Ligand-controlled preparation and fundamental understanding of anisotropic gold nanostructures

Xia, Jing

2018

Xia, J. (2018). Ligand-controlled preparation and fundamental understanding of anisotropic gold nanostructures. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/75887>

<https://doi.org/10.32657/10356/75887>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**LIGAND-CONTROLLED PREPARATION AND
FUNDAMENTAL UNDERSTANDING OF ANISOTROPIC GOLD
NANOSTRUCTURES**

XIA JING

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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FUNDAMENTAL UNDERSTANDING OF ANISOTROPIC GOLD
NANOSTRUCTURES**

XIA JING

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.

10/01/2018

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Date

Xia Jing

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Xia Jing

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Dong ZhiLi

Authorship Attribution Statement

This thesis contains material from a paper submitted in the following peer-reviewed journal where I was the first author.

Chapter 5 is submitted substantially as J. Xia, Z. L. Dong, X. Hu and M. Y. Han. Morphological growth and theoretical understanding of gold and other noble metal nanoplates. *Chemistry – A European Journal*. 2018.

The contributions of the co-authors are as follows:

- I prepared the manuscript, designed and conducted experiments, characterized samples and analyzed results.
- Prof Dong Zhili conducted the HRTEM characterization, analyzed results and revised the manuscript.
- Dr Cai Yongqing conducted partial simulation.
- Dr Guan Guijian conducted partial simulation.
- Dr Zhang Shuangyuan designed partial synthetic method.
- Dr. András Kovács conducted the HRTEM characterization.
- Dr. Chris Boothroyd analyzed the HRTEM results.
- Dr. In Yee Phang conducted the AFM characterization.
- Dr. Liu Shuhua analyzed partial results of UV-vis-NIR absorption.
- Wu Mingda conducted partial SAED characterization.
- Dr Zhang Yong Wei analyzed and interpreted the simulation results.
- Prof Hu Xiao supervised student, analyzed results and revised manuscript.
- Dr. Han Ming-Yong revised the manuscript, designed experiments and analyzed results.

10/01/2018

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Date

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Xia Jing

Abstract

In these decades, Au nanostructures have been demonstrated to be promising nanomaterials in catalysis, detection and biomedicine. The merit of these applications mainly arises from the expression of properties with strong correlations to their shape and size. Thus, well control of Au nanostructures in shape and size is important in improving their properties and applications. To synthesize morphology-controlled Au nanostructures, well understanding of their growth mechanism is crucial. Therefore, the main objective of this thesis is to prepare anisotropic Au nanostructures and understand their growth mechanism behind.

Colloidal growth of Au nanostructures has been exploring for decades via chemical reduction of AuCl_4^- . The intermediate process is very difficult to investigate during the fast reduction of Au^{3+} to Au^0 , and thus it is of importance to explore the slow reduction for study of intermediate process with a series of weak reducing agents possessing typical aldehyde groups (i.e., HCOH , HCOOH , HCONH_2 , HCOCH_3 and $\text{HCON}(\text{CH}_3)_2$). The binding energies of Au^{n+} ($n = 3, 1$ and 0) to ligands are simulated to exhibit binding different affinities to starting, intermediate and final Au species. In an optimized slow reaction in which ligands show stronger binding affinities to Au^+ than Au^{3+} and Au^0 , intermediate process that the formation and disproportionation of Au^+ is demonstrated. For example, formic acid has much stronger binding affinity to Au^+ than Au^{3+} so that intermediate Au^+ is able to be captured during the slow reduction of Au^{3+} .

Upon the disproportionation of Au^+ to Au^0 and Au^{3+} , the binding affinity of ligands to different Au facets and Au^0 is crucial in controlling growth of anisotropic Au nanostructures. The adsorption of various ligands causes substantially decreased surface energies on different Au planes. There are much higher energies on $\{110\}$ planes compared to the other two $\{111\}$ and $\{100\}$ planes with certain ratios in these energies, leading to morphological growth of Au nanoplates by various organic ligands. Meanwhile, ligands with stronger binding energies to Au^0 have stronger effect in controlling the anisotropic growth of Au nanostructures.

Furthermore, Ag, Pd and Pt nanosheets are successfully prepared via this facile synthetic method. In addition, using the as-prepared Au nanoplates as templates, ultrathin Au nanosheets with average thickness of ~1.5 nm and bimetallic nanostructures maintaining the plate-like shape are also produced.

Lay Summary

Because of the relative rarity, easy fabrication and distinctive color, Au is regarded as valuable metal, and it has been used for coinage, jewelry and other arts historically. In nanoscale, Au also has attracted much attention, since it shows promising applications in detecting toxic chemicals and killing cancer cells. To prepare Au nanostructures, it is vital to understand how Au nanostructures are formed. Therefore, this project aims to synthesize Au nanoplates and demonstrate their formation mechanism.

In this thesis, a formation mechanism of Au nanoplates is suggested based on the comparative results of various ligands controlled synthesis of Au nanostructures. In the growth of Au nanostructures, Au^{3+} is first reduced to intermediate Au^+ followed by disproportionation of Au^+ to form Au atoms, and surface energies of ligand-bound gold planes with certain energy ratios together with binding affinities play an important role in the anisotropic growth of Au nanostructures. Meanwhile, this simple synthetic method is successfully utilized to prepare Ag, Pd and Pt nanosheets. Furthermore, ultrathin Au nanosheets which are approximately 1.5 nm in average thickness and Au based bimetallic nanoplates are also prepared by using the as-prepared Au nanoplates as templates. Overall, in this work, the growth of Au and bimetallic nanostructures are experimentally demonstrated and the understanding of their growth mechanism behind is provided by controlling the interaction between various organic ligands (i.e., HCOH , HCOOH , HCONH_2 , HCOCH_3 and $\text{HCON}(\text{CH}_3)_2$) and different Au species (i.e., Au^{3+} , Au^+ and Au^0). This novel method for investigating the growth of Au nanostructures provides an approach to study the formation of other metal nanostructures and guide the fabrication of Au nanostructures.

Acknowledgements

Here in, I would like to show great gratitude to my supervisors, Associate Professor Dong Zhili, Dr. Han Mingyong and Prof. Hu Xiao for their patience, immense knowledge, guide and encouragement during my PhD career since the beginning of 2014. Their ideas and recommendations helped me a lot during this project.

My appreciation goes out to lab members in Associate Professor Dong Zhili's group, Shunkuang, Wu Mingda, Yao Bingqing, Wen Cong, Yuan Zhe, Wang Fei and Disha, for their help during my study. I did enjoy my research life here on the campus of NTU. Moreover, I will never forget the help from all staffs in IMRE. I would like to thank all my lab mates, for all moments we spend together. In particular, I am grateful to Dr. Zhang Shuangyuan, since he was my mentor when I started this project in IMRE.

Many thanks go to Dr. Andras Kovacs and Dr. Christopher Brian Boothroyd, the scientists from Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Peter Grunberg Institute, Forschungszentrum Julich, Germany, who assisted me to characterize and analyze my samples.

Besides, I would like to thank school of Materials Science and Engineering and FACTS for providing well-equipped laboratories and advanced equipment for my research.

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Abbreviations

NIR	Near InfraRed
PPT	Plasmonic Photothermal Therapy
ROS	Reactive Oxygen Species
CTAB	Cetyltrimethylammonium Bromide
PEG	Polyethylene Glycol
SERS	Surface Enhanced Raman Scattering
CCD	Charge-Coupled Device
NaBH ₄	Sodium Borohydride
TOAB	Tetraoctylammonium Bromide
GA	Gum Arabic
TOAB	Tetradodecylammonium Bromide
BDAC	Benzyltrimethylhexadecylammonium Chloride
UPD	Underpotential Deposition
SPR	Surface Plasmon Resonance
LSPR	Localized Surface Plasmon Resonance
TERS	Tip-Enhanced Raman Scattering
DNA	Deoxyribonucleic Acid
ROS	Reactive Oxygen Species
TEM	Transmission Electron Microscopy
HRTEM	High Resolution Transmission Electron Microscopy
EDX	Energy Dispersive X-Ray
SEM	Scanning Electron Microscopy
AFM	Atomic Force Microscopy
XRD	X-Ray Diffraction
ESI-MS	Electrospray Ionization Mass Spectrometry
UV	Ultraviolet
I ₀	Incident Light
I	Transmitted Light
T	Transmittance

A	Absorbance
FTIR	Fourier Transform Infrared Spectroscopy
ATR	Attenuated Total Reflectance
VASP	Vienna Ab initio Simulation Package
PVP	Polyvinylpyrrolidone
HCOOH	Formic Acid
HCOH	Formaldehyde
HCOCH ₃	Acetaldehyde
HCONH ₂	Formamide
HCON(CH ₃) ₂	N, N-dimethylformamide
DFT	Density Functional Theory
NPL	Nanoplate
γ	Surface Energy
E _b	Binding Energy
fcc	Faced Centred Cubic
PDMS	Polydimethylsiloxane

Chapter 1

Introduction

In this chapter, the background in the preparation of gold nanostructures is first presented. Gold nanostructures have been demonstrated to be promising nanomaterials in catalysis, biomedicine and detection. To improve their properties and applications, it is of importance to understand their growth mechanism. On the basis of above, the hypotheses, objectives and scope of this work are presented. This is followed by the dissertation overview of this thesis and main outcomes of this work.

1.1 Problem Statement and Hypothesis

1.1.1 Problem Statement

Au nanostructures with at least one dimension less than 100 nm, [1] display unique properties which are faded in their molecular or bulk structures. They have promising diverse applications in catalysis, imaging, detection and therapeutics. [2-11] The merit of these applications mainly arises from the expression of properties with strong correlations to their size, shape, structure and dispersity. [1] For example, morphology control provides an effective method to maneuver optical applications of Au nanostructures. [12] Therefore, preparation of high-quality Au nanostructures with well-controlled shape, size and structure is of importance. To fabricate Au nanostructures with high quality, it is crucial to have a sufficient understanding of their growth mechanism.

As a facile and easy-controlled method [13-15], colloidal growth has been widely applied to prepare Au nanostructures via chemical reduction of HAuCl_4 [16-19]. In the reduction of HAuCl_4 , strong reducing agents [20, 21] (e.g., sodium borohydride) are commonly used. However, with strong reducing agents, the reduction of Au^{3+} to Au^0 is rapid and thus difficult to reveal its intermediary process, which greatly hinders the investigation of the mechanism for Au nanostructure growth and in turn hampers their applications. Meanwhile, thermal decomposition of solid $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ for preparation of Au nanoparticles in artificial air is via the formation of intermediate AuCl . [22] As such, this implies that intermediate Au^+ could also be observed and further captured in liquid phase during reduction of Au^{3+} . To improve the understanding of growth mechanism of Au nanostructures, it is crucial to explore the intermediate Au^+ in liquid phase during the growth of Au nanostructures which has been seldom reported.

In addition, advances in developing synthetic methodologies and understanding underlying formation mechanisms of anisotropic Au nanoplates which show diversity applications in biomedicine and detection [23-27] have been realized recently. Generally, plate-like seeds mediated mechanism is suggested to explain the formation of Au nanoplates. [1, 28] However, this mechanism only investigates the nucleation and emphasizes the influence of seeds in the formation of Au nanoplates. The role of other

factors such as ligands is ignored in this mechanism. To enrich the understanding of formation mechanism, novel methods for investigating the formation mechanism of Au nanoplates are needed.

1.1.2 Hypothesis

1. In a slow reduction of Au^{3+} to Au^0 with weak reducing agents, intermediate process may be observed in liquid phase at optimized conditions during growth of Au nanostructures.
2. Intermediate Au^+ may be captured before reducing to Au^0 by ligands with appropriate coordination ability to Au^{n+} ($n = 3, 1, 0$).
3. The mechanism for morphological growth of Au nanoplates may be demonstrated experimentally and computationally by using a series of organic molecules with similar HCO-R formula ($\text{R} = \text{-H, -OH, -NH}_2, \text{-CH}_3$ and $\text{-N(CH}_3)_2$) that possess different coordination capability to Au as ligands for achieving comparative data.

1.2 Objectives and Scope

The main objective of this project is to experimentally demonstrate and theoretically understand the growth of anisotropic Au nanostructures through tuning interactions between a series of similar ligands and Au species with variable valence (i.e., Au^{3+} , Au^+ and Au^0).

To achieve this objective, the research work was carried out as follows:

1. Design a simple reaction system to synthesize anisotropic Au nanostructures in which only three basic parameters, Au precursors, ligands and stabilizers were included, making it easy to study the formation of anisotropic Au nanostructures experimentally and theoretically.
2. Choose a series of simple organic molecules with similar HCO-R formula ($\text{R} = \text{-H, -OH, -NH}_2, \text{-CH}_3$ and $\text{-N(CH}_3)_2$) that possess weak reducing and different coordination capability as ligands for obtaining comparative data.

3. Investigate the intermediate process during the formation of Au nanostructures through evaluating the binding affinities of various ligands and Au^{n+} ($n = 3, 1, 0$) computationally and monitoring the reaction by TEM, UV-vis-NIR spectrometer, ESI-MS experimentally.
4. Study the morphological growth of anisotropic Au nanostructures through comparing ligands-bound surface energies, binding energies between different ligands and Au atoms, and morphology of Au nanostructures after adsorption of different ligands.
5. Explore the influence of ligands on morphologies of formed Au nanoplates through heating as-prepared Au nanoplates in the solution of ligands.

1.3 Dissertation Overview

There are 7 chapters included in this thesis and they are introduced briefly as follows:

Chapter 1 states the problems in the formation of Au nanostructures. The hypotheses, overall scope, and objectives of this project are presented. It also lists the dissertation overview and innovative outcomes.

Chapter 2 reviews the current research of Au-based monometallic and bimetallic nanostructures. The synthetic strategies and applications of Au nanostructures, and a brief introduction of Au-based bimetallic nanostructures are presented in this chapter.

Chapter 3 describes the methods to calculate the Au amount in the experiment and the techniques used for material characterization.

Chapter 4 demonstrates a facile method to prepare Au nanoplates and other noble metal nanoplates. The structural characterization and optical properties of Au nanoplates are analyzed, and approaches to optimize the reaction system are also discussed.

Chapter 5 demonstrates anisotropic growth of Au nanoplates experimentally by using various organic ligands with weak reducing and coordination capability, and further provides insights to understand their growth mechanism behind.

Chapter 6 presents the synthesis of ultrathin Au nanoplates and Au-based bimetallic nanoplates. Their structural characterizations are conducted and formations are discussed.

Chapter 7 summaries the research findings and suggests methods for future research.

1.4 Findings and Outcomes

This research led to several novel outcomes by:

1. Providing a facile one-step method to fabricate Au and other noble metal nanoplates, and exploring the optical property of Au nanoplates.
2. Demonstrating experimentally and understanding theoretically the morphological growth of anisotropic Au nanostructures by using a series of organic ligands with similar HCO-R formula (R=H, -OH, -NH₂, -CH₃ and -N(CH₃)₂) that possesses weak reducing and coordination capability through tuning interactions between various ligands and variable valence Au species (i.e., Au³⁺, Au⁺ and Au⁰).
3. Demonstrating the formation and disproportionation of intermediate Au⁺ during the growth of Au nanostructures by capturing the intermediate Au⁺ in an optimized condition.
4. Fabricating ultrathin Au nanosheets and Au-based bimetallic nanoplates by using as-prepared Au nanoplates as templates.

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Chapter 2

Literature Review

This chapter presents the current research progress on gold-based nanostructures in literatures. It starts with a brief introduction of the synthetic methods of gold nanostructures, including the fabrication of gold nanoparticles, gold nanorods, gold nanoplates, gold nanopolyhedra and branched gold nanostructures. Their applications in optical, catalytic and biological fields are then discussed. Finally the synthesis and applications of gold based bimetallic nanostructures containing Au/Pt, Au/Pd and Au/Ag bimetallic nanostructures are summarized.

2.1 Synthetic Methodologies of Gold Nanostructures with Different Morphologies

In these decades, increasing attention has been paid to develop synthetic methods to prepare Au nanostructures with diversity morphologies due to the strong correlations between morphologies of Au nanostructures and their applications. For example, lots of methods to fabricate Au nanorods and branched nanostructures which show unique optical and biomedical applications, have been reported. In this part, a brief overview of synthetic methods to prepare Au nanoparticles, nanorods, nanoplates, nanopolyhedra and branched nanostructures are provided.

2.1.1 Gold Nanoparticles

In creating Au nanoparticles, numerous synthetic strategies have been developed. In this section, we briefly describe different synthetic methods for successfully preparation of Au nanoparticles.

Typically, the preparation of Au nanoparticles includes the reduction of Au ions to Au atoms by a reducing agent and stabilizing of nanostructures by a stabilizer or surfactant. In 1951, Turkevich *et al.* synthesized Au nanoparticles by reducing HAuCl_4 in boiling water with citric acid which acts as both stabilizer and reducing agent. [1] Frens further employed this method to prepare Au nanoparticles with different sizes by adjusting the Au/citrate ratio. [2] Nowadays, this citrate-stabilized method has been widely utilized to prepare Au nanoparticles. [3, 4]

Figure 2.1 Schematic formation mechanism for Au nanoparticles [8]. © 2010 American Chemical Society

For the shape and size control of Au nanoparticles, the well-understanding mechanism of the growth of Au nanoparticles is required. As a classical and facile protocol, several mechanistic explanations for the formation of Au nanoparticles synthesized through citrate-stabilized method have been reported. [5-8] For example, Kraehnert *et al.* proposed a four-step formation mechanism for Au nanoparticles in the classical citrate synthesis (**Figure 2.1**). [8] The sequential four steps include 1) fast nucleation of small nanoparticles, 2) aggregation of small nuclei to form bigger nanoparticles, 3) slow growth of nanoparticles accompanied by sustaining reduction of Au precursors, and 4) fast growth ending when Au precursors are completely consumed. Of four steps, the aggregation of nuclei to form larger nanoparticles is important and determines the polydispersity of final Au nanoparticles. The formation rate of Au nanoparticles can be accelerated dramatically by increasing initial Au precursor concentration or reaction temperature.

Figure 2.2 Schematic illustration of two reaction pathways for synthesis of Au nanocrystals by citrate reduction [7]. © 2007 American Chemical Society

Ji and co-workers have shown the third role of citrate in the formation of Au nanoparticles. [7] Except as the stabilizer and reducing agent, sodium citrate also acts as pH mediator in the reaction system. The solution pH can be changed by sodium citrate and HAuCl_4 concentrations. At varied pH values, the formation of Au nanoparticles undergoes different pathways (**Figure 2.2**). When the pH is below ~ 6.5 , Au nanoparticles are formed through nucleation, aggregation and smoothing. However, the formation of Au nanoparticles contains nucleation and growth at pH above 6.5.

Figure 2.3 a-e) TEM and f) SEM images of Au nanoparticles with different average sizes. Au nanoparticles are synthesized using a mixture of sodium citrate and ascorbic acid as reductant and stabilizer [11]. © 2011 American Chemical Society

Size control plays a vital role in the application of Au nanoparticles, since size affects properties (e.g., optical property) of Au nanoparticles significantly. [9] However, traditional citrate-stabilized method can only prepare monodispersed and quality Au nanoparticles with average size less than ~50 nm [10], which hampers applications of Au nanoparticles. To expand the size range and improve size and shape dispersion of Au nanoparticles, several modified citrate methods are provided to synthesize Au nanoparticles. For instance, Eychmüller' group reports a seed-growth method to produce Au nanoparticles with average sizes ranging from 15 to 300 nm (**Figure 2.3**). [11] In their research, a mixture of sodium citrate and ascorbic acid is used as stabilizer and reducing agent, which improves the uniformity and size range of Au nanoparticles. In addition, a Hydroquinone-assisted synthesis is presented to prepare uniform Au nanoparticles of 50 to 200 nm in the citrate method (**Figure 2.4**). [12]

Figure 2.4 Representative TEM images of Au nanoparticles in different sizes. Au nanoparticles are synthesized through Hydroquinone-assisted method [12]. © 2009 American Chemical Society

It is well known that sodium borohydride (NaBH_4)-synthesized method is also widely employed in the preparation of Au nanoparticles. [13, 14] In 1994, Brust *et al.* presented a biphasic reduction method to synthesize alkanethiol-stabilized Au nanoparticles. [15] NaBH_4 acts as reducing agent and Tetraoctylammonium bromide (TOAB) is used as phase transfer in this synthetic system (**Figure 2.5**). The sizes and dispersity of Au nanoparticles can be easily changed by varying Au/thiol ratio, reaction temperature and addition rate of NaBH_4 . [16]

Figure 2.5 Two-phase preparation of Au nanoparticles in the presence of alkanethiols and NaBH_4 [17]. © 2012 The Royal Society of Chemistry

This NaBH_4 -reduced synthesis of Au nanoparticles also provides a simple method to produce Au nanoparticles with various surfactants such as 3-mercaptopropionic acid, 3-mercaptopropylamine, 2-(2-mercaptoethoxy)ethanol and 2-[2-(2-mercaptoethoxy)ethoxy]ethanol, which significantly expands the applications of Au nanoparticles. [13, 18] For example, Urban shows a simple procedure to prepare phospholipid-capped Au nanoparticles by stirring Au precursor, NaBH_4 and surfactant at

room temperature (**Figure 2.6**). [19] These lipid protected Au nanoparticles with good biocompatibility have potential applications in biomedicine. [20]

Figure 2.6 Schematic illustration of phospholipid-capped Au nanoparticles [19]. © 2005 American Chemical Society

The polymer-assisted approach of Au nanoparticles has attracted much attention, since Au nanoparticles capped by polymers provide good stability and narrow dispersion. Hyperbranched [21], linear [22], amphiphilic [23, 24], and pH-responsive [25] polymers have been used as surfactants to produce Au nanoparticles. For instance, a one-step method to prepare monodispersed Au nanoparticles is presented by Brust's group. [26] The Au nanoparticles are capped by functionalized poly(methacrylic acid) and the sizes of products can be controlled by Au/polymer ratio. The monodispersed Au nanoparticles with varied sizes are shown in **Figure 2.7**.

