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Nanoporous Gold Nanostructures: Morphological Design and Their Energy Conversion Applications

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the requirement for the degree of Doctor of Philosophy**

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Abstract

Nanoporous gold (NPG) is interconnected porous gold nanostructures with high surface area, extraordinary catalytic activity and unique optical properties. The objectives of my thesis is to synthesize high-performance NPG-based functional nanostructures, investigate the relationship between the structures and their performances, and boost their performance in energy conversion applications. In chapter 2, I prepare Pt-nanoporous gold bowl (Pt-NPGB) hybrids and demonstrate the superiority of Pt-NPGB as catalysts in electro-oxidation of methanol. The d-band interaction between NPGB and Pt is studied to elucidate the origin of its excellent catalytic activity. This study is important in promoting the catalytic performance for diverse electro-chemical applications, especially in the field of energy, synthetic chemistry, and also environmental toxin degradation. In chapter 3, I prepare bowl-shaped, tube-shaped and plate-shaped NPG particles, and compared their photothermal effect. I also demonstrate the application of NPG's strong photothermal effects by the light-controlled movement of NPG coated shape memory polymer, which can be utilized in actuator applications. The detailed controllability of NPG coated shape memory polymer movement is systematically studied in chapter 4. In chapter 5, I directly synthesize NPG-molybdenum sulfide hybrid structure by exploiting the photothermal effect to significantly increase localized temperature to initiate reduction of molybdenum sulfide precursors. The excellent catalytic activity of the obtained NPG-molybdenum sulfide hybrid in hydrogen evolution reaction is demonstrated.

Lastly, chapter 6 summarizes research works in my 4-year PhD study and provides an outlook of the potential future direction in this field.

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Chapter 1

Introduction

ABSTRACT. Nanoporous gold is a porous network composed of interconnected nanosized gold ligaments. Owing to its high surface-to-volume ratio, good thermal and electrical conductivity, and intriguing optical properties, nanoporous gold has been applied in various fields. In this chapter, we first introduce the synthetic strategies of nanoporous gold. Next, we discuss the unique properties of nanoporous gold and corresponding characterization methods. This will be followed by a review on the applications of nanoporous gold in the fields of catalysis, sensors, photothermal heating and actuators. Finally, we identify the current challenges in the research of nanoporous gold and establish the objectives of this thesis.

1.1 SYNTHESIS METHODS OF NANOPOROUS GOLD

Research of nanoporous materials have been developing rapidly due to its wide range of applications in energy storage, catalysis, purification, drug delivery, environmental remediation, sensors, electronic devices.¹⁻⁸ Nanoporous materials can be categorized into microporous materials (pore size < 2 nm), mesoporous materials ($2 \text{ nm} < \text{pore size} < 50 \text{ nm}$) and macroporous materials (pore size $> 50 \text{ nm}$), as according to the definition from the International Union of Pure and Applied Chemistry (IUPAC).⁹

Gold nanostructure, has been a hot topic in the research field of catalysis, sensors and biomedical applications due to its large surface area, plasmonic effect and good biocompatibility.¹⁰ The shape of gold nanostructure is of great importance in tuning its catalytic activity and light-matter interaction.¹¹ For example, gold nanorods are known to absorb near infrared region light, thus favorable for the photothermal effect in biomedical applications.¹² Among all shapes, nanoporous gold (NPG), which are bicontinuous porous gold nanostructures with interconnected gold ligaments, has attracted considerable interest due to its high surface area, extraordinary catalytic activity and unique optical properties.^{4,13,14} NPG has shown great potential in various important research fields including sensing, fuel cells, actuation and drug delivery.¹⁵⁻¹⁸ The surface energy of Au is very high compared to other metals, therefore NPG structures are hard to be synthesized compared to other porous metal structure. Notably, the performance of NPG in various applications is largely affected on their morphology such as ligament size and pore size, which is in turn dependent on the synthesis

methods. In the following section, I will discuss the different synthesis methods of NPG.¹⁹⁻²¹ The synthesis methods can be categorized into five methods: dealloying method, template method, self-assembly method, electrochemical method and wet chemistry method.

1.1.1 Dealloying method

Dealloying method is one of the most commonly used method for nanoporous metal preparation. The history of this method starts from the mechanism study of metal corrosion. Swann and Pickering first reported the formation of nanoporous structure during dealloying process of gold-based alloy when they were studying the mechanism of alloy corrosion.^{22,23} By dealloying Ag-Au alloy in nitric acid, Forty prepared NPG membrane with a pore size of approximately 20 nm.²⁴ Newman et al. systemically discussed the importance of parting limit and critical potential in dealloying process: parting limit determines the starting dealloying concentration of noble metal in alloy, and critical potential defines the voltage threshold required for dealloying process.²⁵ With these pioneering works, dealloying is established as a method for preparing porous metal nanostructure. Depending on the means of alloy etching, the dealloying methods can be categorized into chemical dealloying and electrochemical dealloying.

1.1.1.1 Chemical dealloying

Chemical dealloying is achieved by selectively etching the less noble constituent in the alloy under specific experimental conditions. NPG can be obtained by selectively dealloying $\text{Ag}_x\text{Au}_{1-x}$ alloy in concentrated nitric acid, which is similar to the preparation of Raney Ni via etching Al from Ni-Al alloy (Figure 1.1A).^{4,26} The

process of NPG formation by chemical dealloying $\text{Ag}_x\text{Au}_{1-x}$ alloy is shown schematically in Figure 1.1B. First, Ag atoms are selectively leached in concentrated nitric acid, generating Au adatoms and vacancies. The exposed Au atoms with high surface energy diffuses to the surface to form a pit-and-mound surface which further evolves into three-dimensional porous nanostructure.¹⁵

Figure 1.1 (A) SEM image of chemically dealloyed NPG. (B) Schematic representation of the NPG formation mechanism during chemical dealloying.¹⁵ Reprinted with permission from The Royal Society of Chemistry and American Chemical Society.

Besides Ag-Au alloy, Cu-Au^{27,28} and Al-Au^{29,30} alloy can also be chemically dealloyed in a similar manner to obtain NPG. Though these alloys can be chemically etched into NPG, the porosity and composition varies with the starting alloy, which is closely related to their phase diagrams, lattice structure and surface passivation

behavior. For example, Al₁Au alloy exhibits faster dealloying speed than Al₂Au alloy.^{29,30} Over 20% residual Cu or Al is found in the obtained NPG using Cu-Au or Al-Au alloy due to the surface passivation during the dealloying progress.

1.1.1.2 Electrochemical dealloying

Electrochemical dealloying is another way of providing selective dissolution of Ag from Ag-Au alloy. Erlebacher et al. used electrochemical dealloying method to investigate the formation process of NPG and proposed the dealloying process model with three steps: Ag dissolution, Au surface diffusion and coarsening of ligaments.²⁶ Weissmüller et al. reported that the potential applied in electrochemical dealloying method plays an important role in controlling NPG morphology.^{31,32} At the potential of 600 mV vs Ag/AgCl, gold hydroxide is formed and the coarsening of NPG ligaments is hindered.

Cao et al. reported an NPG preparation method that involves Zn alloying followed by dealloying of Zn.³³ They performed cyclic voltammetry (CV) in ZnCl₂/DMSO electrolyte and used Au plate, Pt plate and Zn plate as working electrode, counter electrode and reference electrode, respectively. Zn is reduced on the surface of Au working electrode during the reduction process of CV cycles, and then stripped out from alloy during the reverse scan. They found that higher dealloying temperature, faster scan rate and more scan cycles dramatically increases the porosity of NPG film.

1.1.2 Template method

1.1.2.1 Hard template method

Template method is another commonly used method for the preparation of porous materials, and is widely applied in the synthesis of porous materials ranging from macroporous to microporous.

