmonic materials are irradiated, electrons oscillate with irradiated light and cause generation of hot electrons; these electrons can participate in chemical reactions, this is how the solar energy can be turned into chemical energy. To increase the solar to chemical energy conversion rate, modifications were made to these plasmonic nanoparticles. For example, anisotropic nanoparticles experience different LSPR properties compare with spherical nanoparticles. The LSPR optical properties of plasmonic metal nanoparticles can be tuned with changing the nanoparticles' shape, size and environment. In this thesis, nanoprisms made of silver and gold (AgAu) were employed as plasmonic part, and the nanoprisms were combined with semiconductor and form hybrid nanostructures. The plasmonic properties and the photocatalytic ability of these nanostructures were studied.

First, AgAu nanoprisms were combined with TiO_2 nanoparticles on only one side of the AgAu nanoprisms; this structure can be referred to as Janus nanostructure. Janus structure means two or more components integrated at small junctions with other regions exposed. AgAu/ TiO_2 Janus nanostructure can provide enhanced photocatalytic efficiency in hydrogen generation compare with AgAu@ TiO_2 core-shell nanoprisms. The unique Janus structure provides a shortcut for plasmon generated hot electrons to the reactive site, which locates at the three-phase interphase of nanostructure where connecting the AgAu

nanoprisms, TiO_2 and the environment. The photodeposition location of gold nanoparticles also showed the same conclusion.

Second, AgAu@TiO_2 core-shell nanoprisms were employed as the templet, anisotropic nanostructures experience unique properties, and the AgAu nanoprisms have a stronger electric field on tips and edges under LSPR excitation. However, the relationship between the intensity of the electric field and distribution is not well studied. In this experiment, the AgAu@TiO_2 nanoprisms were mixed with gold ions and irradiated under LSPR wavelength to promote the hot electron generation. The electrons can reduce gold cations and cause the deposition of gold nanoparticles, the gold nanoparticles deposition locations point out the reaction site on AgAu nanoprisms, which also indicate the concentration of hot electrons. The gold nanoparticles preferentially deposited on tips and edged of the AgAu nanoprisms; therefore there is a positive correlation relationship between the electric field intensity and hot electrons distribution for an anisotropic plasmonic nanoparticle.

Third, AgAu nanoprisms were employed as the plasmonic core, titanium dioxide (TiO_2) was employed as a semiconductor shell, and the photocatalytic ability of core-shell structures was studied. Nanoprisms with thin TiO_2 shell experience higher photocatalytic efficiency under visible light, this is due to the hot elections were easier accessed to the chemical reaction site with thin semiconductor filter. With some platinum (Pt) nanoparticles deposited on the AgAu@TiO_2 nanoprisms as co-catalyst, the photocatalytic ability increased for AgAu@TiO_2 nanoprisms with different TiO_2 shell thickness. However the nanoprisms with thin TiO_2 shell did not experience the highest efficiency, the reason is the Pt nanoparticles were too close to the AgAu nanoprisms and caused damping of the usable ratio of hot electrons. This result provides a new thought in the rational design of plasmonic nanostructures for photocatalytic reactions.

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Table of Contents

Abstract.....	i
Lay Summary	iii
Acknowledgements	v
Table of Contents	vii
Figure Captions	xi
Abbreviations	xvii
Chapter 1 Introduction	1
1.1 Hypothesis	2
1.2 Objectives and Scope	3
1.3 Dissertation Overview	5
1.4 Findings and Outcomes/Originality	6
References	7
Chapter 2 Literature Review	9
2.1 Overview	10
2.2 Optical Properties of Metal Nanoparticle.....	10
2.2.1 Localized Surface Plasmon Resonance	10
2.2.2 Plasmon Coupling Between Metal Nanoparticles.....	16
2.3 Controlling the Synthesis of Silver nanostructure and Metal/Semiconductor Nanostructure	18
2.3.1 Introduction to Silver Nanoprisms	18
2.3.2 Gold Coating of Ag Nanoprism	21
2.3.3 Hybridization of Metal Nanoparticles and Semiconductor Nanostructure	24

2.4 Plasmon Enhanced Photocatalytic Reactions.....	27
2.4.1 Photocatalysis on Semiconductor.....	28
2.4.2 Hybrid Plasmonic Metal/Semiconductor Photocatalyst.....	30
References	33
Chapter 3 Experimental Methodology.....	43
3.1 Rationale for selection of Method and Material.....	44
3.2 Chemical and Synthesis Process	45
3.2.1 Chemicals	45
3.2.2 Synthesis of Silver Nanoparticles	45
3.2.3 Synthesis of Silver Nanoprisms	46
3.2.4 Gold Coating of Silver Nanoprisms	47
3.2.5 Synthesis of Ag@Au/TiO ₂ Janus Nanostructure	48
3.2.6 Synthesis of Ag@Au@TiO ₂ /Au Nanostructure.....	48
3.2.7 Synthesis of AgAu@TiO ₂ core-shell Nanostructures	49
3.2.8 Platinum Photodeposition onto AgAu@TiO ₂ Nanoprisms.....	50
3.2.9 Photocatalytic Hydrogen Generation	52
3.3 Characterization	52
3.3.1 Ultraviolet–visible Spectroscopy (UV-Vis).....	53
3.3.2 Transmission Electron Microscopy (TEM).....	53
References	54
Chapter 4 Janus AgAu/TiO₂ Nanostructure: Synthesis and Site-Dependent Photocatalytic Reactions under Visible-Light.....	57
4.1 Introduction	58
4.2 Result and Discussion	59
4.2.1 Synthesis and Characterization of Janus AgAu/TiO ₂ nanostructure.....	59
4.2.2 Photocatalytic ability of Janus AgAu/TiO ₂ Nanostructure	62

4.3 Conclusion.....	65
References	66
Chapter 5 Plasmon Controlled Facet-selective Deposition of Gold on AgAu@TiO₂ Nanoprisms.....	69
5.1 Introduction	70
5.2 Results and Discussion.....	71
5.3 Conclusion.....	76
References	76
Chapter 6 Distance Dependence of Plasmon Enhanced Photocatalytic Hydrogen Evolution of AgAu@TiO₂ and AgAu@TiO₂/Pt Nanoprisms.....	79
6.1 Introduction	80
6.2 Result and Discussion	81
6.2.1 Synthesis and Characterization of AgAu@TiO ₂ Nanoprisms	81
6.2.2 Synthesis and Characterization of AgAu@TiO ₂ /Pt Nanoprisms	85
6.2.3 Photocatalytic of AgAu@TiO ₂ Nanoprisms and AgAu@TiO ₂ /Pt Nanoprisms	88
6.3 Conclusion.....	91
References	92
Chapter 7 Discussion and Future Work	95
7.1 General discussion.....	96
7.1.1 Discussion on the AgAu@TiO ₂ , AgAu@TiO ₂ /Pt and their photocatalytic ability.....	98
7.1.2 Discussion on the facet-selective gold photodeposition onto AgAu@TiO ₂ nanoprisms	96
7.1.3 Discussion on the Janus AgAu/TiO ₂ nanostructure for photocatalysis.....	96
7.2 Reconnaissance	98
7.2.1 Controlling hot electrons via plasmon coupling	100

7.2.2 Plasmon induced hot holes from anisotropic nanostructures	100
7.2.3 Anisotropic growth of TiO ₂ onto AgAu nanoprisms for plasmon enhanced photocatalytic reactions	100
References	101

Figure Captions

- Figure 2. 1** Schematic of LSPR for a spherical metal nanoparticle, the negative electrons are displaced from the positively charged nuclei.[9] 11
- Figure 2. 2** Quality factor (Q) of the LSPR for a metal/air interface. Higher Q represents less damping and stronger plasmon resonance. [10, 30] 12
- Figure 2. 3** a) Calculated UV-visible spectra for Au ellipsoids with increasing aspect ratio, b) experimental spectra of Au nanorods of varying aspect ratio. [44]...... 14
- Figure 2. 4** (a - d) TEM images of silver triangular nanoplates with decreasing tip sharpness. The sharp corner nanoprisms in a) were rounded until the nanoparticles had a circular disk shape shown in d). e) UV-Vis extinction spectrum of silver nanoplates, blue-shift of LSPR peak with decreasing tip sharpness. [47] 14
- Figure 2. 5** DDA simulation of the extinction efficiency of triangular nanoprisms based on nanoprisms with edge length of 100 nm with snip of 0 nm, 10 nm, and 20 nm. The thickness of nanoprism is 16 nm. [9, 48, 49]...... 15
- Figure 2. 6** a) Calculated extinction spectrum of a pair of silver nanosphere (36 nm in diameter) with a gap of 2 nm. Solid lines represent polarization parallel and perpendicular to the symmetry axes, the dash line represents the overall extinction spectrum of the dimer. b) Electric field enhancement contours external of the dimer at 430 nm and 520 nm respectively. In 3-D plots, the axis perpendicular to the plane represents the amount of electric field enhancement. [56]...... 17
- Figure 2. 7** a) Calculated extinction spectrum of a pair of “tip to tip” silver nanoprisms (60 nm in edge length and 12 nm in thickness) with a gap of 2 nm. Polarization along x and y axis respectively. b) Electric field enhancement contours external of the “tip to tip”

nanoprisms dimer at 932 nm and 550 nm respectively. In 3-D plots, the axis perpendicular to the plane represents the amount of electric field enhancement. [56]..... 18

Figure 2. 8 Schematic demonstration of photo-mediated growth pathway of silver nanoprisms from spherical silver nanoparticles [68]. 20

Figure 2. 9 a) TEM images of triangular nanoparticles, deformation of nanoprisms can be observed [90]. b) TEM image of Ag@Au core-shell nanoprisms with full gold shell and c) schematic illustration of the formation of Ag@Au nanoprisms [91]. d) & e) TEM images of Ag@Au core-shell nanoprisms and growth intermediates of the Ag@Au nanoprisms. Different gold growth rate along different facets result in a truncated triangular product [92]. 23

Figure 2. 10 TEM images of various plasmonic core@TiO₂ shell nanostructures. a-b) Au@TiO₂ core-shell nanoparticles [99, 103]. c-d) Ag@TiO₂ core-shell nanoprisms [101, 102]. e-f) Bimetallic AuAu@TiO₂ core-shell nanorods [104, 105]. 25

Figure 2. 11 TEM images of various anisotropic plasmonic metal /semiconductor nanostructures. a-b) Au/TiO₂ Janus nanostructures [106-108]. c) Anisotropic growth of TiO₂ onto gold nanorods [109]. d) Anisotropic growth of Cu₂O onto heteronanocrystals [112]. e-h) Anisotropic growth of SiO₂ onto gold nanorods and nanobipyramids, SiO₂ can be selectively deposited on tips and sides of gold nanostructure by chosen different kind of surfactant [110, 111]. 27

Figure 2. 12 a) Photo-electrochemical cell for water splitting. Under irradiation by photons with energy exceeding the BG, excited charge carriers are generated in semiconductor photoanode. Holes participate in the oxygen-evolution reaction half-reaction and electrons travel to counter-electrode and evolved in hydrogen evolution half-reaction. b) Semiconductor photocatalyst with co-catalyst for water splitting, generated charge carrier diffuse to the co-catalyst surface and participate in half-reactions. [2] 29

Figure 2. 13 a) Localized surface plasmon decay radiatively and re-emitted of photons. b) Localized surface plasmon decay non-radiatively via excitation of hot e-, which can occur via interband excitations within the CB or via interband excitations caused by transitions between other bands (for example, d bands) and the CB. [136].....	30
Figure 2. 14 Schematic PMET process of a plasmonic metal/semiconductor hybrid structure for efficiency conversion of irradiation energy to chemical energy, hot electrons with higher energy can overcome the Schottky barrier and be injected into the CB of the semiconductor component.	31
Figure 2. 15 Schematic plasmon mediated direct electron transfer processed in Au/CdSe nanorod system [140].....	32
Figure 2. 16 Optical absorption maps of Janus Au/TiO ₂ nanostructures, gold nanoparticles with diameter of a) 70nm, b) 50 nm and c) 30nm. The maps show the power absorbed under LSPR excitation, with incident polarization along the x-axis and the incident intensity of 0.5 W cm ⁻² [109].....	32
Figure 3. 1 Scheme of crystal twinning that leads to plate-like growth of nanostructures (side view and top-down view). Crystal twinning leads to the formation of a re-entrant groove A that serves as a site for preferential crystal growth over B. Crystal growth occurs parallel to the major {111} planes, preferentially at A sites over the B sites, leading to triangular, plate-like crystals.....	47
Figure 3. 2 Scheme of (a) reductive photodeposition and (b) oxidative photodeposition. D, sacrificial electron donor; A, sacrificial electron acceptor; M, metal. [164]	51
Figure 3. 3 Schematic illustrating the internal components of a UV-Vis spectrophotometer.	53

Figure 4. 1 TEM images of AgAu/TiO₂ nanostructure synthesized with different amount of titanium dioxide precursor: (a) 10 μ L (b) 50 μ L (c) 100 μ L (d) 500 μ L. 60

Figure 4. 2 UV-Vis spectrum of bare AgAu nanoprisms and AgAu/TiO₂ Janus nanostructure. 61

Figure 4. 3 TEM images of AgAu/TiO₂ nanostructure synthesized with different amount of ammonia as hydrolysis catalyst: (a) 10 μ L (b) 100 μ L (c) 500 μ L. 62

Figure 4. 4 Hydrogen generation volume of core-shell nanoprisms and Janus nanostructures under visible irradiation. 63

Figure 4. 5 Proposed photocatalytic process of efficient H₂ production of Janus AgAu/TiO₂ nanostructures as photocatalyst under visible light. Hot electrons generated from the plasmonic AgAu nanoprisms are filtered by TiO₂ and transferred to nearer reactive site, where also experience stronger plasmon enhanced local EM field. 64

Figure 4. 6 TEM images of AgAu/TiO₂/Au nanostructure by photodeposition of Au nanoparticles (a) in darkness (b) under visible light (c) under full spectrum light. 65

Figure 5. 1 TEM images of (a) AgAu core-shell nanoprisms, (b) AgAu@TiO₂ core-shell nanoprisms with TiO₂ shell thickness at 5-8 nm. 72

Figure 5. 2 UV-Vis spectrum of AgAu@TiO₂ nanoprisms and AgAu@TiO₂/Au nanoprisms with gold nanoparticles deposited on tips of AgAu@TiO₂ nanoprisms. Red-shift and broadening of LSPR peak can be observed. 74

Figure 5. 3 TEM images of AgAu@TiO₂/Au nanoprisms. (a-c) Photodeposition of Au nanoparticles under visible light (> 650 nm) with increase Au precursor amount (a) 20 μ L, (b) 50 μ L, and (c) 100 μ L. (d-e) Photodeposition of Au nanoparticles under UV light with low Au precursor amount at (d) 20 μ L, (e) 50 μ L and (f) 100 μ L. Site-selectively deposition

of Au nanoparticles can be observed at low Au precursor concentration on tips and edged under irradiation of visible light. 74

Figure 5. 4 Structure and mechanism of Au nanoparticles photodeposition onto AgAu@TiO₂ nanoprisms under visible light. Hot electrons generated from plasmonic AgAu nanoprisms skip out at tips of AgAu nanoprisms where support stronger E field enhancement and induce site-selective photodeposition of Au nanoparticles..... 75

Figure 6. 1 TEM images of a) Ag nanoprisms. b) Ag@Au core-shell nanoprisms. Diameter of AgAu nanoprisms as plasmonic core is around 50 nm and gold shell thickness is around 3 nm. c) UV-Vis spectrum of silver nanoprisms and AgAu core-shell nanoprisms..... 82

Figure 6. 2 TEM images of AgAu@TiO₂ nanoprisms with different TiO₂ shell thickness. (a) 5 nm. (b) 10 nm. (c) 15 nm. (d) 20 nm. 84

Figure 6. 3 UV-Vis spectrum of AgAu nanoprism before and after TiO₂ coating, red-shift of LSPR peaks as the AgAu nanoprisms were coated by amorphous TiO₂ and further red-shift of LSPR peak as TiO₂ shell at 5 nm, 10 nm, 15 nm and 20 nm. 84

Figure 6. 4 TEM images of AgAu@TiO₂/Pt nanoprisms with different TiO₂ shell thickness. (a) 5 nm. (b) 10 nm. (c) 15 nm. (d) 20 nm, Pt nanoparticles loaded on AgAu@TiO₂ nanoprisms evenly. 85

Figure 6. 5 UV-Vis spectrum of AgAu@TiO₂/Pt nanoprism with different TiO₂ shell thickness at 5nm, 10nm, 15nm, 20nm. 86

Figure 6. 6 UV-Vis spectrum of AgAu@TiO₂ nanoprisms and AgAu@TiO₂/Pt nanoprisms. TiO₂ shell thickness at a) 5 nm, b) 10 nm, c) 15 nm, d) 20 nm. Red-shift and damping of LSPR peak can be observed, FWHM increase after Pt deposition. 86

Figure 6. 7 TEM images of AgAu@TiO₂ nanoprisms with unevenly loaded Pt nanoparticles for core-shell nanostructure with a) 5 nm TiO₂ shell, b) 20 nm TiO₂ shell.88

Figure 6. 8 UV-Vis spectrum of photodeposition of Pt nanoparticles onto AgAu@TiO₂-10 nm nanoprisms a) with methanol as sacrificant agent b) without methanol as sacrificant agent..... 88

Figure 6. 9 Volume of H₂ generated under visible light irradiation (>600nm) using a) AgAu@TiO₂ nanoprisms and b) AgAu@TiO₂/Pt nanoprisms with different TiO₂ shell thickness..... 90

Figure 6. 10 Schematic photocatalytic process for H₂ generation under visible light using a) AgAu@TiO₂ nanoprisms and b) AgAu@TiO₂/Pt nanoprisms. 91

Abbreviations

3-D	Three-dimensional
AgAu	Silver@Gold
ATR	Attenuated Total Reflectance
BEI	Backscatter Electron Images
BSE	Backscattered Electron
BSPP	Bis(p-sulfonatophenyl)phenylphosphine dihydrate dipotassium
CB	Conduction Band
CTAB	cetyl trimethylammonium bromide
D ₂	Deuterium
DDA	Discrete Dipole Approximation
EM	Electromagnetic
H ₂	Hydrogen
HER	Hydrogen Evolution Reaction
IPA	Isopropyl Alcohol
LSPR	Localized Surface Plasmon Resonance
M	Metal
N ₂	Nitrogen
NaCi	Sodium Citrate
NIR	Near-Infrared
NP	Nanoparticle
NW	Nanowire
PMET	Plasmon Mediated Electron Transfer
PVP	Polyvinylpyrrolidone
SPR	Surface Plasmon Resonance
TEM	Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
TiO ₂	Titanium Dioxide
TDAA	titanium diisopropoxide bis(acetyltonate)
UV	Ultraviolet

UV-Vis Ultraviolet-Visible

VB Valence Band

Vis Visible

Chapter 1

Introduction

The increasing demand of energy pushed the scientific community to investigate efficient photocatalysts. Plasmonic metal materials are gaining much attention because of their ability to interact with solar irradiation with a wide wavelength range from UV, visible to NIR region. Plasmon generated hot electrons play a crucial role for plasmonic nanostructures to convert solar energy into chemical energy. However, the behaviors of hot electrons remain elusive in photochemistry. Hence, the objective of this thesis is to investigate the behaviors of plasmon-induced hot electrons on anisotropic nanostructures based on AgAu@TiO₂. This chapter describes the background and motivation behind the work undertaken in this thesis. The objectives and scope of the entire thesis are provided, while the originality is also demonstrated.