Figure 2.7 TEM images of Au nanoparticles in different sizes. The Au nanoparticles are capped by functionalized poly(methacrylic acid) [26]. © 2005 American Chemical Society

Polymers not only are good surfactants to protect and shape Au nanoparticles, they also can be used as reducing agents to simplify the synthetic method. For example, Nagasaki *et al.* produce monodispersed Au nanoparticles by stirring functionally Polyethylene glycol (PEG) and HAuCl_4 aqueous solution at room temperature without additional reductant (**Figure 2.8**). [27] These Au nanoparticles capped by functionally PEG are extremely stable at very high concentration of salt. Meanwhile, Poly(diallyl dimethylammonium) chloride also can act as both surfactant and reducing agent in the synthesis of stable and uniform Au nanoparticles. [28]

Figure 2.8 Synthetic process and TEM image of Au nanoparticles with addition of functionalized PEG [27]. © 2004 American Chemical Society

Recently, “green chemistry” becomes a hot topic in the synthesis of nanomaterials, because it is eco-friendly. With an increasing effort to protect environment, numerous green methods to synthesize Au nanoparticles have been presented.

Room temperature ionic liquids which are potential “green” recyclable solvents have attracted much attention in nanochemistry. [29, 30] Recently, Naka’s group synthesizes and functionalizes Au nanoparticles in ionic liquid. [30] The hydrophilic Au nanoparticles can be easily changed to hydrophobic Au nanoparticles through anion exchange.

Figure 2.9 Synthesis of Au nanoparticles with addition of chitosan [31]. © 2007 Springer Science Business Media, LLC

Over the past decade, polysaccharides like chitosan, gum Arabic, gellan gum, guar gum, xanthan gum, and gum karaya, have also been employed to synthesize Au nanoparticles. [31-33] For example, Pokharkar *et al.* produce Au nanoparticles by heating chitosan and

Au precursor aqueous solution in the presence of acetic acid, as shown in **Figure 2.9**. [31] In the reaction system, the biocompatible chitosan acts as both surfactant and reducing agent, and the obtained Au nanoparticles are quite stable. In addition to chitosan, gum Arabic (GA) also has been reported to prepare Au nanoparticles. As an example, Boote and co-workers fabricate GA-stabilized Au nanoparticles in a simple method. [32] The obtained Au nanoparticles show high stability in phosphate-buffered solution, water, saline solution, and even solid state.

Figure 2.10 a) Formation process of gelatin-capped Au nanoparticles. b) TEM images of gelatin-capped Au nanoparticles in various sizes. Gelatin concentrations: 1) 0%, 2) 0.05%, 3) 0.10%, 4) 0.25%, 5) 0.50%, 6) 1.0% [34]. © Springer Science Business Media B.V. 2010.

Watari *et al.* present a “green” method to prepare size-controlled Au nanoparticles in the presence of gelatin. [34] The sizes of Au nanoparticles can be easily tuned from 10 to 15 nm through varying the concentrations of gelatin. The formation process of Au nanoparticles and TEM images of Au nanoparticles in different sizes via change of gelatin concentrations are shown in **Figure 2.10**. It can be noticed that silk fibroin, collagen and plant extract of cinnamomum, gymnema sylvestre, hibiscus sabdariffa, and nerium oleander also demonstrate the ability to synthesize Au nanoparticles in “green” methods. [35-40] As a lot of studies have reported, Au nanoparticles can be produced in the photoreduction process. [41-45]

2.1.2 Gold Nanorods

As one of the most popular anisotropic nanostructures, the synthesis of Au nanorods has been widely studied. Wang *et al.* reported the electrochemical approach to prepare Au nanorods in the 1990s, which was the main method to prepare Au nanorods in high yield before the use of seed-mediated process. [45, 46] In their research, an Au plate acts as anode while a Pt plate is used as cathode. Meanwhile, surfactant cetyltrimethylammonium bromide (CTAB) and co-surfactant like TOAB are added into the electrolytic solution. Au ions are reduced at cathode and the surfactants which form cylindrical micelle help to facility rod-like nanostructures. [45, 47-50] The ratio of length and width of Au nanorods can be adjusted by inserting of an Ag plate in electrolytic solutions. [45, 46]

Another common and early synthetic protocol to prepare Au nanorods is photochemical synthesis. [51-53] As an example, Yang and co-workers produce Au nanorods through irradiation of a solution containing Au precursor and surfactants with a 254 nm UV light. [51] The aspect ratio of Au nanorods can be easily controlled via the concentration of silver added into the reaction solution (**Figure 2.11**).

Figure 2.11 TEM image of Au nanorods with different aspect ratios prepared with addition of a) 15.8 μL , (b) 23.7 μL , (c) 31.5 μL of silver nitrate via photochemical method. d) HRTEM image of a Au nanorod [51]. © 2002 American Chemical Society

The seed-mediated method, which is facile and provides high quality Au nanorods with controlled aspect ratio, is the most popular synthetic strategy for preparation of Au nanorods. [54, 55] In 2001, Murphy *et al.* firstly reported the current concept of seed-mediated synthesis of Au nanorods. [54, 55] In their research, the Au nanorods are obtained through addition of as-prepared 3-4 nm Au nanoparticles capped by NaBH_4 to a growth solution containing HAuCl_4 , CTAB, silver nitrate, and ascorbic acid. The as-prepared Au nanoparticles act as seeds and the average aspect ratio of Au nanorods can be adjusted via the amount of seed.

Later, some modifications are made in this seed-mediated synthesis. [56] For example, EI-Sayed and co-workers use CTAB instead of sodium citrate as the capping agent to

prepare small Au nanoparticles in the seed formation step. [57] The CTAB-stabilized seeds provide higher yield in formation of Au nanorods, as compared to citrate-stabilized seeds. Meanwhile, Au nanorods with aspect ratios ranging from 1.5 to 5 can be obtained via change of silver nitrate concentrations added in the growth solution. To get Au nanorods with various aspect ratios, mixed surfactants with CTAB and a co-surfactant like benzyldimethylhexadecylammonium chloride (BDAC) [57, 58] are introduced to seed-mediated growth of Au nanorods. For instance, Au nanorods with an aspect ratio about 20 are obtained with addition of co-surfactant Pluronic F-127. [58]

Figure 2.12 Three-step seed-mediated method for the preparation of Au nanorods with a controlled aspect ratio. The TEM image shows the Au nanorods with an average length of 500 nm [59]. © 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Murphy's group also improves their seed-mediated process with a multi-step Ag-free synthesis to prepare Au nanorods with aspect ratio up to 25. [59] **Figure 2.12** shows the

typical procedure of this method. The Au nanorods obtained in first step act as seeds in the next step. Similarly, the second-step obtained Au nanorods are the seeds of final step. However, this method produces Au nanorods in presence of a large fraction of Au nanoparticles.

To improve the quality of Au nanorods, deep understanding of the formation mechanism is required in the seed-mediated synthesis of Au nanorods. In these decades, three mechanisms for seed-mediated synthesis of Au nanorods have been reported. Murphy *et al.* propose a surfactant-preferential-binding-directed growth mechanism for anisotropic Au nanorods in the absence of Ag ions (**Figure 2.13 A**). [59, 60] They explain that citrate-capped seeds contain pentatetradedral twins leading to anisotropic nanoparticles. In the growth step, CTA⁺ headgroup adsorbs on the {100} facets of Au seeds, which retards the growth of {100} facets. As a result, Au atoms adsorb on {111} facets leading to growth of rod-like Au nanostructures.

The other explanation for rod-like growth is the electric-field-directed mechanism (**Figure 2.13B**). [61] AuCl₄⁻ firstly reacts with CTAB to form AuCl₂⁻-CTAB micelles, followed by collisions between positively charged seeds capped by CTAB and negatively charged AuCl₂⁻. The faster collisions at tips than sides of the CTAB-capped seeds lead to formation of Au nanorods.

In the presence of Ag ions, Murphy *et al.* report an Ag underpotential deposition (UPD) mechanism to explain the rod-like growth (**Figure 2.13C**). [62] In this mechanism, a faster adsorption of Ag ions on {110} Au side facets than {100} end facets facilitates the anisotropic growth of Au nanorods.

Nowadays, some other methods to synthesize Au nanorods have also been presented, such as one-step seedless approach, biochemical synthesis, and solvothermal method. [63-66]

Figure 2.13 Mechanisms for growth of Au nanorods via seed-mediated synthesis. A) Surfactant-preferential-binding-directed growth mechanism for Au nanorods without addition of Ag ions. B) electric-field-directed mechanism without addition of Ag ions. C) UPD mechanism with addition of Ag ions [55]. © 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

2.1.3 Gold Nanoplates

In recent years, Au nanoplates have been widely studied because of their strong plasmon band in the NIR region, enhanced electric field at vertices, anisotropic electrical conductivity and atomically flat surfaces. Au nanoplates with these properties have possible applications in sensing, imaging, photonics and optoelectronics, surface enhanced raman scattering (SERS), and tip-enhanced raman scattering (TERS). [67-71] It is also reported that Au nanoplates provides new possibilities for fundamental studies and potential applications in catalyzing, and new nanodevices. [72-77]

Many methods have been exploited to get these anisotropic Au nanoplates. The most common method in the formation of Au nanoplates is the seed-mediated approach. [78, 79] However, this two-step process is too complex, compared with polyol process which is a typical one-step method to fabricate Au nanoplates. [80, 81] While the high reaction temperature, low yield, unclean surface of Au nanoplates and wide distribution of size are the drawbacks of this method. Recently, more attempts have been made to develop the fabrication of Au nanoplates, such as template assisted synthesis, microwave assisted synthesis, photochemistry method, sonochemistry method, polymer assisted synthesis and surfactant-free synthesis. [82-85] But most of these new methods still cannot provide clean Au nanoplates in high yield or low dispersion of size.

In 2006, Mirkin and co-workers [78] utilized the seed-mediated approach to prepare 2D Au nanoplates with the edge lengths from 114 nm to 220 nm. The 5.2 nm Au nanoparticles (the seeds) were firstly prepared. The initial Au nanoplates (average edge length and thickness are approximately 114 nm and 7.5 nm respectively) were fabricated by adding the seed solution into the growth solution containing $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, CTAB, ascorbic acid and NaOH. The edge lengths of the nanoplates can increase while the thicknesses keep unchanged through serial addition of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ into the initial Au nanoplate solution. **Figure 2.14** shows the TEM images of Au nanoplates with different edge lengths.

Figure 2.14 TEM images of Au nanoplates with different sizes synthesized through seed-mediated method. Edge length: A) ~114 nm, B) ~148 nm, C) ~192 nm, D) ~207 nm, and E) 220 nm [78]. © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

In order to control the size of Au nanoplates, Gu *et al.* added I^- into the growth solution through the seed-mediated approach. Briefly, the citrate-capped Au seed was obtained firstly. Then the seed solution, $HAuCl_4 \cdot 3H_2O$, reducing agent ascorbic acid and KI were added into the CTAB solution. Their results indicated that the edge length of the Au nanoplates can easily decreased from 140 to 30 nm by simply increasing the amount of seed and I^- in the growth solution, while the thickness of nanoplates kept the same. [86] In their research, I^- was of great importance to suppress {111} facets, leading to faster growth of other facets. [87] Recent years, the I^- -assisted method is widely used to prepare several-hundred nanometers Au nanoplates. [88, 89]

Polyvinylpyrrolidone (PVP) was found to be an excellent surfactant to keep 2D Au nanoplates stable, well-dispersed and prohibiting aggregation. [90] Qian and co-workers fabricated Au nanoplates via seed-mediated approach and use PVP as the surfactant to displace CTAB by adding PVP into the purified Au nanoplate colloids. At last, the Au

nanoplates with an average edge length of 95 nm were fabricated. [91] On the other hand, Akrajas *et al.* used the mixture of CTAB and PVP as the surfactant in the growth solution. [92] The results showed that the edge length of Au nanoplates depends on the concentration of CTAB, while the yield of nanoplates was relating to PVP concentration. High CTAB concentration led to large Au nanoplates and the optimize PVP concentration was 0.5 mM with a yield of 60%. The resulting nanoplates were the mixture of triangles, hexagons and truncated triangles. Hsu *et al.* prepared Au nanoplates through a modified seed-mediated method. [93] In their research, PVP was used as both the reducing agent and surfactant. Firstly, 6.0 nm Au seeds were prepared by heating a mixed solution of HAuCl_4 and PVP at 130 °C. To obtain Au nanoplates, the growth solution containing seed solution, HAuCl_4 and PVP was aged at room temperature.

Apart from the fabrication of Au nanoplates in solution, Au nanoplates can also be prepared on glass and Si/SiO_x surfaces directly through the seed-approach method. Zamborini and co-workers placed thiol-functionalized substrates into 4 nm diameter Au nanoparticle (seeds) solution to immobilize seeds on substrate, and then seeds can grow to larger nanoplates by immersing those substrates into growth solution containing $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, CTAB and ascorbic acid. [94, 95] The average width and height of nanoplates were approximately 200 nm and 35 nm, respectively.

The glycol process was a typical and simple one-step method to synthesize Au nanoplates with the edge length ranging from hundreds of nanometers to tens of micrometers. [81, 96-98] In a typical synthesis, AuCl_4^- ions and PVP were firstly added into ethylene glycol and then the mixture solution reacted at above 120 °C for several hours. The resulting Au nanoplates were a mixture of triangles, hexagons, and truncated triangles. In a polyol process, both ethylene glycol and PVP were of great importance to form Au nanoplates. Ethylene glycol was the reducing agent and solution in this experiment. It can also absorb preferentially on the {111} surfaces of Au nanoplates, which decreased the surface energy of {111} facets and enhances the growth along $\langle 110 \rangle$ directions. [81, 97] Surfactant PVP can stabilize the Au nanoplates to prevent them aggregating. In addition, PVP can selectively interact with different crystallographic planes of Au nanocrystals, leading to the reduced growth rate on {111} surfaces and preferential growth along $\langle 110 \rangle$

directions. [99] Thus, ethylene glycol and PVP favored the formation of Au nanoplates. Some modifications had been realized in some polyol process. For example, Liu *et al.* used ultrasonic irradiation instead of heating to provide power in the polyol method. Hartland and co-workers slightly modified the polyol process to fabricate Au nanoplates. In their research, a mixture of PVP and CTAB was used as the surfactant. [100] The average edge length and thickness of triangular and hexagonal nanoplates were $5 \pm 2 \mu\text{m}$ and $107 \pm 30 \text{ nm}$, respectively.

In the synthesis of one-step Au nanoplates, CTAB was a common surfactant. 2D Au nanoplates can be synthesized in a system containing HAuCl_4 , lyotropic liquid crystal (LLC) poly (ethylene oxide)-poly(propylene oxide)-poly (ethylene oxide) block copolymers, and surfactant CTAB. In this system, surfactant CTAB selectively absorbed on certain planes of the Au nanostructures, leading to the formation of triangular and hexagonal nanoplates. Meanwhile, LLC provided an ordered structure which confined the surfactant and nascent Au nuclei. Thus the Au atoms directionally attached to nuclei and formed larger nanoplates. [101] Years later, Pereira reported that the average edge length can be easily changed by varying the concentration of surfactant CTAB in a photocatalytic approach. [102] The tin (IV) porphyrin and triethanolamine were used as the photocatalyst and final electron donor, respectively.

Sodium citrate was also a common reductant to synthesize Au nanoplates with the appearance of surfactant CTAB. [103-105] Francois and Deckert fabricated Au nanoplates with an edge length of a few micrometers by adding CTAB and HAuCl_4 into a hot sodium citrate solution. [103, 104] In their research, the HAuCl_4 was reduced by sodium citrate to form seed particles and the platelike morphology was obtained under the template effect of CTAB. [104]

Efforts in the synthesis of Au nanoplates increased rapidly these years. The platelike Au nanostructures can be obtained without additional reductant. Sun *et al.* synthesized the 2D triangular and hexagonal Au nanoplates with the edge length of several nanometers through a simple method. [106] In a typical experiment, tannic acid (TA) and HAuCl_4 reacted at room temperature. A few minutes later, the platelike nanostructures were

obtained. The results indicated that the Au^{3+} was reduced to Au^0 by the phenolic hydroxyls of tannic acid and the bayberry tannin can be used to stabilize the Au nanostructures. [107, 108] In a α -D-glucose assisted method, bulk and shape-controlled Au nanoplates can be obtained by high-intensity microwave irradiating a mixture of HAuCl_4 and α -D-glucose solution for 30-45 s. [109] In this system, α -D-glucose was both the reductant and surfactant. Microwave irradiation provided rapid and uniform heating of reagents, solvents, and intermediates.

Recently, a PVP-based polymer (PQ11) was utilized to prepare Au nanoplates. [110] In this system, the PVP part of PQ11 functioned as the reducing agent. Additionally, this polymer absorbed on the crystallographic planes selectively, which kinetically controlled the growth of different surfaces leading to the fabrication of large Au nanoplates.

Figure 2.15 Atomic force microscopy (AFM) images of Au nanoplates with different thicknesses controlled by HAuCl_4 concentrations in the DGI-templated method [111]. © 2013 American Chemical Society

Jin and co-workers reported a template-directed synthesis of ultrathin 2D Au nanoplates with the help of template dodecylglyceryl itaconate (DGI). [111] Briefly, the HAuCl_4 was first added into the stable and well-dispersed DGI solution. Then the mixed solution reacted at 45 °C for 24 h. The thicknesses of these resulting Au nanoplates were only several to tens of nanometers while the areas were more than 100 μm^2 . The thickness of Au nanoplates can be controlled through changing the HAuCl_4 concentrations in reaction

solution (**Figure 2.15**). Their results demonstrated that HAuCl_4 can be reduced to Au^0 by the hydroxyl groups of DGI. In addition, the self-assembled DGI formed the lamellar bilayer membrane in water functioning as a soft template to induce an oriented growth of Au nanoplates.

In recent years, more and more simple and novel approaches had been exploited to fabricate Au nanoplates, such as amyloid-mediated synthesis [112], starch-mediated synthesis [71], chitosan-assisted synthesis [82], sodium sulfide synthesis [83, 84] and surfactant-free synthesis [85].

2.1.3 Gold Nanopolyhedra

Figure 2.16 Electron microscopy images of Au nanopolyhedra: a) octahedrons, b) truncated tetrahedrons, c) icosahedrons, d) decahedrons, e) truncated nanocubes and f) nanocubes [117]. © 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Au nanopolyhedron is also a main morphology in the family of Au nanostructures. In the past decades, numerous synthetic strategies have been presented to prepare Au nanopolyhedra like octahedron, cube, tetrahedron, cuboctahedron, icosahedron, and ditetragonal prism. [99, 113-116] **Figure 2.16** shows some typical morphologies of Au nanopolyhedra. [117]

Figure 2.17 SEM images of elongated tetrahedral Au nanostructures. a) Typical SEM image and schematic model of elongated tetrahedral Au nanostructures. b) Side and c) end facets of elongated tetrahedral Au nanostructures [118]. © 2009 American Chemical Society

Modified seed-mediated synthesis is a common method to prepare Au nanopolyhedra. [118-121] For an instance, Yan and co-workers report the synthesis of elongated tetrahedral Au nanostructures through seed-mediated method in the presence of Ag ions. [118] **Figure 2.17** shows the morphology of elongated tetrahedral Au

nanostructures enclosed by 24 $\{037\}$ facets. In this reaction system, the acid growth solution is of great importance to the growth of elongated tetrahedral Au nanostructures.

Figure 2.18 SEM images of Au nanopolyhedra prepared through Mirkin's method. A) Octahedra, B) rhombic dodecahedra, C) truncated ditetragonal prisms, and (D) concave cubes. Scale bars: 200 nm [120]. © 2011 American Chemical Society

Mirkin *et al.* also present a seed-mediated process to produce Au nanopolyhedra. [120] Octahedra, rhombic dodecahedra, truncated ditetragonal prisms, and concave cubes (**Figure 2.18**) have been produced through simply changing Ag ions concentration in growth solution and the deposition of Ag on Au facets stabilizes the obtained Au nanopolyhedra.

Polyol process, in which ethylene glycol is generally used as both solvent and reducing agent, is also the main method to produce Au nanopolyhedra. [99, 113, 122] For example, Cho and co-workers apply a polyethylene glycol 600 based polyol method to successfully produce Au octahedron with an average edge length of 50 nm. [122] Meanwhile, a series of polyhedral Au nanostructures with controlled shape and size are synthesized via a polyol process with addition of silver nitrate. In this method, octahedra, higher polygons, cubes, truncated octahedra and cuboctahedra have been produced through simply adjusting concentration of silver nitrate. [113] Other methods like galvanic replacement reaction [123] or surfactant-assisted approach [124] have been also reported to prepare Au nanopolyhedra.

2.1.4 Branched Gold Nanostructures

In this part, particular attention is paid to branched Au nanostructures which show enhancement of properties as compared to other anisotropic Au nanostructures. Nowadays, branched Au nanostructures like nanostars, nanoflowers, urchins, dendritic nanostructures and nanocrosses have been successfully produced. [125, 126] To create branched Au nanostructures, three main synthetic strategies, which are classified as seed-mediated, seedless and template growth, are provided.

Figure 2.19 TEM images of a) Au octahedral seeds and b) Au nanoheptapod. The Au nanoheptapod is prepared through a seed-mediated method [127]. © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Seed-mediated synthesis, in which as-prepared seeds act as nucleation points, is a common method to prepare branched Au nanostructures, and the final morphologies of products can be controlled by addition of seeds with various size and shape. Xia *et al.* report a facile seed-mediated process to synthesize Au nanohexapods by using single-crystal Au octahedra as seed and N,N-dimethylformamide as reducing agent (**Figure 2.19**). [127] In the growth of Au nanohexapods, the newly reduced Au atoms prefer to adsorb on the six vertices of as-prepared Au octahedra, since the vertices have higher energy. The lengths of the arms in Au nanohexapods can be easily tuned through changing the concentrations of HAuCl_4 or reaction temperatures.