For instance, Masuda et al. fabricated highly ordered NPG nanohole array by a two-step replication of the honeycomb structure of anodic porous alumina.³⁴ Colvin et al. prepared macroporous gold structure using well-assembled silica particles as templates.³⁵ The macroporous gold is obtained by electroless deposition and subsequent etching of silica using hydrofluoric acid. However, the as-prepared macroporous gold samples are poor in mechanical strength and not thermally stable.

Shen et al. synthesized nanoporous gold film using layer-by-layer assembled Ag nanoparticles as templates.³⁶ In their method, multilayered Au nanoparticles / Ag nanoparticles films were first prepared by alternatively depositing Au nanoparticles and Ag nanoparticles with 1,5-pentanedithiol. Ag nanoparticles in the multilayered film was then etched in mixed solution of HAuCl_4 and NaCl , obtaining NPG film (Figure 1.2).

Figure 1.2 Schematic illustration of the preparation of multilayers of colloidal Au/Ag and the subsequent removal of colloidal Ag templates to form porous Au films.³⁶

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1.1.2.2 Soft template method

Yamauchi et al. recently developed a novel NPG preparation method using polystyrene-block-poly(oxyethylene) (PS-b-PEO) block copolymer micelles as soft-templates.³⁷ In electrolyte solution mixed with HAuCl_4 and PS-b-PEO micelles, positively charged micelles are formed as H_3O^+ is attached on the PEO shell of micelles via hydrogen bonding. At -0.5 V (vs Ag/AgCl), the positively charged micelles are directed towards the working electrode surface, acting as soft templates, while at the same time AuCl_4^- ions are reduced onto the surface of micelles (Figure 1.3A). After removing micelle templates using ultraviolet ozone cleaner or O_2 plasma, NPG film is obtained. As the size of micelles can be controlled by the amount of THF in solution, pore size of NPG can be controlled from 19 nm to 25 nm by tuning the volume of THF from 1 mL to 3 mL (Figure 1.3 B-D). The amount of swelling agent and molecular weight of PS block in PS-b-PEO are also able to control the pore size of NPG.

Figure 1.3 (A) Schematic illustration of formation mechanism of mesoporous Au films through micelle assembly. (B-D) Top-surface SEM images of mesoporous Au films prepared with three electrolytes containing $\text{PS}_{18000}\text{-b-PEO}_{7500}$ micelles and different THF amounts ((B) 1 ml, (C) 2 ml and (D) 3 ml, respectively).³⁷ Reprinted with permission from Nature Publishing Group.

1.1.3 Self-assembly method

NPG can also be obtained via controlling the self-assembly and coalescence process of gold nanoparticles. Zhang et al. reported an NPG preparation method that utilized the self-assembly initiated by evaporation of water in Au nanoparticle solution.³⁸⁻⁴⁰ By simply allowing water of Au nanoparticle solution to evaporate at ambient conditions, single layer of porous gold film can be obtained. The authors

studied the mechanism of the formation of porous gold structure and found the process could be defined as three steps: (1) Concentration of Au nanoparticles at solution surface due to evaporation, (2) wire-like morphology formation due to the coalescence of Au nanoparticles, (3) the formation of single layer porous gold film due to the diffusion-limited aggregation and cluster-cluster aggregation. The pore size of as-obtained NPG by this method can be tuned by size and concentration of Au nanoparticle and solution temperature.

Burpo et al. prepared monolithic porous gold aerogel via self-assembly strategy.⁴¹ The authors found that, as long as HAuCl_4 solution is above the threshold salt concentration, gel structure composing of gold is formed when the gold ions are reduced by dimethylamine borane (DMAB) and sodium borohydride (NaBH_4). Monolithic NPG aerogel can be obtained after freeze-drying. SEM results indicate that the pore size of the as-prepared NPG aerogel ranges from 50 nm to 600 nm while BET analysis indicates an average pore diameter of 85.4 nm in NPG aerogel (Figure 1.4).

Figure 1.4 (A) Proposed mechanism of noble metal gel formation. Synthesis proceeds via (a) initial nucleation of nanoparticles, (b) rapid growth of nanoparticles, (c)

densification of nanoparticles due to hydrogen gas evolution, (d) fusion of nanoparticles, and finally (e) surface energy minimization and equilibration of resulting gel. (B-C) SEM images of gold aerogel.⁴¹ Scale bars indicate (B) 500 nm and (C) 10 μm . Reprinted with permission from Materials Research Society.

1.1.4 Electrochemical method

Li et al. developed an electrochemical method to synthesize NPG film. Their method involves only a one-step potential sweep of gold substrate, which requires no dealloying or template.⁴² By simply sweeping applied potential from the open circuit potential to 0.9 V (vs saturated mercurous sulfate electrode) in HCl solution for about 1 min, NPG film is obtained. This process can be categorized into three steps. The first step is the electro-dissolution of gold, which roughens the surface of gold substrate. Second step involves the disproportion formation of Au^* atoms. The third step is the deposition of Au^* atoms, forming Au nanoparticles with passivated protection layer on the surface. Due to the presence of Au oxide layer on Au nanoparticles, electro-dissolution process is able to proceed continuously under the reacted surface thus forming nanopores in the deeper region of gold substrate. After the removal of applied potential, the passivated protection layer on Au nanoparticles will disappear spontaneously due to the recovery of HCl concentration (Figure 1.5).

Sukeri et al. prepared NPG film using gold electrode via a similar electrochemical strategy.⁴³ In their work, pre-polished gold electrode was swept from 0 V to 2 V (vs Ag/AgCl) at 0.02 V/s in 0.5 M sulfuric acid and held at 2 V for 1 h in order to form

Au oxide film on electrode surface. Then, reverse potential sweep was carried out to reduce the Au oxide layer to obtain NPG film. The pore size of the as-obtained NPG film is ~32 nm in average.

Figure 1.5 Scheme of the fabrication mechanism of NPG film via electrochemical method.⁴² Reprinted with permission from Elsevier.

1.1.5 Wet chemistry method

As compared with the methods described above, wet chemistry method offers a simpler and more cost-effective strategy to prepare NPG. Ling et al. developed a one-step wet chemistry method to prepare zero-dimensional (0D) NPG hollow spheres.⁴⁴ By simply mixing PVP solution with hydroquinone, HAuCl_4 and AgNO_3 solution under ambient condition, 0D NPG nanospheres can be obtained (Figure 1.6). The sphere diameter and ligament size can be easily controlled by tuning the concentration

of hydroquinone. The mechanism of this process involves the formation of cubic AgCl sacrificial template upon the mixing of AuCl_4^- and Ag^+ , followed by the growth of nanoporous gold structure on AgCl surface due to the preferred heterogeneous growth of Au on AgCl seeds. After etching AgCl by ammonia solution, hollow NPG spheres are obtained.

Figure 1.6 Mechanism of 0D NPG formation using wet chemistry method. (a–c) Synthetic route scheme of the formation process of hollow 0D NPG involving AgCl nanocube as sacrificial template. (d–f) SEM images of corresponding stages of hollow 0D NPG formation process. (d–f) Scale bars indicate 200 nm.⁴⁴ Reprint permission from Nature Publishing Group.

1.2 PROPERTIES AND CHARACTERIZATION OF NANOPOROUS GOLD

1.2.1 Surface area

Nanoporous materials possess much larger surface areas than solid materials of equivalent mass. With the increase of surface area per mass of a material, a higher amount of the material is able to come into contact with surrounding reactants, thus

influencing the reactivity.^{7,18} Therefore, the high surface area of NPG offers great potential in material functionality. The surface area of NPG can be characterized by electrochemical methods and Brunauer–Emmett–Teller (BET) method.