1.1 Hypothesis

Clean and renewable energy is vital and demand for the modern industry because of the growing population and economy. At present, about 80% of the world energy consumption depends on the limited and unrenewable fossil fuels including coals and natural gas, which can lead to many environmental problems such as water pollution, global warming and air contamination. Solar energy is considered as abundant, free and environmentally friendly energy; therefore efficient utilization of solar energy is one of the most concerns for scientists. After the publication of Fujishima and Honda's ground-breaking work on photocatalysis in 1972 [1], photocatalysts based on semiconductor have been extensively studied for photochemical applications including water splitting [2, 3] and CO₂ reduction [4, 5]. However, the main limitation for semiconductor photocatalysts is their wide bandgap which can only absorb UV light [6-8]. To extend the utilization of full spectrum solar light, plasmonic materials experience wide and tunable optical properties through the visible light are drawing more attention [7]. The plasmonic properties can be tuned by changing the size, shape and dielectric environment of plasmonic nanoparticles [9]. The localized surface plasmon resonance can be visualized as the enhanced electric field coupled with the oscillation of free electrons of a plasmonic nanoparticle. The local electric field induced by excitation of LSPR around silver nanoparticles and dimers have been investigated via discrete dipole approximation, the result of a monomer nanoprism indicated that the most significant fields for the dipole resonance at tips followed by edges, the base facets experience less stronger electromagnetic field enhancement [10]. This phenomenon applies to all kinds of anisotropic nanoparticles such as nanorods and nanospheroids. Besides the local field enhancement under excitation, hot carriers can be produced and further participate in photocatalytic chemical reactions. Thus, incorporating plasmonic nanoparticles into photocatalytic systems is a promising strategy to enhance the solar light use ratio. The extremely short lifetime of hot electrons makes many photochemical reactions directly occur on plasmonic nanoparticles impractical, hybridizing plasmonic nanoparticles with semiconductor is a common strategy to elongate the lifetime of hot electrons. The surface plasmon produced hot electrons can be transferred to the adjacent semiconductor via a plasmon mediated electron transfer (PMET) process

[11]. In a hybrid nanostructure, the yield of hot electrons that can participate in a photocatalytic reaction is significantly increased, and photocatalytic ability can be enhanced [12, 13]. However, there is no experimental evidence shows the relationship between the SPR induced electromagnetic field enhancement and hot electron generation of an anisotropic nanoparticle and many questions need to be answered about the transfer of plasmon resonance generate hot electrons to the photochemical reaction site.

This thesis tests the hypothesis that for anisotropic plasmonic nanoparticles, the enhancement of electromagnetic field under plasmon excitation is related to the hot electron generation and recombination of plasmon-induced hot carriers. Take silver nanoprisms as an example, nanoprisms experience heterogeneous electromagnetic field enhancement, the tips of a silver nanoprisms experience the strongest electromagnetic field enhancement followed by the edges, and the two top and bottom facets. The hot electron generation site is positively related with the electromagnetic field, therefore for a silver nanoprism under LSPR excitation, more hot electrons are ejected at the tips than edges, and less hot electrons are ejected from the base facets of the nanoprisms where experience less strong electromagnetic field enhancement. The photochemical site of a silver nanoprism as a photocatalyst is also located at the tips as plasmon electron accumulate there. The electromagnetic field enhancement also impedes the re-combination of plasmonic generated hot carriers. Therefore the reactive site should be close to the plasmonic nanostructure surface, where the oscillation of surface plasmon resonance enhances the electromagnetic field.

1.2 Objectives and Scope

The objective of this thesis is to develop the understanding and utilization of anisotropic plasmonic material for photocatalytic applications by rational design of plasmonic metal/semiconductor hybrid nanostructures. Silver nanoprisms have been studied for decades because of their unique plasmon properties, and they are ideal subjects for anisotropic plasmonic nanostructure studies. It has been reported that the resonant optical excitation of surface plasmon produced hot electrons which can be involved in

photocatalysis chemical reactions. Under plasmon excitation, hot electrons can be generated via the dephasing of free electrons oscillation. The hot electron is the key to the conversion of irradiation energy to chemical energy; therefore many studies have been carried out to get a clear picture of plasmon resonance induced hot electron. However, there are still many unexplained questions about the hot electron. Based on the hypotheses that have been proposed, the objectives and the scope of this thesis are listed below:

First, a Janus nanostructure consisting of AgAu nanoprism and TiO_2 will be synthesized. Unlike core-shell nanostructure, the Janus nanostructure exposes both parts of the plasmonic metal and semiconductor components. The Janus AgAu/ TiO_2 nanostructure will be characterized by transmission electron microscopy and UV-Vis spectrophotometer and finally evaluated for photocatalytic ability via hydrogen generation under visible light.

Second, AgAu@ TiO_2 core-shell nanoprisms with narrow size distribution will be synthesized. The as-synthesized AgAu@ TiO_2 nanoprisms will be mixed with precise gold precursor and irradiated under LSPR wavelength of AgAu@ TiO_2 nanoprisms. Under irradiation of LSPR wavelength, in another word, under plasmon excitation, gold nanoparticles will be selectively deposited on the tips of the nanoprism, which experiences the strongest electric field enhancement. With the increase of gold precursor amount, gold nanoparticles will growth along the edges, follow by the planes of the nanoprisms. Meanwhile, control experiments will be conducted under full-spectrum irradiation and darkness. Under full-spectrum irradiation, gold nanoparticles should be loaded onto the nanoprisms without site preference and in darkness, no photodeposition reaction will happen and no gold nanoparticles should be deposited onto the AgAu@ TiO_2 nanoprisms.

Third, silver nanoprisms with narrow size distribution will be synthesized and further coated with a layer of gold to enhance the stability; the Ag@Au nanoprisms are used as the anisotropic plasmonic metal templates. TiO_2 shell with well-controlled thickness will be further coated onto the AgAu nanoprisms as electron filter. To further enhance the photocatalytic ability, Pt nanoparticles will be evenly deposited onto the AgAu@ TiO_2 nanoprisms as co-catalyst. The core-shell nanostructure will be used as photocatalyst for

HER under visible light. The as-prepared AgAu@TiO₂ and AgAu@TiO₂/Pt nanoprisms will be characterized by TEM and UV-Vis spectrophotometer.

1.3 Dissertation Overview

This thesis consists of seven chapters in total.

Chapter 1 provides a rationale for the plasmonic properties and their localized surface plasmon resonance properties. The objectives and motivations of this thesis are also illustrated in chapter 1.

Chapter 2 first reviews the literature concerning plasmonic nanoparticles and their optical properties, followed by the current published synthesize methods of silver nanoprisms and the gold coating protocols. After that, recent research progress of synthesis and design photocatalysts including semiconductor and plasmonic metal/semiconductor nanostructures will be introduced, the mechanisms of different kinds of photocatalysts will also be reviewed.

Chapter 3 discusses the principles underlying the synthesis and characterization techniques employed. Why silver nanoprisms were chosen as the plasmonic metal template for plasmonic metal/semiconductor nanostructure will be discussed. The detailed synthetic procedure and the characterization techniques used will be described in detail.

Chapter 4 elaborates the synthesis of Janus AgAu/TiO₂ nanostructure composed of an AgAu nanoprism and a TiO₂ nanosphere. The TiO₂ component connects on only one side of AgAu nanoprisms with the other side exposed. The photocatalytic activity towards HER under visible light was evaluated.

Chapter 5 elaborates the plasmon controlled facet selective photodeposition of gold nanoparticles onto AgAu@TiO₂ core-shell nanoprisms.

Chapter 6 elaborates the synthesis method of core-shell AgAu@TiO₂ nanoprisms and

AgAu@TiO₂/Pt nanoprisms with different TiO₂ shell thickness. The photocatalytic efficiency was tested via hydrogen generation under visible light to evaluate the effect of semiconductor shell thickness and distance between AgAu plasmonic core and Pt nanoparticles as co-catalyst.

Chapter 7 conclude the overall thesis and elaborates the reconnaissance studies which can be conducted in the future.

1.4 Findings and Outcomes/Originality

This research led to three novel outcomes by:

1. For the first time, a new Janus nanostructure which is composed of an AgAu nanoprism and a TiO₂ nanosphere was synthesized. The TiO₂ nanosphere as semiconductor component attached on only one side of anisotropic AgAu nanoprism as the plasmonic metal component. The photocatalytic activity of the Janus nanostructure toward HER under visible light was enhanced compared with ordinary core-shell nanostructures.
2. For the first time, successfully selective deposition of metal nanoparticles onto an anisotropic plasmonic metal nanostructure was achieved via plasmon control. Gold nanoparticles can be selectively deposited onto the tips and along the edges of AgAu@TiO₂ nanoprisms by taking advantage of unbalanced hot charge carrier distribution of an anisotropic plasmonic nanostructure under LSPR excitation. This process also verifies the positive correlation between electric field enhancement and hot electron generation rate of anisotropic plasmonic nanoparticles.
3. Plasmonic metal/semiconductor hybrid nanostructures Ag@Au@TiO₂ with controlled semiconductor shell thickness were developed. Photocatalytic ability increases with the decrease of semiconductor shell thickness. With Pt nanoparticles deposited onto AgAu@TiO₂ nanoprisms as co-catalyst, photocatalytic ability can

be enhanced by hinder the hot carriers recombination. However, the plasmonic coupling between AgAu nanoprism core and Pt nanoparticles result in damping of the electric field, especially when the distance between AgAu nanoprisms and Pt nanoparticles is short.

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Chapter 2

Literature Review

Plasmonic metal nanoparticles have been explored for over 1500 years since a red stained glass containing gold nanoparticles was made. However, the term “plasmon” was coined just decades ago, and the tremendous amount of studies on plasmonic material recently manifest that plasmonic material is a long-standing topic. This chapter first reviews the optical properties of plasmonic metal nanoparticles and the factors that affect the LSPR properties of a single nanoparticle, followed by reviewing the studies on plasmon coupling between nanoparticle dimers. After that, the synthesis methods of the most well-known plasmonic material: silver and gold nanoparticles are reviewed as well as their hybrid nanostructures with semiconductors. Finally, mechanism of plasmonic nanostructures as photocatalyst are discussed for both single component semiconductor catalysts and plasmonic metal/semiconductor hybrid nanostructures.

2.1 Overview

For a long time, the understanding of the interaction between matter and light was restricted to visible light which can be observed by human eyes. The oldest known artifact related to plasmonic nanoparticles is the Lycurgus Cup, a glass vessel produced around 300 A.D. It contains gold nanoparticles inside the glass matrix which have a plasmon peak at green wavelengths; therefore the glass looks red when light passes through, but the glass strainers did not know the reason of this phenomenon. With the development of technology and science, telescopes and microscopes were invented to observe nebula and blood cells, down to the single atom, until recently, come to “nano-optics”. The peculiarity interactions between metal nanoparticles and light draw more attention in the past decades and applications of plasmonic metal nanoparticles were developed. The ability of plasmonic metal nanoparticles can focus light into the nanometer regime and produce a strong electromagnetic field at the nanoscale has inspired a tremendous amount of researches on plasmonic nanostructures as photocatalysts. Considerable effort has been devoted to developing the high efficient photocatalyst, and significant progress has been achieved, understanding of plasmon resonances in metal nanostructures and further promoting the photocatalytic efficiency remain challenging.

2.2 Optical Properties of Metal Nanoparticle

2.2.1 Localized Surface Plasmon Resonance

Localized surface plasmon resonance refers to a nano-optical phenomenon. As light incidents onto a metal nanoparticle, the electrons in this metal nanoparticles are attracted to one side by an electric field, leaving a positive core. The negatively charged electrons are attracted by the positive charge from the other side, when the electrons are pulled back, they will oscillate back and forth with a certain frequency (Figure 2.1) [1, 2]. At certain incident light frequency which matches the nature oscillation frequency of the metal nanoparticle, the oscillations of the free electrons reach as maximum; this wavelength refers as the “LSPR wavelength” of this kind of metal nanoparticle [3]. The collective

oscillation of the electrons bring about electric field in the vicinity of the metal nanoparticle, the enhanced electric field also reinforcing the oscillation. The charge oscillation inside the metal nanoparticle and the electromagnetic field outside the metal nanoparticle are LSPR (or plasmon resonance) [1-4].

Figure 2. 1 Schematic of LSPR for a spherical metal nanoparticle, the negative electrons are displaced from the positively charged nuclei.[2]

The LSPR of a metal nanoparticle is dependent on the composition [5-7], size [8, 9], shape [2, 10, 11], and the dielectric environment of the nanoparticle [12-14], and the proximity of other plasmonic nanoparticles [15-20]. Metal with a high density of free electrons including silver, gold, copper, aluminum, platinum and palladium experience plasmon resonance, more conduction electrons interacting with light, stronger restoring force and higher resonant frequency [21, 22]. Among all the LSPR materials, silver and gold are particularly suitable material for plasmonic studies because of their high-quality plasmon resonance at visible frequencies (Figure 2.2) [3]. Silver has the lowest losses of plasmon while gold is more stable at both chemically and physically. The resonance frequency can be tuned from UV region, throughout the visible region, and into the NIR region of the solar spectrum by changing the size and the shape of silver and gold nanoparticles [21].

Figure 2. 2 Quality factor (Q) of the LSPR for a metal/air interface. Higher Q represents less damping and stronger plasmon resonance. [3, 23]

For small plasmonic metal nanoparticle ($r \ll \lambda$, where r is the radius of the nanoparticle and λ is the incident light wavelength), the LSPR of plasmonic metal nanoparticles can be described by Mie's theory to calculate the extinction cross-section, C_{ext} ($C_{ext} = C_{abs} + C_{sca}$ = absorption cross-section + scattering cross-section):

$$C_{ext} = \frac{24\pi^2 r^3 \epsilon_m^{3/2}}{\lambda} \left[\frac{\epsilon_i}{(\epsilon_r + \chi \epsilon_m)^2 + \epsilon_i^2} \right] \quad (1)$$

where ϵ_r and ϵ_i represent the real dielectric component and the imaginary dielectric component of the metal respectively, and $\epsilon = \epsilon_r + i\epsilon_i$ is the dielectric constant of the bulk metal material. ϵ_m is the relative dielectric constant of the external environment, λ is the wavelength of the incident light, and the factor χ accounts the shape of the nanoparticle, it equals to 2 as the nanoparticle is spherical[24], but can be as large as 20 for highly anisotropy nanoparticles[1, 25]. The external environment and the wavelength of the incident light are often fixed under a specific situation; therefore the material properties are the key factors that determine the plasmonic property of the nanoparticle. As indicated in equation (1), the SPR raises when $\epsilon_r = -\chi \epsilon_m$ and ϵ_i is small, the plasmonic peak is approximated by ϵ_i .

The absorption and the scattering amount of plasmonic nanoparticles increase as the size of the particle increases. For larger nanoparticles ($2r > 30\text{nm}$), the optical properties cannot be adequately described by Equation (1), and the full Mie equation is required to model the absorption spectra [26]. The scattering dominates over absorption for larger nanoparticles as the absorption cross-section and scattering cross-section is proportional to r^3 and r^6 , respectively [27]. There is a red-shift and a broadening of the LSPR spectrum peak as the nanoparticle becomes larger, which is due to the radiative damping: the dipole moment results from the charge oscillation increase, lead to increase of dipole decay rate. The radiative damping degree is proportional to the polarization of the nanoparticles and thus is positively related to the particle size [28, 29]. Typically there is only dipole excitation in small nanoparticles while higher-order multipole excitation present for larger nanoparticles [30-32]. Compared with spherical plasmonic nanoparticles; anisotropic nanoparticles show typically larger electric field due to their ability to support plasmon resonance at broader and longer wavelength with the same composite and volume[33]. The plasmon resonance splits into multi-mode for non-spherical plasmonic metal nanoparticles, which can be characterized by additional absorption band in the spectrum [34, 35]. Figure 2.3 shows both the calculated and the experimental UV-Vis spectrum of gold nanorods with increasing aspect ratio from 2 to 3, the electrons oscillating perpendicular to the major axis give rise to the transverse excitation mode, which corresponding to the high energy absorption peak. Meanwhile, free electrons oscillating along the gold nanorod causes the lower energy longitudinal LSPR mode. The higher the aspect ratio is, the more pronounced the two LSPR absorption peaks are, the extinction spectra under longitude excitation shift to longer wavelength [29, 35, 36]. Similar to nanorod, silver nanoprisms experience three plasmon modes according to different polarized direction: along the triangular side, perpendicular bisector and short axis [2, 37].

Figure 2. 3 a) Calculated UV-visible spectrum for Au ellipsoids with increasing aspect ratio, b) experimental spectra of Au nanorods of different aspect ratio. [36]

The sharpness of the corners and edges of the plasmon nanoparticle also gave a significant effect on the LSPR properties [38]. Experimental measurements of silver nanoprisms with increase tip sharpness are shown in Figure 2.4. A red-shift of the LSPR wavelength from 400nm to 800nm can be observed as the roundish nanoplates are tuned to nanoprism plates [39]. This is due to the increase of charge separation and reduction of the restoring force for the dipole oscillation. The resonance frequency of electron oscillation is reduced; therefore a red-shift of the LSPR wavelength can be predicted.[2, 40].