Figure 2.20 TEM images of star-like Au nanostructures synthesized with addition of different Au:Ag ratios. a) 3:1, b) 10:1, c) 15:1, d) 30:1, e) 50:1 and f) 100:1 [128]. © The Royal Society of Chemistry 2012.

Seedless synthesis for nanostructures is a common and facile one step method. Branched Au nanostructures produced through seedless synthesis have also been reported recently.

For instance, Liu's group synthesizes star-like Au nanostructures through a seedless approach in the presence of AgNO_3 . [128] In the reaction, reduced Ag atoms adsorb on Au cores and act as active sites for further growth of thorns on Au cores. As shown in **Figure 2.20**, the morphologies of branched Au nanostructures are controlled by tuning the ratio of Au and Ag. Similarly, Au nanocrosses are produced via a seedless method with addition of Cu ions which break the symmetry of fcc Au. [129]

Figure 2.21 The illustration of formation of Au multipods [130]. © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

In the past decades, branched Au nanostructures synthesized with the assist of template have also been reported. Xia *et al.* presents a simple templated-assisted method to produce Au multipods. [130] In this method, self-assembled Fe nanoparticles, as shown in **Figure 21**, act as the three-dimensional template. As the addition of Au^+ precursors to the template, the void space among Fe nanoparticles are filled with Au^+ and Au atoms are formed through the galvanic replacement between Au ions and Fe. The reduced Au atoms nucleate and further grow in the void space. As the volume expansion of the template and consumption of Fe, the self-assembled Fe nanoparticles fall apart and the final Au

multipods (**Figure 21**) are released. **Figure 21** shows the schematic illustration for the formation of Au multipods.

Graphene oxide nanosheets which are two-dimensional monolayers can also be used as a template to synthesize branched Au nanostructures with enriched {111} facets. [131] In the growth of branched Au nanostructures, the oxygen-containing moieties are the active sites for nucleation and limit the diffusion of Au atoms. As a comparison, irregular Au nanostructures are formed without addition of graphene oxide nanosheets. Meanwhile, other templates such as deep eutectic solvent have been presented to prepare Au nanostructure with tips. [126, 132, 133]

2.2 Properties and Applications of Gold Nanostructures

Nanoscale Au shows unique and fascinating properties as compared to bulk Au, making it a promising material in a wide range of applications. In this section, the properties and applications of Au nanostructures are highlighted in optics, biochemistry, and catalysis.

2.2.1 Optical Properties and Applications

Due to the interaction between electromagnetic waves of incident light and conduction band electrons of Au, Au nanostructures show obvious surface plasmon resonance (SPR). The SPR-based optical properties depend strongly on the morphology of Au nanostructures. [55] Au nanoparticles show a strong absorption in the visible region, and the wavelength of absorption can be easily tuned by the size of Au nanoparticles. [55]

However, some anisotropic Au nanostructures like Au nanorods and nanoplates show different SPR properties as compared to Au nanoparticles. [78] For example, Au nanorods exhibit plasmon resonance along both short and long axes. The plasmon resonance along the short axis refers to the transverse band, which is in the visible region like the plasmon resonance of Au nanoparticles. The plasmon resonance along the long axis refers to the longitudinal band and ranges from visible to near-infrared region. The transverse plasmon resonance can be tuned by Au nanorod size while the longitudinal plasmon resonance is sensitive to the aspect ratio of Au nanorods. [55] The plasmon resonance of other Au nanostructures with intricate morphologies (e.g., nanostars,

nanobelts, nanohexapods and nanocages) has recently been studied. [123, 127, 134-137] For instance, Hafner and co-workers explore the plasmon resonance of Au nanobelts with rectangular cross sections, and the obtained Au nanobelts show transverse plasmon resonance at visible region. [136] The dark-field images of Au nanobelts in **Figure 2.22** show the colors of Au nanobelts change from green to red with the increase of cross-sectional aspect ratio. Meanwhile, the plasmon resonance, which is perpendicular to the length of Au nanobelt (blue line in **Figure 2.22**), can be controlled by changing the aspect ratio of cross section.

Figure 2.22 (left) Dark field micrographs and (right) corresponding spectra of single Au nanobelt with different cross-sectional aspect ratio [136]. © 2011 American Chemical Society.

Due to the strong plasmon resonance, Au nanostructures have potential applications in cancer therapy, detection and imaging. [138-141] As an example, Zamborini *et al* reported a high-yield synthesis of Au nanoplates by nanostructures growing directly on a substrate. The maximum extinction ($\lambda_{\max}$) of localized surface plasmon resonance (LSPR) band changed when the anti-IgG bound to the edges of these Au nanoplates. [95] The shift in $\lambda_{\max}$ was several times larger in comparison with that of Au nanoparticles. [142] Their results also showed that shifts in $\lambda_{\max}$ mainly depended on the binding coverage, location, and binding distance. [94] For the detection of IgG, $\lambda_{\max}$ changed more than 40 nm while the anti-IgG functionalized nanoplates exposed to a 10 pg/mL IgG solution. [95] The detection limit of IgG was extremely low compared to related reports. [143] The results indicated that the LSPR spectrum of Au nanoplates was sensitive to even low concentration of binding proteins, therefore, Au nanoplates may be used to monitor proteins by LSPR.

In addition, Au nanostructures have been found to show SERS, making them promising candidates for Raman sensors. For instance, Hsu and co-workers [93] utilized Au nanoplates as SERS platform to detect pyrene which was a potential carcinogen. In their experiment, SERS activities were enhanced dramatically on the Au nanoplates substrates, and the enhancement factor was as high as 7.30×10^7 . In the further detection of pyrene, a remarkable low detection limit was achieved, which was 5×10^{-10} M. Compared with silver nanoparticle SERS platforms, Au nanoplate substrates were more sensitive in the detection of pyrene. [144-148] Meanwhile, the SERS-active Au nanoplate substrate was also an excellent detector for label-free deoxyribonucleic acid (DNA) with a low detection limit of 10^{-6} mg/mL. [91] These results showed that Au nanoplates were potential SERS substrates in the applications of biomolecule sensing and toxic molecules detecting.

2.2.2 Catalysis

Au has been applied as catalysis to facilitate numerous chemical reactions for a long period of time. As the development of nanotechnology, noble metal nanostructures with high surface-to-volume ratios attract much attention as catalysts. In these decades, Au

nanostructures have been widely employed in catalysis of CO oxidation, 4-nitrophenol reduction, alcohol oxidation and so on. [149-153] The catalytic efficiency and activity greatly depend on the size, exposed facet and shape of Au nanostructures. [124, 154]

Figure 2.23 The normalized absorption of p-nitrophenol with the increase of reaction time catalyzed by Au decahedra [154]. Reproduced with permission from the Royal Society of Chemistry © 2013.

Huang and co-workers study the size-dependent catalysis of Au nanostructures through a typical reduction of p-nitrophenol to p-aminophenol in the presence of Au decahedra. [154] **Figure 2.23** shows the normalized absorption of p-nitrophenol with the increase of reaction time catalyzed by Au decahedra. It is clearly that the reaction rate and the conversation rate of p-nitrophenol are improved as the reduction of Au decahedra sizes. The authors suggest that the surface area and amount of edge atoms in single Au decahedra affect the catalytic efficiency of Au nanostructures.

In addition, Au nanostructures enclosed by different facets have been synthesized and proved to show different catalytic activity. [124] For example, Han *et al.* successfully synthesize 12 {110}-faced Au dodecahedra and the obtained Au nanostructures show enhanced catalytic capability as compared to Au nanoparticles enclosed with {111} facets. [124] The improved catalytic ability is due to the larger binding force between reactant and high energy {110} surfaces on Au dodecahedra. To study the facet-

dependent catalytic ability of Au nanostructures, Wand and co-workers make a comparison of catalytic capability of Au nanostructures enclosed by various high-index surfaces. [121] The results demonstrate that Au elongated tetrahedra mainly bounded by {730} facets exhibit the highest catalytic rate for the reduction of 4-nitrophenol, followed by Au concave cubes mainly enclosed by {520} facets. The {221} faced Au trisoctahedra show the lowest catalytic rate. However, all these Au nanostructures bounded by high-index facets possess better catalytic ability than {111} and {100} faced Au nanostructures. Generally, Au nanostructures with high energy facets possess high catalytic capability. [155]

The shape of Au nanostructures is significantly important to their catalytic efficiency and activity. Thus the catalysis of Au nanostructures with various morphologies has been studied in these decades. [156-158] As an example, the catalytic ability of single-walled helical Au nanotubes Au(5,3) is studied by the oxidation of CO. [157] The oxidation of CO undergoes two steps including initiation by O₂ and formation of peroxo-intermediates. The electronic resonance between intermediates and Au atoms, and the strain inherent in Au(5,3) lead to the enhanced catalytic ability. Furthermore, the catalytic capabilities of Au nanostars, nanoflowers, nanowire, and dendrites have been reported. [158-160]

2.2.3 Biological Applications

Due to the promising optical properties, Au nanostructures have wide applications in biosensing. [161, 162] Typically, biosensors are functionalized Au nanostructures which can recognize specific analytes. When the biosensor interacts with analyte, the plasmon resonance or SERS intensity of the Au nanostructures indicate a change. For example, Lee *et al.* have reported that anti-thrombin functionalized Au nanocubes, nanorods and nanoparticles can be utilized as SPR biosensors for efficient detection of thrombin. [161] **Figure 2.24** shows the process for detection of thrombin via functionalized Au nanostructures. The 11-mercaptoundecanoic acid functionalized Au nanostructures (e.g. nanoparticles, nanocubes and nanorods) firstly link to anti-thrombin through cross-linker and N-hydroxysulfosuccinimide (**Figure 2.24a**). Then the Au SPR chip is attached by a 5'-end aminemodified DNA aptamer through prolinker B or PEG (**Figure 2.24b**). Finally,

the thrombin can be detected by a simple sandwich sensor containing anti-thrombin functionalized Au nanostructures and an aptamer-modified Au chip (**Figure 2.24c**). The detection limit for thrombin is as low as ~ 1 aM through the SPR measurements.

Figure 2.24 The process for detection of thrombin via functionalized Au nanostructures [161]. © 2012 American Chemical Society

In addition to SPR biosensors, SERS biosensors have also been presented. For instance, Kim *et al.* have developed an Au nanowire SERS sensor for detection of pathogenic fungi in high sensitivity. [163]

Up to now, Au nanostructures are one of the most remarkable nanomaterials for phototherapy and biomedical imaging owing to their simple functionalization, long body circulation times, absorption in near-infrared region, and selective accumulation. [129, 141, 155, 164] EI-Sayed and co-workers have demonstrated the anti-EGFR antibody-functionalized Au nanorods to contrast agents for biomedical imaging and photothermal therapy for cancer. [164] In a vitro experiment, cancer cells can be clearly

visualized and more easily photothermally destroyed than nonmalignant cells in the presence of the functionalized Au nanorods.

Figure 2.25 Schematic illustration of drug delivery system using Au nanocages as support [165].
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Recently, Au nanostructures have been utilized as biocarriers for drug release. [165, 166] Wan et al. have developed a drug delivery system using functionalized Au nanocages as support. [165] The surfaces of Au nanocages are functionalized with thiol-modified singlestranded oligonucleotides (SH-DNAs). Then SH-DNAs on Au nanocages hybridize with two ends of ATP aptamers, capping the pores of Au nanocages. The addition of ATP triggers the release of drugs, because ATP competitively interacts with ATP aptamer and the pores of Au nanocages are opened (**Figure 2.25**).

2.3 Gold and Other Metal Based Bimetallic Nanostructures

Recently, increasing efforts have been made to Au based bimetallic nanostructures due to their enhanced catalytic and optical properties as compared to single component. In the section below, the morphologies and applications of Au-based 1) Pt, 2) Pd, and 3) Ag bimetallic nanostructures are presented.

2.3.1 Gold and Platinum

Among the Au and Pt bimetallic nanostructures reported, nanorods which exhibit enhanced therapeutic efficacy and unique optical properties, are one of the most common

Au and Pt bimetallic nanostructures. [167-169] For example, EI-Sayed and co-workers prepare Au nanorods with tips coated by Pt shells through simply reducing Pt precursors in as-prepared Au nanorods solution at 40 °C. [167] The Pt coated Au nanorods show high stability when exposed to NIR laser and their plasmon resonance can be tuned by changing the amount of Pt on Au nanorod tips. Besides, the Au and Pt bimetallic nanorods are biocompatible and have enhanced thermal response to laser as compared to the original Au nanorods, indicating they are useful agents for plasmonic photothermal therapy (PPT). In addition to kill cancer cells through PPT efficiently like original Au nanorods, Pt coated Au nanorods can simultaneously scavenge reactive oxygen species (ROS) produced in PPT, as shown in **Figure 26**. The reactive oxygen species have been demonstrated to harm DNA and proteins in healthy cells irreversibly. Therefore, the Pt coated Au nanorods produced by EI-Sayed are suggested to be ideal candidates for PPT with high therapeutic efficacy and ability to scavenge reactive oxygen species. The Pt tipped Au nanorods have also been reported to produce hydrogen efficiently under visible-NIR light due to the formation of hot electrons in Au nanorods. [169]

Figure 2.26 The plasmonic photothermal therapy by using Pt coated Au nanorods and original Au nanorods. ROS are scavenged in the presence of Pt coated Au nanorods while ROS are remained by using original Au nanorods as agents [167]. © 2016 American Chemical Society

Another example for Au/Pt bimetallic nanorods is reported by Yang's group. [168] In their research, Pt nanocubes are used as seeds to prepare anisotropic Au nanorods with length of ~185 nm. The authors suggest that the larger lattice mismatch for Pt/Au leads to the non-conformal growth of Au nanorods which contain Pt nanocubes at their perimeter.

Recently, Au/Pt nanowires with an average length of 140 nm are produced by Arben. [170] They can be used as real-time glucose detector with high sensitivity, due to the oxidation of glucose on Au and reduction of hydrogen peroxide on Pt.

In addition, Zheng and coworkers fabricate Pt covered Au nanopentagams through epitaxial growth. [171] In their reaction system, as-prepared Au nanopentagams are used as seeds and Pt grow on the high-index surfaces of the seeds. The obtained Au/Pt nanopentagams are excellent electrocatalyst for oxidation ethanol in alkaline condition, due to the surface electronic interaction. As compared to commercial Pt/C for oxidization of ethanol, the Au/Pt bimetallic nanopentagams show higher specific and mass activities, and better durability and anti-poisoning ability.

2.3.2 Gold and Palladium

Recently, Zhang's group produces Pd covered Au nanorods through the epitaxial growth. [172] As shown in **Figure 27**, Au nanorods are firstly synthesized by reducing HAuCl_4 in oleylamine at 70 °C. Secondly, Pd covered Au nanorods are obtained through reduction of Pd precursors in the presence of as-prepared Au nanorods. The resulted Au nanorods are thoroughly coated by 2-7 nm Pd shell. The authors suggest that the growth of Pd covered Au nanorods through the Stranski-Krastanov mode which is a mixture of uniform layered deposition and island-like growth. Meanwhile, the Pd covered Au nanorods exhibit excellent mass activity for oxidation of ethanol, which is 3.9 and 5.2 times more than those of commercial Pt/C and Pd black, respectively.

Figure 2.27 Schematic illustration for fabrication of Pd covered Au nanorods [172]. © 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

In addition, Au/Pd bimetallic nanorods have been reported as catalyst for Suzuki coupling reaction. For instance, Yan and co-workers fabricate Au/Pd nanorods through a two-step method in which Au nanorods are synthesized firstly and used as seeds for growth of Pd. [173] The resultant Au/Pd nanorods have rough ends and relatively smooth side surfaces after the growth of $\sim 3\text{--}5\text{ nm}$ Pd nanoparticles on original Au nanorods. Meanwhile, the longitudinal plasmon peak of Au/Pd nanorods is blue-shift as compared to original Au nanorods. Upon plasmon excitation, the Au/Pd bimetallic nanorods show efficient catalysis for Suzuki coupling reaction and the yield of this reaction is about 2 times that obtained when the reaction is conducted without Au/Pd nanorods. In this reaction, the Au nanorods inside absorb light efficiently under illumination of laser and the Pd nanoparticles outside catalyze Suzuki coupling reactions. Due to Au and Pd are in one nanocrystal, light energies absorbed by Au nanorods can be transferred to Pd nanoparticles directly. Thus, plasmonic photocatalysis and photothermal conversion play roles simultaneously in Suzuki coupling reaction.

Besides Au/Pd bimetallic nanorods, Tian *et al.* successfully synthesize Au@Pd nanocubes. [174] They use as-prepared Au nano-octahedras with size of 30 nm as seeds and monodispersed Au@Pd nanocubes are fabricated through overgrowth of Pd precursors on Au seeds in the presence of CTAB. The obtained Au@Pd nanostructures show a great cubic shape and the average size is about 41.5 nm . Meanwhile, Au@Pd

porous cuboid-like nanostructures with Au nanorods as cores have also been reported. [175]

Another example for Au/Pd bimetallic nanostructures is presented by Zheng and co-workers. [176] They report Pd@Au nanoplates which can be used as theranostic agent. In the synthesis of Pd@Au bimetallic nanoplates, as-prepared hexagonal Pd nanoplates, which are about 15 nm and 1.8 nm in edge length and thickness respectively, act as seeds, and Au precursors grow on as-prepared Pd nanoplates in the assistance of hydrazine hydrate and N,N-dimethylformamide. The final morphology of Pd@Au nanoplates is still hexagonal with an average diameter of approximately 30 nm and thickness of about 4 nm which is larger than original Pd nanoplates. The authors have demonstrated that the PEG modified Pd@Au nanoplates have wide applications in biomedicine, such as photothermal ablation of tumors and computed tomography contrast agent.

2.3.3 Gold and Silver

Au/Ag bimetallic nanoclusters stabilized by adenosine monophosphate are produced by Wu and co-workers through a facile hydrothermal protocol recently. [177] The obtained Au/Ag bimetallic nanoclusters with strong fluorescence emission exhibit a Stokes shift of about 200 nm. In the formation of Au/Ag bimetallic nanoclusters, Au atoms act as cores while Ag atoms grow on Au as shells, as shown in **Figure 28**. Under irradiation of sunlight, the color of Au/Ag bimetallic nanoclusters changes from colorless to orange and their fluorescence emission is quenched slightly. Meanwhile, the size of Au/Ag bimetallic nanoparticles increases to 10.0 nm (**Figure 28**), which is accompanied by the appearance of an absorption ranging from 400 to 500 nm. The authors suggest that the increase of nanoparticle size under sunlight is due to the reaction between hydroxyl on stabilizer and Ag ions on nanoclusters.

Figure 2.28 Schematic illustration for formation of Au/Ag bimetallic nanoclusters and their size increase under sunlight [177]. ©The Royal Society of Chemistry 2017

Wang and co-workers provide another example for Au and Ag bimetallic nanocluster. [178] They find that the electrochemiluminescence can be easily improved by adding Ag atoms into Au nanoclusters. When the molar ratio of Au and Ag is 6:1 in bimetallic nanoclusters, the electrochemiluminescence is 5-fold that of original Au nanoclusters. The obtained Au and Ag bimetallic nanoclusters can act as signal-off sensor to detect Hg^{2+} with low detection limit and high sensitivity, due to the metallophilic interaction between analyte and Ag or Au.

Furthermore, Au/Ag bimetallic nanopolyhedra have also been reported. For example, Xia *et al.* produce Au/Ag bimetallic octahedrons with uniform morphology successfully by using Au nanorods as seeds. [179] In their research, Au@Ag core-shell octahedrons can be easily fabricated via addition of AgNO_3 into Au nanorods solution in the assistance of PVP and CTAB. The average diagonal length of final products is about 64.8 nm and the size of Au@Ag core-shell octahedrons can be easily tuned by changing the size of Au seeds and amount of Ag precursors. Tian and co-worker present another example for synthesis of Au/Ag bimetallic nanopolyhedra by using Au nano-octahedra as seeds. [174] The final products are monodispersed Au@Ag core-shell nanocubes with smooth surfaces.

Recently, a facial approach for preparation of Au/Ag bimetallic nanowires on silicon surface is presented by Parlapalli and co-workers. [180] They find that the amount of Ag used to modify the silicon surface play a vital role in the final morphology of Au/Ag

bimetallic nanowires and the bimetallic nanowires can act as SERS substrates for bio-detection.

2.4 Questions Remaining

Nowadays, advances have been developed in the applications of Au based nanostructures. These Au based nanostructures with various morphologies can be synthesized through diverse methods. However, the mechanism underlying the growth of Au nanostructures is still a challenge, which hampers the precise control of shape and size in the synthesis of Au nanostructures. Therefore, developing facile method to experimentally demonstrate and theoretically understand the formation of Au nanostructures is important, which will in turn improve the properties and applications of Au nanostructures.

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Chapter 3

Experimental Methodology

In this chapter, the details of experiments and characterizations are presented. The methods to calculate the concentrations of gold nanoplates and the amount of gold atoms on gold nanoplate surfaces, which are important for the correct analysis of experimental results, are first demonstrated. The principles and the roles of characterization techniques employed in this project including TEM, SEM, XRD and AFM, are discussed in the second part.

3.1 Calculation of Gold Nanoplates Concentration

To calculate the Au nanoplates concentration, the as-prepared Au nanoplates were completely oxidized to Au^{3+} by aqua regia first. Then the concentration of Au^{3+} in the above solution was measured through UV-vis-NIR spectrophotometer. Since the Au^{3+} originates from oxidized Au nanoplates, the concentration of Au nanoplates can be calculated from Au^{3+} concentration.