Electrochemical surface area (ECSA) is one of the most commonly used parameter describing the surface area of gold. Cyclic voltammetric (CV) determination of the Au ECSA is based on the charges to form surface gold oxide monolayers according to the oxygen adsorption measurement method⁴⁵. Chen et al. reported an ECSA of 9.3 m²/g in NPG with ~25 nm ligament diameter.⁴⁶ Rouya et al. compared surface area of NPG with various pore sizes determined by three different electrochemical methods: Cu under-potential deposition (Cu UPD), the oxygen adsorption of gold and electrochemical impedance spectroscopy (EIS). They found that Cu UPD method and Au oxygen adsorption method yield surface areas in good agreement, while EIS indicates a ~1.5-fold larger surface area value.⁴⁷

BET method is a commonly used method for characterizing surface area of porous material, which determines material surface area using gas adsorption-desorption isotherms. Stine et al. investigated NPG surface area using BET method. They found that NPG shows typical type IV material isotherms and H1 type hysteresis, which is typical of mesoporous materials. Barrett-Joyner-Halenda (BJH) pore size distribution analysis implies that the nitrogen adsorption behavior within NPG pores is closely related to pore blockage effects. They also report that surface area determined by BET compares well with ECSA determined by gold oxide stripping at low scan rates.⁴⁸

1.2.2 LSPR

Metallic nanoparticles are known to possess the unique ability to manipulate light-matter interactions, owing to the effect of localized surface plasmon resonance (LSPR).^{49,50} Metallic nanoparticles with LSPR, such as silver or gold nanoparticles, are also termed as plasmonic nanoparticles. Surface plasmon resonance (SPR) is the collective oscillation of electron cloud aroused by electromagnetic radiation onto the surface of metallic nanoparticles (Figure 1.7).⁵¹ LSPR is capable of concentrating light within a very small volume at the surface of plasmonic nanoparticles. This is attributed to the free electron oscillation that is confined within only a few nanometers at the surface of metal nanoparticles, giving rise to an increased electromagnetic field strength of 100 to 10000 times.⁵² The regions with greatly enhanced localized electromagnetic fields are not distributed homogeneously at the surface of nanoparticles, and the areas with highly enhanced electromagnetic fields is known as “hot spots”.

Figure 1.7 Scheme illustration of localized surface plasmon resonance (LSPR).⁵¹

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Plasmonic nanoparticles triggered the interest of researchers from various fields because of the potential application of light-matter interactions. The application of

plasmonic nanoparticles can be dated back to the Roman period. An example is the “Lycurgus Cup” which is now exhibited at the British Museum. With Ag and Au nanoparticles embedded in its glass, the “Lycurgus Cup” has a dichroic effect, which appears red in transmission state and green in reflected light.⁵³ The investigation of the “Lycurgus Cup” was first reported by Brill et al. in 1965, and the origin of the color in the “Lycurgus Cup” was studied by Freestone et al. using TEM.^{54,55} Mie et al. pioneered in explaining the light absorption behavior using Maxwell equations.⁵⁶ Mie’s theory is successfully applied in analyzing the effect of SPR in various systems. Based on the fundamental study of SPR, plasmonic nanoparticles are now widely applied in the fields of sensing, photodetection and information storage.

Plasmonic coupling between different plasmonic nanostructures is found to be able to generate more ‘hot spots’.⁵⁷ Therefore, abundant ‘hot spots’ are present in NPG, whose interconnected porous gold nanostructure is favorable for plasmonic coupling. The LSPR of NPG can be characterized using UV-vis spectroscopy. Chen et al. investigated the LSPR of dealloyed NPG which was found to have two characteristic SPR bands.⁵⁸ The position of band at around 590 nm arising from LSPR is dependent on the NPG pore size and ligament size, and a redshift is observed when pore size increases. On the other hand, the band at about 490 nm is ascribed to the resonant absorption of gold films. De Hosson et al. further investigated the peak shifts using both experimental and computation methods, and established that the peak shift of LSPR in NPG should be described by the ratio between ligament size and pore size, rather than merely the size of ligaments or pores.⁵⁹

1.2.3 Catalytic activity

Gold is a noble metal and it is well-known for its chemical inertness resulting from the weak interactions between gold surfaces and adsorbates. Thus, gold has very good anti-corrosion abilities and remains chemically stable in its metallic form. Therefore, gold was previously considered to be catalytically inactive.⁶⁰ However, this stereotype is overthrown by the pioneering works that utilized nanosized gold particles to catalyze the hydrogenation of olefins, low-temperature oxidation of CO and chlorination of olefins.⁶¹⁻⁶³ The origin of catalytic activity of gold nanoparticles is discussed by Nørskov et al. using density functional calculations.⁶⁴ They found that particle size greatly affects the chemical activity of gold, and the fraction of low-coordinated gold atoms is in accordance with the catalytic activity, indicating that the atoms at corners and edges of gold nanoparticles are active sites.

Nanoporous gold, with abundant curvatures structure, possess great amount of steps and kinks on the surface which consist of low-coordinated gold atoms that is highly catalytically-active (Figure 1.8A).⁴ These active sites can be characterized using TEM and electrochemical methods.

For example, Chen et al. studied the surface atomic structure of dealloyed NPG using high-angle annular dark-field spherical-aberration-corrected scanning TEM (HAADF-STEM).⁶⁵ Large amounts of steps and kinks structures can be observed on the dealloyed NPG surface (Figure 1.8B and C). Using in situ environmental TEM, the authors found that these steps act as catalytic active sites in the oxidation of CO and the residual silver plays an important role in stabilizing these surface defects.

Ling et al. used Pb underpotential deposition for the investigation of distinguishing the surface atoms with various activity.⁶⁶ As atoms from different facets possess different surface energy, the potential needed in depositing Pb on various facets is different. Therefore, the comparative atom ratios of steps, (111), (100) and (110) facets can be determined using Pb underpotential deposition method (Figure 1.8D).

Figure 1.8 (A) Scheme illustration of Terrace, step and kink site atoms in NPG and their corresponding coordination number (CN).⁴ (B, C) HAADF-STEM images demonstrating stepped surface beside (111) terraces.⁶⁵ Scale bars indicate 2 nm. (D) Cyclic voltammograms of Pb underpotential deposition and corresponding NPG facets.⁶⁶ Reprinted with permission from The Royal Society of Chemistry, Nature Publishing Group and John Wiley and Sons.

1.3 APPLICATIONS OF NANOPOROUS GOLD

1.3.1 Catalysis

The catalytic activity of NPG is first reported in the oxidation of CO by Bäumer et al. and Ding et al. independently.^{67,68} Prior to this discovery, catalytic activity of gold nanoparticles was only reported to occur when supported by oxide materials. The catalytic activity of NPG is the first example of gold catalysis without any oxide support. This discovery demonstrated that NPG is highly catalytically active for CO oxidation with excellent long-term stability, even at temperatures as low as $-30\text{ }^{\circ}\text{C}$. The catalytic activity of NPG originates from the low-coordination number atoms at the steps and kinks of surface curvatures. Ding et al. also reported high activity of preferential CO oxidation in hydrogen-rich stream using NPG as catalyst.⁶⁹ At $20\text{ }^{\circ}\text{C}$, the final concentration of CO could be reduced from 1% to lower than 2 ppm with a turnover frequency (TOF) of $4.1 \times 10^{-2}\text{ s}^{-1}$. The mechanism proposed by the authors involves O_2 activation followed by highly oxidative intermediate OOH^* formation and then OH^* and CO_2 formation upon reaction of OOH^* with CO. H^* and CO_2 are then formed as OH^* reacts with CO, and finally H_2 is evolved due to the recombination of H^* (Figure 1.9). These results implies the potential of NPG in the hydrogen purification steps of fuel cell applications.

Figure 1.9 Reaction mechanism of CO oxidation in hydrogen-rich flow over NPG catalyst.⁶⁹ Reprinted with permission from Nature Publishing Group.