Figure 2. 4 (a - d) TEM images of silver triangular nanoplates with decreasing tip sharpness. The sharp corner nanoprisms in a) were rounded until the nanoparticles had a round disk shape shown in d). e) UV-Vis extinction spectrum of silver nanoplates, blue-shift of LSPR peak with decreasing tip sharpness. [39]

Beside experimental evidence, Schatz and coworkers used a quasistatic approximation model to figure out the optical properties of perfect triangular nanoprisms and “snipped” nanoprisms. Discrete dipole approximation (DDA) calculations were carried out for nanoprisms with a diameter of 100 nm and thickness of 16 nm, for “snipped” nanoprisms, the ends of all three tips have been removed. The results shown in Figure 2.5 indicate that there was an apparent red-shift of the main peak with increased tip sharpness. The perfect triangular nanoprisms’ spectrum consisted of a long wavelength peak centered at 700 nm, a weak one at 460 nm and a small but sharp one at 335 nm. The main peak is very sensitive to snip of tips, a blue shift of 100 nm was observed for 20 nm snipped nanoprisms. The other peaks are less affected by snipping [2, 40, 41].

Figure 2. 5 DDA simulation of the extinction efficiency of triangular nanoprisms based on nanoprisms with an edge length of 100 nm with snips of 0 nm, 10 nm, and 20 nm. The thickness of nanoprism is 16 nm. [2, 40, 41].

The near-field distribution and the electromagnetic fields that confined within the nanoscale environment of the nanostructure are also affected by the corner sharpness [3]. The near-field intensity can be dramatically enhanced by a factor of 1000 times for nanostructure with sharp corner feature compare with spherical and elliptic nanostructures. Plasmon nanorice and nanobipyramid are ideal for applications of SERS and SEF, which take advantage of the enhanced near-field [42, 43]. The SERS performance of gold nanobipyramid with sharp ends and gold nanorod with similar LSPR wavelength around 785nm were compared. The peak intensity at 1080 cm^{-1} for sharp gold nanobipyramid is

≈ 6 times and ≈ 18.2 times of that nanorod in solution and on substrates respectively [44, 45].

The environment around nanoparticles also exerts a tremendous influence in determining the plasmonic properties. In the air, dielectric constant ϵ_m is equal to 1, as a matter of fact, the plasmon nanoparticles are either suspended in liquid, or embedded in the dielectric material, or even deposited on a substrate in most experiments. Assuming the plasmon nanoparticles are surrounded by a homogeneous material with $\epsilon_m > 1$, Red-shift of LSPR wavelength over spherical nanoparticles could be observed with larger ϵ_m (Equation (1)). The shift of LSPR wavelength happens due to the dielectric environment screens the local fields around the plasmonic nanostructure, thereby the restoring forces of charge oscillation are reduced [35].

2.2.2 Plasmon Coupling Between Metal Nanoparticles

Individual nanoparticles have many intriguing plasmonic properties, how the morphologies of metal nanoparticles infusing the plasmon resonance and enhanced local electromagnetic field were discussed in the previous section. When a single plasmonic nanoparticle get to near another plasmonic nanoparticle until they spectrally overlapped with each other, the two plasmon resonances will emerge into one new resonance, which can result in new LSPR mode and further enhancement of local electromagnetic fields [46, 47]. Plasmon coupling between two nanoparticles is caused by Coulomb interaction between the surface charges of the nanoparticles and increases as the distance between the nanoparticles is shortened, and capacitive coupling is stronger when high charge density parts of the nanoparticles are closer to each other [48, 49]. Charge dipoles can be developed between the gap of two coupled nanoparticles, where experiences stronger local electromagnetic field compare with single nanoparticles. The regions with the intense electromagnetic field are known as “hot spot” or “hot site” [50-52].

The “hot spots” were investigated by performing DDA calculations of single silver nanosphere and nanosphere dimer. Figure 2.6 a) shows the calculated extinction spectrum

of a dimer of 36 nm Ag nanospheres with a gap of 2 nm. One spectrum shows one strong peak locates at 520 nm and another shoulder peak locates at 430 nm is for polarization parallel to the dimer, the other shows a peak at 410 represents the perpendicular polarization. The dashed line is corresponding to the overall extinction spectrum. The induced polarization depends on the interfacial distance strongly, with dipoles in the gap being influenced mainly by the inter-nanoparticle coupling as the particles are close to each other. The contours of the electromagnetic field around the silver dimer are shown in Figure 2.4 b) at 430nm and 520 nm, the maximum enhancement of local field occur at the gap between the two nanospheres for dipole resonance and quadrupole resonance respectively. The most considerable local field enhancements are 3500 times and 11000 times the applied field at 430 nm and 520 nm, which are much higher than Ag monomer (10^2 enhancement). The field enhancement is related to peak extinction, which is distinct for a specific nanoparticle combination [48].

Figure 2. 6 a) Calculated extinction spectrum of a pair of silver nanosphere (36 nm in diameter) with a gap of 2 nm. Solid lines represent polarization parallel and perpendicular to the symmetry axes, the dash line represents the overall extinction spectrum of the dimer. b) Electric field enhancement contours external of the dimer at 430 nm and 520 nm respectively. In 3-D plots, the axis perpendicular to the plane represents the amount of electric field enhancement. [48]

For anisotropic nanoparticle which already experiences typically larger electric field, the non-spherical nanoparticles dimer shows even higher local field enhancement. Extinction spectrum of one pair of triangular prisms with corresponding tips toward against each other, the gap between two tips is 2 nm. The spectrum and electric field enhancement

perpendicular to the triangular facets and perpendicular to the interparticle axis are similar to that of isolated nanoprisms [2, 10], while there is an apparent red-shift for the spectrum of polarization along the inter-particle axis (Figure 2.7). The peak location shifts from 653 nm to 932 nm for dipole polarization, meanwhile a weaker peak locates at 550 nm for quadrupole appears [53]. Figure 2.5 shows the electric field contours for the tip to tip configuration of the silver prisms at 550 nm and 932 nm, large enhancements occur at the tips and interfaces, while the strongest enhancement takes place at the interface between the two tips of two nanoprisms. The largest electric field at 932 nm and 550 nm are 53000 and 5700 times of the applied field. Alike to spherical dimers, smaller separation produces dramatically increase near-field intensity [48].

Figure 2. 7 a) Calculated extinction spectrum of a pair of “tip to tip” silver nanoprisms (60 nm in edge length and 12 nm in thickness) with a gap of 2 nm. Polarization along x and y axis respectively. b) Electric field enhancement contours external of the “tip to tip” nanoprisms dimer at 932 nm and 550 nm respectively. In 3-D plots, the axis perpendicular to the plane represents the amount of electric field enhancement. [48]

2.3 Controlling the Synthesis of Silver nanostructure and Metal/Semiconductor Nanostructure

2.3.1 Introduction to Silver Nanoprisms

Many silver nanoparticles have been synthesized and observed including nanosphere and quasi-sphere [54-56], nanoprisms [10, 57-62], nanorod [63, 64], nanocube [65, 66],

nanowire[67, 68] and hollow nanostructures [69]. Applications of silver nanostructures include catalysis [70-72], electronics [73], surface enhanced Raman scattering (SERS) [74, 75]. Prism-like nanostructures are particularly interesting because the decreased symmetry of the nanostructure usually gives rise to unique physical and chemical properties. In general, silver nanoprisms are highly anisotropic silver nanoparticles with a triangular plate-like morphology with three sharp tips, which contribute vitally to the optical property of the nanostructure [2, 41, 76]. When significant rounding of the vertices occurs, nanostructures are generally described as nanoplates or nanodisks. Silver nanoprisms synthesized to date typically exhibit edge length ranging from 40 nm to 1 μ m and thickness in the 5 nm to 50 nm [41]. The optical properties highly depend on the geometry of silver nanoprisms; therefore nanoprisms with precisely controlled dimensions and high yield are desired [2].

A photochemical route was the first high yielding and reliable method for the synthesis of silver nanoprisms in solution phase by Zheng et. al [10]. Using this method, the edge length of silver nanoplate can be tuned by excitation wavelength. Mechanism studies proposed that in the light-induced transformation of small Ag nanoparticles to silver nanoprisms, existing of citrate, oxygen and light are crucial. Figure 2.8 presents the schematic formation process of silver nanoprisms: Firstly, LSPR excitation of silver nanoparticles cause charge transfer via plasmon decay. In the presence of oxygen, small silver nanoparticles with size less than 2 nm are oxidized to Ag^+ and followed by being reduced by plasmon excited hot electrons. The reduction of silver cations by citrate is extremely slow at room temperature without irradiation, however, irradiated with visible light can initiate this reaction. As silver nanoparticles grow to the point where they can absorb a significant amount of visible light, the transformation of anisotropic from isotropic silver seeds accelerates. With continuous irradiation, dipole plasmon excitation leads to ultrafast charge separation on silver nanoparticles surface, which causes facet selective silver deposition until the silver seeds grow into anisotropic triangular nanoprisms. As the silver nanospheres experience shape transformation, growth of silver nanoprisms proceed at the same time. The lower surface free energy of (1 1 1) facet than (1 0 0) and (1 1 0) is responsible for lowest growth rate,

the prisms edges and tips grow preferentially over thickness. After all the small Ag nanosphere seeds are consumed, nanoprisms stop growing.

Figure 2. 8 Schematic demonstration of photo-mediated growth pathway of silver nanoprisms from spherical silver nanoparticles [60].

One interesting finding is that, if the silver nanospheres are irradiated by single excitation wavelength, two different sizes of silver nanoprism can be obtained, with the larger nanoprisms have an edge length of about twice of the smaller ones. For example, visible light at 550 nm is resonated with both the dipole plasmon of 70 nm edge length nanoprisms and quadrupole plasmon mode of 150 nm nanoprisms. Single nanoprism size can be controlled by using two excitation wavelength with careful chosen. By adjusting other reaction such as pH environment can control the silver nanoprism growth, if the solution pH is adjusted to 11.2 and excited with 550 nm visible light, unimodal growth was observed. Resulting silver nanoprisms with a primary plasmon band red-shifted from the increasing excitation wavelength [59].

Beside photochemical methods, chemical reduction methods (thermal syntheses) were also applied for silver nanoprisms syntheses [62, 77, 78]. In a typical experiment, aqueous solution includes AgNO₃, trisodium citrate, poly(vinylpyrrolidone), H₂O₂ and varying amount of NaBH₄ were mixed under vigorous string. Spherical nanoparticles can be formed after 20 to 30 mins followed by a rapid transformation to silver nanoprisms within 5 seconds. The NaBH₄ concentration has a dramatic effect on the degree of Ag nanoprisms formation. In general, red-shift of plasmon peak was observed with increased NaBH₄ concentration from 0.3 to 0.8 mM. PVP acts as stabilizes to prevent aggregation; it does not play a direct shape role in this reaction [62]. A two-step process for controlled growth of silver nanoprisms with high aspect ratio and narrow size distribution was proposed by Yin Yadong and co-workers [78]. The synthesis procedure is designed on the basis of preferential adhesion to different facets of PVP and citrate. Seed-mediated growth process

was applied to get silver plate-like seeds. Silver nanoplates seed were mixed with L-ascorbic acid and sodium citrate as reductant and surfactant; the AgNO_3 solution was added slowly together with citric acid and sodium citrate. Nanoplates size increase with multiple growth routes and the plasmon band of obtained silver nanoprisms can be precisely tuned from the visible region to the infrared spectrum by controlling the aspect ratio [78]. A robust synthesis for nanoprisms was reported by the same group for large-scale production of silver nanoprisms, different volume of seed solution were injected into a growth solution containing acetonitrile, sodium citrate, ascorbic acid and AgNO_3 aqueous solution, citrate as capping agent determine the growth dimensions of the seed and lead to high yield of triangular nanoprisms with sharp tips. Silver nanoprisms synthesized following this routine have a relatively large size ranging from 150 nm to 1.5 μm in edge length and the extinction spectrums locate beyond 1000 nm [77]. Another aqueous method based on a combination of biological organisms, molecules and environments had been developed for the synthesis of silver nanoprisms. Klaus and co-workers have prepared silver nanoprisms in a bacterium as an organism accumulating silver ions in its intracellular space [79]. Bacteria were grown on the agar substrate containing silver nitrate; the silver ions were reduced and formed silver nanoprisms either within the bacteria or in the growth medium. Beside solution phase syntheses, solid phase syntheses method like lithographic fabrication [80, 81] also have been applied for large scale of silver nanoprisms fabrication.

2.3.2 Gold Coating of Ag Nanoprism

Although silver has high-quality plasmon resonance through the visible spectrum, stability and chemical resistance of silver nanostructures are much weaker compare with other plasmon materials such as gold, especially for highly anisotropic silver nanostructures include silver nanoprisms, which limit their performance in many applications. Therefore simple methods to enhance the stability without weakening the plasmon properties of silver nanostructure are desired. Coating a thin layer of gold onto silver nanoprisms fits the requirements of better stability without changing the morphology and retain high-quality plasmon resonance. A few gold coating methods have been developed in the past decades. In 2005, Sanedrin et al. published a method for preparing triangular nanoprisms made of

silver and gold [82]. In this experiment, silver nanoprisms were added to growth solutions containing HAuCl_4 , CTAB, L-AA, and NaOH. With controlled $\text{Ag}^+ : \text{Au}^{3+}$ ratio, AgAu core-shell nanoprisms can be obtained. However, the core-shell nanostructure has a morphology of pseudo-triangular shape with a thicker coating on the vertex of the silver nanoprisms. Meanwhile, a significant amount of truncation and pseudo-disc shape nanoparticles formed using this method, shown in Figure 2.9 a) [82]. Mohammad and co-workers modified the gold coating method and preserve the triangular shape of silver nanoprisms [7]. In this method, the gold shell coating process was carried out by slowly injecting HAuCl_4 solution as gold precursor and hydroxylamine (HyA) solution as reductant simultaneously, the concentration of the chemicals and the injection speeds were carefully controlled. Shown in Figure 2.9 c), four stages were performed through the gold coating process: firstly, gold deposited on the tips and edges of silver nanoprisms, this deposition is due to the higher surface energy of the (1 1 0) planes on the silver nanoprism edges, therefore at first stage, gold atoms preferentially on along the edges of the silver nanoprisms; secondly silver nanoprisms surfaces were oxidized and pin-hole can be observed; in the third stage, Ag^+ ions along with Au^{3+} ions were reduced and formed an alloy surface on the original silver nanoprisms; finally in the last stage, silver nanoprisms were thoroughly coated by gold shells, and Ag@Au core-shell nanoprisms can be obtained. TEM confirmed the core-shell structure; gold shell thickness is less than 5 nm (Figure 2.9 b). This method is the first successful approach of entirely gold coated core-shell Ag@Au nanoprisms which maintain the triangular morphology. Using the same method with minor modification, edge coated silver nanoprisms and ultrathin gold nanoframe can be synthesized [83]. A robust method for etching free gold coating on silver nanoprisms was demonstrated by Yin Yadong et al [84]. In this study, sulfite (SO_3^{2-}) was chosen as an appropriate ligand and reducing agent. Gold sulfite complex $\text{Na}_2\text{Au}(\text{SO}_3)_2$ was formed as a gold plating agent [85], this complex has high stability and low reduction potential under alkaline conditions. It is also benign to the silver nanoprisms, which allows etching free epitaxial growth of gold. Gold shell thickness can be easily tuned by adjusting the gold precursor amount, TEM images show that uniform gold shell with well-defined facets on silver nanoprisms, no voids and pinhole due to galvanic replacement and etching were observed (Figure 2.9 d). One interesting finding is that as the growth rate of gold onto silver

nanoprisms exhibited site selectivity, the growth of gold preferentially on the edges over the tips (Figure 2.9 e). Therefore a truncated triangular core-shell nanoprisms were obtained for thicker shell Ag@Au core-shell nanostructures. Ag@Au nanoprism synthesized using this method displayed excellent stability against chemical oxidation due to the gold shell, which allows many practical plasmon based applications for enhanced performances [84].

Figure 2.9 a) TEM images of triangular nanoparticles, deformation of nanoprisms can be observed [82]. b) TEM image of Ag@Au core-shell nanoprisms with full gold shell and c) schematic illustration of the formation of Ag@Au nanoprisms [83]. d) & e) TEM images of Ag@Au nanoprisms and growth intermediates of the Ag@Au nanoprisms. Different gold growth rate along different facets result in a truncated triangular product [84].

2.3.3 Hybridization of Metal Nanoparticles and Semiconductor Nanostructure

Hybrid nanostructures which are composed of plasmonic metal components and semiconductor components are gaining extensive attention for their synergistic interactions between two components [86-89]. In this section, preparation methods of plasmonic metal@semiconductor core-shell nanostructures and anisotropic plasmonic metal/semiconductor nanostructures will be reviewed; semiconductor species will focus on titanium dioxide because of the wide applications of titanium dioxide in photocatalysis.

Plasmonic metal@semiconductor core-shell nanostructure has been attracting attention because of their extensive potential photocatalysis applications. To date, various hybrid nanostructures have been designed and successfully synthesized. In a gold core-titania shell synthesize route demonstrated by Wang Jianfang and co-workers, Au@TiO₂ core-shell with different morphologies have been prepared, gold nanorods and nanospheres were prepared using a seed-mediated growth method and wrapped with poly(sodium 4-styrenesulfonate) layer then stabilized with CTAB. TiCl₃ was chosen as the titanium precursor for its low rate of hydrolysis in water, which is assisted by dissolved O₂ in the reaction system [90]. The TiO₂ shell has a relatively uniform thickness (53 nm) on gold nanospheres and nanorods, and the TiO₂ shell is in compact contact with the gold core. Same TiO₂ coating approach can be applied to other plasmonic metal core such as Pd, Pt and Au-based nanocrystals [91]. An ethylene glycol-assisted coating of TiO₂ on relative small nanoparticles was established [92]. In this simple route for depositing a titanium-glycolate coating on Au and Ag nanoparticles (15 to 20 nm in diameter), titanium *n*-butoxide (TBOT) in ethylene glycol (EG) as titanium precursor was injected into metal nanoparticle acetone solution over a course of half an hour, followed by refluxing the core-shell nanostructures or calcination for crystallization of the TiO₂ shell. Different thickness of titanium glycolate coating on metal nanoparticles can be controlled by adjusting the amount of metal nanoparticles contained in the coating solution[92]. A sol-gel method has been employed for coating TiO₂ shell on silver nanoprisms, the thickness of the TiO₂ shell can be varied from 1 to 15 nm by controlling the amount of TiO₂ precursor and reaction time [93]. Directly coating of mesoporous TiO₂ on CTAB capped gold nanorod in aqueous

solution was demonstrated. In this method, titanium diisopropoxide bis(acetylacetonate) (TDAA) in methanol was carefully added into the reaction solution by multi times at a small amount to maintain mild hydrolysis. Reaction solution pH and CTAB concentration were carefully controlled at 10.5 and 0.18 mM respectively [94]. With fixed titanium precursor amount, TiO_2 shell thickness increases with the decrease aspect ratio of gold nanorod [94]. Beside single component metal nanoparticles, the TiO_2 coating was successfully achieved on Au/Ag bimetallic nanorods [95, 96]. Titanium-(triethanolaminate) isopropoxide (TTEAIP) isopropyl alcohol solution can be used as the TiO_2 precursor for CTAC stabilized gold nanorod and Au/Ag nanorod, the resulted TiO_2 shell is amorphous [96]. In another TiO_2 coating procedure on Au/Ag nanorods, titanium tetraisopropoxide (TTIP) methanol was used as the TiO_2 precursor. TiO_2 shell thickness can be tuned by adjusting the precursor concentration [95].