Taking the calculation of 0.5 mM Au nanoplates as an example, 2 mL of Au nanoplates aqueous solution, the absorption intensity of which at 1100 nm is 0.4 a.u., was first oxidized by freshly prepared 1mL of aqua regia. The obtained solution was named as oxidized Au nanoplates solution. **Figure 3.1** shows the UV-vis-NIR absorption spectra of original Au nanoplates and oxidized Au nanoplates solution. The absorption of original Au nanoplates at 1100 nm is 0.4 a.u. (**Figure 3.1**). After oxidization by aqua regia, their peak at 1100 nm is zero, indicating the complete oxidization of Au nanoplates (**Figure 3.1**).

Figure 3.1 UV-vis-NIR absorption spectra of original Au nanoplates and oxidized Au nanoplates.

Then, the concentration of oxidized Au nanoplates solution was diluted to 10 times that of original solution with addition of 17 mL of deionized water. The above solution was named as ‘oxidized Au nanoplates solution x 10’. In this solution, $[\text{AuCl}_4]^-$ complex was formed due to oxidization of Au nanoplates in aqua regia. Due to a ligand-metal transition of $[\text{AuCl}_4]^-$ complex, strong peaks at about 303 nm are detected in ‘oxidized Au nanoplates solution x 10’ (black line) and 0.05 mM HAuCl_4 aqueous solution (red line), as shown in **Figure 3.2**. [1] The absorption of $[\text{AuCl}_4]^-$ complex at about 303 nm in “oxidized Au nanoplates solution x 10” is similar to that in 0.05 mM HAuCl_4 aqueous solution (**Figure 3.2**). Therefore, the concentration of “oxidized Au nanoplates solution x 10” is 0.05 mM and the original Au nanoplates concentration is 0.5 mM. It should be noted that 5% (volume%) aqua regia is included in the 0.05 mM HAuCl_4 aqueous solution to make the pH similar with “oxidized Au nanoplates solution x 10”. [1]

Figure 3.2 UV-vis-NIR absorption spectra of “oxidized Au nanoplates solution x 10” and 0.05 mM HAuCl_4 aqueous solution.

3.2 Calculation of the Amount of Gold Atoms on Gold Nanoplate Surfaces

Figure 3.3 The 3D model of triangular Au nanoplate.

In the method of calculation, Au nanoplate was assumed as regular triangle with edge length of 860 nm and thickness of 25 nm (**Figure 3.3**), which was based on the TEM and AFM results in **Figure 4.1a and f**. The mass (m) of an individual Au nanoplate can be calculated according to **Equation 3.1**, in which V is the volume and ρ is the density. Since ρ_{Au} is 19.30 g/cm^3 and V_{Au} can be calculated from the size of Au nanoplate, the mass of an individual Au nanoplate is $1.54 \times 10^{-13} \text{ g}$. According to **Equation 3.2**, where N is atom number, M is the molar mass and N_A is Avogadro constant, the amount of Au atoms in one Au nanoplate is 4.7×10^8 .

$$m = V\rho \quad (3.1)$$

$$N = \frac{m}{M} N_A \quad (3.2)$$

$$N = \rho^a S \quad (3.3)$$

As for the Au atoms on both top and bottom surfaces of one nanoplate, their amount can be calculated from **Equation 3.3**. ρ^a is atomic packing density, which equals to $1.387 \times 10^{15} \text{ atoms/cm}^2$ for Au (111) facet and S is the area. [2] Thus, the amount of Au atoms on

the surface of an individual nanoplate is 8.88×10^6 . This result shows approximately 2% Au atoms are on the surfaces of Au nanoplates.

3.3 Characterization Techniques

3.3.1 Transmission Electron Microscopy (TEM)

Figure 3.4 Schematic illustration of a TEM [6]. © 1992 by Butterworth-Heinemann, a division of Reed Publishing (USA) Inc.

TEM is a kind of microscopies which is similar to optical microscopy, but the light source is replaced by electron beams in TEM that extremely improve the resolution. When the electron beams transmit through samples, images are formed and can be recorded by photographic film or charge-coupled device (CCD) camera. Since the appearance of first TEM in 1931, this technique has been widely used in material characterization. [3-5]

A schematic of a TEM is shown in **Figure 3.4**. Electron gun, a series of lenses with different functions, specimen stage and imaging system are included in a TEM. [6]

In the electron gun, electrons are generated and accelerated by high voltage which is usually 200 kV. Higher resolution can be achieved in higher accelerated voltage. Generally, thermionic emission gun with tungsten filament or lanthanum hexaboride as the cathode, and field emission gun are the basic types of electron guns. In a thermionic gun, cathode is heated to high temperature to release electrons and the temperature can determine the intensity of electron beams. The generation of electrons on metal surfaces in a field emission gun occurs under an extremely high electric field through tunneling effect. As compared to thermionic emission gun, intensity of electron beams generated by field emission gun is higher. [7]

Different types of TEM images such as bright-field, dark-field images, diffraction pattern, and high resolution TEM (HRTEM) image can be created through different modes. If only transmitted beams pass the objective aperture, bright field images (**Figure 3.5a**) are created. However, the pass of only diffraction beam leads to the formation of dark field image (**Figure 3.5b**). These two kinds of images can be obtained by changing objective aperture in operation. When the TEM is operated in diffraction mode, the diffraction pattern (**Figure 3.5c**) which is generated on the back-focal plane of the objective lens can be recorded. For crystal materials, HRTEM image (**Figure 3.5d**) can be produced through phase contrast. In the formation of HRTEM image, the diffraction and transmitted beams participate simultaneously to generate a phase difference. [7]

Figure 3.5 a) Bright field, b) dark field TEM images, c) electron diffraction pattern and d) HRTEM image. [8, 9] a, b) © 2016 Wiley-VCH Verlag GmbH & Co. c, d) © 2014 Macmillan Publishers Limited.

Energy dispersive X-ray (EDX) spectroscopy which is an attachment of TEM, is a technique to analyze chemical composition of samples. When the incident electrons interact with the specimen, the characteristic X-ray which is specific for each element, is generated from the sample surface. Elemental composition of samples is identified via analyzing the characteristic X-ray by EDX system.

Morphology and structure characterization, and elemental analysis of products were conducted by TEM (Philips 300 FEGTEM) with accelerating voltage 300 kV. TEM samples were prepared by depositing 10 μL of product solution on a copper grid and drying at room temperature.

3.3.2 Scanning Electron Microscopy (SEM)

Figure 3.6 Schematic illustration for the operation of an SEM [7]. © 1992 by Butterworth-Heinemann, a division of Reed Publishing (USA) Inc.

In an SEM, electron beams are focused on specimen surface through the raster, as shown in **Figure 3.6**. When the electron beams pass the specimen surface, electrons from the surface are emitted due to the interaction between incident electrons and specimen surface. The emitted electrons from the surface of specimen can be captured by a detector. Therefore, an image is formed by recording every point (i.e. scanning the sample) that incident electrons hit on the surface of specimen. [7]

When electron beams penetrate the surface of samples, diverse signals such as secondary electrons, backscattered electrons, and characteristic X-rays are generated through interactions between incident electrons and specimen (**Figure 3.7**). Secondary electrons with several keV energies are generated via inelastic scattering and from the surface of sample with a depth less than 50 nm. Morphological and topographical images are commonly created by detecting secondary electrons. Elastic scattering produces the

backscattered electrons with similar energy level to that of electron beams. The backscattered electrons are mostly used for rapid phase discrimination. Since backscattered electrons escape from deeper level (50-300 nm) of sample surface, images created by them show worse spatial resolution, as compared to secondary electron images. When the incident electrons interact with electrons discrete orbitals (shells) of atoms in the specimen, inelastic collisions between them produce X-ray. The wavelength of the emitted X-ray is specific for each element, thus the characteristic X-ray can be used to analyze chemical composition of sample.

Figure 3.7 The interaction zone of electrons and specimen atoms below a specimen surface.

To achieve high resolution in SEM imaging, accelerating voltage is critical. With the increase of accelerating voltage, the probe size is reduced and electron beam brightness is improved, resulting in formation of images with more details on samples. Meanwhile, higher accelerating voltage will decrease the lateral spatial resolution in SEM imaging, because of interactions between electron probe and sample. [7]

In this work, SEM was conducted by JEOL 7600F with accelerating voltage of 15 kV to get the morphological analysis of samples. The samples were prepared via depositing a drop of product solution on silicon substrate and drying at ambient condition.

3.3.3 Atomic Force Microscopy (AFM)

Figure 3.8 Detection of cantilever deflection [7]. © 2004 Springer-Verlag GmbH

In an AFM, the topography of specimen can be mapped through detecting near-field forces between the sharp tip in and specimen. A cantilever with a sharp tip acts as a sensor to detect force through a beam deflection method, as shown in **Figure 3.8**. The elastic bending of the cantilever caused by the force between the specimen and sharp tip is recorded by photodiodes via receiving the laser beam which is reflected by cantilever. The cantilevers are commonly made from silicon nitride or silicon. [7]

In general, the AFM works in either static mode, in which the deflection of cantilever is maintained, or dynamic mode, in which the cantilever is in oscillation. Images produced in static mode show low resolution and the sample surface will be damaged in this mode. On the contrary, dynamic mode can resolve these problems.

In the dynamic mode, three types are included. They are non-contact, tapping and contact modes. **Figure 3.9** shows the schematic illustration of three AFM working modes and the force between tip and sample surface detected in different modes. In the non-contact mode, the cantilever vibrates at its resonant frequency when it is near the specimen surface and detects the attractive force (**Figure 3.9b**) between the specimen and sharp tip. High vertical resolution can be provide in this mode, while the disadvantage is that liquid samples cannot be analyzed. In a tapping mode, the cantilever slightly touches the sample surface followed by leaving away. This intermittent contact produces images with high resolution while avoids damaging the sample surfaces. In the dynamic contact mode, a force modulation image can be produced to reveal the stiffness or elasticity of sample surfaces when the sharp tip oscillates at a low frequency to contact the sample surface. [7]

Figure 3.9 a) Three modes in AFM operation and b) the corresponding force between tip and sample surface.

For the research in this thesis, topography images and corresponding height profiles of products were obtained by AFM Asylum Research Cypher S through tapping mode. The

samples for AFM were produced via dropping 10 μL of product solution on flat silicon wafer. After drying at ambient condition, the samples were analyzed by AFM.

3.3.4 X-Ray Diffraction (XRD)

Since the discovery of X-ray diffraction by crystal, this technique has been well developed to analyze crystal structures. X-ray is a kind of electromagnetic radiation with short wavelength in an order of 0.1 nm, and it is generated by an X-ray tube including electron source and metal electrons.

Figure 3.10 Bragg diffraction by crystal surfaces [7]. © 2008 John Wiley & Sons Inc.

Wave interferences are the basic principle for X-ray diffraction technique. When two waves with the same frequency travel in a phase difference of integer (n) times of wavelength (λ), constructive interference is generated. The planes in a crystal will diffract the incident X-rays. As the illustration shown in **Figure 3.10**, X-ray 1 and 2 are diffracted by facet A and B. If the phase difference of deflected X-rays satisfies the Bragg's Law (**equation 3.4**, d is spacing of two planes and θ is an angle as shown in **Figure 3.10**), constructive interference will occur. [7]

$$n \lambda = 2d \sin \theta \quad (3.4)$$

In modern nomenclature, it is unnecessary to retain n in the Bragg equation. It is usually more convenient to divide both sides of the Bragg equation by n and to define d/n as d_{hkl} . This makes Bragg's law look like the **equation 3.5**.

$$\lambda = 2d_{hkl}\sin \theta \quad (3.5)$$

According to the Bragg's Law, the spacing of crystal planes can be obtained when the angle and wavelength of incident X-ray are given. Thus the crystal information of materials is provided by X-ray diffraction.

Figure 3.11 shows the compositions of an X-ray diffractometer, in which X-ray tube, sample stage and detector are three main parts. Before interact with samples on a flat plate, X-rays produced by tube are first collimated by soller slits (**Figure 3.11**) to make them convergent. Diffracted X-rays pass through receiving slits to form convergent beams and then recorded by a detector (**Figure 3.11**). [7]

Figure 3.11 Illustration of an X-ray diffractometer [7]. © 2008 John Wiley & Sons Inc.

In an X-ray diffractometer, the angle of incident X-ray with designed wavelength is continuously changed to obtain the diffraction pattern revealing the relationship between

diffraction intensity and 2θ (2θ is the angle between incident and diffracted X-rays). The structure and quality of crystals can be identified through comparing the obtained diffraction pattern with that of known crystals.

Besides crystal phase identification, other crystal information such as preferential orientation, crystallite size and residual stress can be obtained from the result of X-ray diffraction.

X-ray diffraction for structure characterization in this thesis was conducted by using Shimadzu Thin Film X-ray diffractometers with Cu-K α radiation. The samples for X-ray diffraction were fabricated by depositing several drops of product solution on glass substrates and then drying at ambient condition.

3.3.5 Electrospray Ionization Mass Spectrometry (ESI-MS)

ESI-MS with high sensitivity and reliability is a technique to analyze molecular structure and mass. In the mass spectrometry, molecules are first converted to ions with either positive or negative charges before they pass through the mass analyzer. Since the ions have different mass/charge (m/z) ratios, they will be separated and sorted in the mass analyzer. Finally, they reach different positions of the detector, which can generate useable signals. The signals are recorded as mass spectrum showing the m/z ratios of the ionized molecules. [10]

Typically, an ESI-MS contains three main parts, which are ion source, mass analyzer and detector as shown in **Figure 3.12**. Due to the extremely high reactivity of ions in the gas phase, high vacuum is required in mass analyzer and detector. [11]

Figure 3.12 The three main components of the ESI-MS and the illustration of final spectrum [11].
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To ionize the analyte in ESI-MS, the solution of analyte in low concentration is first injected to a needle. Then 2-6 kV voltage is applied to the tip of the needle relative to a heated capillary (**Figure 3.13**). Due to the strong electric field, the sample solution converts to highly charged electrospray droplets, as shown in **Figure 3.13**. With the assist of nitrogen flow, the solvent of the charged droplets evaporates and the analytes arrive at the mass analyzer (**Figure 3.13**). If the analyte ions enter into the mass spectrometer at optimized instrumental conditions from the spray needle, the structure of ions remain intact in general. Recently, techniques have been improved to modify the sprayer. For example, pneumatically assisted electrospray and nanoelectrospray have been reported. [12-18]

In the mass analyzer, where static or dynamic magnetic/electric field are generated, ions are sorted based on their ratios of mass and charge. Nowadays, a number of mass analyzers, such as linear quadrupole ion trap and time-of-flight mass analyzer, have been developed based on Lorentz force law or Newton's second law of motion. Different mass analyzers provide results with different resolution, detection limit and mass range. [11]

Finally, the separated ions arrive at the detector, in which the ions are detected by a Faraday cup or an electron multiplier which can analyze ion flux in low amount.

Figure 3.13 The ionized process of analyte in ESI-MS [11]. © 2012 S. Banerjee and S. Mazumdar.

In this thesis, ESI-MS (Thermo Fisher mass spectrometer) was used to analyze the structures of Au complexes. The analytes were first converted to ions with positive charges, and the time of flight was analyzed. In the preparation of samples, 0.05 mL of 1mM analyzer was diluted in 1 mL of methanol. The samples were analyzed immediately after the preparation.

3.3.6 Ultraviolet-Visible-Near Infrared (UV-vis-NIR) Spectroscopy

UV-vis-NIR spectroscopy is a widely used technique to analyze molecules qualitatively and quantitatively through measuring the UV-vis-NIR absorption of analytes. UV light from 180 to 400 nm (**Figure 3.14**) and visible light from 400 to 750 nm (**Figure 3.14**) originates from the excitation of electronic states. Information of π -electron conjugation in the molecules is provided by UV absorption. In general, molecules with larger π -electron conjugation show absorption at longer wavelength and stronger intensity. The wavelength of near infrared light is from 750 to 2500 nm (**Figure 3.14**). Their absorption with inherently weak intensity is due to combinations of fundamental vibrations together with excitation of overtones. Though the causes for light absorption of molecules at UV, visible and NIR regions are different, principles of instruments for three types of light are

similar, and the measurement of absorption from 180 to 2500 nm can be conducted together.

Figure 3.14 The wavelength of different types of light.

In the UV-vis-NIR spectroscopy, the quantity of absorbed light by samples is defined as the difference between radiation of incident light (I_0) and that of transmitted light (I). It is expressed as transmittance (T) as shown in **equation 3.6** or absorbance (A) which is commonly used in research. The relationship between transmittance and absorbance is demonstrated in **equation 3.7**. The UV-vis-NIR spectroscopy can be applied to identify the structure by comparing the absorption wavelength of samples with that of known molecules and analyze samples quantitatively based on Beer's law.

$$T = \frac{I}{I_0} \quad (3.6)$$

$$A = -\log T \quad (3.7)$$

In this research, UV-vis-NIR spectroscopy was conducted with Shimadzu UV-1800 spectrophotometer. Liquid samples were analyzed in quartz cells and the reference was the solvent.

3.3.7 Fourier Transform Infrared Spectroscopy (FTIR)

In the FTIR which is a vibrational spectroscopic technique, the infrared radiation absorbed by samples is measured through Fourier transform method. The components and structures of molecules can be identified by the absorption wavelength.

Under irradiation of infrared light, molecules are excited to a higher vibrational state. The wavelengths of infrared light absorbed by molecules are characteristic, which is based on the structures of molecules. The final FTIR spectrum, which is a plot of transmittance versus wavenumber is Fourier transformed by computer from an interferogram obtained by the detector in FTIR spectrometer. The examples of an interferogram and FTIR spectrum are shown in **Figure 3.15**. [7]

Figure 3.15 a) Interferogram obtained by FTIR spectrometer and the corresponding b) FTIR spectrum after Fourier transform [7]. © 1996 CRC Press LLC

FTIR spectrometer contains three main parts which are infrared light source, beam splitter and infrared detector. Wideband radiation is produced in infrared light source via heating solid materials like *Nernst glower* and *Globar*. Beam splitters are semi-transparent to infrared light. Half percent infrared light is reflected by them to a moving mirror and the remained light is transmitted by them to a fixed mirror at the same time. The infrared detector, which is usually a thermal or semiconductor detector, is used to analyze the energy of infrared light from the specimen through converting signals of light to that of electricity.

In an attenuated total reflectance (ATR) FTIR spectrometer, samples are in contact with the surface of an ATR crystal intimately, as shown in **Figure 3.16**. When the infrared light is directed into the ATR crystal, reflection of infrared light is generated from the internal surface of the ATR crystal and an evanescent wave is created. The evanescent wave projects into the specimen on the crystal orthogonally and absorbed by specimen partially. The remaining reflected infrared light is measured by a detector. This ATR process is illustrated in **Figure 3.16**. ATR-FTIR shows several advantages such as simple sample preparation, excellent analysis of thick specimens.

Figure 3.16 Schematic illustration of a multiple reflection ATR process.

A Perkin Elmer Frontier spectrophotometer was applied to obtain FTIR and ATR-FTIR spectra in this thesis. The samples for FTIR were obtained by dropping product solutions on KBr wafer and drying. Solid samples were used for ATR-FTIR through drying ethanol solutions of products at 50 °C.

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Chapter 4

Formic Acid-Assisted Synthesis of Gold and Other Noble Metal Nanoplates

Chapter 4 presents the synthetic strategy of Au nanoplates through a facile one-step method. The morphology, structure and optical property of gold nanoplates are studied. This is followed by the understanding of formation mechanism of plate-like gold nanostructures. And then the approaches for optimizing the synthetic method are discussed by investigating the influence of reactant concentrations, reaction temperature and pH on the growth of gold nanoplates. Finally, the synthesis of silver, palladium and platinum nanosheets is provided through this one-step method.

4.1 Introduction

In the past decades, Au nanostructures have been widely studied due to their unique size and morphology dependent electronic, chemical, physical, and optical properties. [1-4] To date, a myriad of Au nanostructures, such as nanoparticles [5, 6], nanorods [7], nanorings [8, 9], nanowires [10], nanodisks [11], nanocubes [12] and branched nanocrystals [13, 14], have been synthesized. Anisotropic Au nanoplates are a specifically interesting class among Au nanostructures, due to their unique optical properties which provide possible applications in cancer hyperthermia, sensing, imaging, and biological assays. [15-17] Nowadays, the most common method in the fabrication of Au nanoplates is the two-step seed-mediated approach with the assistance of surfactants with complex structures like CTAB. [18] However, it is complicated to prepare Au nanoplates through this two-step method in which small Au seeds are synthesized in advance. Moreover, synthesis with multiple steps makes it difficult to understand the formation of Au nanoplates theoretically.

Herein, a facile one-step method to prepare Au nanoplates with high yield in the presence of formic acid was presented. The formation mechanism was also discussed. Furthermore, this synthetic method was extended to prepare silver, palladium and platinum nanoplates. This formic acid assisted synthesis provides a simple method to prepare noble metal nanoplates and explore the mechanism underlying their growth.

4.2 Experimental Methods

4.2.1 Materials

Formic acid (HCOOH , $\geq 96\%$), tetrachloroauric(III) acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.9\%$), chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$), sodium hydroxide (NaOH , 97%) and polyvinylpyrrolidone (PVP, $M_w \approx 55,000$) were purchased from Sigma-Aldrich. Silver nitrate (AgNO_3) was purchased from Fluka.

4.2.2 One-Step Synthesis of Gold Nanoplates

4.2.2.1 HCOOH Concentration Dependent Synthesis of Gold Nanoplates

Typically, 2.5 mL of PVP solution (4 mM) and 2 mL of HCOOH solution (0.05mM) were thoroughly mixed at 50 °C. Then 0.5 mL of HAuCl₄ solution (10 mM) was rapidly added into the above solution followed by strong shaking of the mixture for 30 s. After reacting at 50 °C for 4 h, Au nanostructures were obtained. The Au nanostructures were finally centrifuged with ethanol twice and dispersed in ethanol. To explore the effects of HCOOH concentrations on fabrication of Au nanostructures, a series of similar experiments were conducted through changing HCOOH concentrations to 1 mM, 2 M and 10 M, respectively.