Following the reports of NPG's high catalytic activity, Friend et al. presented the high selectivity using NPG as catalyst in oxidative coupling of methanol.⁷⁰ They found that more than 97% of methanol is selectively oxidized into methyl formate. They also discovered high TOF at temperatures lower than 80 °C and low O_2 pressure (Figure 1.10A-B). By comparing the catalytic activity and selectivity of oxidative coupling reactions of alcohols with longer chain lengths, they found that both esters and aldehydes are formed in ethanol system while only aldehydes is selectively formed in n-butanol system (Figure 1.10C-D).⁷¹ Ligament sizes also affects the catalytic performance of NPG. For example, in the aerobic oxidation of D-glucose using NPG as catalyst, ligament sizes of 6 nm and 30 nm were found to be optimal for catalytic activity and structure stability, respectively.⁷² On the other hand, residual Ag atoms ratio did not influence the catalytic activity of NPG.

Figure 1.10 (A) Temperature-dependent conversion rate of methanol into methyl formate. (B) Selectivity of methanol oxidation using NPG as catalyst at different oxygen concentrations.⁷⁰ (C) Temperature-dependent conversion rate of ethanol. (D) The relationship between alcohol chain length and product species / selectivity.⁷¹ Reprinted with permission from The American Association for the Advancement of Science and John Wiley and Sons.

The catalytic performance of NPG in electrochemical reactions has also been investigated. Ding et al. reported the electro-oxidation of methanol, which could be used in direct methanol fuel cells, using dealloyed NPG as catalyst.⁷³ There are three advantages of using NPG as catalyst as compared to other gold nanostructures: (1) the high surface-to-volume ratio of NPG is favorable for providing more contact between electrolyte and electrodes, (2) the porous structure offers easier mass transport for the diffusion of reacting species, (3) the steps and kinks of NPG surface facilitates the

adsorption of oxygen species like OH^- which is essential for the methanol oxidation process.

1.3.2 Sensors

Raman scattering signals of the molecules close to or adsorbed onto the surface of plasmonic nanoparticles is known to be amplified by the electromagnetic field. Such enhanced Raman scattering is called surface-enhanced Raman scattering (SERS).⁷⁴⁻⁸⁰ Compared with other sensing techniques, SERS provides much higher sensitivity as well as molecular structural information. NPG, which has strong LSPR due to its porous interconnected nanostructure, holds great potential in SERS sensing applications.

Chen et al. compared the SERS enhancement of NPG with pore sizes ranging from 5 nm to 700 nm using Rhodamine 6G (R6G) and crystal violet as probe molecules.⁸¹ They found that SERS enhancement increases with decreasing NPG pore size, and NPG with 5-10 nm exhibits the highest SERS enhancement. In another report, the knife-cut fracture surfaces of dealloyed NPG sheet achieved ten times enhancement of SERS intensity at fracture surface with tip structures compared to other areas.⁸² This is due to the highly intensified SPR at the fracture surface, and validates that the SERS enhancement in NPG is ascribed to the electromagnetic field rather than chemical enhancement.

Weiss et al. fabricated large area two-dimensional arrays of patterned NPG and studied its SERS enhancement using benzenethiol as probe molecule.⁸³ They applied a one-step stamping method onto the dealloyed NPG, obtaining NPG with periodic

NPG gratings and mechanically densified NPG area. Such NPG platform exhibits about 100-fold increase in SERS enhancement factor as compared with normal NPG. Shih et al. created monolithic NPG nanodisks using a method involving top-down sputter etching of polystyrene beads coated with Au-Ag alloy and bottom-up dealloying.⁸⁴ The authors found the as-obtained NPG nanodisks exhibit a SERS enhancement factor of $\sim 10^8$ using benzenethiol as probe molecule, which is 517 times compared to that of unpatterned NPG. Chen et al. prepared wrinkled NPG by utilizing the thermal contraction force of polystyrene substrate attached under NPG.⁸⁵ There is no obvious porosity change and the length of wrinkles can be controlled by tuning the thermal contraction ratios. The wrinkled area yields a local enhancement factor of $\sim 10^9$, which is attributed to the abundant nanogaps and tips at the wrinkled area (Figure 1.11).

Figure 1.11 (A) Scheme of the preparation process of wrinkled NPG utilizing the thermal contraction force of polystyrene layer. (B) STEM image of the wrinkled area in NPG. The inset shows sharp nanotips. The scale bar is 200 nm. (C) SERS intensity

comparison between wrinkled area and non-wrinkled area in NPG with various pore sizes.⁸⁵ Reprinted with permission from American Chemical Society.

NPG is also increasingly employed as electrochemical biosensors owing to four main reasons.⁸⁶ (1) In the biosensor systems where enzymes are needed, the nanosized porous structure of NPG offers enzymes protection from high temperature and organic solvents. (2) NPG endows biosensors with fast electron transfer and quick electrochemical response due to its good conductivity and active surface sites. (3) NPG is easier for the binding of thiol-molecules monolayers than conventional smooth Au electrodes due to the abundance of highly active surface defects of NPG. (4) NPG systems can minimize biofouling as their porous nature can forbid the access of large protein molecules into the internal area.

Both enzyme-based NPG biosensors and nonenzymatic NPG biosensors have been reported. Gao et al. prepared a NPG based glucose biosensor by physically adsorbing glucose oxidase (GOD) onto the NPG surface.⁸⁷ This GOD-NPG modified glassy carbon electrode shows a good linear range from 1 mM to 18 mM ($R = 0.996$), a sensitivity as low as $0.049 \mu\text{A mM}^{-1}$ and the detection limit of $196 \mu\text{M}$ ($S/N = 3$). In another work, GOD is immobilized onto NPG surface using thiol-linking method.⁸⁸ It is found that the sensitivity and selectivity of the glucose sensor is enhanced when using GOD-thiol-NPG electrode compared to GOD-NPG electrode. On the other hand, non-enzymatic NPG glucose biosensor is designed based on the direct electro-oxidation of glucose. The reaction proceeds through the following pathway (1.1)-(1.4):

In neutral environment:

In alkaline environment:

Yan et al. reported that in 0.1 M NaOH alkaline environment, NPG exhibits much lower onset potential (-0.9 V vs SCE) than smooth gold electrode (-0.6 V vs SCE), which indicates the high catalytic activity of NPG.⁸⁹ When comparing the catalytic current density of NPG with various pore sizes, it was determined that NPG with pore size of 12 nm possess 1.5-fold and 17-fold higher current response than NPG with pore size of 35 nm and smooth gold electrode, respectively.⁹⁰

1.3.3 Photothermal effect

SPR excitations of plasmonic nanoparticles significantly increase the light absorption and lead to the occurrence of ‘hot electrons’ which jump to excited state from ground state. As a result of instability of high energy excited state, the excited ‘hot electrons’ go through radiative decay or non-radiative decay. Radiative (electromagnetic radiation) decay corresponds to the enhanced scattering, while non-radiative decay proceeds with the loss of coherence to the incoming light, corresponding to the adsorption of light. Photothermal effect of plasmonic nanoparticles originate from non-radiative decay after SPR excitation. Non-radiative decay triggers the collision of atoms, which raises up the temperature of metal lattice.⁹¹

NPG, with intense SPR and abundant ‘hot spots’, possess high photothermal efficiency and can be utilized in various photothermal applications.

Shih et al. investigated the photothermal effect of NPG nanodisks coated on glass substrate.⁹² Maximum photothermal temperature increase (ΔT) of NPG nanodisks is found to be ~ 60 °C using $0.10 \text{ W} \cdot \text{mm}^{-2}$ laser with tunable wavelength 700–900 nm and the photothermal conversion efficiency of NPG nanodisks is calculated to be 56%. The advantage of this photothermal effect is then demonstrated via the effective multi-stepped light-gated release of R6G.