Figure 2. 10 TEM images of various plasmonic core@ TiO_2 shell nanostructures. a-b) Au@ TiO_2 core-shell nanoparticles [90, 94]. c-d) Ag@ TiO_2 core-shell nanoprisms [92, 93]. e-f) Bimetallic AuAg@ TiO_2 core-shell nanorods [95, 96].

Comparing with the numerous published method on the synthesis of plasmonic core-shell metal@semiconductor nanostructures, not many methods of anisotropic growth of TiO_2 onto plasmonic metal nanoparticles have been reported [97-100]. Anisotropic dumbbell structures of gold nanorods with two ends covered by TiO_2 were synthesized by using CTAB as the surfactant. Bilayers of surface-capping agents like C_{16}TAB are more closely packed on gold nanorods' side than on tips, which allow gold nanorod tips accessible to Ti species. By controlling the hydrolysis rate of TiCl_3 as titanium precursor, Ti^{3+} is catalytically oxidized and attached on the gold nanorod tips. The concentration of C_{16}TAB as surfactant plays an important role for successful partially coating, otherwise fully titanium dioxide gold nanorods or TiO_2 coated on only ends of the gold nanorods [100]. A series of Janus gold nanoparticle/titanium dioxide hybrid nanostructures were synthesized [97-99]. Janus nanostructure integrates two or more component at small junctions with other regions exposed. By controlling the hydrolysis of titanium diisopropoxide bis(acetylacetonate), a titanium precursor with relatively slow hydrolysis rate, on pre-grown gold nanospheres and nanorods, Au@TiO_2 core-shell nanostructure, Au@TiO_2 yolk-shell nanostructure and Au/TiO_2 Janus nanostructure can be obtained. The amount and addition manner of titanium precursor has been found critical for the final structure of products. The balance between gold surface energy, TiO_2 surface energy and Au- TiO_2 interface energy determine the morphologies of Au/TiO_2 hybrid nanostructure [97-99]. Besides TiO_2 , other kinds of semiconductor have also been successfully site-selectively deposited onto plasmonic metal nanoparticles [101, 102]. Site-selective silica coating was achieved on both gold nanorod and gold nanobipyramids. Silica can be selectively coated at the two ends or on the side of the gold nanorod and nanobipyramids by choosing different surfactant. Han and co-workers successfully deposited Cu_2O selectively at the tips of hexoctahedral gold nanoparticles, CTAB/SDS binary stabilizer system was employed [103].

Figure 2. 11 TEM images of various anisotropic plasmonic metal /semiconductor nanostructures. a-b) Au/TiO₂ Janus nanostructures [97-99]. c) Anisotropic growth of TiO₂ onto gold nanorods [100]. d) Anisotropic growth of Cu₂O onto heteronanocrystals [103]. e-h) Anisotropic growth of SiO₂ onto gold nanorods and nanobipyramids, SiO₂ can be selectively deposited on tips and sides of gold nanostructure by chosen different kind of surfactant [101, 102].

2.4 Plasmon Enhanced Photocatalytic Reactions

The ability to interact with visible light of plasmonic nanostructure draws growing interest from scientists to solve the energy crisis and pollution issues. Numerous photochemical studies on plasmonic nanostructures have attempted to develop the efficiency convert visible radiation into chemical energy. LSPR excitation of plasmonic metal nanoparticles results in elevated electric fields at the surface of the nanoparticles via light-matter interaction, the enhanced electric field yield energetic charge carriers (hot carriers), which can further participate in photochemical transformations through localized heating or transfer of the hot carriers. The optical properties of these plasmonic metal nanostructures can be tuned across the entire visible spectrum (43% of solar irradiation) [104], therefore incorporating plasmonic metal nanostructures into photocatalytic systems provides great promise for efficient conversion of solar to chemical energy.

Under LSPR excitation, the quick dephasing of oscillation of free electrons in metal nanoparticles results in the generation of two kinds of carriers: an electron and a hole. The

carriers which carry more substantial energy than carriers of thermal excitations at ambient temperature are considered “hot”. The ratio of formed hot carriers to cold carriers depends on the photon energy and the plasmonic structure. The generation of hot carriers is on a timescale in the range of 1 to 100 fs [105-108] followed by rapidly thermalize to a Fermi-Dirac distribution by electron-electron and electron-photon scatterings at a timescale of 100 fs to 10 ps and lead to an increase of lattice temperature [106, 107, 109]. The heat dissipates to the surrounding environment slowly from 100ps to 10 ns [106, 110]. Electrons with enough energy can transfer from the metal nanoparticles to nearby adsorbate’s electron-accepting orbital or connected semiconductor.

2.4.1 Photocatalysis on Semiconductor

Photocatalytic materials for converting solar energy to chemical energy are mostly semiconductors (e.g. TiO_2 , Fe_2O_3). The mechanism of photocatalysis applications induced by UV-Vis light, including water splitting, degradation of pollutant and reduction of carbon dioxide, were firstly demonstrated by Fujishima and Honda [111]. In these systems, photons absorbed by the semiconductor yield high energy electrons and holes in the semiconductor. The electrons and holes separate from each other and diffuse to the chemical reaction site, usually at the semiconductor-liquid interface. The electrons are involved in reduction half-reaction such as hydrogen generation; meanwhile, the holes drive the oxidation half-reaction. The schematic mechanism of photocatalytic reaction process is shown below in Figure 2.12.

Figure 2.12 a) Photo-electrochemical cell for water splitting. Under irradiation by photons with energy exceeding the BG, excited charge carriers are generated in semiconductor photoanode. Holes participate in the oxygen-evolution reaction half-reaction and electrons travel to counter-electrode and evolved in hydrogen evolution half-reaction. b) Semiconductor photocatalyst with co-catalyst for water splitting, generated charge carrier diffuse to the co-catalyst surface and participate in half-reactions. [112]

Ideal photocatalyst should be affordable, have high efficiency and high stability; however, most of the single component semiconductor materials cannot fit all the requirements. N-type titanium dioxide as one of the most promising semiconductor photocatalyst has a relatively large bandgap of $\sim 3.2\text{eV}$; therefore only photons of UV-region can be absorbed. As UV region only represent 5% of the sun's total irradiance spectrum, TiO_2 as a photocatalyst is not quite efficient under sunlight. Co-catalysts are commonly used to prevent the fast recombination of generated electron and hole pairs and provide reactive sites for photo-catalytic reactions [113]. With decorated by metal nanoparticles on semiconductor, the recombination rate of electron-hole pairs is restrained as the electrons migrate to co-catalyst site, as well as reaction sites. Commonly used materials as co-catalyst include nanoparticles of Pt [115], Au [116], Ag [117] and various metal oxide.

2.4.2 Hybrid Plasmonic Metal/Semiconductor Photocatalyst

Incorporating plasmonic metal with semiconductor can vastly improve the photocatalytic ability of semiconductor by utilizing the LSPR of the plasmonic metal under visible light [118-121]. As plasmonic nanostructures under LSPR excitation, the absorption of photons can electromagnetically decay radiatively into re-emitted photons or non-radiatively by generating hot pairs (Figure 2.13) [122-125]. Without surrounding adsorbate or semiconductor, the hot electron/hole pairs will relax into heat within nanoseconds and cause increased lattice temperature and further dissipates into the surrounding area [126]. The lifetime of generation and emission of the hot electron are at a timescale of femtoseconds to nanoseconds, which mismatch with the timescale of chemical reactions (approximately microseconds to seconds) [127-129]. Therefore elongation of hot electrons lifetime is requested for efficient photocatalytic reactions.

Figure 2. 13 a) Localized surface plasmon decay radiatively and re-emitted of photons. b) Localized surface plasmon decay non-radiatively via excitation of hot e^- , which can occur via interband excitations within the CB or via interband excitations caused by transitions between other bands (such as d bands) and the CB. [130]

In hybrid plasmonic metal/semiconductor nanostructure, semiconductor acts as hot electron filter; plasmonic generated hot electrons can be transferred to the CB of a semiconductor via plasma mediated electron transfer (PMET) process. The Schottky barrier formed at the interface of metal and semiconductor can trap the hot electrons from

travelling back to metal and elongate the lifetime of hot electrons at the CB of the semiconductor. The filtered hot electrons can be involved for surface chemical reactions.

Figure 2. 14 Schematic PMET process of a plasmonic metal/semiconductor hybrid structure for efficient conversion of irradiation energy to chemical energy, hot electrons with higher energy can overcome the Schottky barrier and be injected into the CB of the semiconductor component.

Besides the conventional proposed indirect electron transfer mechanism, evidence has been found that implying other underlying electron transfer pathways from metal to connected semiconductor [110]. Furube and co-workers investigated the hot electron transfer timescale on Au/TiO₂ nanostructure by using *fs* transient absorption spectroscopy with an infrared probe, the plasmon excited hot electron transferred from 10 nm gold nanoparticles to TiO₂ takes less than 240 fs with a yield at about 40%, which is much higher than the theoretical calculated efficiency at 8% for indirect electron transfer mode [131, 132]. Lian et al. published the experimental evidence of plasmon-induced metal/semiconductor interface charge transfer pathway in an Au/CdSe nanorod heterostructure. In this newly proposed mechanism, plasmon decay by creating an electron in semiconductor CB directly, and the hot holes were left in metal (Figure 2.14) [133, 134].

Figure 2. 15 Schematic plasmon mediated direct electron transfer processed in Au/CdSe nanorod system [134].

Figure 2. 16 Optical absorption maps of Janus Au/TiO₂ nanostructures, Au nanoparticles with a diameter of a) 70nm, b) 50 nm and c) 30nm. The maps show the power absorbed under LSPR excitation, with the incident polarization along the x-axis and the incident intensity of 0.5 W cm⁻² [100].

Hot electrons that were transferred from metal to semiconductor and part of them can participate in chemical reactions including water splitting [112, 121, 135-141], CO₂ reduction [142-144], organic transformation [145, 146] and degradation of organic pollutants [99, 147-149]. The interfacial Schottky barrier facilitates the hot electron/hole separation. However, the re-combination of transferred hot electrons in semiconductor and hot holes left in the plasmonic metal nanoparticle still limit the efficiencies of photocatalytic reactions. The required photovoltage for overall water splitting is 1.23V [150, 151], which is much higher than the ~0.2V photovoltage of Au/TiO₂ photoanode under SPR excitation [136, 152]. Several strategies were applied to prevent the recombination hot electrons transferred to semiconductor and hot holes left in plasmonic nanoparticles [141, 153-155]. Moskovits and co-workers developed a hybrid nanostructure, beside of gold nanorod as plasmonic metal and neighboring TiO₂ as hot electron filter, a cobalt-based oxygen evolution catalyst (Co-OEC) is loaded on gold

nanorod as a hole consumer, and Pt nanoparticles were deposited on TiO₂ as hot electron sink and photocatalytic reaction site. Plasmonic generated hot holes and electrons were trapped in Co-OEC and Pt nanoparticles separately, the increase of difficulty for electron/hole pair recombination lead to noticeable enhancement of H₂ evolution under visible light without scavengers [153]. It has also been proposed that plasmon enhanced electromagnetic field might facilitate electron-hole separation in plasmonic metal/semiconductor hybrid nanostructures [19, 97, 99, 100]. Anisotropic growth of TiO₂ on gold nanosphere and gold nanorod was successfully synthesized by Han and co-workers to form a plasmonic metal/semiconductor Janus nanostructure [97, 99]. The excitation of gold nanoparticle under visible light results in enhancement of electromagnetic field localized at Au/TiO₂ interfaces, at which region hot electrons were transferred from gold nanoparticles to the semiconductor. An increase of Au nanoparticle diameter would give rise to the photocatalytic ability of the hybrid nanostructures as larger plasmonic metal nanoparticles provide a stronger electric field in the immediate vicinity of gold nanoparticles, shown in Fig 2.14 [97]. Moskovits and co-workers selectively deposited TiO₂ onto the tips of gold nanorods and found that this dumbbell-like nanostructure experience much higher hydrogen generation rate under visible light compare with Au@TiO₂ core-shell nanostructures and single component Au and TiO₂ nanostructures. The plasmonic induced electric field was concentrated at the tips, which promote the hot carriers separation [100].

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Chapter 3

Experimental Methodology

All of the synthesis methods and characterization techniques used in the experiment throughout the whole thesis are summarized in chapter 3. Silver nanoprism is employed as the anisotropic plasmonic template and further modified with a gold coating to enhance the stability. The unique triangular shape of AgAu nanoprism fits very well with the studies on anisotropic plasmonic nanostructures. The metal nanoprisms are hybridized with TiO₂ to form Janus and core-shell hybrid nanostructures. The morphologies of the hybrid nanostructures can be well controlled. The photocatalytic ability of hybrid nanostructures with different morphologies are evaluated via hydrogen generation under visible light. The synthetic methods to construct AgAu/TiO₂ hybrid nanostructures together with the characterization methods will be introduced in detail in this chapter.

3.1 Rationale for selection of Method and Material

This thesis demonstrates plasmonic nanostructures based on silver nanoprisms for photocatalytic reactions. Among all of the plasmonic metal materials, silver supports high-quality plasmon resonances at visible wavelength range with a reasonable price [1]. The anisotropic triangular shape silver nanoprisms contain multiple plasmon modes, and this unique structure can provide diverse interiorly plasmon properties [2]. Silver nanoparticles were synthesized via a high yield seed-mediated growth method and light-induced into silver nanoprisms. Gold coating of silver nanoprisms can enhance the stability of silver nanoprisms, which was performed using a wet chemical method [3]. A sol-gel method was applied for the titanium dioxide coating of the plasmonic metal core to form a core-shell nanostructure. Titanium diisopropoxide bis(acetylacetonate) (TDAA) was chosen as the titanium precursor because of its relatively slow hydrolysis rate [4], the thickness of titanium dioxide can be readily tuned. Titanium dioxide can trap the plasmon generated hot electron and provide deposition site in photocatalytic reactions. However, the thickness of the TiO_2 shell also plays an important role in hot electron transfer pathway[5]. Noble metals are the most commonly used co-catalysts in photocatalyst for higher photocatalytic efficiency [6]. Pt nanoparticles as electron sinks were deposited to manipulate the hot electrons in the semiconductor and to improve the activity of metal/semiconductor nanostructures.

It has been proposed that plasmonic metal nanoparticles can enhance the electric field in the vicinity under excitation, especially at the tips and gaps of the nanostructures as hot spots [7]. Meanwhile, hot electrons can be generated and participate in various photocatalytic reactions, the hot electron generation location of anisotropic plasmonic metal particles can be assumed as the reaction site of photocatalytic reactions. By photo-deposit metal nanoparticles under surface plasmon resonance excitation onto highly anisotropic AgAu nanoprisms, the in-situ growth of metal nanoparticles can indicate the reaction site intuitively. Therefore, find a metal precursor that can be precisely controlled photo-deposited was desired. Several common metal sources were attempted including gold, platinum and palladium.

Beside metal@semiconductor core-shell hybrid nanostructure, incorporating titanium dioxide with AgAu metal core anisotropic, intriguing morphology dependent properties can be exhibited. Janus nanostructure integrating plasmonic metal and semiconductor at a small junction and exposing other regions to the environment, the characteristic three-phase interface connecting metal, semiconductor and environment. Once again TDAA was used as the titanium precursor for its slow hydrolysis rate.

3.2 Chemical and Synthesis Process

3.2.1 Chemicals

Silver nitrate (AgNO_3 , 99.9%, Sigma-Aldrich), Tri-sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, 99%, Sigma-Aldrich), Sodium borohydride (NaBH_4 , 99.99%, Sigma-Aldrich), Bis(p-sulfonatophenyl)phenylphosphine dihydrate dipotassium (BSPP, 97%, Sigma-Aldrich), Gold(III) chloride hydrate (HAuCl_4 , 99.995%, Sigma-Aldrich), Sodium sulfite (Na_2SO_3 , Sigma-Aldrich), Polyvinylpyrrolidone (PVP, mol wt 40,000, Sigma-Aldrich), L-Ascorbic acid (99.0%, Sigma-Aldrich), Sodium hydroxide (NaOH , 98%, Sigma-Aldrich), Titanium diisopropoxide bis(acetylacetonate) (TDAA, 75 wt. % in isopropyl alcohol, Sigma-Aldrich), Ammonia solution (NH_4OH , 25wt% solution, Sinopharm Chemical), Chloroplatinic acid hydrate ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, 99.9%, Sigma-Aldrich), isopropyl alcohol (99%, Sigma-Aldrich), methanol (AR) and formic acid (>98%, Sigma-Aldrich) were used as received without further purification. All glasses wears were washed Aqua Regia, $\text{HCl}:\text{HNO}_3=3:1(\text{v}:\text{v})$, and rinsed with ethanol and Milli-Q water. Deionized water ($18.2 \text{ k}\Omega \cdot \text{cm}$, Milli-Q System, Millipore, Billerica) was used in all the experiments.

3.2.2 Synthesis of Silver Nanoparticles

Seed-mediated growth method was used for the synthesis of silver nanoparticles.