4.2.2.2 HAuCl₄ Concentration Dependent Synthesis of Gold Nanoplates

Typically, 2.5 mL of PVP solution (4 mM) and 2 mL of HCOOH solution (5 M) were thoroughly mixed at 50 °C. Then 0.5 mL of HAuCl₄ solution (1 mM) was rapidly added into the above solution followed by strong shaking of the mixture for 30 s. After reacting at 50 °C for 4 h, Au nanostructures were obtained. The Au nanostructures were finally centrifuged. To explore the effects of HAuCl₄ concentrations on fabrication of Au nanostructures, a series of similar experiments were conducted through changing HAuCl₄ concentrations to 0.2 mM, 1 mM and 4 mM, respectively.

4.2.2.3 Temperature Dependent Synthesis of Gold Nanoplates

In a typical preparation, 2.5 mL of PVP solution (4 mM) and 2 mL of HCOOH solution (5 M) were thoroughly mixed at 0 °C. Then 0.5 mL of HAuCl₄ solution (10 mM) was rapidly added into the above solution followed by strong shaking of the mixture for 30 s. After reacting at 0 °C for 4 h, Au nanostructures were obtained. The Au nanostructures were finally centrifuged with ethanol. Besides the reaction temperature at 0 °C, higher reaction temperatures at 25 °C, 50 °C, and 75 °C were also chosen to prepare Au nanoplates in the same synthetic method.

4.2.2.4 pH Value Dependent Synthesis of Gold Nanoplates

Briefly, 0.38 mL of HCOOH and 1.926 mL of 5 M NaOH were added in 2.194 mL of water at 50 °C. Then 0.5 mL of HAuCl₄ solution (10 mM) was rapidly added into the above solution followed by strong shaking of the mixture for 30 s. After reacting at 50 °C for 4 h, Au nanostructures were obtained. The Au nanostructures were finally centrifuged with ethanol and dispersed in ethanol. In another case, the pH value was adjusted to 11.5 while the concentrations of HCOOH and HAuCl₄ are kept at 2 M and 1mM, respectively.

4.2.2.5 Surfactant-Free Synthesis of Gold Nanoplates

Typically, 0.38 mL of HCOOH was added in 4.12 mL of water at 50 °C. Then, 0.5 mL of 10 mM HAuCl₄ was rapidly added into the above solution followed by strong shaking of the mixture for 30 s. After reacting at 50 °C for 4 h, Au nanostructures were obtained. Finally, the products were washed by ethanol three times and disperse in ethanol.

4.2.3 One-Step Synthesis of Other Noble Metal Nanoplates

4.2.3.1 Silver Nanoplates

Briefly, 2 mL of 5 M HCOOH aqueous solution was firstly added into 2.5 mL of 4 mM PVP solution at 75 °C. After reacting for 3 min, 0.5 mL of 10 mM AgNO₃ aqueous solution was added into the mixed solution rapidly. After strong shaking for 30 s, the mixture reacted at 75 °C for 1 d. The products were finally centrifuged with ethanol twice and dispersed in ethanol.

4.2.3.2 Palladium Nanoplates

Firstly, PdCl₂ (89.6 mg, 0.5 mmol) was dissolved in 1 mL of 37% HCl aqueous solution. Then the above PdCl₂ solution was diluted by adding water to required concentration. Typically, 2.5 mL of PVP solution (4 mM) and 2 mL of HCOOH solution (5 M) were thoroughly mixed at 50 °C. Then 0.5 mL of PdCl₂ aqueous solution (10 mM) was rapidly added into the above solution followed by strong shaking of the mixture for 30 s. After reacting at 50 °C for 4 h, Pd nanoplates were obtained. The Pd nanoplates were finally centrifuged with ethanol twice and dispersed in ethanol.

4.2.3.3 Platinum Nanoplates

Typically, 2.5 mL of 4 mM PVP solution was mixed with 2 mL of 5 M HCOOH at RT firstly. Then 0.5 mL of 10 mM H_6PtCl_2 solution was rapidly added into the mixed solution followed by strong shaking of the mixture for 30 s. After reacting at RT for 2 d, irregular Pt nanoplates were obtained. The irregular Pt nanoplates were finally centrifuged with ethanol twice and dispersed in ethanol.

4.2.4 Sample Preparation for Characterization

UV-vis-NIR absorbance spectra were obtained with a Shimadzu UV-1800 spectrophotometer. Well-dispersed solutions of Au nanostructures were dropped on Si wafers to prepare AFM and SEM samples. AFM images were collected on an AFM Asylum Research Cypher S and SEM imaging was performed by a JEOL 7600F field-emission scanning electron microscope. TEM images were collected on a Philips 300 FEGTEM and the samples were prepared by immobilizing 10 μL of Au nanostructures solution on Cu grids. X-ray Diffraction was collected by using Shimadzu Thin Film X-ray diffractometers and the sample was obtained by deposition a drop of Au nanostructures solution on a glass slide and dried under ambient conditions. The structures of Au complexes, samples of which were prepared by adding a drop of Au complexes aqueous solution into 1 mL of methanol, were determined with a Thermo Fisher mass spectrometer. The (ATR) FTIR spectral analysis was performed using a Perkin Elmer Frontier spectrophotometer and the sample was prepared by drying Au nanoplates solution at ambient conditions.

4.2.5 Simulation Methods of Interactions between HCOOH and Gold

The first-principles calculations are performed via the Vienna ab initio simulation package (VASP) package [19] within the framework of density functional theory to calculate the surface energies (γ) of Au facets. Electronic cutoff energy of 400 eV and the PW91 functional [20] as the exchange-correlation functional are adopted. The surfaces of Au are simulated by creating slab models constructed from the bulk Au with a lattice constant of 4.18 Å. Nine atomic and eleven layers are included for (111) and (110)

surface, respectively, together with a vacuum layer with a thickness of 20 Å. Only the top surface in the slab is allowed to relax and the three atomic layers in the bottom surface are fixed at bulk position. We use the k-point samplings of $6 \times 6 \times 1$ and $3 \times 4 \times 1$ for (111) and (110) surfaces, respectively. The surface energy (γ_{surface}) of Au surfaces is calculated through the following formula $\gamma_{\text{surface}} = (E_{\text{slab}} - n_{\text{total}} \times E_{\text{Au}} - E_{\text{bottom}})/S_{\text{surface}}$, where E_{slab} and E_{Au} are the total energies of the one-side relaxed slab and a bulk Au atom, respectively. n_{total} and S_{surface} are the number of Au atoms in the slab and the area of the slab surface. E_{bottom} is formation energy of the bottom surface with fixing atoms calculated by $E_{\text{bottom}} = (E_{\text{fixed}} - n_{\text{total}} \times E_{\text{Au}})/2$, where E_{fixed} is the total energy of pristine unrelaxed symmetric slab with atoms being fixed in bulk position. For the X molecular decorated Au surface (denoted as Au-X), the γ_{surface} is calculated as: $\gamma_{\text{surface}} = (E_{\text{Au-X}} - n_{\text{total}} \times E_{\text{Au}} - E_{\text{bottom}} - mE_X)/S_{\text{surface}}$, where $E_{\text{Au-X}}$ is total energy of the Au slab adsorbed with X molecule at the top surface, m is the total number of X molecules adsorbed, and E_X is the energy of each X molecule.

4.3 Results and Discussion

4.3.1 Structural and Optical Study of Gold Nanoplates

Figure 4.1 Morphology characterization of Au nanoplates synthesized at 50 °C in an aqueous solution with 1 mM HAuCl₄, 2 M HCOOH and 2 mM PVP for 4 h. a) Representative TEM and (inset) SEM images of Au nanoplates. b - d) Morphology characterization of individual nanoplate in three shapes (triangle, truncated triangle and hexagon). For each shape, 1) TEM image and 2) SEM image. e) AFM image and f) the corresponding height profile of Au nanoplate.

Figure 4.1a shows the typical TEM and SEM images of Au nanoplates prepared at 50 °C in an aqueous solution with 1 mM HAuCl₄, 2 M HCOOH and 2 mM PVP for 4 h. The average edge length of Au nanoplates is ~860 nm. As shown in **Figure 4.1b-d**, these Au nanoplates are a mixture of triangles, truncated triangles and hexagons. The representative AFM image (**Figure 4.1e**) and corresponding height profile (**Figure 4.1f**) of Au nanoplate show that the average thickness of Au nanoplate is ~25 nm.

Figure 4.2 Morphology and structure characterization of Au nanoplates. a) HRTEM image of Au nanoplate and the inset shows the electron diffraction pattern of corresponding Au nanoplate. b)

TEM image of an individual Au nanoplate and the HRTEM is taken in the red square area. c) XRD pattern of Au nanoplate.

A HRTEM (**Figure 4.2a**) taken from one of the Au nanoplates (**Figure 4.2b**) reveals the Au nanoplate to be single-crystalline. The fringe spacing of 0.14 nm is indexed to $\{220\}$ reflections of fcc Au. [21, 22] The inset in **Figure 4.2a** shows a typical electron diffraction pattern recorded by directing the electron beam perpendicular to the flat face of an individual nanoplate. The hexagonal diffraction spots indicate that the top and bottom facets of nanoplates are presented by $\{111\}$ planes. [18] **Figure 4.2c** shows XRD pattern of Au nanoplates. The overwhelmingly strong (111) diffraction peak at $2\theta = 38.2^\circ$ and the (200) diffraction peak can be clearly seen. The other weak peaks, assigned to (220) and (311), originated from a small number of Au nanoparticles. As shown in **Figure 4.3**, each nanoplate is bounded by two $\{111\}$ planes as the top and bottom faces and a mixture of $\{111\}$ and $\{100\}$ planes as the side faces. [23, 24]

Figure 4.3 3D models of Au nanoplate from side and top views.

Figure 4.4 Absorption spectrum of Au nanoplates measured by using FTIR. The Au nanoplates were prepared with 2 M HCOOH, 1 mM HAuCl₄, 2 mM PVP at 50 °C for 4 h. And the sample for FTIR was obtained by dropping Au nanoplates solution on KBr wafer.

By the way, the UV-vis-NIR absorption of Au nanoplates mixed into KBr sample is measured by FTIR instead to investigate their very wide absorption up to 5.7 μm (**Figure 4.4**). The properties of Au nanoplates in liquid solution are studied but with a limited spectroscopic range due to the strong absorption of solvent in this near- and infrared range.

4.3.2 Formation Mechanism of Gold Nanoplates

Besides the above morphological and structural study of Au nanoplates, the mechanism behind for the formation of Au nanoplates is investigated theoretically. It is reported that the adsorption of an appropriate ligand can control the morphology of nanostructures through interaction between ligands and metal facets. [25-27] As shown in **Figure 4.5**, the surface energies of Au facets with HCOOH are calculated. The surface energies of ligand-bound Au follow a sequence of $\gamma_{\{110\}} > \gamma_{\{100\}} > \gamma_{\{111\}}$, which means it favors the formation of $\{111\}$ facets dominated Au nanostructures. At the same time, HCOOH

bounded $\{111\}$ and $\{100\}$ facets have similar surface energies ($\gamma_{\{100\}}$ is approximately only 0.3 times more than $\gamma_{\{111\}}$ after binding of HCOOH on Au facets), which means these two facets with lowest surface energies can be expressed simultaneously in the final morphology. Therefore, $\{111\}$ and $\{100\}$ faced Au nanoplates with $\{111\}$ dominated facets are formed (**Figure 4.3**). Further discussion and investigation on growth mechanism of Au nanoplates including the role of γ ratios are presented in chapter 5 through controlling the interactions between ligands and Au species (**Figure 5.1** and **5.14**).

Figure 4.5 Simulation of the binding of HCOOH on three Au facets. a) Simulated surface energies after the binding of HCOOH on Au $\{111\}$, $\{100\}$ and $\{110\}$ facets. b) The optimized binding formats of HCOOH on different Au facets.

Figure 4.6 ATR-FTIR spectra of PVP and purified Au nanoplates prepared with 2 M HCOOH, 1 mM HAuCl₄, 2 mM PVP at 50 °C for 4 h. ν - stretching motion, $\nu_{as/s}$ – asymmetric/symmetric stretching, δ - bending motion.

The ATR-FTIR spectrum of purified Au nanoplates prepared with 2 M HCOOH, 1 mM HAuCl₄, 2 mM PVP at 50 °C for 4 h is shown in **Figure 4.6**. Peaks at 2914, 1538 and 1465 cm⁻¹ are the $\nu(\text{CH})$, $\nu_{as}(\text{OCO})$ and $\nu_s(\text{OCO})$ modes of HCOOH, respectively. [28] In addition, the absence of $\delta(\text{CH})$ mode of PVP at 1287 cm⁻¹ implying that few PVP remains in the Au nanoplates. [29] These ATR-FTIR results experimentally demonstrate the adsorption of HCOOH on Au nanoplates.

4.3.3 Optimized Synthesis of Gold Nanoplates

4.3.3.1 Influence of Surfactant PVP

With the use of a large amount of HCOOH at 2M, they intimately interact with Au due to their small molecular size and high surface adsorption density due to strong interaction. With a large molecular weight, PVP is not allowed to closely interact with Au ions due to its large molecular size, and low surface adsorption/binding density due to stereo

hindrance (less space to bind functional groups of PVP to Au surfaces). The ATR-FTIR result of obtained Au nanoplates also suggests that only HCOOH adsorbs on the surfaces of Au nanoplates (**Figure 4.6**). With the use of a large amount of 2 M HCOOH as both coordination and reducing ligand, a small amount of 2 mM PVP as stabilizer does not play a major role as coordinator to bind Au surfaces but stabilizer to stabilize resulting nanostructures from agglomeration and precipitation. Meanwhile, Au nanoplates were also formed in the absence of PVP (**Figure 4.7**), indicating its stabilization effect during the formation of Au nanoplates.

Figure 4.7 TEM and optical images (insets) of Au nanoplates obtained at 50 °C in an aqueous solution with 1 mM HAuCl₄, 2 M HCOOH for 4 h. More products were sticky on the internal surface of bottle in the absence of PVP as stabilizer.

4.3.3.2 Influence of pH Value

It is known that HCOOH can ionize in aqueous solution and it shows different formula at various pH. Thus the influence of pH value on the growth of Au nanoplates should be considered.

With addition of 2 M HCOOH and 1mM HAuCl₄ at 50 °C, the pH value of reaction system is about 1.5 and Au nanoplates are obtained (**Figure 4.1a**). To investigate the influence of pH, NaOH is added into the reaction system to adjust the pH to 6.5 and 11.5, respectively, while other reaction conditions are the same. It should be noted that the reactions at pH 6.5 and 11.5 are conducted in the absence of PVP, since PVP precipitates with addition of NaOH. The detailed synthetic method is shown in 4.2.2.4.

Figure 4.8 pH dependent synthesis of Au nanostructures. The TEM images and corresponding photos (insets) of Au nanostructures prepared in an aqueous solution with 1 mM HAuCl₄, and 2 M HCOOH at a) pH = 6.5, and b) pH = 11.5.

Figure 4.8 shows the TEM images of Au nanostructures prepared at different pH. Non-uniform Au nanoparticles in the absence of Au nanoplates are obtained at pH 6.5 (**Figure 4.8a**) and 11.5 (**Figure 4.8b**). The purple solution of products (**Figure 4.8 inset**) also indicates the formation of Au nanoparticles.

Figure 4.9 The equilibrium form of formic acid as a function of pH at 50 °C. Reprinted with permission from. [30] © Journal of Mining and Metallurgy

When the pH value of reaction system is 1.5, HCOOH (**Figure 4.9**) is the main formula in reaction mixtures. [30] As discussed above, the adsorption of HCOOH on Au facets leads to the formation of Au nanoplates (**Figure 4.5**). However, at pH higher than 6.5, HCOOH is totally ionized to HCOO⁻ (**Figure 4.9**). In the presence of HCOO⁻, surface energies of Au facets after binding of HCOO⁻ follow an order of $\gamma_{\{110\}} < \gamma_{\{111\}} < \gamma_{\{100\}}$ (**Figure 4.10**). [31] The change of surface energies in HCOO⁻ bound Au facets leads to the failed synthesis of Au nanoplates. This result demonstrates that lower pH facilitates the formation of Au nanoplates since HCOOH which assists to prepare Au nanoplates prefers to form at lower pH.

Figure 4.10 The surface energies (J/m^2) of different Au facets bounded with HCOO^- .

4.3.3.3 Influence of HCOOH Concentration

Table 4.1 Synthesis conditions of HCOOH concentration dependent Au nanoplates.

	HAuCl ₄	HCOOH	PVP ($M_w \approx 55,000$)	Temperature	Time	pH value
1	1 mM	0.01 M	2 mM	50 °C	4 h	3.00
2	1 mM	0.1 M	2 mM	50 °C	4 h	2.50
3	1 mM	2 M	2 mM	50 °C	4 h	1.50
4	1 mM	10 M	2 mM	50 °C	4 h	0.80

Figure 4.11 illustrates the UV-vis-NIR absorption spectra of Au nanoplates synthesized in different HCOOH concentrations. The spectra clearly show an increase of Au nanoplates absorption at 1100 nm, as the increase of HCOOH concentrations from 0.01 to 2 M. Meanwhile, the solution of products becomes yellow, light orange and eventually orange, when HCOOH concentrations range from 0.01 to 2 M (**Figure 4.11 inset**). These results mean that the yield of Au nanoplates raises with increase of HCOOH

concentrations. In **Figure 4.11**, the peaks at approximately 600 nm are the absorption of Au nanoparticles formed in products (**Figure 4.1a** and **4.12**).

Figure 4.11 Absorption spectra of Au nanoplates obtained at 50 °C for 4 h with 1 mM HAuCl₄, 2 mM PVP and different concentrations of HCOOH from 0.01 M to 10 M. Inset: corresponding optical images of Au nanoplates.

Figure 4.12 SEM images of Au nanoplates prepared at 50 °C in an aqueous solution with 1 mM HAuCl₄, 2 mM PVP, a) 0.01 M HCOOH, b) 0.1 M HCOOH and c) 10 M HCOOH for 4 h.

As shown in **table 4.1**, the pH increases with reduce of HCOOH concentration. When the pH in reaction system increases, HCOOH is more likely to ionized to HCOO⁻ which hinders the formation of Au nanoplates (**Figure 4.9** and **4.10**). Therefore, yield of Au

nanoplates reduces with decrease of HCOOH concentration. However, the peak of Au nanoplates at 1100 nm decreases when HCOOH concentration continues to increase (**Figure 4.11**). This is because Au nanoplates are etched at high HCOOH/HAuCl₄ ratio (etching of Au nanoplates is discussed in chapter 6). **Figure 4.1a** and **4.12** show SEM images of Au nanoplates obtained with addition of different HCOOH concentrations which have little influence on size of Au nanoplates.

4.3.3.4 Influence of HAuCl₄ Concentration

Table 4.2 Synthesis conditions of HAuCl₄ concentration dependent Au nanoplates.

	HAuCl ₄	HCOOH	PVP (M _w ≈ 55,000)	Temperature	Time	pH value
1	0.1 mM	2 M	2 mM	50 °C	4 h	1.50
2	0.2 mM	2 M	2 mM	50 °C	4 h	1.50
3	1 mM	2 M	2 mM	50 °C	4 h	1.50
4	4 mM	2 M	2 mM	50 °C	4 h	1.50

To explore the influence of HAuCl₄ concentrations on the growth of Au nanoplates, the reactions are conducted with addition of various amount of HAuCl₄ while the other reaction conditions are the same (**Table 4.2**).

Figure 4.13 TEM images of Au nanoplates prepared at 50 °C in an aqueous solution with 2 M HCOOH, 2 mM PVP, a) 0.1 mM HAuCl₄ and b) 0.2 mM HAuCl₄ for 4 h.

Figure 4.14 SEM image of Au nanoplates prepared at 50 °C in an aqueous solution with 2 M HCOOH, 2 mM PVP and 4 mM HAuCl₄ for 4 h.

The morphologies of Au nanostructures prepared in different HAuCl₄ concentrations are shown in **Figure 4.13** and **4.14**. When the concentration of HAuCl₄ is as low as 0.1 mM, only non-uniform Au nanoparticles are formed (**Figure 4.13a**). Correspondingly, the absorption of Au nanostructures synthesized in 0.1 mM HAuCl₄ only shows a peak at about 538 nm which is the absorption of Au nanoparticles (**Figure 4.15**). As the HAuCl₄ concentration increases to 0.2 mM, small Au nanoplates with average size of ~100 nm begin to form (**Figure 4.13b**). Meanwhile, when the HAuCl₄ concentration is 0.2 mM, a weak absorption at 1100 nm is observed, indicating the growth of Au nanoplates (**Figure 4.15**). With the increase of HAuCl₄ concentrations to 1 mM and 4 mM, the average edge lengths of Au nanoplates grow to ~860 nm (**Figure 4.1a**) and ~8 µm (**Figure 4.14**), and the absorption of Au nanoplates at 1100 nm grows (**Figure 4.15**). However, when the HAuCl₄ concentration is as high as 4 mM, Au³⁺ cannot be totally reduced during the reaction time, which is proved by the absorption of Au³⁺ at about 310 nm after reacting for 4 h (**Figure 4.15**). The color change of Au nanostructure aqueous solutions from purple to brown also demonstrates that the shape of Au nanostructures changes from nanoparticles to nanoplates with the increase of HAuCl₄ concentrations (**Figure 4.15 inset**).

Figure 4.15 Absorption spectra of Au nanoplates obtained at 50 °C for 4 h with 2 M HCOOH, 2 mM PVP and different concentrations of HAuCl₄ from 0.1 mM to 4 mM. Inset: corresponding optical images of Au nanoplates.