Interestingly, the photothermal effect can also be employed to tune the morphology of NPGs (Figure 1.12).⁹³ As the laser is applied, the localized temperature of NPG is effectively increased, and this induces the coarsening of NPG ligaments. Through simulations and experiments, the influence of substrate, laser mode and laser power on the thermal coarsening of NPG was investigated. It is found that the use of silicon substrate and continuous-wave irradiation provide better control over NPG morphology, while the degree of coarsening can be well controlled by tuning laser power. In addition, the authors fabricated an on-chip NPG library consisting of 9 different morphologies, which could be useful in morphology–property relationships study.

Figure 1.12 (a) Scheme of the preparation process of NPG material library. (b) SEM images of the NPG morphology using different laser mode and laser power.⁹³ Reprinted with permission from The Royal Society of Chemistry.

Photothermal effect of NPG is also useful in the inactivation of bacteria.⁹⁴ A 785 nm NIR laser (0.085 W/mm²) irradiated onto NPG grown with bacteria results in the destruction of all three types of bacteria within 25 s due to the heat produced, demonstrating the effectiveness of NPG in bacteria inactivation (Figure 1.13).

Figure 1.13 SEM images of *E. coli* (a-c), *B. subtilis* (d-f) and *Exiguobacterium* sp. AT1b (g-i) cells deposited on the NPG substrate. Images (a, d and g) show the bacteria

before laser irradiation. Images (b, c, e, f, h and i) show the bacteria after 25 s of laser irradiation.⁹⁴ Reprinted with permission from The Optical Society (OSA).

1.3.4 Actuators

NPG can also be exploited as actuators due to their excellent thermal and electrical conductivity. Jin et al. reported a NPG/paraffin wax hybrid actuator which can overcome the problem of low response rate in traditional pure paraffin actuators.⁹⁵ Using a Au/(paraffin/NPG) bilayer structure, the actuation movement is caused by the difference in thermal expansion/contraction rate between the two layers. The authors found that embedding dealloyed NPG sheet in paraffin greatly increases the response speed, which is ascribed to the improved thermal conductivity after the introduction of NPG. They also found that the actuation performance of Au/(paraffin/NPG) bilayer structure is related with NPG ligament size, whereby smaller NPG ligament size leads to higher actuation stress.

Figure 1.14 (a) Scheme of Au/(paraffin/NPG) bilayer structure. (b) Reversible rotation of a spring-type actuator in response to cyclic temperature changes between 100 °C to

20 °C. (c) The continuous bending and straightening of a cantilever-type actuator above hot water with temperature of around 90 °C. Scale bars in (b) and (c) are 10 mm.⁹⁵ Reprinted with permission from IOP Publishing.

De Hosson et al. developed a novel electrolyte-free metallic muscle using NPG/polyaniline (PANI) bulk junction actuator.⁹⁶ In this design, doped PANI is coated onto the surface of NPG and the counterions of dopant is in the PANI coating matrix. This metallic muscle is controlled using electricity and when dopant counterions (sulfate ions) are present in the PANI coating, they interact with NPG substrate, creating a charge-induced relaxation/contraction of NPG. The actuation rate of this NPG/PANI hybrid electrolyte-free metallic muscle is about 1000 times higher than that of conventional metallic muscles operating in aqueous electrolytes.

Figure 1.15 (a) Scheme of NPG/PANI bulk junction actuator in the Au/PANI/NPG configuration. SEM images of (b) NPG whose edge is linked with anode side; (c) NPG with PANI coating of ~5 nm; (d) NPG with PANI coating of ~10 nm. (e)

Electrolyte-free actuation curve in NPG/PANI, indicating 50 expansion/contraction cycles.⁹⁶ Reprinted with permission from American Chemical Society.

1.4 MOTIVATION AND OBJECTIVES

Nanoporous gold is an emerging porous nanostructure that have attracted extensive research interest in various fields. The versatile preparation strategies of NPG offer great opportunities in designing material structures for various applications. The unique properties of high surface-to-volume ratio, surface sites with high activity and light-matter interaction render NPG the ability to convert one form of energy into another. For instance, NPG-based applications have been developed in the fields of energy conversion, such as heterogeneous catalysis in fuel cell (converts chemical energy into electrical energy), photothermal heating (converts luminous energy into thermal energy) and actuators (converts thermal or other types of energy into mechanical energy).

Despite the potential of NPG, three main challenges still remain in the research of NPG-based functional hybrid materials. (1) Although NPG is an intriguing platform for functional hybrid structure design due to its highly conductive and thermally stable porous structure, the interaction between NPG substrate and the other component in hybrid remains unknown. Understanding the mechanism of such interactions is of great importance in enhancing the performance of functional hybrid materials. Up to now, there is no research reporting the factors that affect the synergistic effects in NPG-based hybrid. (2) Current morphology dependent studies of NPG are only restricted to

pore size and ligament size. However, the different shapes of NPG can notably affect the mass transfer behavior and optical properties. Thus, it is of interest to systemically investigate the shape dependent properties of NPG. (3) The preparation strategy of NPG-based hybrid materials is restricted to ‘top-down’ methods which is fabricated based on macro-sized 2D NPG sheets. However, the morphology of nanostructure prepared by ‘top-down’ strategy is usually limited to the shape of the masks. Particle-based ‘bottom-up’ strategy provides more flexibility in the morphology design of nanostructures. Currently no particle-based NPG hybrid nanostructure, which is more advantageous in ‘bottom-up’ structural construction, has been developed. To conclude, the mechanism of NPG-based hybrid synergistic effects, the effect of NPG shape and the possibility of preparing particle-based NPG hybrid, which all restricts the potential of high-performance functional NPG hybrid design, are yet to be investigated in detail.

The objective of my thesis is therefore to address the aforementioned limitations in the research of NPG-based functional hybrid structures, and boost their performance in energy conversion applications. (1) The synergistic effects in NPG-based hybrids can be studied in detail by characterizing the electronic structure, surface area and conductivity of NPG-based hybrid using valence band XPS and electrochemical tests. (2) This thesis aims to prepare NPG with different shapes using templates with different shapes and study the shape-dependent performance of NPG in photothermal effect. (3) Zero-dimensional NPG particles can be prepared using wet chemistry method, therefore particle-based NPG hybrid nanostructure can be prepared by utilizing the photothermal effect of NPG particles. This thesis aims to find out the

mechanism of synergistic effects and shape-dependent photothermal effect of NPG nanostructures and enhancing their performance in energy conversion applications.

In chapter 2, I deposit Pt onto the surface of open-structured nanoporous gold bowls (NPGBs) and demonstrate the superiority of Pt-NPGB as catalyst in electro-oxidation of methanol. Notably, I investigate the d-band interaction between NPGB and Pt to elucidate the origin of its excellent catalytic activity. In chapter 3 and 4, NPG is exploited in designing photo-mechanical materials. In chapter 3, I compare the photothermal effect of bowl-shaped, tube-shaped and plate-shaped NPG particles. I also employ the strong photothermal effects of NPG for light-controlled movement of shape memory polymer/NPG. Chapter 4 focuses on the systematic study of the shape memory polymer/NPG composite, and parameters that affects its light-induced movement will be discussed in detail. Chapter 5 involves the direct synthesis of a NPG-hybrid structure by exploiting the photothermal effect to significantly increase localized temperature. Remarkably, molybdenum sulfide is deposited onto NPG surface using photothermal heat without any reducing agent. In addition, excellent activity of obtained molybdenum sulfide/NPG hybrid in hydrogen evolution reaction is demonstrated. Lastly, chapter 6 concludes the thesis and provides an outlook of the potential future direction of this field.