AgNO_3 solution (1 mL, 30 mM) was dispersed into Millipore water (190 mL) in a glass 500-mL three-neck flask. The glass flask was immersed in an ice bath and degas using N_2 gas with vigorous stirring for 20 minutes. Trisodium citrate solution (2 mL, 25 mM) was

injected into the flask drop by drop, followed by the fast injection of the NaBH_4 solution (2 mL, 60 mM). Over the next 10 minutes, 500 μL of NaBH_4 solution was added into the flask with an interval of 2 minutes for five times. Then bis(p-sulfonatophenyl) phenylphosphine dehydrate dipotassium (BSPP) (1.5 mL, 5 mM) and 2 mL of NaBH_4 solution were injected dropwise into the reaction solution. The mixed solution of Ag nanoparticles was kept stir for one hour and then allowed to age for 8 hours refrigerated in darkness.

3.2.3 Synthesis of Silver Nanoprisms

A photo-mediated approach was used to synthesize the silver nanoprisms.

Ag nanoparticles solution was transferred into a 20 mL vial and irradiated with 150W halogen lamp with a bandpass optical filter of 500 ± 20 nm for 2 hours, then the 500 ± 20 nm bandpass optical filter was replaced with a 600 ± 20 nm bandpass optical filter and the irradiation continued for 1 hour. The as-synthesized Ag nanoprisms were collected via centrifuge and stored in darkness before gold coating.

As the synthesized silver nanoparticle colloid was irradiated by 500 ± 20 nm visible light, hot electrons generated on the surface of silver nanoparticles due to plasmon excitation [8-10]. The adsorbed Ag^+ ions combine with the hot electrons and were reduced onto the surfaces of silver nanoparticles. With the presence of oxygen, ultra-fine silver nanoparticles were oxidized to Ag^+ and subsequently complexed with BSPP, which is used as the silver source in the photoreaction. Under SPR excitation, the dipole plasmon excitation causes ultrafast charge separation on silver nanoparticle surfaces [11], which induce facet selective silver deposition, in consequence, anisotropic growth into silver nanoprisms [12]. Many researchers also suggested that the parallel twin planes and reentrant groove are the key factors determining the plate-like structures (Figure 3.1). Coalescence between two 111 faces yields stacking faults, which can result in lateral crystal growth parallel to the major 111 planes. As the silver nanoprisms grow, strong electromagnetic fields generated at the tips due to dipole excitation, the nanoprisms tips experience higher growth rate

compare with edges, which explain the final prism structure with sharp tips. A 150W halogen lamp was used for the photoreaction to expedite the photochemical growth without causing superfluous thermal growth. By changing 500 ± 20 nm filter to another 600 ± 20 nm filter, cluster fusion and bimodal size distribution can be prevented [13]. The prisms growth stops as the small size silver nanoprisms are completely consumed, the synthesized silver nanoprisms need to be stored at 4°C in darkness to prevent deformation and oxidation.

Figure 3. 1 Scheme of crystal twinning that leads to plate-like growth of nanostructures (side view and top-down view). Crystal twinning leads to the formation of a re-entrant groove A that serves as a site for preferential crystal growth over B. Crystal growth occurs parallel to the major $\{111\}$ planes, preferentially at A sites over the B sites, leading to triangular, plate-like crystals.

3.2.4 Gold Coating of Silver Nanoprisms

To prepare gold growth solution, $400\ \mu\text{L}$ of HAuCl_4 (25 mM), $240\ \mu\text{L}$ of NaOH (200 mM) and 3mL of Na_2SO_3 (10 mM) were added into 4.36mL DI water in sequence. Gold growth solution was left undisturbed for 4 hours. Silver nanoprisms were centrifuged from 20mL to one mL. A solution was prepared by mixing 1.5mL DI water, 0.5mL PVP (5 wt%), 0.5mL L-AA (100 mM), 0.25mL NaOH (200 mM), 0.25mL Na_2SO_3 (10 mM), one mL of concentrated silver nanoprisms and one mL of gold growth solution were added at same time. The mixture was stirred overnight, and AgAu core-shell nanoprisms were collected via centrifuge and washed with DI water for three times.

By using this epitaxial deposition method for the gold coating of Ag nanoparticles, the chemical stability and LSPR properties of Ag nanoprisms are enhanced [3]. The thickness of the gold shell can be precisely tuned by controlling the amount of gold growth solution.

Sulfite was chosen as an appropriate ligand to coordinate with gold ions and forms a stable complex with lowered reduction potential. Sulfite also functions as a reducing agent to form $\text{Na}_2\text{Au}(\text{SO}_3)_2$ as an Au plating agent [14], which has a low reduction potential ($E=0.111\text{ V}$ vs SHE) within alkaline condition. The Au complex undergoes a redox reaction with the mild reductant agent ascorbic acid instead of silver nanoprisms; therefore galvanic replacement and etching of silver nanoprisms can be prevented.

3.2.5 Synthesis of Ag@Au/TiO₂ Janus Nanostructure

AgAu nanoprisms were synthesized following previous procedure, the solution of AgAu nanoprisms (2 mL) was mixed with 8 mL isopropyl alcohol, 100 μL of ammonia solution (28-30 wt %) was added under vigorous stirring. 100 μL of TDAA isopropyl alcohol solution (10mM) was injected into it under stirring. After 4 hours, the AgAu/TiO₂ Janus nanostructures were collected by centrifugation at 8,000 rpm for 10 min and washed three times with isopropyl alcohol to remove excess TiO₂ nanoparticles, and then the Janus nanostructures were transferred into the water. To investigate the growth process of TiO₂ nanosphere onto AgAu nanoprisms, different amount of titania precursor and ammonia solution were tested. The geometry of AgAu/TiO₂ nanostructure can be tuned by controlling the amount and adding manner of TDAA. Without ammonia as the catalyst for the hydrolysis of TDAA, the growth of TiO₂ was isotropically and an even TiO₂ shell can be coated onto AgAu nanoprisms on both facets and edges. By adjusting the pH of the reaction mixture to 9-10 using ammonia solution, the hydrolysis rate of TADD was facilitated. Spherical TiO₂ nanoparticles were formed anisotropically on one side of AgAu nanoprism facets, leaving the other facet exposed. The formation of this AgAu/TiO₂ Janus nanostructure is a consequence of balancing of surface energies of AgAu nanoprisms and TiO₂ nanoparticles, and the AgAu/TiO₂ interfacial energy. The size of TiO₂ nanosphere can be tuned by adjusting the volume of the TDAA solution.

3.2.6 Synthesis of Ag@Au@TiO₂/Au Nanostructure

AgAu nanoprisms and AgAu@TiO₂ nanoprisms were synthesized following the previous procedure. The thickness of the TiO₂ shell is controlled between 3-5 nm. The as-synthesized AgAu@TiO₂ nanoprisms were redispersed into 5 ml DI water in a 20 ml glass vial, and the glass vial was covered with aluminium foil, 10 μ L of HAuCl₄ solution (10 mM) was added. Three batches of the mixed solution were placed (A) in darkness; (B) under irradiation of full spectrum light using a 150W tungsten lamp; (C) under visible light with a wavelength range of 600-700 nm bandpass filter (or a cut off filter >600 nm) coupled a 150W tungsten lamp respectively. After 30 min, AgAu@TiO₂/Au nanoparticles were collected via centrifugation at 10,000 rpm for 10 min and then washed with ultrapure water for three times.

3.2.7 Synthesis of AgAu@TiO₂ core-shell Nanostructures

For titanium dioxide coating, the solution of AgAu nanoprisms (1 mL) was mixed with 4 mL isopropyl alcohol, 100 μ L of TDAA isopropyl alcohol solution (10 mM) was added rapidly under vigorous stirring; the mixture was left to stir overnight at ambient temperature. After washing with isopropyl alcohol 3 times, AgAu@TiO₂ nanoprisms were dispersed into 1 mL DI water. The thickness of the titanium dioxide shell can be increased by repeating this coating process.

The coating of an even layer of a TiO₂ shell onto AgAu nanoprisms was performed using TDAA, a TiO₂ precursor with slow hydrolysis rate [4]. This less reactive precursor helps separate the nucleation and growth of TiO₂ for controlled synthesis of AgAu@TiO₂ nanoprisms. Plasmonic metal core AgAu nanoprisms were dispersed in a mixed solvent of isopropyl alcohol and DI water, isopropyl alcohol was used as a homogenizing agent because of the poor miscibility between TDAA and water. To achieve an even and better smoothness of TiO₂ shell surface, vigorous stirring of the reaction system was necessary. AgAu@TiO₂ nanoprisms with different TiO₂ shell thickness can be achieved by repeatedly

coating of TiO₂. Directly increasing the TDAA amount can cause extra free TiO₂ nanoparticles instead of an increase of TiO₂ shell thickness.

3.2.8 Platinum Photodeposition onto AgAu@TiO₂ Nanoprisms

Pt nanoparticles were deposited on AgAu@TiO₂ by using a photo-deposition method. AgAu@TiO₂ core-shell nanoprisms with different TiO₂ shell thickness were synthesized following the previous procedure. The core-shell nanoprisms were dispersed into a mixture of 4.5 ml DI water and 1.5 ml of methanol in a 20 mL glass bottle. 10 µL of H₂PtCl₆ aqueous solution (10 mM) was added. A 150 W Tungsten lamp (MAX-150, Asahi Spectra Company, Ltd.) was used as the light source. The glass vial was irradiated for up to 2 hours before the sample was collected via centrifugation at 8,000 rpm for 10 mins. The sample was washed with DI water three times. Photodeposition is a promising and straightforward technique for loading of metal nanoparticles [15, 16]. In a photodeposition process, photo-excited charge carriers reduce or oxidize metal ions to form metal and metal oxide nanoparticles [17]. A generalized equation for the photodeposition of metal nanoparticles is:

As TiO₂ is irradiated without methanol, adsorbed Pt species are reduced and form PtO or Pt(OH)₂ indicated as following equations:

A schematic representation of photo-deposition mechanism is shown in Figure 3.2.

Figure 3. 2 Scheme of (a) reductive photodeposition and (b) oxidative photodeposition. D, sacrificial electron donor; A, sacrificial electron acceptor; M, metal. [16]

Photodeposition happens only when the CB of the semiconductor must be more negative than the reduction potential of the metals, and the valence band must be more positive (E vs NHE scale) than the oxidation potential of the metal ion or sacrificial agents. The absorbed photon energy must exceed the band gap of the semiconductor, which is 3.2 eV for TiO_2 ; therefore ultraviolet light is required for photodeposition of Pt nanoparticles onto AgAu@TiO_2 nanoprisms. For the deposition of metal nanoparticles, a sacrificial agent including methanol[18, 19], ethanol and 2-propanol [20] is often used during the photodeposition. There are four steps of photodeposition of Pt nanoparticles onto AgAu@TiO_2 nanoprisms, firstly PtCl_6^{2-} are adsorbed on the surface of TiO_2 without irradiation, secondly small amount of PtCl_6^{2-} deposited on the surface of TiO_2 under irradiation, thirdly a sharp increase of photodeposition within a few minutes, followed by complete reduction of PtCl_6^{2-} .

Methanol favours the adsorption equilibrium and changes the surface of TiO_2 , without the existence of methanol, a higher concentration of H_2PtCl_6 and much longer irradiation time is required. Under irradiation with TiO_2 , oxidation of methanol occurs and forms methoxy-radicals:

The Pt species PtO and Pt(OH)_2 are further reduced to metallic Pt nanoparticles according to reactions

The reduction of Pt^{4+} to Pt^0 is driven not only by photogenerated electrons but also methanol radicals, which is a much stronger reductant than the CB electrons [19].

Deposited Pt nanoparticles as electron sinks expedite the transfer of photogenerated hot electrons from TiO_2 as the catalyst and facilitate the growth of Pt nanoparticles.

3.2.9 Photocatalytic Hydrogen Generation

The photocatalytic activity was evaluated using above synthesized hybrid nanostructures as photocatalysts and formic acid as sacrificing reagent. The synthesized nanoparticles as photocatalysts were dispersed into 10 ml DI water containing 10 μL of formic acid solution (98%). The mixture was sealed in a 20 ml glass vial and purged with N_2 for 20 min to remove O_2 and other gases. A 300 W Xenon lamp (MAX-302, Asahi Spectra Company, Ltd.) was used as the light source. The glass vial was exposed under the light coupled with a cut-off filter ($>600\text{ nm}$). The generated hydrogen was analysed by periodically injection 0.5 ml gas into the gas chromatograph (GC, Agilent 7890A).

3.3 Characterization

After different kinds of nanostructures were obtained, proper techniques were required to characterize the features including the optical properties and morphologies of the nanostructure. Ultraviolet-visible Spectroscopy is a common technique to test the extinction spectrum of the nanostructures and transmission electron microscopy with atomic resolution can reveal the detail of nanostructure morphologies. Shimadzu UV-1800 UV-Vis Spectrophotometer and JEOL JEM-2010 200kV and JEOL TEM-2100 200kV

were used for characterization. The basic principles of UV-Vis and TEM will be introduced in this section.

3.3.1 Ultraviolet–visible Spectroscopy (UV-Vis)

UV-Vis spectroscopy is based on the measurement of the absorbance of solution contained in a cuvette. Figure 3.3 shows the construction details of a typical double-beam UV-Vis spectrophotometer. A deuterium lamp (190-400 nm) and a tungsten filament lamp (300-2500nm) are used as UV, visible and near-IR light source. Monochromatic light is split into 2 beams, one as the reference, and the other beam simultaneously passes through the sample. The transmitted ration of the beam is recorded by the signal processor and shown on readout devices. The UV-Vis spectrometer measures the intensity of light passing through a sample and compare the intensity of reference for two beam spectrophotometer. In this thesis, all nanostructures were dispersed in DI water and contained in quartz cuvette for sample preparation.

Figure 3. 3 Schematic illustrating the internal components of a UV-Vis spectrophotometer.

3.3.2 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy is a kind of technique that use electron beam instead of visible light to observe ultra-thin specimens. For conventional optical microscopes, the

maximum resolution is limited by the wavelength of photons, by using electrons as “light source”, the resolution is largely enhanced. As the electrons emitted from the electron source, the TEM uses electromagnetic lenses to focus the electrons. The electrons are focused into a very thin beam and transmit through the specimen. Parts of the electrons are scattered depending on the density of the specimen material. The unscattered electrons which pass through the sample hit the fluorescent screen and give rise to an image. The various darkness of the images is dependent on the absorption of the electrons from the specimen's part.

Bright field imaging mode is the most common mode for TEM usages. In this mode, the imaging is formed by direct absorption of the sample, a sample with higher thickness or with a higher atomic number will appear darker. Regions with no sample will appear bright since most of the electrons are not scattered or absorbed. The background without the sample is bright; therefore it is known as bright field mode. Another mode is known as dark field imaging mode. In dark field images, a tilting incident electron beam interacts with the sample and the diffracted beam passes the object aperture in the objective lens rear focal plane and ends up projected onto the imaging apparatus. Sample exhibits diffraction contrast due to differences of the lattice orientation in the specimen. Only parts of the specimen that cause Bragg scattering and those electrons can be selected and appear bright images. Where there is no sample scattering, the images appear darker. Under the condition of dual beam diffraction, the image brightness contrast is opposite to each other of the bright field imaging mode and dark field imaging mode.

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Chapter 4

Janus AgAu/TiO₂ Nanostructure: Synthesis and Site-Dependent Photocatalytic Reactions under Visible-Light

Plasmonic metal/semiconductor heterostructures are strongly desired for exploring the plasmon-induced application. Herein, synthesis of Janus AgAu/TiO₂ nanostructure integrating AgAu nanoprisms and TiO₂ nanosphere is realized through selective deposition of TiO₂ onto AgAu nanoprisms. Size of TiO₂ component can be tuned by controlling the addition manner and amount of TiO₂ precursor titanium diisopropoxide bis(acetylacetonate)(TDAA). The Janus AgAu/TiO₂ nanostructures show plasmon-enhanced hydrogen generation under visible light and NIR light compared with the AgAu@TiO₂ core-shell nanostructure. The exposure of AgAu provides the plasmon-induced hot electron with the direct access to the photocatalytic reaction site, where is believed to locate at the three-phase interface of AgAu nanoprism, amorphous TiO₂ component and the environment. The photocatalytic reaction site location was further investigated by the photodeposition of metal nanoparticles onto the Janus nanostructure under UV light and visible light. It is believed that the Janus nanostructure would have great potential application in the plasmonic photocatalysis applications.

4.1 Introduction

Plasmonic metal nanoparticles are of great of interest because of the unique reactions to light based on LSPR, which is caused by the collective oscillations of free electrons at the surface of the plasmonic nanoparticles [1]. The optical properties of plasmonic nanostructure are related to the component [2, 3], size [4], shape [5, 6] and dielectric environment [7] of the nanostructure, LSPR wavelength can be tuned through the visible light to the infrared by adjusting these factors. However, the ultrafast generation and thermalization process of plasmon generated hot charge carriers keeps plasmonic nanostructure from being directly used for many photocatalysis applications. To close the gap of fleet hot electrons and time needed for the chemical reaction, incorporating plasmonic metal nanoparticles with semiconductors is a proven technique [8]. The enhanced efficiency if solar energy conversion of metal/semiconductor nanostructures is attributed to the elongation plasmon induced hot electrons' lifetime. The plasmon resonance resulted in hot electrons can be transferred to the connected semiconductor CB through plasmon-induced hot electron transfer (PHET) process [9]. Therefore, rational design and synthesis of hybrid nanostructures of plasmonic metal and semiconductor have attracted considerable interest because of their fascinating combined synergistic properties and wide applications of water splitting [8, 10], CO₂ reduction [11, 12], degradation of organic pollutants [13, 14] and so on. Common hybrid nanostructures including metal nanoparticles decorated semiconductor nanostructures [15-17], plasmonic metal@semiconductor core-shell and yolk-shell nanostructures [18-21], Janus nanostructures [13, 22] and other nanostructure of semiconductor partially coated metal nanoparticles [23, 24]. Among all hybrid plasmonic metal/semiconductor nanostructure, Janus nanostructures are gaining importance due to the non-centrosymmetric plasmon coupling of a metal component and a semiconductor component. Although numerous kinds of core-shell nanostructures have been studied, LSPR characteristic of Janus nanostructures with connected joint and exposure of both component remains relatively undeveloped.