This shows that the size of Au nanoplates increases as the increase of HAuCl₄ concentrations from 0.2 mM to 4 mM (**Figure 4.13b**, **4.1a** and **4.14**), due to more Au atoms reduced from Au precursors can adsorb on Au nanoplates in higher HAuCl₄ concentrations. However, Au nanoplates cannot be fabricated in low HAuCl₄ concentration (i.e., 0.1 mM, **Figure 4.13a** and **4.15**). This is interesting and will be discussed in chapter 6.

4.3.3.5 Influence of Reaction Temperature

Table 4.3 Synthesis conditions of temperature dependent Au nanoplates.

	HAuCl ₄	HCOOH	PVP (M _w ≈ 55,000)	Temperature	Time
1	1 mM	2 M	2 mM	0 °C	4 h
2	1 mM	2 M	2 mM	25 °C	4 h
3	1 mM	2 M	2 mM	50 °C	4 h
4	1 mM	2 M	2 mM	75 °C	4 h

Figure 4.16 UV-vis-NIR absorption and optical images (insets) of Au nanoplates prepared at different temperatures in an aqueous solution with 1 mM HAuCl_4 , 2 M HCOOH and 2 mM PVP for 4 h.

Figure 4.17 SEM images of Au nanoplates prepared at a) RT and b) 75 °C in an aqueous solution with 1 mM HAuCl_4 , 2 M HCOOH and 2 mM PVP for 4 h.

The influence of temperature on the formation of Au nanoplates is further investigated (Table 4.3). At 0 °C, the reaction mixture is still yellow even after reacting for 4 h (Figure 4.16inset). Meanwhile, the absorption of Au nanoplates centered at 1100 nm is not detected and the absorption peak of HAuCl_4 at 313 nm is still observed, indicating the

reduction of HAuCl_4 to form Au nanoplates cannot occur at 0 °C (**Figure 4.16**). With the increase of reaction temperatures from 0 °C to 50 °C, the absorption of Au nanoplates at 1100 nm grows while the absorption of HAuCl_4 at 313 nm decreases, indicating the increase of yield in Au nanoplates (**Figure 4.16**). This is because HCOOH and HAuCl_4 are more active at higher temperature and the reaction rate is improved, leading to increase of yield in Au nanoplates at the same reaction time. As compared to Au nanoplates prepared at 50 °C, a slight decrease is observed in the absorption of Au nanoplates at 1100 nm (**Figure 4.16**) and the amount of Au nanoparticles is increased when reaction temperature is 75 °C (**Figure 4.1a** and **Figure 4.16b**). The solution of Au products synthesized at 75 °C turns to purple instead of orange the color of Au nanoplates, due to the increased amount of Au nanoparticles (**Figure 4.16 inset**). With the increase of temperature to 75 °C, the reaction rate is too quick and the concentration of metal atoms in solution is too high so that less plate-like seeds are generated, resulting in lower yield in Au nanoplates and increased Au nanoparticles. [24, 32, 33] As shown in **Figure 4.1a** and **4.17**, the size of Au nanoplates prepared at different temperatures is similar.

4.3.4 One-Step Synthesis of Other Metal Nanoplates

Figure 4.18 Morphologies of noble metal nanoplates synthesized by using HCOOH as ligand. a) TEM image of Ag nanoplates prepared at 75 °C in an aqueous solution with 2 M HCOOH, 1 mM AgNO_3 , and 2 mM PVP for 1 d. b) TEM image of Pd nanoplates prepared at 50 °C in an aqueous solution with 2 M HCOOH, 1 mM PdCl_2 , and 2 mM PVP for 4 h. c) TEM image of irregular Pt nanoplates prepared at RT in an aqueous solution with 2 M HCOOH, 1 mM H_6PtCl_2 .

This synthetic strategy has been further extended to prepare other noble metal nanostructures. As shown in **Figure 4.18**, triangular Ag (**Figure 4.18a**), round Pd

(**Figure 4.18b**) and irregular Pt (**Figure 4.18c**) nanoplates are obtained in similar reactions with HCOOH as ligand. The mechanism for the formation of these nanoplates is still under research.

4.4 Conclusions

A simple one-step method has been provided to produce Au nanoplates with average edge length of ~860 nm and thickness of ~25 nm through heating HCOOH and HAuCl₄ aqueous solution. The structural characterization of Au nanoplates demonstrates that the Au nanoplates are atomically flat and enclosed by {111} facets as the top and bottom surfaces and a mixture of {111} and {100} facets as side surfaces. The formation of plate-like Au nanostructures is due to the adsorption of HCOOH on the facets of Au nanostructures, which results in a similar $\gamma_{\{111\}}$ and $\gamma_{\{100\}}$. Additionally, the pH, HCOOH concentration, HAuCl₄ concentration and reaction temperature are found to be important for the synthesis of Au nanoplates. The optimal condition to synthesize Au nanoplates is heating 1 mM HAuCl₄ and 2 M HCOOH aqueous solution at 50 °C in the presence of PVP. Such Au nanoplates with extremely flat surfaces and unique optical properties have potential applications in detecting and biomedicine. Meanwhile, this simple reaction system in which small organic molecules services as both reducing agents and ligands provides a possibility to further explore the formation of Au nanostructures. Furthermore, the synthetic method has been used to prepare Ag, Pd and Pt nanosheets.

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Chapter 5*

Morphological Growth and Theoretical Understanding of Gold Nanoplates through Binding Simple Aldehyde-Containing Ligands to Gold Species with Variable Valences

In this chapter, the growth of gold nanostructures and their formation mechanism are presented through tuning the interactions between various ligands and Au^{n+} ($n = 3, 1$ and 0). The morphology control of gold nanostructures is first discussed through investigating the binding of ligands and gold. This is followed by exploring the intermediate process via capture of Au^+ during reduction of Au^{3+} to Au^0 . Furthermore, a formation mechanism of ligand mediated synthesis of anisotropic gold nanostructures is provided, which could guide the fabrication of gold nanostructures in further study.

*This section was submitted substantially as J. Xia, Z. L. Dong, X. Hu and M. Y. Han. Morphological Growth and Theoretical Understanding of Gold and Other Noble Metal Nanoplates. *Chemistry – A European Journal*. **2018**.

5.1 Introduction

More advances in morphological formation of Au nanostructures have been realized in recent years after many decades' efforts in developing synthetic methodologies and understanding underlying growth mechanisms, which in turn lead to promising diverse applications in catalysis, imaging, sensing, detection and therapeutics. [1-10] In particular, there is great success to produce Au nanostructures via chemical reduction of widely used chloroauric acid [11-14] (i.e., HAuCl_4) by different reducing agents. With strong reducing agents [15, 16] (e.g., sodium borohydride), the reduction of Au^{3+} to Au^0 is rapid and thus difficult to reveal its intermediary process during growth of Au nanostructures. As such, it is of importance to explore slow reduction of Au^{3+} to Au^0 with weak reducing agents, in which intermediate may be captured in liquid phase at optimized conditions during growth of Au nanostructures. As demonstrated earlier in solid phase, thermal decomposition of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in artificial air proceeds via three consecutive steps to produce AuCl_3 , AuCl and Au^0 at 180, 240 and 320 °C, respectively. [17] As an intermediate, AuCl is only obtained above 190 °C by slowly cleaving AuCl_3 in solid phase. This exhibits that AuCl has a higher chemical stability than AuCl_3 , in agreement with its higher binding energy (E_b) of Au^+-Cl^- (5.07 eV) than $\text{Au}^{3+}-\text{Cl}^-$ (4.61 eV) as simulated. As such, this implies that Au^+ intermediate could also be captured in liquid phase during slow reduction of Au^{3+} with weak reducing agents.

With appropriate coordination ability, weak reducing agents may substitute Cl^- in AuCl_4^- . As an example, formic acid with aldehyde group (i.e., $\text{HCO}-\text{OH}$) has much weaker binding affinity to Au^{3+} than Cl^- (1.15 eV vs. 4.61 eV) (**Table 5.1**), and only replaces Cl^- partially. Interestingly, HCOOH has stronger binding affinity to Au^+ than Au^{3+} (1.75 eV vs. 1.15 eV) so that intermediate Au^+ may be captured before reducing to Au^0 during growth of Au nanostructures. In comparison, other ligands such as formaldehyde, acetaldehyde, formamide and dimethylformamide (i.e., $\text{HCO}-\text{H}$, $\text{HCO}-\text{CH}_3$, $\text{HCO}-\text{NH}_2$ and $\text{HCO}-\text{NH}(\text{CH}_3)_2$) with aldehyde groups (**Table 5.1**) have similar trend in binding affinities to both Au^+ and Au^{3+} . Upon disproportionation of Au^+ to Au^0 and Au^{3+} , the binding affinity of ligands to Au^0 is crucial in controlling growth of Au nanostructures. These selected ligands with aldehyde groups have much weaker affinity to Au^0 compared

to Au^{3+} and Au^+ , and thus is difficult to be dissociated from the Au complexes until reduction to Au^0 . In comparison, HCOOH has the strongest affinity to Au^0 while other ligands have much weaker ones. Correspondingly, HCOOH has strong effect in anisotropic growth of Au nanostructures than other ligands. As simulated, HCOOH -bound $\{111\}$ and $\{100\}$ planes of Au^0 have close surface energies that are much lower than HCOOH -bound $\{110\}$ planes, resulting in the growth of $\{111\}$ and $\{100\}$ -faceted Au nanoplates. In contrast, HCONH_2 -bound $\{111\}$ planes have much lower surface energy than HCONH_2 -bound $\{100\}$ and $\{110\}$ planes, leading to the formation of $\{111\}$ -faceted Au nanoparticles. Similarly, $\text{HCON}(\text{CH}_3)_2$ -bound $\{100\}$ planes have lower surface energy than $\text{HCON}(\text{CH}_3)_2$ -bound $\{111\}$ and $\{110\}$ planes, leading to non-uniform faceted Au nanostructures. However, the very weak affinity of HCOH and HCOCH_3 to Au^0 results in smaller Au nanoplates together with more Au nanoparticles.

In this research, anisotropic growth of Au nanostructures was demonstrated experimentally by using a series of organic ligands with similar HCO-R formula ($\text{R}=\text{H}$, OH , NH_2 , CH_3 and $\text{N}(\text{CH}_3)_2$) that possess weak reducing and coordination capability for achieving comparative data. Further, the binding affinities of ligands to various Au species with variable valences and Au surfaces with different surface planes were investigated computationally. Together with different binding affinities of ligands to Au^{n+} ($n = 3, 1$ and 0), the substantially decreased surface energies of ligand-bound Au planes with certain energy ratios play an important role in the anisotropic growth of Au nanostructures. Overall, a facile method to synthesize and investigate the morphological growth of Au nanostructures has been developed through experimental and computational understanding of interactions between various ligands and variable Au species (i.e., Au^{3+} , Au^+ and Au^0). This provides more insights to reveal the underlying growth mechanism via the formation of Au^+ intermediate/intermediate states during retarded reduction process with weak reducing agents.

5.2 Experimental Methods

5.2.1 Materials

Formaldehyde (HCOH, 36.5-38% aqueous solution), formic acid (HCOOH, $\geq 96\%$), tetrachloroauric(III) acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.9\%$), and polyvinylpyrrolidone (PVP, $M_w \approx 55,000$) are purchased from Sigma-Aldrich. Formamide (HCONH_2 , 98%) and N,N-dimethylformamide ($\text{HCON}(\text{CH}_3)_2$, 99%) are obtained from Alfa-Aesar. Acetaldehyde (HCOCH_3 , 99.5%) is purchased from Acros.

5.2.2 Ligand Controlled Synthesis of Gold Nanostructures

In a typical preparation, 2.5 mL of PVP solution (4 mM) and 2 mL of HCONH_2 solution (5 M) were thoroughly mixed at 50 °C. Then 0.5 mL of HAuCl_4 solution (10 mM) was rapidly added into the above solution followed by strong shaking of the mixture for 30 s. After reacting at 50 °C for 4 h, Au nanostructures were obtained. The Au nanostructures were finally centrifuged with ethanol. To explore the effects of different ligands on morphologies of Au nanostructures, a series of similar experiments were conducted through replacing HCONH_2 by HCOH, HCOOH, HCOCH_3 and $\text{HCON}(\text{CH}_3)_2$, respectively.

5.2.3 Sample Preparation for Characterization

UV-vis-NIR absorbance spectra were obtained with a Shimadzu UV-1800 spectrophotometer. Well-dispersed solutions of Au nanostructures were dropped on Si wafers to prepare SEM samples. SEM imaging was performed by a JEOL 7600F field-emission scanning electron microscope. TEM images were collected on a Philips 300 FEGTEM and the samples were prepared by immobilizing 10 μL of Au nanostructures solution on Cu grids.

5.2.4 Simulation Methods of Interactions between Ligands and Gold

5.2.4.1 Calculations of Binding Affinity of Different Species on Gold Ions

For studying the binding affinity of ligands on Au^{3+} ions, the binding energies of various species on Au^{3+} ions were calculated by using the plane wave code Vienna *ab initio* simulation package (VASP) within the framework of density functional theory (DFT). The individual energy of species and compounds were obtained through conformation optimization by using the projector augmented wave method with the PW91 functional. For one Au^{3+} ion, this calculation was difficult to produce a stable conformation due to its high charge. For really reflecting the binding of species on Au^{3+} ions, $[\text{AuCl}_2]^+$ was chosen to replace Au^{3+} ion for the calculation. Therefore, the binding energy between species and Au^{3+} ions was determined with $E_b = -(E_{[\text{AuCl}_2]\text{-species}} - E_{[\text{AuCl}_2]} - E_{\text{species}})$. For each compound, three different conformations were chosen and the conformation with the lowest energy was used to calculate the binding energy. For the calculations of binding energies between ligands and other Au ions, similar method was used.

5.2.4.2 The Calculation of Surface Energies of Gold Facets

The method is the same with that in section 4.2.5.

5.3 Results and Discussion

5.3.1 Morphology Control of Anisotropic Gold Nanostructures

Figure 5.1 Surface energies and morphologies of Au nanostructures after binding of different ligands on three Au facets. Simulated surface energies after the binding of a) HCONH₂, b) HCOH and c) HCOOH on Au {111}, {100} and {110} facets. TEM images of Au nanostructures synthesized by using d) CHONH₂, e) HCOH and f) HCOOH as ligands. The inset in Figure 1f shows a representative TEM image of Au nanoplates synthesized by using HCOOH as ligand.

Appropriate organic ligands not only interact with Au species but also act as reducing agents when containing reducing entities. A series of such ligands in the formula of HCO-R (R=H, OH, NH₂) with aldehyde groups were chosen to investigate their influence on the growth of Au nanostructures. First, the surface energies of different Au planes adsorbed with ligands including HCO-H, HCO-OH and HCO-NH₂ were simulated (**Figure 5.1a-c**). [18] As compared to pristine Au planes (**Figure 5.2**), all the surface energies of ligand-bound Au planes are greatly decreased while remaining the same surface energy sequence of $\gamma_{\{110\}} > \gamma_{\{100\}} > \gamma_{\{111\}}$. The much higher $\gamma_{\{110\}}$ than $\gamma_{\{100\}}$ and $\gamma_{\{111\}}$ indicates that the more stable $\{111\}$ and $\{100\}$ planes play an important role in controlled growth of Au nanostructures. For HCONH₂, $\gamma_{\{111\}}$ is much lower than $\gamma_{\{100\}}$ and $\gamma_{\{110\}}$ by 35% and 66%, respectively so as to only form Au nanoparticles exposed with $\{111\}$ planes (**Figure 5.1a**). For HCOH or HCOOH, $\gamma_{\{111\}}$ is close to $\gamma_{\{100\}}$ but they are much lower than $\gamma_{\{110\}}$ (**Figure 5.1b and c**), indicating the co-existence of $\{111\}$ and $\{100\}$ -exposed planes in resulting Au nanostructures, i.e. nanosheets.

Figure 5.2 Comparison in surface energies of Au a) $\{111\}$, b) $\{100\}$ and c) $\{110\}$ facets before and after binding with different typical ligands.

To demonstrate this morphosynthesis with different ligands, Au nanostructures were prepared at 50°C by using 1 mM HAuCl₄ and 2 M ligands for 4 h. In agreement with the above simulated results, Au nanoparticles were obtained with HCONH₂ while Au nanosheets were produced with HCOH or HCOOH, as shown in TEM images in **Figure 1d-f**, respectively.

Figure 5.3 Temporal evolution of UV-vis-NIR absorption spectra of reaction mixtures by using a) HCOOH, b) HCOH, and c) HCONH₂ as ligands respectively.

To further understand the growth of Au nanosheets, the absorption spectra of reaction mixtures containing HCOOH or HCOH were monitored immediately upon addition of HAuCl₄ solution (**Figure 5.3a** and **b**). A great increase in absorption was observed above 500 nm as a function of time due to the formation of Au nanostructures. As there is no absorption of Au nanoparticles beyond 800 nm in the absence of aggregates, the formation of Au nanoplates was monitored by the change in absorption intensity at 1100 nm (**Figure 5.4**), which comes from a wide absorption range from 700 to 1100 nm with almost equal absorption intensity. An obvious absorption of Au nanoplates was detected after reaction at 30 and 60 min by using HCOOH and HCOH, respectively. At 240 min, the absorption of HCOOH-adsorbed Au nanoplates is stronger than that of HCOH-adsorbed Au nanoplates, indicating faster formation of more Au nanoplates in the presence of HCOOH than HCOH. For HCONH₂, there is absorption observed at shorter wavelength (i.e., formation of Au nanoparticles) rather than absorption at longer wavelength region, indicating no formation of Au nanoplates (**Figure 5.3c**).

Figure 5.4 Temporal evolution of absorption intensities of Au nanoplates prepared by using different ligands with the increase of reaction time.

In addition to the surface energies of Au planes adsorbed with ligands, the binding affinities of ligands to Au^0 atoms produced in solution were also considered for the growth of Au nanostructures (**Figure 5.5**). [18] Among various ligands, HCOOH has the highest binding affinity to Au^0 atoms as simulated. Its binding energy of 0.50 eV is 25 or 16 times as high as that between Au^0 and HCOH or HCOCH_3 . Comparing to HCOH (**Figure 5.1e**), HCOOH interacts with Au^0 atoms more strongly and then bind specifically more on certain Au planes with greatly reduced surface energy (**Figure 5.1b** and **c**). These greatly modulate the shape/size of Au nanostructures, leading to the formation of more and larger Au nanoplates accompanied with a less number of Au nanoparticles (**Figure 5.1f inset**). As observed, HCOOH-adsorbed nanoplates have a larger edge length of ~ 860 nm in average (**Figure 5.1f inset**) while HCOH-adsorbed nanoplates have a smaller edge length of ~ 118 nm in average (**Figure 5.1e**).

Figure 5.5 a) Structures of ligands used to prepare Au nanostructures. From up to down: formaldehyde, acetaldehyde, formic acid, formamide and N,N-dimethylformamide. b) Binding energies between various ligands and Au⁰.

Similar observation was seen with HCOCH₃ (**Figure 5.6a**) to exhibit weaker control in anisotropic growth of Au nanostructures, leading to the formation of more nanoparticles accompanied with small nanoplates due to weak interaction with Au⁰ and close $\gamma_{\{111\}}$ and $\gamma_{\{100\}}$ but much weaker than $\gamma_{\{110\}}$. Also, HCONH₂ has much higher binding affinity to Au⁰ than HCOH and HCOCH₃, but the greatly reduced surface energy specially on $\{111\}$ planes with the lowest surface energy results in the formation of Au nanoparticles predominantly (**Figure 5.1a**) in agreement with the surface plasmonic band at shorter wavelength in **Figure 5.3c**.

Figure 5.6 Surface energies and morphologies of Au nanostructures after binding of different ligands on three Au facets. 1) Simulated surface energies and 2) TEM images of Au nanostructures after the binding of a) HCOCH₃ and b) HCON(CH₃)₂ on Au {111}, {100} and {110} facets.

HCON(CH₃)₂ has relatively lower binding affinity to Au⁰ than HCONH₂ (i.e., lower binding density of ligands on Au planes), leading to weaker control in anisotropic growth of Au nanostructures, i.e., non-uniform faceted Au nanostructures (almost no nanosheets observed) (**Figure 5.6b**) due to the lowest $\gamma_{\{100\}}$ instead of $\gamma_{\{111\}}$ together with greatly reduced $\gamma_{\{110\}}$. The weaker absorption intensities of Au nanoplates at 1100 nm prepared with addition of HCOCH₃ or HCON(CH₃)₂ also indicate lower yields of Au nanoplates, as compared to addition of HCOOH or HCOH (**Figure 5.7a**). These above results exhibit ligand-dependent formation of Au nanosheets in agreement with the spectroscopic evidence in **Figure 5.4**. In addition, UV-vis-NIR absorption spectra of various Au

nanostructures prepared with all the ligands were plotted together for convenient comparison (**Figure 5.7b**).

Figure 5.7 a) Absorption intensities of Au nanoplates at 1100 nm in aqueous solutions prepared by using different ligands. b) UV-vis-NIR absorption spectra of Au nanostructures obtained by using different ligands.

5.3.2 Disproportionation of Intermediate Au⁺

Figure 5.8 UV-vis-NIR absorption intensities of H[AuCl₄] and Au nanoplates as a function of time in the reactions with 2 M HCOOH at 50 °C.

Time-dependent evolution in absorption spectra upon mixing AuCl_4^- into 2 M HCOOH at 50 °C (**Figure 5.3a** and **5.8**) was monitored to further investigate the growth of Au nanosheets. The absorption intensity of AuCl_4^- centered at ~ 313 nm, decreases sharply in the first 30 min (**Figure 5.8**). For the same period of time, the absorption intensity of Au nanoplates at 1100 nm remains almost zero. From 30 to 70 min, there is no obvious change in the absorption of AuCl_4^- (balanced consumption and re-formation of Au^{3+} at equal reaction rate) while the absorption of Au nanoplates increases continuously (**Figure 5.8**). During further reaction up to 120 min, the absorption intensity of Au^{3+} decreases again because of the faster consumption than re-formation of Au^{3+} . The reaction completes after 120 min, indicated from the unchanged absorption of Au^{3+} and Au nanoplates.