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Chapter 2

Manipulating the d-band Electronic Structure of Platinum-Functionalized Nanoporous Gold Bowls: Synergistic Intermetallic Interactions Enhance Catalysis**

ABSTRACT. Bicontinuous nanoporous gold (NPG) is a high-performance catalyst characterized by its excellent electrochemical stability and immense active surface area with high electrolyte accessibility. However, the intrinsic catalytic activity of NPG is still lower compared to other metal (such as Pt), thus impeding its applicability in commercial catalytic system. Herein, we incorporate secondary Pt metal with inherently strong catalytic activities into zero-dimensional (0D) nanoporous gold bowl (NPGB) to develop Pt-NPGB bimetallic catalyst. Our strategy effectively exploits the highly accessible surface area of NPGB and the manipulative d-band electronic structure brought about by the synergistic intermetallic interaction for enhanced catalytic performance and durability. Deposition of Pt in the bimetallic catalyst directly modulates its d-band electronic structure, with the electronic energy of 1%Pt-NPGB (-4.24 eV) approximating that of chemically-resistance gold (-4.35 eV). This is vital to weaken the binding strength between Pt active sites and intermediate poisoning species. Together with the high Pt ECSA of 17.1 mA/ μ gPt facilitated by NPGB co-catalyst, such synergistic effect enables the superior performance of Pt-NPGB hybrids over commercial Pt/C in methanol oxidation reaction (MOR), where a 11-fold and 227-fold

better catalytic activity and durability are demonstrated even after an extended duration of 3600 s. Our study is therefore the first demonstration on the exploitation of precisely-modulated synergistic effect at the electronic level to control and boost catalytic performance. Furthermore, the chemically-inert NPGB possesses intrinsically higher gold surface area and electrolyte accessibility unique to 0D nanoparticle, hence empowering it as an immensely attractive co-catalytic platform extendable to a wide range of secondary metals. This is important to promote the catalytic performance for diverse electro-chemical applications, especially in the field of energy, synthetic chemistry, and also environmental toxin degradation.

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2.1 INTRODUCTION

Nanoporous gold (NPG) is a three-dimensional bicontinuous porous gold nanostructure interconnected by nanosized ligaments.¹⁻⁹ It exhibits good electrochemical stability and large active surface area with high electrolyte accessibility, making it a high-performance catalyst promising in electrocatalytic reaction for energy applications.¹⁰ Notably, reducing the size of NPGs from conventional two-dimensional (2D) sheets to zero-dimensional (0D) nanoparticles has increased its surface-to-volume ratio and shortened electrolyte diffusion path in all three dimensions, giving rise to $\sim 40\%$ enhanced catalytic activity in methanol oxidation reaction (MOR).^{11,12} However, the intrinsic catalytic activity of NPG is still lower compared to other metal (such as Pt), thus impeding its applicability in commercial catalytic system.

The introduction of secondary metal with inherently strong catalytic properties to form bimetallic NPG catalysts is anticipated to produce synergistic effects that can further boost the catalytic performance of such hybrid systems. This is due to the modification of bimetallic system's d-band structure which directly manipulates the binding strength between the catalyst and reacting adsorbate species to improve their catalytic efficiency.^{13,14-18} Such synergistic effects mainly arise from ligand effect and strain effect; ligand effect refers to the direct electron interactions between two constituent metals, while strain effect refers to the electronic structure change caused by lattice strain change.^{16,19-21} Bimetallic catalysts with tunable intermetallic interaction are therefore vital to regulate lattice strain and ligand effect for optimal

synergistic effect, which is especially advantageous for electrochemical reactions in energy-related applications.²² Among various metal co-catalytic platforms, gold (Au) is immensely attractive due to its high chemical resistance and its potential in enhancing catalytic activity imparted by synergistic effects.²³⁻²⁶ For instance, 2D NPG sheets were reported to promote the catalytic activity of Pt by 2-fold and 380-fold in methanol and formic acid oxidation, respectively.^{27,28} However, there is a lack of fundamental study on the origin of synergistic effects in bimetallic NPG catalytic systems, especially on the understanding of relationship between surface electronic structure and catalytic activity. This is crucial for the design of bimetallic hybrids with optimal synergistic effects and catalytic performance, ultimately expediting their future incorporation into commercial fuel cell applications.

Herein, I develop 0D Pt-NPG bimetallic system with manipulative d-band electronic structure brought about by the synergistic intermetallic interaction for catalytic reaction enhancement and modulation. I choose Pt as the secondary metal owing to its high intrinsic catalytic activities, which also generally suffer from severe blockage by strongly bound intermediate species (the “poisoning” effect) that limit their applicability. The aim is to effectively exploit the synergistic benefits and the highly accessible surface area of 0D NPG co-catalyst platform to boost Pt catalytic activity and durability. I first demonstrate the template-assisted synthesis of 0D NPG, which are subsequently deposited with precisely-regulated Pt contents to yield the hybrid Pt-NPG systems. The valence band electronic structures of Pt-NPG bimetallic catalysts are then characterized using X-ray photoelectron spectroscopy (XPS) to elucidate the tunable d-band center positions of the hybrid with respect to NPG-loading.

I further evaluate the electrochemical surface area (ECSA) and Pt utilization of our Pt-NPG systems. Using methanol electro-oxidation (MOR) as a model study, the importance of both synergistic effect and highly accessible electrochemical surface to boost catalytic performance of Pt-NPG bimetallic system are systematically exemplified. Such synergistic engineering of bimetallic catalysts is highly promising for improving the catalytic reactions in diverse electro-chemical applications.

2.2 RESULTS AND DISCUSSION

Morphology, structure and composition of NPGB and Pt-NPGB bimetallic catalysts

I fabricate bimetallic catalysts by depositing Pt on NPG co-catalytic platform to modulate their synergistic effects for enhanced electrocatalytic performance. Open-structured 0D nanoporous Au bowls (NPGBs) are first prepared using a template-assisted method.¹¹ In this synthesis, AgCl nanocubes are used as sacrificial templates (average length = 301 ± 49 nm),²⁹ HAuCl₄ as gold precursor, polyvinylpyrrolidone (PVP) as surfactant and hydroquinone as reducing agent (Figure 2.1). Upon the reduction of Au precursor, porous Au structures are observed to grow mainly at the corners of AgCl nanocubes due to their higher surface energy.³⁰ Such Au structures exhibit a bowl-like morphology because of the non-epitaxial growth of Au arising from the large lattice mismatch between Au and AgCl ($\sim 26\%$).³¹ The AgCl templates are subsequently etched off using ammonia solution to obtain NPGBs characterized by their hollow half-sphere open structures interconnected with bicontinuous nanoscale

ligaments (Figure 2.1). NPGB exhibits average diameter and ligament size of (288 ± 29) nm and (12 ± 2) nm (Figure 2.2), respectively. X-ray diffraction (XRD) pattern of NPGB reveals the sharp diffraction peaks of metallic gold (JCPDS 04-0784)¹¹, demonstrating the high crystallinity of NPGB (Figure 2.3). NPGB's crystallite size is calculated at ~ 11 nm according to Scherrer equation,³² which is consistent with the ligament size measured using scanning electron microscopy (SEM). Elemental analysis using inductively-coupled plasma optical emission spectrometry (ICP-OES) affirms the successful removal > 97 wt% of Ag from NPGBs. X-ray photoelectron spectroscopy (XPS) survey spectrum indicates 5 wt % of Ag on NPGB surface. Such near-complete Ag removal is essential to minimize its potential interference on later Pt deposition and electrochemical evaluation.

Figure 2.1. (A) Schematic synthetic route of open-structure 0D NPGB. SEM images of (B) AgCl nanocubes and (C) AgCl-NPGB hybrid. (D, E) SEM image of NPGB demonstrating the porous structure.

Figure 2.2. Distribution curve of (A) AgCl cube size, (B) NPGB particle diameter and (C) NPGB ligament size.

Figure 2.3. XRD pattern of as prepared NPGB.