Herein, a Janus nanostructure composed of AgAu nanoprism as plasmonic part and titanium dioxide nanosphere as semiconductor part was synthesized. Photocatalytic

efficiency of Janus AgAu/TiO₂ nanostructures was evaluated and compared with core-shell AgAu@TiO₂ nanoprisms via HER under visible light irradiation. The pathway of plasmon generated hot electrons and photocatalysis reaction site of the Janus nanostructure was investigated by plasmon controlled site-selective photodeposition of metal nanoparticles.

4.2 Result and Discussion

4.2.1 Synthesis and Characterization of Janus AgAu/TiO₂ nanostructure

Wet chemistry approaches are the most commonly employed method for anisotropic growth of semiconductor onto metal nanostructures. AgAu nanoprisms were synthesized following the previous method [25, 26]. Morphology of TiO₂ component can be tuned by adjusting the addition manner of titania precursor solution and ammonia solution as the catalyst to control the hydrolysis rate of titanium dioxide precursor. The stirring rate of the reaction system and the addition manner of ammonia as hydrolysis catalyst also affect the final geometry of the AgAu/TiO₂ nanostructure. Experimentally, the as-synthesized AgAu nanoprisms approximately 54 nm in edge length were dispersed into a mixture containing 2 ml DI water and 8 ml of isopropyl alcohol under vigorous stirring, 100 μ L of titanium diisopropoxide bis(acetylacetonate) isopropanol solution (10 mM) as titanium dioxide precursor was added in one portion, after stirred for half an hour, 100 μ L of ammonia (28 wt%) was injected into the mixture, subsequently stirred for overnight. The TiO₂ was found to grow anisotropically on only one side of the AgAu nanoprisms, leaving the other side exposed, forming Janus AgAu/TiO₂ nanoprisms. The TEM images indicate that the TiO₂ component is hemispherical, the flat side connects with one facet of AgAu nanoprism and the arcuate part of TiO₂ is exposed to environment, this geometry can achieve the minimum surface energy of the nanostructure (Figure 4.1). The LSPR properties of AgAu@TiO₂ core-shell nanoprisms and AgAu/TiO₂ Janus nanostructure were examined and studied. The bare AgAu bimetallic nanoprisms exhibit LSPR wavelength at 721 nm, after hybridizing with TiO₂, the in-plane mode LSPR peak red-shifted to 773 nm due to the change of the dielectric environment (Figure 4.2). To better understand the growth process, the relation between the TDAA amount and the growth of TiO₂ was studied. Figure 4.1

shows the TDAA amount effect on TiO₂ growth. When TDAA precursor volume is as low as 10 μ L, a thin layer of the TiO₂ shell can be observed grow isotopically on AgAu nanoprisms and form a core-shell nanostructure; the TiO₂ shell is extremely thin (Figure 4.1 a). As TDAA precursor volume reached 50 μ L, the thickness of TiO₂ on one side of AgAu nanoprism facet start to increase and start to form an arched surface (Figure 4.1 b). The TiO₂ component continuous growth with increasing TDAA amount and larger TiO₂ nanosphere are formed and attached on one side of the AgAu nanoprisms (Figure 4.1 c). When TDAA precursor amount added reached 500 μ L, large spherical TiO₂ nanoparticles with a diameter of 200 nm were formed, metal nanoparticles were embedded at one side of the TiO₂ nanoparticles, free large TiO₂ nanoparticles started to appear at the same time (Figure 4.1 d). After TDAA solution was added into the reaction system, TDAA started to hydrolysis on the surface of AgAu nanoprisms until all titania precursor was consumed. The Janus structure is a result of balancing the interfacial energy between the two components and surface energy of overall nanostructures.

Figure 4. 1 TEM images of AgAu/TiO₂ nanostructure synthesized with different amount of titanium dioxide precursor: (a) 10 μ L (b) 50 μ L (c) 100 μ L (d) 500 μ L.

Figure 4. 2 UV-Vis spectrum of bare AgAu nanoprisms and AgAu/TiO₂ Janus nanostructure.

The pH also influences the geometry of the final structure, without ammonia facilitating the hydrolysis rate of TDAA, AgAu@TiO₂ core-shell nanostructure with a thin layer of amorphous TiO₂ shell coated evenly on the surface of AgAu nanoprisms at low TDAA concentration. With a higher amount of TDAA, dissociate TiO₂ nanoparticles are formed instead of the AgAu@TiO₂ nanostructure with a thicker shell. To investigate the effect of ammonia as the hydrolysis catalyst, different amount of ammonia was added into the reaction mixture with a fixed volume of TDAA (10mM, 100 μ L). As shown in Figure 4.3, an appropriate amount of 100 μ L ammonia solution facilitate the formation of TiO₂ nanosphere to obtain Janus nanostructures. On the condition of low pH, strip shape TiO₂ nanostructures germinated from AgAu nanoprisms; on the other hand, high volume of ammonia gave rise to fast hydrolysis of TDAA and generate small size TiO₂ nanoparticles on AgAu nanoprisms and in solution.

Figure 4. 3 TEM images of AgAu/TiO₂ nanostructure synthesized with different amount of ammonia as hydrolysis catalyst: (a) 10 μ L (b) 100 μ L (c) 500 μ L.

4.2.2 Photocatalytic ability of Janus AgAu/TiO₂ Nanostructure

The photocatalytic activity of Janus AgAu/TiO₂ nanostructures was investigated using hydrogen generation from formic acid aqueous solution. Various nanostructures were irradiated under a tungsten halogen lamp with a cut-off optical filter ($\lambda > 600$ nm). The photocatalytic ability of bimetallic AgAu nanoprisms and amorphous TiO₂ nanosphere were very low under irradiation of visible light. Since TiO₂ has a band gap of 3.2 eV, amorphous TiO₂ nanospheres as semiconductor photocatalysis can only absorb photons from UV light. The hybridization of plasmonic metal and semiconductor can significantly increase the hydrogen production rate under visible light. LSPR induced hot electrons generated in AgAu nanoprisms were filtered by the TiO₂ shell and participate in photocatalytic hydrogen generation. The synergistic interaction between AgAu nanoprism and TiO₂ enhance the photocatalytic ability to 103 μ L hydrogen generation for core-shell nanostructure after irradiation of 6 hours. Under the circumstances of Janus nanostructure, hydrogen generation volume was further increased to 152 μ L, which is 1.48 times higher compared with core-shell nanostructures.

Figure 4. 4 Hydrogen generation volume of core-shell nanoprisms and Janus nanostructures under visible irradiation.

The photocatalytic reaction mechanism of Janus AgAu/TiO₂ nanostructure was proposed (Figure 4.5). Different from AgAu@TiO₂ core-shell nanostructure, the junction between the plasmonic metal and semiconductor component provide transfer pathway for plasmon generated hot electrons, this junction also has a direct connection to formic acid molecules, which allows prompt chemical reactions. As indicated in the previous chapter, hot electrons concentrate at where experience larger local electric field, in other words along the edges and at the tips of the AgAu nanoprisms, where overlays the metal-semiconductor junctions. The heightened hot electron generation and expedite linkage to reagent conjointly enhance the photocatalysis efficiency. Note that the difference of photocatalytic activity does not result from the volume of the amorphous component as the visible light cannot be absorbed by TiO₂.

Figure 4. 5 Proposed photocatalytic process of efficient H₂ production of Janus AgAu/TiO₂ nanostructures as photocatalyst under visible light. Hot electrons generated from the plasmonic AgAu nanoprisms are filtered by TiO₂ and transferred to nearer reactive site, where also experience stronger plasmon enhanced local EM field.

To verify the hypothesis that three-phase interface is the reaction site, photo-deposition of gold nanoparticles onto the AgAu/TiO₂ Janus nanostructure was performed. As-synthesized AgAu/TiO₂ nanostructures were re-dispersed into 10 mL of DI water in a 20ml glass bottle, 10 μ L of HAuCl₄ solution (1mM) were added in darkness. The glass vials were irradiated cooperating with a 150W tungsten lamp and a 600nm cut-off filter to allow only visible light to pass. Control experiments were taken with irradiate the mixture under full spectrum irradiation and without irradiation in darkness. After one hour, the sample was collected via centrifuge and be washed with DI water.

TEM images show that small Au nanoparticles with a diameter of around 5 nm can be deposited under irradiation with both visible light and full spectrum light. Under visible light irradiation, plasmonic excited AgAu nanoprisms can generate hot charge carriers and injected into the connected TiO₂, as the dissemination distance of hot electrons are only within tens of nanometers before they lose their energy, the hot electrons accumulate in the CB of semiconductor near the interface between plasmonic metal and semiconductor, followed by transfer to nearest reaction site and involved in photocatalytic reactions. Another factor that exerts an effect on the reaction site may be the local electromagnetic field. Plasmonic nanostructures can cause enhanced electric field in the vicinity upon

excitation, for anisotropic plasmonic metal nanostructures, the tips and edges experience higher electric field. Hot spots of AgAu nanoprisms boost the probability of site-selective deposition of gold nanoparticles near tips and edges of AgAu nanoprisms on AgAu/TiO₂ nanostructure. In the case of irradiated under the full-spectrum light, the generation of the electron in semiconductor component TiO₂ dominate instead of plasmon generation. The photon absorbed by the semiconductor yield high energy electrons and holes for gold nanoparticles deposition, followed by reductant of gold precursors to gold nanoparticles. With hybridizing with AgAu bimetallic nanoprisms as electron sink and co-catalyst, generated electrons migrate to metal component and induced photo-deposition. Therefore Au nanoparticles can be found on both the semiconductor component and metal component of Janus AgAu/TiO₂ nanostructures. The plasmon enhanced local field at the adjacent of AgAu nanoprisms also contribute to hinder the recombination of electron-hole pairs, which can augment the probability of site-selective photo-deposition of gold nanoparticles at the three-phase interface of AgAu/TiO₂ Janus nanostructures.

Figure 4. 6 TEM images of AgAu/TiO₂/Au nanostructure by photodeposition of Au nanoparticles (a) in darkness (b) under visible light (c) under full spectrum light.

4.3 Conclusion

In conclusion, Janus nanostructure composed of AgAu nanoprism as plasmonic metal component and titanium dioxide nanosphere as semiconductor component was successfully synthesized. The photocatalytic efficiency under visible light is enhanced compared with bare AgAu nanoprisms, TiO₂ nanosphere and a relatively simple hybrid nanostructure AgAu@TiO₂ core-shell nanoprisms. The enhancement of the photocatalytic

ability of Janus nanostructure is believed on account of the shortcut of plasmon-induced hot electrons to the reactive site on the Janus nanostructure. The plasmon induced hot electrons were generated concentrated at the tips and edges of AgAuTiO₂ nanoprisms, where are also close to the three-phase interphase between plasmonic metal component, semiconductor and the environment. The close-by reaction site from hot electron generation site avails the high usage ratio of hot electrons with a short lifetime and travel distance. This approach is a promising strategy for designing plasmon based anisotropic metal/semiconductor hybrid nanostructures.

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Chapter 5

Plasmon Controlled Facet-selective Deposition of Gold on AgAu@TiO₂ Nanoprisms

The localized surface plasmon resonance of anisotropic metal nanoparticles is highly dependent on the size, morphological and chemical compositions. Previously studies have shown that LSPR excitation of a gold or silver nanoparticles can induce strongly enhanced local electric field, and generate hot electrons for redox reactions. In particular, for the anisotropic nanostructures, plasmon excitation re-distributes local field enhancement on different crystal facets, as such, the correlation between the local electric field enhancement and the hot electron distribution becomes critical in order to control the plasmon derived chemical processes. In this chapter, triangular AgAu@TiO₂ core-shell nanoprisms were synthesized, which have easily identified surface site with direct correlation to the plasmon mode and electric field intensity, and thereby can serve as an ideal platform to explore the distribution and behaviour of plasmon-induced hot electrons. In the presence of gold precursor, dipole plasmon excitation of AgAu@TiO₂ core-shell nanoprisms (at~700nm) induces selectively deposition of Au nanoparticles on the prism tips and edges. This observation suggests that the surface sites with the stronger electric field can provide more hot electrons, which can diffuse through the thin TiO₂ shell and reduce Au³⁺ on its surface. This study provides a new avenue of harvesting low-energy photons for chemical reactions.

5.1 Introduction

Plasmonic nanostructures have been studied for a long time and much progress was made in the fine-tuning of plasmonic metal nanoparticles synthesis protocols, structure characterisation and understanding of their optical properties [1-8]. The most attracting property of plasmonic nanostructure refers to as LSPR is known to be highly dependent on morphologies and chemical composition of the nanostructures [9]. Single and multicomponent metal nano-architectures with high anisotropic structures including rod [10], cubic [11, 12], disk [13], pyramid [14] and octahedron [15] have been successfully synthesized with high yield and narrow size distribution. Compared with isotropic nanosphere, anisotropic plasmonic nanostructures process broader range of plasmon tunability and versatile surface functionalities [9, 16], which bring about intriguing applications in biological and chemical sensing [17], photocatalysis [6, 9, 18-21], surface-enhanced Raman scattering [22] and metal-enhanced fluorescence [7, 23, 24].

In a spherical nanoparticle, the negative charge accumulating on one side of the spherical particle and positive charge accumulating on the other side under SPR excitation, forming a dipole-like mode [5]. Field lines converge at the regions where the charge accumulate, corresponding to strong local enhancement of electric field [8, 25]. In the case of anisotropic nanoparticles, higher order SPR mode can be supported [8]. Taking silver nanoprisms as an example, in-plane dipole, in-plane quadrupole and out-of-plane quadrupole modes will be supported when an external field drives the charges along the silver nanoprisms edges, along facets and perpendicular to facets [26, 27]. At the resonant state, enhancement on the intensity of the local electric field can reach $10^2 \sim 10^3$ at the surface of the nanoprism due to charge accumulation [26, 28]. Discrete dipole approximation (DDA) calculations have been done for silver nanosphere and silver nanoprisms [26, 27]. For small silver nanosphere with radius less than 20 nm, DDA results show that the maximum local electric field enhancement is less than 200 times at plasmon resonance at about 410 nm, for larger silver nanosphere with radius at 90 nm, the SPR occurs at 700 nm, the EM field enhancement is only ~ 25 [27]. However for highly anisotropic silver nanoprisms have plasmon resonance at 700 nm (side length = 60nm,

thickness = 12 nm and snip = 0 nm), the largest field for the dipole resonance are 3500 times of the applied field at tips of silver nanoprisms, the results also indicate that that maximum EM field enhancement for dipole resonance is at tips of the nanoprisms, and for the quadrupole resonance the significant regions of enhancement occur at the side edges [26] [27, 29]. Although the EM fields around non-symmetrical depend on the morphologies, the largest fields for the long wavelength resonance are thousand times of the applied field for all the nanoparticle shapes considered. Besides E-field enhancement, another intriguing peculiarity about plasmonic nanostructures is the generation of hot carriers under plasmon excitation [1]. SPR in nanostructure can be damped radiatively and cause re-emission of a photon, or non-radiatively by inducing the generation of an energetic hot electron-hole pair via Landau damping [30]. Plasmon-induced hot carrier science has been studied since the discovery of the photoelectric effect by Hertz especially for hot electrons and hot electron induced photochemistry in 1887 [3, 31]. However, very little has been reported the correlation between the local EM field enhancement and the distribution of the hot electron in an anisotropic plasmonic nanostructure. Here an experimental method was developed to discover the strong relationship between the E-field enhancement and hot electron generation site within a single anisotropic nanoparticle under plasmon excitation.

5.2 Results and Discussion

AgAu@TiO₂ nanoprisms were synthesized followed by previous procedure. Silver nanoprisms with narrow size distribution were synthesized via a light-induced method [32, 33], and the obtained silver nanoprisms were coated with a thin layer of gold to enhance the stability [34]. AgAu core-shell nanoprisms were employed as the plasmonic core for generation of surface plasmon driven hot electrons, pinholes and flaws on the AgAu nanoprisms should be avoided as the mismatch of the lattice will cause unconventional generation of hot electrons. The AgAu nanoprisms collaborate with semiconductor shell. The thickness of the TiO₂ shell was controlled below 10 nm for efficient ejection and transfer of plasmonic generated hot electrons. Upon excitation, the generated hot elections will decay on timescales of picoseconds via a series of ultrafast processes [35]; therefore the lifetimes of hot electrons are not long enough to participate in photocatalysis chemical

reactions. By coating a thin layer of semiconductor such as TiO_2 as the electron acceptor, the Schottky barrier between semiconductor and metal can trap the hot electron in CB of semiconductor and prevent the electron-hole re-combination to elongate the lifetime of the hot electrons. Despite being “hot” with extra energy, the travel distance of hot electrons is no longer than tens of nanometers before they lose their energy via thermalization [36]. Hence the thickness of the TiO_2 shell is a crucial factor for successful site-selective photodeposition of metal nanoparticles. Titanium diisopropoxide bis(acetylacetonate) (TDAA) was chosen as the titanium dioxide precursor for its slow hydrolysis rate, the thickness of the TiO_2 shell on AgAu nanoprism can be tuned precisely within 5-8 nm. As-synthesized AgAu@ TiO_2 nanoprisms were well dispersed into 10 ml of DI water in a 20 ml glass vial. Different amount of HAuCl_4 aqueous solution was injected as the gold precursor in darkness, and the glass bottles contain different amount of gold precursor was irradiated under full spectrum light and visible light ($>650\text{nm}$) respectively, one set of glass vial was stored in darkness as the control experiment. The LSPR wavelength of AgAu@ TiO_2 nanoprisms as Au deposition templet is at around 680 nm, therefore a cut-off filter which only allows light with the wavelength longer than 650 nm was used to filter out high energy photon. After the glass vials were irradiated for 30 mins, samples were collected via centrifuge and washed with ultrapure water for three times.

Figure 5. 1 TEM images of (a) AgAu core-shell nanoprisms, (b) AgAu@ TiO_2 core-shell nanoprisms with TiO_2 shell thickness at 5-8 nm.

Figure 5.1 shows the TEM images of the prepared AgAu nanoprisms and AgAu@TiO₂ core-shell nanoprisms with AgAu nanoprisms as the plasmonic core, the side length of AgAu nanoprisms is around 54 nm, snip of tips can be observed. The thickness of the titanium dioxide shell is within 5-8 nm. The starting hybrid nanoprisms process uniform morphologies and narrow size distributions, which are critical for successful site-selective photo-deposition of Au nanoparticles. Without irradiation, no gold nanoparticles were deposited onto AgAu@TiO₂ nanoprisms, even with a relative high Au³⁺ concentration, indicating that the electrons and energy used for deposition of gold nanoparticles are coming from the incident light.