Figure 5.9 Absorption intensities of HAuCl_4 and Au nanoplates as a function of time in the reactions with a) 0.02 mM HCOOH at 50 °C and b) 2M HCOOH at RT.

To interpret this interesting phenomenon, the concentration of HCOOH was decreased to 0.02 M while remaining other reaction conditions. The time-dependent evolution was monitored to exhibit much slower reaction (**Figure 5.9a** and **5.10a**). There is a decrease in absorption of Au^{3+} in the first 2 h and then an increase in the next 2 h, indicating the re-formation of Au^{3+} . Correspondingly, Au^{3+} is first reduced to Au^+ intermediates (**Figure 5.11**) followed by disproportionation to form Au^{3+} and Au^0 . [19] As such, Au nanoplates (**Figure 5.9a**, bottom curve) only starts to be observed at the beginning of the second stage (>2 h), their formation rate is increased quickly up to 4 h and becomes slowly afterwards to produce more products. Further,

a decrease is seen again from 4 to 8 h (**Figure 5.9a**, top curve) due to the faster consumption of Au^{3+} than the re-formation of Au^{3+} .

Figure 5.10 Time-dependent evolution of UV-vis-NIR absorption spectra of Au nanoplates. The Au nanoplates were prepared a) at 50 °C in an aqueous solution with 0.02 mM HCOOH and b) at RT in an aqueous solution with 2 M HCOOH, respectively.

By the way, the ESI-MS was further measured upon the addition of 0.02 mM HCOOH at very low concentration for 1 h (**Figure 5.11**). During the slow reaction, $\text{Au}^{3+}(\text{HCOOH})_2$ at $m/z = 96.49$ (**Figure 5.11a**) was clearly detected when substituting Cl^- with HCOOH. At 1 h, $\text{Au}^+(\text{HCOOH})$ at $m/z = 242.97$ was also observed to further confirm the formation of Au^+ intermediates (**Figure 5.11b**).

Figure 5.11 ESI-MS spectra of the intermediate products after addition of 1 mM HAuCl_4 , 0.02 mM HCOOH and 2 mM PVP at 50 °C for a) 30 min and b) 1 h respectively.

Similarly, the re-formation of Au^{3+} was also observed upon mixing AuCl_4^- into 2 M HCOOH at room temperature rather than 50 °C (**Figure 5.3a**), indicating the much slower formation and disproportionation of Au^+ for the growth of Au nanoplates (**Figure 5.9b** and **5.10b**).

Figure 5.12 UV-vis-NIR absorption intensities of HAuCl_4 as a function of time in reactions with 2 M a) HCOH , b) HCONH_2 , c) $\text{HCON}(\text{CH}_3)_2$ and d) HCOCH_3 as ligands respectively.

Figure 5.13 Simulated binding energies of different ligands with variable valence Au species. Binding energies of different ligands with a) Au^{3+} and b) Au^+ respectively.

The re-formation of Au^{3+} was also observed in the growth of Au nanostructures via disproportionation by using HCOH, HCONH_2 and $\text{HCON}(\text{CH}_3)_2$ (**Figure 5.12** and **5.13**). Upon reduction of Au^{3+} to Au^+ , HCOH and HCOCH_3 starts to weakly bind to Au^+ compared to HCONH_2 and $\text{HCON}(\text{CH}_3)_2$, leading to faster disproportionation of Au^+ to Au^0 after reaction at ~40 min as indicated by the formation of Au nanoparticles/nanoplates (**Figure 5.12** and **5.13**). Interestingly, HCOOH has similar interaction with Au^+ but very stronger interaction of HCOOH with Au^0 compared to HCOH (**Figure 5.5b** and **5.13b**), leading to much faster disproportionation evidenced from the formation of Au nanoparticles/nanoplates at ~20 min (**Figure 5.4**). Similarly, HCONH_2 has relatively stronger interaction with both Au^+ and Au^0 (**Figure 5.5b** and **5.13b**), and this makes the disproportionation obvious at ~20 min as well (**Figure 5.12b**). Further, $\text{HCON}(\text{CH}_3)_2$ has much stronger interaction with Au^+ compared to all the other ligands, and relatively weaker interaction with Au^0 (**Figure 5.5b** and **5.13b**), leading to much slower disproportionation obvious at ~80 min (**Figure 5.12c**). It is noted that all the ligands have the similar trend to interact with both Au^{3+} to Au^+ (**Figure 5.12** and **5.13**).

Table 5.1 Calculated binding energies between different pairs: organic ligands with different Au ions.

Pairs	$\text{Au}^{3+} - \text{HCOH}$	$\text{Au}^{3+} - \text{HCOCH}_3$	$\text{Au}^{3+} - \text{HCOOH}$	$\text{Au}^{3+} - \text{HCONH}_2$	$\text{Au}^{3+} - \text{HCON}(\text{CH}_3)_2$	$\text{Au}^{3+} - \text{Cl}^-$	$\text{Au}^{3+} - \text{HCOO}^-$
Binding energy (eV)	1.15	1.43	1.15	2.06	2.27	4.61	5.54

Pairs	$\text{Au}^+ - \text{HCOH}$	$\text{Au}^+ - \text{HCOCH}_3$	$\text{Au}^+ - \text{HCOOH}$	$\text{Au}^+ - \text{HCONH}_2$	$\text{Au}^+ - \text{HCON}(\text{CH}_3)_2$	$\text{Au}^+ - \text{Cl}^-$	$\text{Au}^+ - \text{HCOO}^-$
Binding energy (eV)	1.39	1.82	1.75	2.11	2.35	5.07	5.69

Pairs	Au ⁰ – HCOH	Au ⁰ – HCOCH ₃	Au ⁰ – HCOOH	Au ⁰ – HCONH ₂	Au ⁰ – HCON(CH ₃) ₂	Au ⁰ – Cl ⁻	Au ⁰ – HCOO ⁻
Binding energy (eV)	0.02	0.03	0.50	0.37	0.25	0.981	0.731

5.3.3 Formation Mechanism of Anisotropic Gold Nanostructures

Figure 5.14 Schematic mechanism for the formation of Au nanostructures from Au³⁺. (1) Chemical reduction of Au³⁺ to Au⁺ and (2) further reduction to Au⁰. (3) Disproportionation of Au⁺ to form Au³⁺ and Au⁰.

Overall, the formation of Au nanostructures in the presence of various HCO-R ($R = \text{OH}$, H , NH_2 , CH_3 and $\text{N}(\text{CH}_3)_2$) involves the reduction of Au^{3+} to intermediate Au^+ in the first stage. Intermediate Au^+ can be captured and temporarily stabilized in the reaction by ligands with relatively stronger affinities with Au^+ than Au^{3+} (**Figure 5.13** and **Table 5.1**), and the disproportionation of Au^+ to Au^{3+} and Au^0 competitively occurs in the following stage (**Figure 5.14**). When Au^0 atoms are formed, two alternative growth pathways (**Figure 5.14**) may proceed to form different Au nanostructures. After adsorption with ligands, Au nanoparticles are formed when the ratio between $\gamma_{\{111\}}$ and $\gamma_{\{100\}}$ is greatly less than 50% because $\{111\}$ -exposed nanoparticles generally have much lower surface energy of Au nanostructures in total. When the ratio is much higher than 50%, Au nanoplates are formed because $\gamma_{\{100\}}$ is close to $\gamma_{\{111\}}$ so that the two facets of $\{111\}$ and $\{100\}$ can be expressed in the final morphology simultaneously to form nanosheets.

5.4 Conclusions

In summary, the anisotropic growth of Au nanosheets was experimentally demonstrated and theoretically understood by using a series of organic ligands with similar HCO-R formula ($R = \text{H}$, OH , NH_2 , CH_3 and $\text{N}(\text{CH}_3)_2$) with weak reducing and coordination capability through tuning interactions between various ligands and variable valence Au species (i.e., Au^{3+} , Au^+ and Au^0). The binding energies of Au^{n+} (3, 1 and 0) to ligands exhibit different affinities for controlled formation of Au nanostructures via the disproportionation of intermediate Au^+ and re-formed Au^{3+} . The surface energies of Au planes adsorbed with ligands are substantially decreased with different ratios in their energies for morphological growth of Au nanosheets. Overall, this work provides a facile strategy to prepare noble metal nanoplates and the finding brings underlying insights to understand the growth mechanism behind.

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Chapter 6

Formic Acid-Assisted Preparation of Ultrathin Gold and Bimetallic Nanoplates via Etching of Templates Gold Nanoplates

The synthesis of ultrathin gold nanosheets through etching of gold nanoplates prepared in chapter 4 is presented. It has been demonstrated that as-prepared gold nanoplates can be etched to form ultrathin gold nanosheets with average thickness of ~1.5 nm in high formic acid concentration. Furthermore, gold/palladium, gold/platinum and gold/Rhodium bimetallic nanoplates are also prepared by using gold nanoplates as templates.

6.1 Introduction

In these decades, etching of templates (i.e., as-prepared metal nanostructures) or incorporated in syntheses has been proved to be a useful method to fabricate metal nanostructures with precise morphologies. One typical example is the synthesis of Au nanoclusters through the etching of as-prepared Au nanoparticles in excess thiol. [1, 2] Nowadays, various Au nanoclusters with high yield have been fabricated via this method, such as $\text{Au}_{18}(\text{SR})_{14}$, $\text{Au}_{38}(\text{SR})_{24}$ and $\text{Au}_{40}(\text{SR})_{24}$. [3-6] Furthermore, bimetallic nanoclusters like $(\text{AuAg})_{144}(\text{SR})_{60}$, $\text{Au}_{24}\text{Pt}(\text{SR})_{18}$ and $\text{Au}_{24}\text{Pd}(\text{SR})_{18}$ have been successfully produced through etching. [7-10] On the other hand, single-crystal Ag nanostructures in high yield have been synthesized through removal of twin seeds which are oxidative etched in the synthetic process. [11] Other examples like the size and shape control of metal nanostructures via etching in the presence of Cl^- or Br^- have been also reported recently. [12, 13] Despite widespread applications of etching in morphological control and various metal nanostructures have been fabricated via etching, ultrathin Au nanosheets (e.g., several atoms in thickness) which may show unique catalytic property synthesized via etching have been seldom presented.

As discussed in previous work (section 4.3.3.3), an interesting phenomena was observed that Au nanoplates cannot be synthesized in low HAuCl_4 concentration (**Figure 4.13a**). Considering this observation and the etching of thiol-stabilized Au nanostructures in excess thiol [1, 2], as-prepared Au nanoplates could also be etched in excess HCOOH resulting in thinner Au nanoplates.

In this research, ultrathin Au nanosheets with thickness of ~ 1.5 nm were fabricated through etching of as-prepared Au nanoplates in HCOOH . The structure and formation of the ultrathin Au nanosheets were also studied. Furthermore, bimetallic nanoplates were obtained by using as-prepared Au nanoplates as templates in the assistance of HCOOH .

6.2 Experimental Methods

6.2.1 Materials

Formic acid (HCOOH , $\geq 96\%$), tetrachloroauric(III) acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.9\%$), Rhodium(III) chloride hydrate ($\text{RhCl}_3 \cdot x\text{H}_2\text{O}$), palladium (II) chloride (PdCl_2 , 99%), chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$), and polyvinylpyrrolidone (PVP, $M_w \approx 55,000$) were purchased from Sigma-Aldrich.

6.2.2 One-Step Synthesis of Gold Nanoplates

A conventional one-step synthetic process of Au nanoplates was employed as described in section 4.2.2. In brief, 2.5 mL of PVP solution (4 mM) and 2 mL of HCOOH solution (5 M) were thoroughly mixed at 50 °C. Then 0.5 mL of HAuCl_4 solution (10 mM) was rapidly added into the above solution followed by strong shaking of the mixture for 30 s. After reacting at 50 °C for 4 h, Au nanoplates were obtained. The as-prepared Au nanoplates were finally centrifuged with H_2O at 1000 rpm twice and dispersed in H_2O .

6.2.3 HCOOH -Assisted Synthesis of Ultrathin Gold Nanosheets

Typical, 0.4 mL of as-prepared Au nanoplates aqueous solution (5 mg/mL) and 1.52 mL HCOOH were added into 18.08 mL water at 50 °C. After stirring at 50 °C for 20 min, the ultrathin Au nanosheets were produced. All the samples were characterized as prepared without any purifying

6.2.4 HCOOH -Assisted Synthesis of Bimetallic Nanoplates

Typically, 0.4 mL of 5 mg/mL as-prepared Au nanoplates was added into 17.88 mL deionized water at 50 °C, followed by addition of 0.2 mL of 10 mM PdCl_2 aqueous solution (the preparation of PdCl_2 aqueous solution was shown in 4.2.3.2) and 1.52 mL HCOOH . After stirring at 50 °C for 120 min, the Au/Pd bimetallic nanoplates were centrifuged at 2000 rpm for 10 min and dispersed in ethanol for further characterization. To obtain Au/Pt and Au/Rh bimetallic nanoplates, a series of similar experiments were developed by addition of H_2PtCl_6 and $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ instead of PdCl_2 , respectively.

6.2.5 Sample Preparation for Characterization

Shimadzu UV-1800 spectrophotometer was used to analyze UV-vis-NIR absorbance of samples. Well-dispersed samples were dropped on silicon substrates to prepare AFM and SEM samples. AFM images were collected on an AFM Asylum Research Cypher S and SEM imaging was performed by a JEOL 7600F field-emission scanning electron microscope. TEM images were collected on a Philips 300 FEGTEM and the samples were prepared by immobilizing 10 μL of sample solution on copper grids. EDX mapping was examined by a JEOL JEM 2100 transmission electron microscope.

6.3 Results and Discussion

6.3.1 HCOOH-Assisted Preparation of Ultrathin Gold Nanosheets

Figure 6.1 Morphologies of Au nanosheets synthesized by etching of as-prepared Au nanoplates in 2 M HCOOH aqueous solution at 50 °C for 20 min. a) TEM and SEM (inset) images of ultrathin Au nanosheets. b) HRTEM of ultrathin Au nanosheet.

The ultrathin Au nanosheets were simply prepared by stirring as-prepared Au nanoplates in HCOOH aqueous solution. Briefly, Au nanoplates were synthesized firstly through a one-step method by using HCOOH as ligands. The morphology and structure characterizations were shown in **Figure 4.1**. The ultrathin Au nanosheets in the presence of some small Au nanoparticles were obtained via stirring 0.5 mM as-prepared Au

nanoplates in 2 M HCOOH aqueous solution at 50 °C for 20 min. **Figure 6.1a** shows the typical TEM and SEM images of ultrathin Au nanosheets. Due to the extremely thin thickness, the ultrathin Au nanosheets are wrinkled and curved like the flexible plastic film. The HRTEM taken from a single ultrathin Au nanosheet (**Figure 6.1b**) indicates it is a single crystalline with a fringe spacing of 0.14 nm which is indexed to {220} reflections of fcc Au. [14, 15] The flat surfaces of ultrathin Au nanosheets are {111} facets, which is demonstrated by the same Au atom arrangement on the flat surfaces of ultrathin Au nanosheets (**Figure 6.1b**) and that of original Au nanoplates (**Figure 4.2a**). As shown in the AFM image and corresponding height profile curve, the thickness of ultrathin Au nanosheets is ~1.5 nm (**Figure 6.2**).

Figure 6.2 a) AFM image and b) corresponding height profile of an ultrathin Au nanosheet.

Figure 6.3 TEM images of ultrathin Au nanosheets prepared by stirring 0.5 mM as-prepared Au nanoplates in 2 M HCOOH aqueous solution at 50 °C for a) 0 min, b) 12 min, c) 16 min and d) 20 min, respectively.

To understand the formation process of ultrathin Au nanosheets, the reaction was monitored by TEM. **Figure 6.3** shows the morphologies of products synthesized through stirring Au nanoplates in 2 M HCOOH at 50 °C for different reaction time. At 12 min, the Au nanoplate (**Figure 6.3b**) is curved as compared to original shape (**Figure 6.3a**) indicating it becomes thinner than original Au nanoplates. The decreased thickness is due to the etching of Au atoms on the surfaces of Au nanoplates. When the reaction time is increased to 16 min, the Au nanoplate is more curved and its plate-like shape begins to

collapse demonstrating it is thinner as compared to the Au nanoplate prepared at 12 min, because more and more Au atoms on the surfaces of Au nanoplate are etched. At the same time, thin Au nanosheets accompanied by formation of small Au nanoparticles appear (**Figure 6.3c**). Finally the ultrathin Au nanosheets are formed at 20 min (**Figure 6.3d**). These results demonstrate that the original Au nanoplates gradually become thinner to form ultrathin Au nanosheets in the etching of as-prepared Au nanoplates. During the etching, some small Au nanoparticles are formed simultaneously.

Figure 6.4 TEM images of Au nanostructures prepared by stirring 0.5 mM as-prepared Au nanoplates and 2 M HCOOH in the presence of 2 mM PVP for 240 min. a) Ultrathin Au nanosheets and b) Au nanoparticles.

During the reaction, the products were aggregated and adhered to glass bottles due to the lack of protection by surfactants, which made it difficult to further explore the formation process of ultrathin Au nanosheets. To solve this problem, the formation of ultrathin Au nanosheets was also investigated in the presence of surfactant PVP. **Figure 6.4** shows the final products fabricated through stirring 2 M HCOOH and 0.5 mM as-prepared Au nanoplates in the presence of 2 mM PVP. Ultrathin Au nanosheets which are wrinkled and folded are obtained (**Figure 6.4a**) while some Au nanoparticles are also formed simultaneously (**Figure 6.4b**).

Figure 6.5 Temporal evolution of UV-vis-NIR absorption spectra of reaction mixtures at 50 °C with addition of 0.5 mM as-prepared Au nanoplates and 2 M HCOOH in the presence of 2 mM PVP.

The absorption spectra of reaction mixtures in the presence of 2 mM PVP were monitored during the reaction, the absorption of Au nanoplates centered at 1100 nm decreases as the increase of reaction time, indicating the consumption of Au nanoplates (**Figure 6.5**). At 40 min, a new peak at about 500 nm appears, which demonstrates the formation of Au nanoparticles (**Figure 6.5**).

As a comparison, the temporal evolution of UV-vis-NIR absorption spectra of reaction mixtures at 50 °C with addition of 0.5 mM as-prepared Au nanoplates and 2 M HCOOH in the absence of PVP was presented in **Figure 6.6**. As the increase of reaction time to 120 min, the absorption of Au nanoplates at 1100 nm decreases gradually, indicating the consumption of Au nanoplates (**Figure 6.6**). This is similar with the reaction in the absence of PVP (**Figure 6.6**). However, since the small Au nanoparticles formed during

the etching of Au nanoplates adhere to glass bottle and aggregate without the protection of PVP, the peak at about 500 nm cannot be detected in the absence of PVP (**Figure 6.6**).

Figure 6.6 UV-vis-NIR absorption spectra of reaction mixtures stirred at 50 °C with addition of 0.5 mM as-prepared Au nanoplates and 2 M HCOOH in the absence of PVP as a function of time.

Overall, as the etching of as-prepared Au nanoplates, the thickness of original Au nanoplates is gradually decreases to produce ultrathin Au nanosheets (**Figure 6.3**) and small Au nanoparticles are formed at the same time (**Figure 6.1a and 6.5**).

To verify the hypothesis in introduction that excess HCOOH may trigger the etching of as-prepared Au nanoplates, the reaction was conducted in different HCOOH concentrations.

Before the discussion and experiments below, it should be noted that the Au nanoplate is in 3D structure in nanoscale. Only Au atoms on top and bottom surfaces, which are exposed to reaction system, can interact with HCOOH. As the calculation in section 3.2,

2% Au atoms are on the surfaces of a single nanoplate. The Au atoms on the surfaces are defined as exposed Au.

Figure 6.7 TEM images of Au nanostructures synthesized by stirring 0.5 mM as-prepared Au nanoplates and 0.5 M HCOOH aqueous solution for a) 20 min, b) 100 min at 50 °C.

As shown in **Figure 6.7a**, when the HCOOH concentration reduced to 0.5 M (**Table 6.1**), the morphology of Au nanostructures etched for 20 min is the same with original Au nanoplates (**Figure 4.1**). Ultrathin Au nanosheets are formed until 100 min in 0.5 M HCOOH solution (**Figure 6.7b**). With further decrease of HCOOH concentration to 0.01 M (**Table 6.1**), the as-prepared Au nanoplates cannot be etched even after stirring for 5 h (**Figure 6.8**). This shows that the formation of ultrathin Au nanosheets through etching of as-prepared Au nanoplates occurs at high HCOOH concentration, and the reaction rate decreases as the reduction of HCOOH concentrations.

Figure 6.8 TEM image of Au nanostructures synthesized by stirring 0.5 mM as-prepared Au nanoplates and 0.01 M HCOOH aqueous solution for 5 h at 50 °C.

Table 6.1 The concentrations of as-prepared Au nanoplates and HCOOH in the etching of Au nanoplates.

	Au nanoplates	Exposed Au	HCOOH	HCOOH : Exposed Au
1	0.5 Mm	2%	2 M	200,000 : 1
2	0.5 mM	2%	0.5 M	50,000 : 1
3	0.5 mM	2%	0.01 M	1,000 : 1

The electrospray ionization mass spectrometry (ESI-MS) of the reaction mixtures were further measured after addition of 2 M HCOOH in 0.5 mM as-prepared Au nanoplates aqueous solution (**Figure 6.9a**). At 5 min, $\text{Au}^+\text{-H}_2$ at $m/z = 198.98$ (**Figure 6.9a**) was clearly detected, demonstrating the formation of Au^+ and H_2 .