I subsequently synthesize a series of Pt-NPGB catalysts of various Pt weight ratios by reducing Pt precursor (1 – 5 wt%) using excess ascorbic acid in the presence of NPGB. This is to evaluate the effect of NPGB-to-Pt ratio on their subsequent catalytic performance. The morphology of Pt-NPGB remains largely unchanged after Pt deposition with no visible Pt aggregations on its surfaces, indicating the deposition of sub-nanometer Pt structures ((Figure 2.4 and 2.5). EDS elemental mappings of all Pt-NPGB bimetallic catalysts demonstrate homogeneous and overlapping distribution of Au and Pt, signifying the even deposition of Pt on NPGB surfaces ((Figure 2.6). The surface composition of Pt-NPGB is further examined using XPS. All Pt-NPGB

samples demonstrate the characteristic doublets of metallic gold at 83.3 eV and 87.0 eV, and metallic Pt at 70.1 eV and 73.5 eV (Figure 2.1F). The peak ratio of the Au/Pt $4f_{7/2}$ peaks decreases from 10.5 to 2.3 as Pt percentage increases from 1 % to 5 % ((Figure 2.7), reflecting an increasing coverage of Pt on NPGB surface at higher Pt percentage.

Figure 2.4. TEM images of (A) 1%Pt-NPGB, (B) 2%Pt-NPGB, (C) 3%Pt-NPGB, (D) 4%Pt-NPGB, and (E) 5%Pt-NPGB. Scale bars indicate 20 nm.

Figure 2.5. SEM images of (A) 1%Pt-NPGB, (B) 2%Pt-NPGB, (C) 3%Pt-NPGB, (D) 4%Pt-NPGB, and (E) 5%Pt-NPGB.

Figure 2.6. SEM-EDS mapping images of (A-C) 1%Pt-NPGB, (D-F) 2%Pt-NPGB, (G-I) 3%Pt-NPGB, (J-L) 4%Pt-NPGB and (M-O) 5%Pt-NPGB. Scale bars indicate 200 nm.

Figure 2.7. (A) XPS spectra of NPGB and Pt-NPGB with different Pt ratios. (B) The Au/Pt peak ratios of various Pt-NPGB samples using XPS characterization.

In addition, I determine the mass composition of our bimetallic catalyst using ICP-OES to ensure the complete deposition of Pt onto NPGB. ICP-OES analysis demonstrates that all reduced Pt on NPGs are in stoichiometric agreement with the added precursors within ± 0.1 wt% accuracy (Figure 2.8; Table 2.1). For instance, the addition of 1 wt% of Pt precursors results in the deposition of (1 ± 0.1) wt% Pt onto NPG. This indicates that nearly all Pt precursors are successfully reduced into metallic form and deposited on NPG surfaces to yield the bimetallic hybrid, with negligible amount of unbounded Pt in the solution. Pt-NPGB bimetallic catalysts with Pt weight ratio of 1 %, 2 %, 3 %, 4 % and 5 % are herein denoted as 1%Pt-NPGB, 2%Pt-NPGB, 3%Pt-NPGB, 4%Pt-NPGB and 5%Pt-NPGB, respectively. Collectively, our results quantitatively affirm the successful deposition of sub-nanometer Pt layer on NPGB surface. Such formation of tiny Pt structures improves the surface-to-volume ratio of Pt, which is especially important for latter electro-catalytic application.

Figure 2.8. Comparison of actual Pt weight percentages of Pt-NPGB with their theoretical values. The elemental composition is determined using ICP-OES.

Table 2.1. Summary of composition of Pt-NPGB with different Pt ratios.

Sample	Theoretical Pt weight ratio(%)	Pt Weight ratio by ICP-OES (%)
1% Pt-NPGB	1.0	1.0 ± 0.0001
2% Pt-NPGB	2.0	2.1 ± 0.0002
3% Pt-NPGB	3.0	3.0 ± 0.0008
4% Pt-NPGB	4.0	4.1 ± 0.0004
5% Pt-NPGB	5.0	5.1 ± 0.0009

Surface electronic structure of Pt-NPGB bimetallic catalysts

To probe the synergistic effects between NPGB and Pt, I study the surface electronic structure of our bimetallic catalysts using valence band XPS evaluations to determine the d-band center position of Pt after incorporating into NPGB co-catalyst platform (Figure 2.9). Using $\int N(\varepsilon)\varepsilon d\varepsilon / \int N(\varepsilon)d\varepsilon$, where $N(\varepsilon)$ is the density of states^{25,33}, the d-band center of control Pt/C and NPGB are positioned at -3.73 eV and -4.35 eV, respectively. The deposition of Pt onto NPGB results in the d-band center of bimetallic system to be altered and falls in between the d-band positions of pure NPGB and Pt/C. As the Pt percentage on NPGB is reduced from 5 % to 1 %, the d-band center decreases from -3.93 eV to -4.24 eV, respectively. I ascribe this evident d-band downshift trend to the increasing contribution of NPGB in valence band. Such downshift in d-band centers is crucial in the precise regulation/reduction of binding strength between the catalysts and adsorbates. This will alleviate strongly adsorbed species away from the Pt catalyst surface, and thus reduce the “poisoning” effects and boost the catalytic activity of Pt.³⁴

Figure 2.9. Analysis of d-band center. (A) Comparison of valence band XPS spectra of Pt-NPGB samples with different Pt ratios, pure NPGB, and Pt/C. Black lines indicate the positions of calculated d-band centers. (B) Comparison of d-band centers among Pt-NPGB bimetallic catalysts, NPGB, and Pt/C. (C) Schematic illustration of synergistic effect-induced downshift of Pt d-band center.

Pt utilization and surface area of Pt-NPGB bimetallic catalysts

Electrochemical active surface area (ECSA) of Pt and Au in Pt-NPGB bimetallic catalysts are quantified using cyclic voltammetry (CV) to demonstrate the effective utilization of Pt for optimal performance-to-cost factor in commercial catalysis (Figure 2.10 and 2.11, Table 2.2). The ECSA of Pt is measured using the total charges under the hydrogen desorption peaks after double layer correction, whereas the ECSA of Au is obtained by measuring the total charges used in gold oxide stripping peak.³⁵⁻³⁷ ECSA

of Pt can be calculated using the measured charge of hydrogen desorption peaks (anodic peaks from around -0.77 V to -0.3 V) after double layer correction (Q_H), 210 $\mu\text{C} / \text{cm}^2$ is used for adsorption charge of monolayer hydrogen on Pt. ECSA of Au can be calculated using the measured charge of gold oxide stripping peak (cathodic peaks between around 0.1 V to 0.4 V), using 450 $\mu\text{C} / \text{cm}^2$ as associated charge of monolayer oxygen on adsorbed on gold ($Q_{\text{Au-O}}$).

Pt utilization is defined as the percentage of Pt atoms being exposed to the surface, which can be calculated using measured Pt ECSA divided by the theoretical surface area of 100% utilized Pt (detail calculation is explained in experimental section). For Pt-NPGB samples, the electro-active surface area of Pt on the NPGB surfaces decreases accordingly from 136 $\text{m}^2/\text{g}_{\text{Pt}}$ to 82 $\text{m}^2/\text{g}_{\text{Pt}}$ as Pt ratio increases from 1 % to 5 %. These correspond to Pt utilization of 58 % to 35 %, respectively.

Assume Pt islands are formed in a layer-by-layer fashion (for example, the third layer will only start formation after the second layer fully covers the first layer), the thickness of Pt islands in 1%Pt-NPGB can be estimated. Pt island thickness is calculated to increase from ~ 1.7 to ~ 2.9 atomic layers as Pt percentage increases from 1% to 5%, respectively. On the contrary, commercial Pt/C sample possesses much smaller Pt ECSA (62 $\text{m}^2/\text{g}_{\text{Pt}}$) and utilization of only 26 %. Our best performing 1%Pt-NPGB therefore demonstrates an enhancement in utilization and effective electro-active surface area by > 2 fold compared to the commercial Pt/C platform. Such higher Pt utilization in Pt-NPGB bimetallic catalysts originates from the sub-nanometer formation of Pt islands which comprises of higher ratio of exposed Pt atoms (Figure 2.10A).