After irradiated at a low Au³⁺ concentration of 20 uM, Au nanoparticles were deposited on AgAu@TiO₂ nanoprisms both under UV light and visible light with the wavelength longer than 650 nm. Site-selective deposition of Au NPs was realized through the irradiation of AgAg@TiO₂ nanoprisms under visible light with the wavelength > 650 nm. Gold NPs were deposited selectively on the tips of the AgAu@TiO₂ nanoprisms (Figure 5.3 a), the diameter of gold nanoparticle is around 5 nm. With increasing Au³⁺ concentration to 50 uM, Au nanoparticles start to grow along the edge facets of the AgAu@TiO₂ nanoprisms, where experience less strong local field enhancement compare with triangular tips, nonetheless stronger than basal facet. Further increase of gold precursor concentration to 100 uM leads to attachment of gold nanoparticles on basal facets of AgAu@TiO₂ nanoprisms.

Instead of visible light, full spectrum irradiation triggers the generation of electrons in semiconductor photocatalyst; therefore gold nanoparticles grow on AgAu@TiO₂ nanoparticles surface randomly with a smaller size. At low gold precursor concentration of 20 uM, a few gold nanoparticles can be found attached on facets of AgAu@TiO₂ nanoprisms without site preference as indicated in Figure 5.3 a), gold nanoparticles have a relatively small diameter of 1-2 nm. An increase of the concentration of HAuCl₄ precursor leads to increase in size and count of gold nanoparticles on each AgAu@TiO₂ nanoprisms.

Figure 5. 2 UV-Vis spectrum of AgAu@TiO₂ nanoprisms and AgAu@TiO₂/Au nanoprisms with gold nanoparticles deposited on tips of AgAu@TiO₂ nanoprisms.

Figure 5. 3 TEM images of AgAu@TiO₂/Au nanoprisms. (a-c) Photodeposition of Au nanoparticles under visible light (> 650 nm) with increase Au precursor amount (a) 20 μ L, (b) 50 μ L, and (c) 100 μ L. (d-e) Photodeposition of Au nanoparticles under UV light with low Au precursor amount at (d) 20 μ L, (e) 50 μ L and (f) 100 μ L. Site-selectively deposition of Au nanoparticles can be observed at low Au precursor concentration on tips and edged under irradiation of visible light.

Photocatalysis reaction sites on AgAu@TiO₂ nanoprisms are intuitively shown by the locations of photo-deposited Au nanoparticles. Proposed mechanism process of plasmon controlled facet-selective photodeposition of Au nanoparticles on AgAu@TiO₂ nanoprisms is demonstrated in Figure 5.4. Upon surface plasmon excitation, collective charge oscillation of free electron in AgAu nanoprisms induce enhanced local E-field around the nanoparticles, especially at tips and edged of anisotropic nanoprisms [27]. Distribution of plasmon-induced hot electrons are positively correlated to local E field enhancement around the plasmonic nanostructure; hot electrons skip out at tips of plasmonic nanostructure at where experience stronger E field. In the case of an anisotropic plasmonic nanostructure, hot electrons accumulate the tips followed by edges. Plasmon generated hot electrons participate in chemical reactions, and photocatalytic reaction site can be plasmon controlled facet selectively. On the condition of being irradiated under higher energy UV light, electron-hole pairs are generated in TiO₂ semiconductor shell; therefore photocatalysis reaction takes place on the surface of semiconductor shell, Au nanoparticles are deposited randomly on AgAu@TiO₂ nanoprisms.

Figure 5. 4 Structure and mechanism of Au nanoparticles photodeposition onto AgAu@TiO₂ nanoprisms under visible light. Hot electrons generated from plasmonic AgAu nanoprisms skip out at tips of AgAu nanoprisms where support stronger E field enhancement and induce site-selective photodeposition of Au nanoparticles.

Selective deposition of metal nanoparticles onto plasmonic nanostructure have been realized before [37, 38]. Gold nanorod and gold bipyramid are partially coated by SiO₂ on body or tips, which can be achieved by applying different kind and amount of surface surfactant. Semiconductor reacts as a blocking material and prevents metal nanoparticles from deposited under this circumstances, hard templates are required before and during the deposition of metal nanoparticles. The plasmon-assisted approach avoids the necessity of surfactant and blocking templates. This finding has potential in the application that can be plasmon controlled.

5.3 Conclusion

In conclusion, facet-selective photodeposition of gold nanoparticles onto AgAu@TiO₂ nanoprisms was successfully achieved. Under irradiation of visible light contain the LSPR wavelength of the nanoprisms, local E field was largely enhanced around the nanoprisms, especially at the tips and along the edges of the nanoprism, which also confirms the gold nanoparticles deposition site with the appropriate gold precursor amount. This result is solid experimental evidence of the positive correlation between plasmon enhanced E field of anisotropic nanostructure and distribution of hot electrons, which provides a new thought making for utilization of solar energy to chemical energy via anisotropic plasmonic photocatalysts. This site-selective surface functionalization approach is a promising strategy for designing and synthesizing of site-selective overgrowth of metal nanoparticles for plasmon-induced applications.

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Chapter 6

Distance Dependence of Plasmon Enhanced Photocatalytic Hydrogen Evolution of AgAu@TiO₂ and AgAu@TiO₂/Pt Nanoprisms

Plasmonic photocatalysis provides a new pathway for efficient conversion of solar energy into chemical energy. It has been extensively studied that plasmonic metal/semiconductor hybrid nanostructures can offer effective visible light absorption and high hot electron transfer rate. Plasmonic generated hot electrons in plasmonic core transferred into the CB of connected semiconductor and participate in photocatalytic reactions. Herein, taking AgAu@TiO₂ nanoprisms and AgAu@TiO₂/Pt core-shell nanoprisms as plasmonic photocatalyst prototypes, the distance between the plasmonic metal core and chemical reactive site were investigated by tuning the TiO₂ shell thickness precisely. Photocatalytic activities of the hybrid nanostructures in the hydrogen generation under visible light ($\lambda > 600$ nm) depends on TiO₂ shell thickness. Without Pt nanoparticles as co-catalyst, photocatalysis ability decreases as TiO₂ shell increases, which block the plasmon generated hot electrons for surface reactions. With Pt nanoparticles deposited onto AgAu@TiO₂ nanoprisms, photocatalysis activity increases with thicker TiO₂ shell up to 10 nm and then decreases with further increase of TiO₂ shell thickness, which was explained by the electric field damping effect of Pt nanoparticles.

6.1 Introduction

Solar photocatalysis plays an essential role in the conversion of solar energy into chemical energy as the energy crisis and the pollution problems are getting more serious [1, 2]. Semiconductor photocatalysts have been extensively studied since the first published work in 1972 by Fujishima and Honda, photo-excited electrons of TiO₂ electrode under VU light irradiation facilitate water splitting [3]. However, the primary concern of using a semiconductor as a photocatalyst is the wide bandgap which can only absorb UV light (4% of solar radiation). Plasmonic nanostructures made of silver and gold are gaining more attention because of their attractive feature of broadly tunable optical properties across the visible light spectrum (44% of solar radiation). Localized surface plasmon resonance of certain metallic nanostructures is a phenomenon that charge density oscillations confined to plasmonic nanostructures when the nanoparticles are excited by incident light at LSPR wavelength [4]. LSPR wavelength of plasmonic metal nanoparticles can be tuned by manipulating the shape and size of the metallic nanostructure [5-7]. Plasmon excitation of the metal nanostructure can generate energetic hot carriers that can participate in photochemical reactions as well as enhance the surrounding electric field. However, these plasmon generated hot carriers have an extremely short lifetime of (on the order of 10 fs) before thermalization and relaxation [2, 8-10]. A prolonged timescale of photo-generated hot carriers is required to match the timescale of chemical reactions (usually ms ~ s) [11-14]. Cooperating plasmonic metal nanoparticles and semiconductor can obtain synergistic interaction between the two components, the Schottky barrier at the interface of metal/semiconductor traps the plasmon generate hot electrons from recombination with the hot hole to elongate the lifetime of energetic electrons [2, 4, 15, 16]. Hybrid core-shell nanostructures including Au@TiO₂ and Ag@TiO₂ have been synthesized for optimum photocatalytic efficiency [17-20]. Despite with relatively high energy, the travel distance of hot electrons is extremely short, manipulation of hot electrons is still challenging. Decorating co-catalyst is a common strategy used to enhance the photocatalytic ability of semiconductor photocatalysts [21], co-catalysts including Pt, Au, Ag nanoparticles can inhibit the fast recombination of charge carriers. This strategy can be applied to surface plasmon driven devices [22]. However, the use of noble metal as co-catalyst lead to

plasmon coupling with other plasmon component and cause variation of the adjacent electric field. To achieve the full optimization of capability to convert solar energy to chemical energy, utilization of surface plasmon generated hot electrons have yet to be improved. Here AgAu@TiO₂ nanostructures with highly anisotropic plasmonic metal nanoprism as core and TiO₂ as semiconductor shell were synthesized to study the transport of hot electrons. Pt nanoparticles were deposited on AgAu@TiO₂ nanoprisms as co-catalyst, the effects of Pt nanoparticles on the spatial and temporal evolution of hot charge carriers have yet to be studied further.

6.2 Result and Discussion

6.2.1 Synthesis and Characterization of AgAu@TiO₂ Nanoprisms

Ag nanoparticles were synthesized according to a reported seed-mediated growth method and were light induced into silver nanoprisms according to a reported method with slight modification [23, 24]. The Ag nanoprisms as templet were further coated by a thin layer of gold to enhance the stability [24-26]. AgAu nanoprisms have multiple plasmon modes corresponding to charge oscillation along triangular edges, along in-plane facets and perpendicular to the facets [6]. Plasmonic properties of AgAu bimetallic nanoprisms can be tuned by changing the size of the prism, in general, larger nanoprisms lead to red-shift of plasmonic peak [27]. The as-prepared highly anisotropic triangular AgAu nanoprisms with an average length of 50 nm and thickness of 10 nm were employed as the plasmonic metal core (shown in Figure 6.1), and the in-plane dipole plasmon mode is located at 642 nm.

Figure 6. 1 TEM images of a) Ag nanoprisms. b) Ag@Au core-shell nanoprisms. Diameter of AgAu nanoprisms as the plasmonic core is around 50 nm and gold shell thickness is around 3 nm. c) UV-Vis spectrum of silver nanoprisms and AgAu core-shell nanoprisms.

Direct coating of amorphous TiO₂ on AgAu nanoprisms can be achieved by control the hydrolysis of titanium dioxide precursor in a mixed solution of isopropyl alcohol and DI water, titanium diisopropoxide bis(acetylacetonate) (TDAA) was used as the TiO₂ precursor for its slow hydrolysis rate. The TiO₂ shell thickness can be readily tuned by increasing the coating attempts instead of simply increasing the TiO₂ precursor amount, and the latter can cause uneven TiO₂ shell and a significant amount of dissociated TiO₂

nanoparticles. Before each attempt, core-shell nanostructures need to be washed via centrifugation to remove excess free TiO₂ particles in solution; otherwise, the subsequent titanium dioxide would grow on dissociate TiO₂ nanoparticles instead of AgAu@TiO₂ nanoprisms. The coating was performed under a vigorous stirring condition to achieve a uniform and smooth TiO₂ shell. This approach is very reproducible and controllable, high yield of AgAu@TiO₂ core-shell nanoprisms can be obtained with good dispersibility, as shown in TEM images.

TEM images indicate that the size of AgAu nanoprism is very uniform and the thickness of TiO₂ semiconductor shell can be tuned precisely with an increased interval of 5 nm. UV-Vis spectrum shows there is a red-shift of the nanostructure LSPR peak after coated with TiO₂, the ensemble LSPR wavelength is 642 nm, 675 nm, 710 nm, 735 nm and 754 nm for AgAu nanoprisms and AgAu@TiO₂ core-shell nanoprisms with TiO₂ shell thickness of 5 nm, 10 nm, 15 nm and 20 nm respectively (shown in Figure 6.3). The red-shift of LSPR peaks is a manifestation of the overall increase of the refractive index of the dielectric environment of plasmonic AgAu nanoprisms. The LSPR peak further shift with increasing TiO₂ shell thickness as the restoring forces of charge oscillation and local fields around the plasmonic nanostructure are screened. This plasmonic metallic core and semiconductor shell nanostructure satisfies the electron refilling requirement and exhibits plasmon-enhanced H₂ evolution from water splitting under visible light. TiO₂ shell works as a hot electrons filter and further enhance the stability of the nanostructure.

Figure 6. 2 TEM images of AgAu@TiO₂ nanoprisms with different TiO₂ shell thickness. (a) 5 nm. (b) 10 nm. (c) 15 nm. (d) 20 nm.

Figure 6. 3 UV-Vis spectrum of AgAu nanoprism before and after TiO₂ coating, red-shift of LSPR peaks as the AgAu nanoprisms were coated by amorphous TiO₂ and further red-shift of LSPR peak as the TiO₂ shell at 5 nm, 10 nm, 15 nm and 20 nm.

6.2.2 Synthesis and Characterization of AgAu@TiO₂/Pt Nanoprisms

Pt nanoparticles were photo-deposited onto the surface of AgAu@TiO₂ nanoprisms under ultraviolet light. TEM indicates Pt nanoparticles with an average diameter of 1-2 nm were loaded evenly on AgAu@TiO₂ nanoprisms with increasing TiO₂ shell thickness from 5 nm to 20 nm with a 5 nm interval. A red-shift and broadening of LSPR peak can be observed with the Pt deposition for various TiO₂ shell thickness. The broadening of plasmonic peak width is mainly caused by the damping of free electron oscillation in Pt nanoparticles. What's more, as the Pt nanoparticle size is smaller or comparable to electron's mean free path in the nanoparticle's corresponding bulk material (about 10~13 nm for Pt), surface scattering of free electron increases, which further heighten the damping of electron oscillation. UV-Vis spectrum measurement revealed that deposition of Pt nanoparticles causes plasmon damping and broaden the plasmon peak (Figure 6.6).

Figure 6. 4 TEM images of AgAu@TiO₂/Pt nanoprisms with different TiO₂ shell thickness. (a) 5 nm. (b) 10 nm. (c) 15 nm. (d) 20 nm, Pt nanoparticles loaded on AgAu@TiO₂ nanoprisms evenly.

Figure 6. 5 UV-Vis spectrum of AgAu@TiO₂/Pt nanoprism with different TiO₂ shell thickness at 5nm, 10nm, 15nm, 20nm.

Figure 6. 6 UV-Vis spectrum of AgAu@TiO₂ nanoprisms and AgAu@TiO₂/Pt nanoprisms. TiO₂ shell thickness at a) 5 nm, b) 10 nm, c) 15 nm, d) 20 nm. Red-shift and damping of the LSPR peak can be observed, FWHM increase after Pt deposition.

Methanol is necessary for the photodeposition process of Pt nanoparticles as sacrifice agents for homogeneous distribution of Pt nanoparticles. Processes for photodeposition of Pt nanoparticles are different with/without sacrifice agents. With the existence of methanol, the plasmonic peak of AgAu@TiO₂ nanoprisms shifts slightly after the H₂PtCl₆ solution was added even in darkness as methanol favors the adsorption equilibrium [28]. Upon irradiation, plasmonic peak slightly shifts a few nanometers to the longer wavelength at first, followed by a sudden shift of 30~40 nm after 15 min of irradiation, then the red-shift of plasmonic peak becomes moderate until the complete deposition of Pt nanoparticles. This might be the reason of methoxy radicals change the surface properties of amorphous TiO₂ and enhance the adsorption of Pt precursors, after the reaction was irradiated under UV light, electrons generated from TiO₂ trigger the in-situ growth of Pt nanoparticles onto the AgAu@TiO₂ nanoprisms and finally achieved the homogeneous loading of Pt nanoparticle on the surface of AgAu@TiO₂ nanoprisms. Without any sacrifice agent, Pt loading process can take 4-12 hours until complete consume of Pt precursor, the plasmonic peak shifted gently throughout the photodeposition process. Instead of evenly deposited on AgAu@TiO₂ nanoprism, Pt nanoparticles assemble along and extend from the nanoprism (Figure 6.7). This is because that, without methanol, Pt deposition rate is slow at first, Pt ions are reduced by TiO₂ generated electron and form Pt nanoparticles. The first batch of deposited Pt nanoparticles work as co-catalyst and electron sinks and perform as well as the new reactive sites for further Pt nanoparticles deposition. With continuous irradiation, free Pt ions deposited beside the original deposited Pt nanoparticles and assembled into chains of Pt nanoparticles, until all Pt source was consumed. This phenomenon occurs for AgAu@TiO₂ core-shell nanoprisms with various TiO₂ shell thickness.

Figure 6. 7 TEM images of AgAu@TiO₂ nanoprisms with unevenly loaded Pt nanoparticles for core-shell nanostructure with a) 5 nm TiO₂ shell, b) 20 nm TiO₂ shell.

Figure 6. 8 UV-Vis spectrum of photodeposition of Pt nanoparticles onto AgAu@TiO₂-10 nm nanoprisms a) with methanol as sacrificial agent b) without methanol as sacrificial agent.