Figure 6.9 Formation mechanism of ultrathin Au nanosheets through etching of as-prepared Au nanoplates in HCOOH aqueous solution. a) ESI-MS of the intermediate products after stirring 0.5 mM as-prepared Au nanoplates in 2 M HCOOH aqueous solution at 50 °C for 5 min. b) Schematic mechanism for the formation of ultrathin Au nanosheets from as-prepared Au nanoplates.

With the understanding of etching of as-prepared Au nanoplates to form ultrathin Au nanosheets, a plausible mechanism is proposed (**Figure 6.9b**). In the reaction, Au atoms on the surfaces of as-prepared Au nanoplates are oxidized to Au^+ by HCOOH, accompanied by formation of H_2 (**Figure 6.9a**). As the Au atoms on the surfaces of as-prepared Au nanoplates are liberated through formation of Au^+ layer by layer, the original Au nanoplates become thinner and thinner, and finally ultrathin Au nanosheets are formed (**Figure 6.9b**).

6.2.2 HCOOH-Assisted Synthesis of Bimetallic Nanoplates

In addition, the Au nanoplates can be used as template to prepare Au-based bimetallic nanostructures in the presence of noble metal precursors with assistance of HCOOH.

6.2.2.1 Gold/Palladium Bimetallic Nanoplates

Figure 6.10 Morphology and chemical composition of Au/Pd bimetallic nanoplates. a) Typical TEM image of Au/Pd bimetallic nanoplates. b) Enlarged TEM image of a single Au/Pd bimetallic nanoplate. c, d) TEM-EDX mapping of an Au/Pd bimetallic nanoplate and the inset shows the TEM image of corresponding Au/Pd bimetallic nanoplate.

In this paper, a simple method was provided to fabricate Au/Pd bimetallic nanostructures. Briefly, the Au/Pd bimetallic nanostructures were prepared by stirring 0.5 mM as-prepared Au nanoplates, 0.1 mM Pd precursor and 2 M HCOOH aqueous solution at 50

°C for 120 min. The morphology of Au/Pd bimetallic nanostructures is shown in **Figure 6.10**. As shown in the typical TEM image of Au/Pd bimetallic nanostructures (**Figure 6.10a**), they have the similar shape with as-prepared Au nanoplates (**Figure 4.1**). The Au/Pd bimetallic nanoplates are totally covered by small Pd nanoparticles with Au nanoplates inside, and their surfaces are coarse as compared to original Au nanoplates (**Figure 6.10a** and **4.1**). Interestingly, the surface of the bimetallic nanoplate presents alternate bright and dark fringes which are the Moiré patterns stemmed from the superposition of misfit Au and Pd lattices (**Figure 6.10b**). [16, 17] Element composition presented by TEM-EDX element mapping indicates an overlapped distribution of Au and Pd, which demonstrates that Au nanoplates are completely covered by Pd nanoparticles (**Figure 6.10c** and **d**).

In order to elucidate the growth of Pd nanoparticles on Au nanoplates more clearly, Au/Pd bimetallic nanoplates prepared at different reaction time were produced and their morphologies were analyzed (**Figure 6.11**). As shown in **Figure 6.11a**, Au/Pd bimetallic nanoplates synthesized for 20 min have rough surfaces, and a small amount of ~6.5 nm Pd nanoparticles grow on Au nanoplates separately. As the reaction time increased to 40 min, the amount of Pd nanoparticles on Au nanoplates increases as compared to Au/Pd bimetallic nanoplates prepared for 20 min (**Figure 6.11a** and **b**). When the reaction time is more than 60 min, Au nanoplates are completely covered by Pd nanoparticles (**Figure 6.11c** and **6.10a**). It is demonstrated that the amount of Pd nanoparticles grown on Au nanoplates can be easily controlled by changing reaction time.

Figure 6.11 TEM images of Au/Pd bimetallic nanoplates prepared for a) 20 min, b) 40 min and c) 60 min. For each reaction time, 1) typical and 2) enlarged TEM images.

6.2.2.2 Gold/Platinum Bimetallic Nanoplates

Figure 6.12 Morphology and chemical composition of Au/Pt bimetallic nanoplates. a) Typical and b) enlarged TEM images. c, d) TEM-EDX mapping of Au/Pt bimetallic nanoplate and the inset shows the corresponding TEM image.

Similarly, Au/Pt bimetallic nanoplates were obtained through reducing Pt precursors by HCOOH in as-prepared Au nanoplates aqueous solution at 50 °C. **Figure 6.12** shows the morphology and chemical composition of Au/Pt bimetallic nanoplates. They are triangular, truncated triangular and hexagonal nanoplates with coarse surfaces (**Figure 6.12a**). As shown in the enlarged TEM image of an individual Au/Pt bimetallic nanoplate, ~3 nm Pt nanoparticles grow on the surface of Au nanoplates (**Figure 6.12b**). The element analysis presented by TEM-EDX mapping indicates small Pt nanoparticles grow on the whole surface of as-prepared Au nanoplates (**Figure 12c and d**).

6.2.2.3 Gold/Rhodium Bimetallic Nanoplates

Figure 6.13 Morphology and chemical composition of Au/Rh bimetallic nanoplates. a) Typical and b) enlarged TEM images. c, d) TEM-EDX mapping of Au/Rh bimetallic nanoplate and the inset shows the corresponding TEM image.

In addition, Au/Rh bimetallic nanoplates were prepared through a similar synthetic method. As shown in the TEM image, Au/Rh bimetallic nanoplates are a mixture of triangle, truncated triangle and hexagon (**Figure 6.13a**). Rh nanoparticles with size of ~2.5 nm grow on the surface of as-prepared Au nanoplates (**Figure 6.13b**). The growth of Rh nanoparticles on the surface of Au nanoplates was also confirmed by the TEM-EDX mapping which shows an overlapped distribution of Rh and Au (**Figure 6.13c and d**).

In general, three growth modes are presented to explain the deposition of a foreign substance on a substrate. [18] In this reaction system, the noble metal precursors are

firstly reduced by HCOOH. Then noble metal atoms heterogeneously nucleate and grow on the surface of Au nanoplates through the island growth mode due to the large lattice mismatch. [17, 19] Due to the protection of foreign noble metal nanoparticles on the surfaces of as-prepared Au nanoplates, etching of Au nanoplates was not observed in these reactions.

6.3 Conclusions

In conclusion, ultrathin Au nanosheets have been fabricated through etching of as-prepared Au nanoplates in HCOOH aqueous solution. Their thickness is ~1.5 nm and flat surfaces are {111} facets which are the same with top and bottom surfaces of original nanoplates. It has also been demonstrated that the high HCOOH concentration triggers the etching of as-prepared Au nanoplates. The formation of ultrathin Au nanosheets is due to the oxidization of Au atoms on the surfaces of as-prepared Au nanoplates by HCOOH layer by layer. The etching of nanostructures in the presence of HCOOH could provide a new and facile method to prepare metal nanostructures. Furthermore, Au/Pd, Au/Pt and Au/Rh bimetallic nanoplates have been produced by using Au nanoplates as templates in the presence of HCOOH.

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Chapter 7

Conclusions and Future Work

This chapter draws together the threads of the thesis. The research work is first briefly summarized. A facile method to prepare anisotropic gold nanostructures is provided experimentally and the growth mechanism is demonstrated. Then the discussion on hypotheses is presented. The three hypotheses have been demonstrated to be correct. Furthermore, recommendations for future work are proposed.

7.1 Conclusions

Firstly, a facile one-step method is provided to prepared Au nanoplates in chapter 4, utilizing HCOOH as both reducing agent and ligand. It is verified that the Au nanoplates are enclosed with {111} facets as the top and bottom surfaces and a mixture of {111} and {100} facets as the side surfaces. Their average edge length and thickness are ~860 and ~25 nm, respectively. For the formation mechanism, it has been demonstrated that the adsorption of ligands on different Au facets plays an important role. When ligands adsorb on Au {111}, {100} and {110} facets, the surfaces energies of these facets decrease in different degrees. In the HCOOH-bound Au nanoplates, $\gamma_{\{111\}}$ is similar to $\gamma_{\{100\}}$ and they are both much lower than $\gamma_{\{110\}}$. Thus, {111} and {100} surfaces can be exposed in the final morphology simultaneously, leading to the formation of Au nanoplates which are enclosed with both {111} and {100} surfaces. Furthermore, the methods to optimize the reaction system are discussed through investigating the influence of stabilizer PVP, pH, HAuCl₄ concentration, HCOOH concentration and reaction temperature on the growth of Au nanoplates. The reaction conducted with addition of 2 M of HCOOH and 1 mM HAuCl₄ at 50 °C in the presence of PVP which acts as stabilizer to prevent aggregation, is found to be the optimized condition to prepare Au nanoplates. By using this method, Ag, Pd and Pt nanosheets are fabricated. Overall, this synthetic system contains only three basic reactants (i.e., HAuCl₄, ligand and stabilizer), making it a simple and feasible system for further study on formation mechanism of Au nanostructures. The role of interaction between HCOOH and Au facets in the growth of Au nanoplates provides a clue to systematically and farther examine the growth of Au nanostructures through controlling the interactions between Au species formed in the reaction and various ligands.

Inspired by the results in chapter 4, the research was extended to investigate the growth of anisotropic Au nanostructures in depth by tuning the interactions between Auⁿ⁺ (n = 3, 1, and 0) and a series of HCO-R formulas (R = -H, -OH, -NH₂, -CH₃ and -N(CH₃)₂) in chapter 5. These HCO-R formulas possess similar aldehyde group with weak reducing ability but different coordination abilities due to various functional groups, thus comparative data is achieved to demonstrate the formation of anisotropic Au

nanostructures. As the simulation of binding energies between Au^{n+} ($n = 3, 1$ and 0) and ligands shows, Au starting, intermediate and final species exhibit different binding affinities to ligands. Since the ligands have much stronger binding affinities to Au^+ than Au^{3+} , the intermediate Au^+ is able to be observed and captured during the slow reduction of Au^{3+} . Upon the disproportionation of Au^+ to Au^0 and Au^{3+} (i.e., the re-formation of Au^{3+}), ligands with much stronger binding affinity to Au^0 show better control of formation of anisotropic Au nanostructures. The adsorption of various ligands causes substantially decreased surface energies on different Au planes. There are much higher energies on $\{110\}$ planes compared to the other two $\{111\}$ and $\{100\}$ planes with certain ratios in these energies, leading to morphological growth of Au nanosheets by various organic ligands. Based on these experimental and computational results, a general formation mechanism for ligand-controlled synthesis of anisotropic Au nanostructures is suggested. Au^{3+} is first reduced to intermediate Au^+ by ligands. If ligands exhibit stronger binding affinities to Au^+ than Au^{3+} , intermediate Au^+ is able to be captured and stabilized by ligands tentatively. In the following step, Au atoms and Au^{3+} form upon disproportionation of intermediate Au^+ . With the formation of Au atoms, growth of Au nanostructures occurs through two modes which are controlled by the interactions between ligands and Au different facets. When the ligand-bounded $\{111\}$ facets show the lowest surface energy which is lower than half of $\gamma_{\{100\}}$, $\{111\}$ -faced Au nanoparticles are produced. If the ratio of $\gamma_{\{111\}}/\gamma_{\{100\}}$ is much larger than 50%, in which case $\{111\}$ and $\{100\}$ facets show similar surface energies, $\{111\}$ and $\{100\}$ faced Au nanoplates are fabricated. In addition, ligands with stronger binding affinities to Au^0 exhibit better ability to modulate the anisotropic growth of Au nanoplates, thus larger Au nanoplates with higher yield are produced. This method of investigating the growth mechanism of Au nanostructures could also be used to explore the growth of other metal nanostructures. Meanwhile, the formation mechanism of ligand-controlled synthesis could guide the preparation of Au nanostructure with well-controlled shape and size.

As the observation in chapter 4, Au nanoplates cannot be produced in low HAuCl_4 concentration. Intrigued by this interesting phenomenon and the dissolution of Au nanoparticles in excess thiol [1, 2], the morphological evolution of as-prepared Au

nanoplates in excess HCOOH solution was investigated in chapter 7. The as-prepared Au nanoplates with average thickness of ~25 nm have been demonstrated to be etched in high HCOOH concentration. Ultrathin Au nanosheets with thickness of ~1.5 nm are fabricated during the etching of as-prepared Au nanoplates. Au atoms on the surfaces of Au nanoplates may dissolve and be liberated in excess HCOOH via reversible disproportionation of Au^+ ($\text{Au}^{3+} + 2\text{Au}^0 \rightarrow 3\text{Au}^+$). As the etching of as-prepared Au nanoplates layer by layer, ultrathin Au nanosheets are finally fabricated. Furthermore, with addition of foreign metal precursors, like Pd, Pt and Rh ions, bimetallic nanoplates are produced by using as-prepared Au nanoplates as template in the HCOOH aqueous solution. The etching of as-prepared Au nanoplates in excess HCOOH provides a novel clue to explore the growth of Au nanostructures. And this synthetic method in which as-prepared Au nanoplates are used templates presents a facile approach to prepare ultrathin and bimetallic nanosheets.

7.2 Discussion on Hypothesis

The aim of this project is to demonstrate the formation of anisotropic Au nanostructures experimentally and explore their growth mechanism behind through tuning the interactions between various ligands with similar formula but different coordination abilities and variable valence Au species via intermediates.

To address the problems faced in the formation of Au nanostructures and achieve the objectives, three hypotheses were provided in this project. Based on the results of this work, the three hypotheses have been proved to be correct.

Hypothesis 1: In a slow reduction of Au^{3+} to Au^0 with weak reducing agents, intermediate process may be observed in liquid phase at optimized conditions during growth of Au nanostructures.

This hypothesis was proven. In the typical reduction of HAuCl_4 to produce Au nanostructures, strong reducing agents (e.g., sodium borohydride or sodium citrate) are widely used. [3-5] **Figure 7.1a** shows the UV-vis-NIR spectra of the reaction mixture with addition of 1 mM HAuCl_4 and 2 M sodium citrate at 50 °C. After the addition of

sodium citrate, Au^{3+} is almost completely reduced immediately, which is demonstrated by the disappearance of the absorption of Au^{3+} at 313 nm (**Figure 7.1a**). At the same time, Au nanoparticles are also formed, indicated by the absorption peak at about 580 nm (**Figure 7.1a**). The color of the reaction solution turns from yellow to black immediately after adding of reducing agent, indicating the fast reaction too (**Figure 7.1b**). In the fast reduction by sodium citrate, in which Au^{3+} is totally reduced and Au nanostructures are produced immediately after addition of reducing agent, it is too difficult to observe the intermediate process during the growth of Au nanostructures.

Figure 7.1 The reduction of 1 mM HAuCl_4 by 2 M sodium citrate at 50 °C in an aqueous solution. a) UV-vis-NIR absorption spectra of reaction mixture before and after addition of sodium citrate at 50 °C. b) Photos of mixed reaction solution before and after addition of sodium citrate at 50 °C.

Organic molecules with aldehyde group are usually used as weak reducing agents to reduce metal ions. In this project, the reaction of the formation of Au nanostructures is slowed down by using HCO-R ($R = -H, -OH, -NH_2, -CH_3$ and $-N(CH_3)_2$) as reducing agents, as compared to the reaction with sodium citrate (**Figure 7.1**) which is a relative stronger reducing agent. It is demonstrated by the appearance of Au products after reacting for at least 20 min and the slower reduction rate of Au^{3+} (**Figure 5.8** and **5.12**). In these slow reactions, the intermediate process is observed. It involves the reduction of Au^{3+} to Au^+ . Au nanostructures are then produced as a result of the disproportionation of Au^+ .

Hypothesis 2: Intermediate Au^+ may be observed and captured before reducing to Au^0 by ligands with appropriate coordination ability to Au^{n+} ($n = 3, 1, 0$).

Figure 7.2 Comparison of binding energies between ligands and Au^{n+} ($n = 3, 1$ and 0).

This hypothesis was verified to be correct. As the calculation showed, ligands used in this project exhibit relatively stronger affinities to Au^+ than Au^{3+} and Au^0 (**Figure 7.2**), indicating ligands prefer to coordinate with Au^+ . Thus, when Au^+ is produced from the reduction of Au^{3+} , ligands are able to capture and stabilize it temporarily before its

disproportionation. Correspondingly, intermediate Au^+ is detected experimentally by ESI-MS in the reaction with ligands possessing stronger binding affinities to Au^+ than Au^{3+} and Au^0 .

Hypothesis 3: The mechanism for morphological growth of Au nanoplates may be demonstrated experimentally and computationally by using a series of organic molecules with similar HCO-R formula ($\text{R} = -\text{H}, -\text{OH}, -\text{NH}_2, -\text{CH}_3$ and $-\text{N}(\text{CH}_3)_2$) that possess different coordination capability to Au as ligands for achieving comparative data.

The third hypothesis was demonstrated to be correct. Firstly, the simulation shows that organic molecules HCO-R with different functional groups have different capabilities to interact with Au. For example, after binding with HCONH_2 , Au {111} facets exhibit extremely low surface energy. $\gamma_{\{111\}}$ is less than 50% of $\gamma_{\{100\}}$ and $\gamma_{\{110\}}$. This indicates {111} faced Au nanoparticles are dominated when HCONH_2 acts as ligand. On the other hand, $\gamma_{\{111\}}$ is close to $\gamma_{\{100\}}$, when HCOOH or HCOH adsorb on the surfaces of Au nanostructures, revealing the formation of Au nanoplates enclosed by {111} and {100} surfaces by using HCOOH or HCOH as ligand. Meanwhile, the higher binding energy between Au^0 and HCOOH than that between Au^0 and HCOH indicates better modulated abilities of HCOOH on the morphology of Au nanoplates. In the following research, the morphologies of various ligands-bounded Au nanostructures were studied experimentally through heating HAuCl_4 in the presence of different ligands. The experimental results are in agreement with the simulation. For example, Au nanoparticles were obtained by using HCONH_2 as ligand. Au nanoplates were fabricated in the presence of HCOOH or HCOH , while HCOOH bounded Au nanoplates have larger size and higher yield. Comparing these simulated and experimental results through using HCOOH , HCOH , HCONH_2 , HCOCH_3 or $\text{HCON}(\text{CH}_3)_2$ as ligand, a possible mechanism for morphological growth of Au nanoplates is suggested. If the ratio of $\gamma_{\{111\}}$ and $\gamma_{\{100\}}$ is less than 50%, Au nanoparticles are produced. When this ratio is much higher than 50%, Au nanoplates are formed. Meanwhile, the stronger binding affinities of Au atoms and ligands result in better morphological control of Au nanoplates.

7.3 Recommendations for Future Work

7.3.1 Gold Nanoplates-Embedded Polymer Substrates for Flexible Chemical Sensors

In the past few years, SERS-based detectors have attracted much attention, because of the highly enhanced detection sensitivity [6]. The deposition of molecules on rough noble metal surfaces can induce great enhancement of Raman scattering, which is a good method to analyze molecules. Theoretically, the Raman scattering can be enhanced sharply when molecules adsorb on metal surfaces with sharp corners and fractal edges [7]. Therefore, anisotropic Au nanoplate is an excellent candidate in the field of SERS.

Until now, Au nanoplates have been widely used as detectors, due to the SERS, and they perform well in detecting pollutants [8-12]. However, in reported methods, the substrates which Au nanoplates deposit on are mainly Si wafer. The hard and fragile Si substrates are difficult to carry and limit the applications of Au nanoplates detector. Thus, the aim of future work is to fabricate flexible Au nanoplates detector. Briefly, the elastomeric Polydimethylsiloxane (PDMS) which is optically clear, inert and nontoxic is planned to be used as the substrate for fabrication of detector. Experimentally, a solution of Au nanoplates is firstly dropped on a flat aluminum substrate to prepare a uniform Au nanoplates film. And then the PDMS pre-polymer is cast onto the Au nanoplates-on-aluminum film followed by curing at certain temperature [13]. Finally, the soft detector, Au nanoplates-in-PDMS, is prepared by dissolving the aluminum

7.3.2 Dimensional Control of Gold Nanoplates through Mixed Ligands

It is well known that size of Au nanostructures play a vital role in their applications. [14, 15] Thus, size control of Au nanoplates is of importance. Nowadays, the common method to adjust the size of Au nanoplates is the seed-mediated approach, in which as-prepared Au nanoplates act as seeds to fabricate larger Au nanoplates. [16] However, in this method, multiple steps are needed, making it complicated to prepare Au nanoplates with required size. So that it is important to provide a facile method to control the size of Au nanoplates.

As the discussion in previous work, HCOOH and HCOH are both ligands to fabricate Au nanoplates. However, the HCOOH and HCOH bounded Au nanoplates show different sizes at the same reaction condition, due to the varied binding affinities of ligands and Au⁰. As such, the size of Au nanoplates could be controlled by using a mixture of HCOOH and HCOH as ligand. Through changing the ratio of HCOOH and HCOH in the mixed ligands, size control could be easily achieved.

7.3.3 Surface Etching of Gold Nanoplates in Various Ligands

Despite ultrathin Au nanosheets were fabricated through etching of as-prepared Au nanoplates in high HCOOH concentration, some problems on the formation mechanism are still obscure. Based on the results of this work, HCOOH, HCOH, HCOCH₃ and HCON(CH₃)₂ have been demonstrated to show different binding abilities to Au and Au nanoplates have been fabricated by using them as ligands. It is verified that as-prepared Au nanoplates are etched in HCOOH solution which also fabricates formation of Au nanoplates. As-prepared Au nanoplates might also be etched in other three ligands, since they have similar structure with HCOOH. The formation mechanism of ultrathin Au nanosheets could be demonstrated more clearly through etching of as-prepared Au nanoplates in different ligands (i.e., HCOH, HCOCH₃ and HCON(CH₃)₂) with similar structure but different binding affinities to Au for obtaining comparative data.

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