6.2.3 Photocatalytic of AgAu@TiO₂ Nanoprisms and AgAu@TiO₂/Pt Nanoprisms

The photocatalytic activity of the nanoprisms was investigated via hydrogen generation from formic acid under visible light. One millilitre of photocatalytic aqueous solution was mixed with 10 μ L of formic acid (98%) and 9 ml DI water; the mixture was irradiated for 6 hours, a 600 nm cut-off optical filter was used in consort with a 300W Xe lamp. The photocatalytic activities of pure AgAu metal nanoprisms and TiO₂ nanoparticles were both extremely low under visible light. Meanwhile hybridizing AgAu@TiO₂ nanostructures can give rise to hydrogen generation, especially for AgAu@TiO₂-5nm core-shell nanoprisms

(Figure 6.10). In the case of AgAu@TiO₂ with TiO₂ shell thickness increases to 10 nm, hydrogen generation volume drop to below half. The photocatalytic ability of AgAu@TiO₂ nanoprisms inverse propagate with TiO₂ shell thickness, as TiO₂ shell reaches 20 nm, little hydrogen can be detected after 6 hours of irradiation. The hybridization of plasmonic metal core and semiconductor shell can promote the process of chemical energy converted from visible light, but the thick TiO₂ shell will drag down the efficiency. Based on the above results, a photocatalysis process for HER using AgAu@TiO₂ core-shell nanoprisms as photocatalysts is proposed. Upon irradiation under visible light, AgAu nanoprisms as the plasmonic core can generate hot electrons with high potential energy; however, those plasmon-induced hot electrons have extremely short lifetimes on the order of 10 fs [8] while the time scale for chemical reactions is approximately microseconds to even seconds. Hybridizing AgAu nanoprisms with amorphous TiO₂ will evade the fast relaxation of hot carriers and bridge the gap between the lifetime of hot electrons and timescale of chemical reactions. The Schottky barriers between AgAu and TiO₂ shell elongate the lifetime of plasmonic generated hot electrons. Amorphous TiO₂ affords efficient electron transport [29] and functions as an electron filter. The photocatalytic ability decreases with increasing TiO₂ shell thickness as less hot electrons pass through the TiO₂ layer and participate in surface chemical reactions. The travel distance of hot electrons can reach as long as 20 nm in amorphous TiO₂ after skipped out of AgAu nanoprisms. A TiO₂ shell can extend the lifetime of plasmon generated hot electrons, however, the recombination of hot electron-hole pairs still hinder the photocatalytic efficiency. SPR enhanced electromagnetic field might also facilitate the photocatalytic reaction, as hot electrons transfer to TiO₂ surface as the reactive site, the nearer the reaction site from the plasmonic core, the stronger the electromagnetic field is [30]. The enhanced electric field hinder the recombination of hot electrons in semiconductor and holes left in metal, which is the main problem inhibit efficient photocatalytic reactions.

The photocatalytic ability can be further enhanced by cooperating with Pt nanoparticles deposited as co-catalyst. After generated in plasmonic AgAu nanoprism and transferred to the CB of TiO₂ shell, a fraction of hot electrons pass through the TiO₂ shell and captured by Pt nanoparticles, following participate in water splitting reactions. Pt nanoparticles serve

as electron sinks and delay hot electrons from travelling back to metal cores [31]. Hot holes were left behind in AgAu and consumed in oxidation half-reaction. Photocatalytic efficiency was dramatically enhanced by 10 times after cooperating with Pt nanoparticles for AgAu@TiO₂-10nm. Pt nanoparticles were loaded as co-catalyst and directly manipulating the pathway of hot electrons. Pt nanoparticles serve as electron storage and delay the re-combination of hot electron-hole pairs.

Figure 6. 9 Volume of H₂ generated under visible light irradiation (>600nm) using a) AgAu@TiO₂ nanoprisms and b) AgAu@TiO₂/Pt nanoprisms with different TiO₂ shell thickness.

An interesting finding that after Pt loading, AgAu@TiO₂ with thin TiO₂ shell at 5 nm does not possess the highest photocatalytic efficiency under visible light among all AgAu@TiO₂/Pt nanoprisms as expected. Without co-catalyst, a thinner layer of TiO₂ coated would trap the hot electron from thermalization and also allow a larger portion of hot electrons to pass and then captured by Pt nanoparticles. This may because the SPR-enhanced electromagnetic field got hindered by adjacent Pt nanoparticles, as EM field might also facilitate the electron-hole pairs' separation and promote the photocatalytic ability. As the distance between the plasmonic core and reactive site increases, lesser hot electrons can pass through the TiO₂ shell; however, more portion of those hot electron would be captured by Pt nanoparticles and participate in photocatalytic chemical reactions. Electromagnetic field damping caused by plasmon coupling between the AgAu and Pt NP become weaker as the gap distances increase. As hot electron transferred yield and recombination ratio of hot carriers achieve equilibrium, photocatalytic efficiency reaches as maximum. As TiO₂ shell between the plasmonic core and reactive site Pt nanoparticles

becomes thicker from 10nm to 15nm, fewer electrons have enough energy to pass through the blockage semiconductor. Further increases of TiO₂ shell thickness will cause insulation of plasmonic AgAu core from visible light as the energy input and converted into chemical energy as water splitting. Proposed photocatalytic process for hydrogen generation under visible light using AgAu@TiO₂ nanoprisms and AgAu@TiO₂/Pt nanoprisms are shown in Figure 6.10.

Figure 6. 10 Schematic photocatalytic process for H₂ generation under visible light using a) AgAu@TiO₂ nanoprisms and b) AgAu@TiO₂/Pt nanoprisms.

6.3 Conclusion

In conclusion, core-shell structures AgAu@TiO₂ nanoprisms and AgAu@TiO₂/Pt nanoprisms with different TiO₂ shell thickness were successfully synthesized. The photocatalytic abilities of the hybrid nanostructures were evaluated via hydrogen generation from formic acid under visible light (> 600 nm). Without Pt nanoparticles, photocatalytic ability decrease with an increase of semiconductor shell as less plasmonic generated hot electrons pass through. With Pt nanoparticles deposited onto the AgAu@TiO₂ nanoprisms surface as co-catalysts, hydrogen generation efficiency increase then decrease with increase TiO₂ shell. The may be caused by plasmon coupling of AgAu nanoprisms nearby Pt nanoparticles, the plasmon damping of Pt nanoparticles hinder the enhancement of electromagnetic field around the nanoprisms and lower the hot electron output. This approach provides a new strategy for designing plasmon-based metal and semiconductor hybrid nanostructures for photocatalytic applications.

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Chapter 7

Discussion and Future Work

In chapter 7, a general discussion is given to conclude the overall thesis. To investigate the behaviors of plasmon-induced hot electrons, plasmonic metal/semiconductor nanostructures based on AgAu nanoprisms and titanium dioxide have been synthesized and introduced. First, the enhanced photocatalysis ability of Janus nanostructure compares with core-shell nanostructure stresses the necessity of rational design of photocatalytic nanostructures. Second, selective photodeposition of gold nanoparticles onto AgAu@TiO₂ nanoprisms explains the relationship between hot electron distribution and electric field enhancement for an anisotropic nanostructure. Third, transfer routes of plasmon-induced hot electrons were studied via investigating the HER efficiency of AgAu@TiO₂ and AgAu@TiO₂/Pt core-shell nanoprisms. The hot electron transfer mechanism, the effect of SPR enhanced electromagnetic field on hot electron distribution and energetic carrier separation have been discussed. However, many questions remained to be answered. Based on the current research status, works that can be done in the near future is also discussed.

7.1 General discussion

This thesis focus on the plasmon-induced hot electron photochemistry based on hybrid AgAu and TiO₂ nanostructures. AgAu/TiO₂ Janus nanostructure, AgAu@TiO₂ core-shell nanostructure were successfully synthesized and investigated for photocatalytic hydrogen generation reactions under visible light.

7.1.1 Discussion on the Janus AgAu/TiO₂ nanostructure for photocatalysis

Rational design of a plasmonic nanostructure for photocatalysis applications is essential for utilization of solar energy to chemical energy transfer efficiency. Hybridization plasmonic metal and semiconductor has been recognized as the typical strategy to facilitate the plasmon-induced charge separation via forming an interfacial Schottky Barrier and trap the hot electrons from travelling back and recombine with hot holes left in metal [3, 7]. The conventional hybrid structures include plasmonic metal@semiconductor core-shell nanostructures and semiconductor decorated with metal particles.

For the first time, a Janus AgAu/TiO₂ nanostructure composed of AgAu nanoprism and TiO₂ nanosphere was reported. TiO₂ nanospheres were attached on only one side of AgAu nanoprisms with the other side exposed. The photocatalytic ability under visible light toward HER was evaluated and compared with AgAu@TiO₂ core-shell nanoprisms. The Janus nanostructure exhibited enhanced photocatalytic activity due to the short distance between hot electron generation location and the reactive site, which is believed at the three-phase interphase of AgAu nanoprism, TiO₂ and environment. Knowing the location of the hot electron is essential for better understanding of photocatalytic reaction process in hybrid nanostructures. Location of the reactive site was verified via plasmon assisted photodeposition of gold nanoparticles under visible light. Gold nanoparticles deposition site was revealed by TEM characterization, and it is confirmed that the gold nanoparticles were selectively deposited at the three-phase area. Upon excitation, hot electron concentrated at the tips and along the edges of AgAu nanoprisms, which was discussed in the previous section. The nanoprisms tips and edges also locate close to TiO₂ hemisphere;

therefore the concentrated hot electrons can be easily transferred to the semiconductor and participate in photocatalytic reactions. In addition, the reaction site locates adjacent to the nanoprism tips and edges, the SPR-enhanced electromagnetic fields also facilitate electron-hole separation and allow high yield of hot electrons participate in photochemical reactions. SPR enhanced electromagnetic field declines dramatically with distance increase from the plasmon nanoparticles surface; therefore the spatial location of the reactive site should be considered. This synthetic strategy of Janus nanostructure opens up a new way to control the plasmon-induced hot electrons for enhanced catalytic reactions. To investigate the relationship between plasmonic generated hot electron distribution and the electromagnetic field was investigated in the second part of this thesis.

7.1.2 Discussion on the facet-selective gold photodeposition onto AgAu@TiO₂ nanoprisms

Anisotropic plasmonic nanostructures can generate hot electrons for redox reactions and induce re-distribute local electromagnetic field enhancement on different crystal facets under plasmon excitation. The correlation between the electric field enhancement on different crystal facets and hot electron distribution become critical. For silver nanoprisms, the local electromagnetic field enhancement is strongest at the three prism tips, followed by the three edge facets and the cover facet under plasmon excitation [6].

In this section, the plasmon controlled facet selective metal deposition was reported, in which gold nanoparticles were successfully grown on tips, along with the side edges and on facets of AgAu@TiO₂ nanoprisms by controlling the irradiation wavelength range and gold precursor amount. As the AgAu@TiO₂ nanoprisms were irradiated under LSPR wavelength, energetic electron-hole pairs were generated and ejected from the plasmonic nanoparticles, and the hot electrons were captured in the CB of TiO₂ shell via PMET process. The acceptor hot electrons then transferred to the surface of the nanostructure and are involved in photochemistry, such as reduction of metal ions. The gold precursor in the reaction system was reduced to gold atoms, and the gold atoms grew into gold nanoparticles which can be observed in TEM images. The gold nanoparticles deposition

site accord with the hot electron concentration ejection location. Under irradiated by visible light with the wavelength longer than 650 nm (LSPR wavelength of AgAu@TiO₂ nanoprisms) and with a small amount of gold precursor, gold nanoparticles were found to be deposited only at the tips of the AgAu@TiO₂ nanoprisms, where experience strongest electromagnetic field enhancement under plasmon excitation. With an increase of gold precursor concentration, photo-deposited Au NPs were observed at the tips and along the edges of the nanoprisms with the cover facets blank or only a few gold nanoparticles attached. Further increase of gold precursor causes the loading of gold nanoparticles all over the AgAu@TiO₂ nanoprisms. To exclude the source of electrons were generated from the semiconductor, gold photodeposition was also performed under UV light and no preference of deposition site of gold nanoparticles was observed. The result illustrates the distribution of plasmon-induced hot electron is correspond to the LSPR enhanced local electromagnetic field of a plasmonic anisotropic nanostructure. For the first time, plasmon controlled site-selective deposition of metal nanoparticles onto plasmonic nanostructure was achieved. This strategy is applicable for precise surface modification of plasmonic nanostructures.

7.1.3 Discussion on the AgAu@TiO₂, AgAu@TiO₂/Pt and their photocatalytic ability

For this part, hybrid plasmonic metal/semiconductor core-shell nanostructures were synthesized to investigate the transfer pathway of plasmon-induced hot electrons and the effect of local electron field to the hot electrons. AgAu nanoprisms were employed as plasmonic core and source of plasmon-induced hot electrons. TiO₂ semiconductor shell was coated on the plasmonic core to form a core-shell nanostructure, and the TiO₂ shell acts as a hot electron filter by trapping the hot electrons in the conduction band [1]. By evaluating the photocatalytic ability of core-shell nanostructure with different semiconductor shell thickness, transfer pathway of plasmon-induced hot electrons can be predicted.

Under plasmon excitation, hot electrons generated in plasmonic metallic AgAu nanoprism core and captured in the conductor band of TiO₂ as a semiconductor shell by Schottky

barrier [2, 3]. However, only the hot electrons with sufficient energy can pass through the TiO_2 shell and reach the photocatalysis reaction reactive site on the AgAu@TiO_2 surface. The recombination of hot carriers is still the primary factor impeding the photocatalytic ability of plasmonic assistant photocatalysts. A short distance between the hot electron generation location and reaction site lessen the recombination rate of hot carriers as more hot electrons can reach the environment before depleting their energy. Furthermore, the local electromagnetic field enhancement given rise by the free electron oscillation around the plasmonic nanostructure decrease progressively with further distance extend into the environment, the stronger local electromagnetic field promotes the separation of hot electrons and hot holes. The AgAu@TiO_2 core-shell nanoprisms with thin TiO_2 shell experience higher photocatalytic ability than nanostructure with TiO_2 shell thickness at 10 nm, 15 nm and 20 nm, and photocatalytic ability decreases with TiO_2 shell thickness increases, in another word, longer distance from the reactive site and weaker local field. The TiO_2 shell serves as an electron acceptor and reactive site provider, whereas the obstruction for electron transfer. This hypothesis was further verified by comparing the hydrogen production rate of $\text{AgAu@TiO}_2/\text{Pt}$ nanoprisms with different TiO_2 shell thickness. In this case, Pt nanoparticles function as co-catalyst, which is a common strategy used in photocatalyst nanostructures design [4]. Pt nanoparticles as electron sinks can hinder the recombination of hot electron/hole pairs and back transfer of the hot electrons to AgAu core. However, Pt as a metal with high imaginary part of Pt's dielectric function at the visible light resonant wavelength, which can cause damping of electromagnetic field enhanced by the plasmonic AgAu core. The plasmon coupling between AgAu nanoprisms and Pt nanoparticles is highly dependent on the interval distance [5]. Unlike AgAu@TiO_2 nanoprisms without the influence of Pt nanoparticles, thinner semiconductor shell would benefit the charge transfer and electron-hole pair separation, photocatalytic ability of $\text{AgAu@TiO}_2/\text{Pt}$ nanoprisms with thin TiO_2 shell at 5 nm is weaker than nanoprisms with a thicker TiO_2 shell of 10 nm. The photocatalytic ability of hydrogen generation under visible light decreases with further increase of gap between AgAu nanoprisms and Pt co-catalyst. The nonlinear relationship between photocatalytic ability and hot electron generation location to reaction site distance is caused by the electromagnetic field

discrepancy. The plasmon damping caused by adjacent Pt nanoparticles might affect the hot electron generation and electron-hole separation.

7.2 Reconnaissance

7.2.1 Anisotropic growth of TiO₂ onto AgAu nanoprisms for plasmon enhanced photocatalytic reactions

In chapter 4, Janus nanostructure with TiO₂ nanoparticle attached on one side of AgAu nanoprisms was successfully synthesized. To further investigate the effect of SPR-enhanced electromagnetic toward hot carriers separation, the anisotropic growth of TiO₂ onto AgAu nanoprisms need to be prepared. TiO₂ can be partially coated on the tips or the cover facets of AgAu nanoprisms. Theoretically, tip-coated nanostructure will have better photocatalytic ability compare with TiO₂ deposited on the flat facets of the AgAu nanoprisms. The hot electrons trapping site is the active site for surface chemical reactions, while the hot electrons are trapped near the tips of AgAu nanoprisms, the enhanced local electromagnetic field at the nanoprism tips contributes to the behaviors of hot electrons, result in enhanced photocatalytic ability compare with cover faced covered nanoprisms.

7.2.2 Plasmon induced hot holes from anisotropic nanostructures

The relationship between SPR enhanced electromagnetic field and hot electron generation distribution was investigated in chapter 5. However, the generation and the transfer path of hot holes was not discussed. So far, a few studies have been reported regarding the dynamics of plasmon-induced hot holes [12, 13]. While the hot electrons participated in photodeposition of gold nanoparticles, the hot holes were consumed in photochemical oxidation reactions. To investigate the distribution of plasmon-induced holes on anisotropic nanostructure, AgAu@TiO₂ nanoprisms can be used as plasmonic phototype. To observe the photogenerated hot hole in this photocatalytic system, photooxidation deposition of PbO₂ nanoparticles under LSPR wavelength can be conducted [13]. The reaction equation of PbO₂ photodeposition is listed as below:

Under irradiate of visible light (LSPR wavelength), hot carriers were ejected from AgAu nanoprisms and participated in photodeposition. The hypothesis is the distribution of plasmon-induced hot holes is same with hot electrons, in other words, positively correlated with the SPR-enhanced electromagnetic field. Therefore theoretically, several PbO_2 nanoparticles will be selectively deposited at the tips of AgAu@TiO₂ nanoprisms with appropriate Pb^{2+} concentration, with the increasing amount of PbO_2 precursor, nanoparticles will start to grow along the three side edges of AgAu@TiO₂ nanoprisms. Upon illumination with full spectrum light, PbO_2 nanoparticles will be loaded on AgAu@TiO₂ nanoprisms without site preference. The reaction site of photooxidation chemical reaction can be characterized via TEM and elemental mapping analysis.

7.2.3 Controlling hot electrons via plasmon coupling

In chapter 6, AgAu@TiO₂/Pt nanoprisms were successfully synthesized. Pt nanoparticles deposited on AgAu@TiO₂ nanoprisms as co-catalyst largely enhanced the photocatalytic ability of the nanostructure towards hydrogen generation under visible light. However, the small gaps between AgAu core and Pt nanoparticles induce strong plasmon coupling [8, 9], the high imaginary part of Pt dielectric constant under visible light caused damping of the electromagnetic field of AgAu nanoprism. So far, most of the studies on plasmon coupling are investigating the dimer of nanoparticles with the same material, nanoparticle size and shape [10, 11]. In the future work, the effect of plasmon coupling between nanoparticles with different size and material can be investigated. AgAu nanoprism can be employed as plasmonic core and coated by a thin layer of SiO₂ as semiconductor shell, plasmonic nanoparticles such as Au, Ag, Pd and Pt can be further loaded onto the core-shell nanostructure. In these systems, plasmon coupling between AgAu core and deposited plasmonic nanoparticles can lead to peculiar properties such as further enhancement of electric field and optical absorption enhancement of surrounding molecules.

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