Figure 2.10. ECSA and Pt utilization. (A) Schematic comparing the Pt utilization of difference sizes of Pt islands. (B) CV curves of various Pt-NPGB samples and Pt/C in 0.5 M KOH. Scan rate = 50 mV/s. (B) Pt ECSA and Pt utilization of Pt-NPGB samples with different Pt ratios, NPGB, and Pt/C.

Figure 2.11. (A) CV curve of NPGB in 0.5 M KOH at 50 mV/s. (B) Comparison of Au ECSA of NPGB and Pt-NPGB with different Pt percentages.

Table 2.2. Summary of electrochemical properties of Pt-NPGB with different Pt ratios.

Sample	Pt ECSA (m ² /g _{Pt})	Pt utilization (%)	Au ECSA (m ² /g _{Au})	Mass current (mA/μg _{Pt})	Specific current (mA/cm ² _P i)	Onset potential (V vs NHE)
1% Pt-NPGB	136	57.5	4.4	17.1	12.6	-0.42
2% Pt-NPGB	115	48.7	3.7	13.3	11.6	-0.42
3% Pt-NPGB	106	45.1	1.9	12.0	11.3	-0.42
4% Pt-NPGB	97	41.4	1.5	10.0	10.2	-0.40
5% Pt-NPGB	82	35.0	1.3	8.0	9.7	-0.39
Pt/C	62	26.3	N/A	1.5	2.3	-0.28

More importantly, the Pt's ECSA of 1%Pt-NPGB is also > 20 % higher compared to reported platinum-decorated two-dimensional NPG leaf (105 m²/g_{Pt}). Such improved Pt's ECSA in Pt-NPGB bimetallic catalysts is attributed to the large Au's ECSA of pure NPGB (11.2 m²/g_{Au}), which is > 200 % of the dealloyed 2D NPG (5.3 m²/g_{Au}).³⁶ Our NPGB therefore surpasses 2D NPG as a co-catalyst platform to enhance the utilization of Pt, demonstrating the importance of enhanced surface area generated by reducing the size of NPG from 2D to 0D. The wide surface coverage of Pt on Au is further supported from the decrease of Au ECSA from 4.4 m²/g_{Au} (1%Pt-NPGB) to 1.3 m²/g_{Au} (5%Pt-NPGB) with increasing Pt percentage (Figure 2.11). The enhancement

to both Pt utilization and its ECSA renders our Pt-NPGB platforms as promising electrocatalyst vital for efficient energy-related applications.

MOR performance of Pt-NPGB bimetallic catalysts

I demonstrate the superior catalytic activities of Pt-NPGB bimetallic catalysts over commercial Pt/C and pure NPGB to highlight the importance of synergistic effect and high Pt utilization for improving catalytic efficiency. Methanol oxidation reaction (MOR) is our model reaction due to their wide application in fuel cell studies. CV measurements in 0.5 M KOH and 2 M MeOH solution indicate that the oxidation peak region of Pt-NPGBs (between -0.4 V to 0.4 V) is similar to that of Pt/C (between -0.3 V to 0.3 V), but is much lower than NPGB's (around 0.1 V to 0.6 V). This implies that the oxidation peak of Pt-NPGB is predominantly attributed to Pt (Figure 2.12) with negligible contribution from NPG. Consequently, catalytic activities are normalized against the mass of Pt for comparison of Pt's catalytic performance (Figure 2.13A). In the presence of NPG as co-catalyst, all Pt-NPGBs exhibit > 5-fold superior catalytic activity (8.0 to 17.1 mA/ μg_{Pt}) as compared to commercial Pt/C (1.5 mA/ μg_{Pt}). We also observe a decrease in mass current as Pt percentage increases in the Pt-NPGB bimetallic catalysts owing to the corresponding reduction of Pt utilization. Notably, 1%Pt-NPGB exhibits the highest current response, i.e. > 11-fold stronger than commercial Pt/C (Figure 2.13B; Table 2.2). I attribute the superior Pt mass-normalized current in our Pt-NPGB to two plausible factors, namely (1) the high Pt ECSA which endows catalysts with more Pt active sites, and (2) the synergistic effects induced via

the modification of catalytically-active Pt's electronic structure upon integration of Pt to NPGB.

Figure 2.12. CV curves of NPGB (enlarged 3 times), Pt/C and Pt-NPGB hybrid with different Pt ratios in 0.5 M KOH + 2 M MeOH at scan rate 50 mV/s. All currents are obtained by normalizing the current responses with the mass of catalyst used.

Figure 2.13. Effect of Pt composition on MOR. (A) CV curves of Pt-NPGB bimetallic catalysts with different Pt ratios and Pt/C in 0.5 M KOH and 2 M MeOH. The plot is normalized using mass of Pt and the CV performed at scan rate of 50 mV/s. (B) Mass current and specific current comparison of Pt-NPGB samples with different Pt ratios, NPGB and Pt/C. (C) Onset potential of Pt-NPGB samples with different Pt ratios and Pt/C. (D) Chronoamperometric curves of Pt-NPGB samples with different Pt ratios and Pt/C in 0.5 M KOH and 2 M MeOH. Potential applied: -0.02 V. Inset is the zoom-in view of the rectangular region. (E) Schematic illustration of the binding strength towards poisoning species.

To evaluate the two aforementioned proposed reasons, I further normalize the current responses against Pt ECSA to eliminate the contribution from enhanced surface area for fair comparison of Pt's intrinsic catalytic activity. Using Pt's ECSA-normalized current, our Pt-NPGB hybrid samples evidently demonstrate similar superior specific catalytic performance (9.7 - 12.6 mA/cm²_{Pt}) which is > 300 % better than Pt/C (2.3 mA/cm²_{Pt}). In particular, the best-performing 1%Pt-NPGB excels over Pt/C by ~ 400 % (Figure 2.13B and Table 2.2). Through such specific current comparison, I therefore ascribe the improved Pt catalytic activity in Pt-NPGB to the synergistic effects between NPGB and Pt which changes the d-band structure. This highlights the highest catalytic activity in 1%Pt-NPGB bimetallic system, characterized by its lowest d-band center, also stems from the weakened binding interaction with poisoning species arising from the Pt-NPGB synergistic effects (Figure 2.13E and 2.14).³⁸ The facilitation of Pt-catalyzed MOR process via such synergistic effect imparted by NPGB co-catalyst platform is again affirmed through the decrease of onset potential for all Pt-NPGB hybrid samples (-0.42 V to -0.39 V) relative to Pt/C (-0.28 V; Figure 2.13C). Collectively, our results clearly emphasize the importance of NPGB as an effective co-catalytic platform to resolve the persistent limitations of conventional Pt catalyst, where the latter is widely known to suffer from the poisoning effect of intermediate species during MOR catalysis process.³⁹

Figure 2.14. Relationship between d-band centers compared to Pt/C and specific current of Pt-NPGB bimetallic catalysts with different Pt ratios.

I conduct chronoamperometric tests to exemplify the superior durability and tolerance of bimetallic catalysts over Pt/C towards poisoning species formed during MOR process. Such studies are crucial to evaluate their suitability for future practical applications. All Pt-NPGB and Pt/C generally exhibit an exponential decrease of current responses with time (Figure 2.13D). Such decay is probably attributed to the inhibition of active sites arising from the accumulation of intermediate poisoning species like CO.⁴⁰⁻⁴² More importantly, all Pt-NPGB bimetallic catalysts are able to retain > 4-fold higher Pt catalytic activity (0.17 – 8.27 mA/μg_{Pt}) than Pt/C (0.04 mA/μg_{Pt}) after 3600 s, whereby 1%Pt-NPGB exhibits the highest remaining current response (227-fold of Pt/C). Moreover, our best performing 1%Pt-NPGB also possesses excellent durability which has 21-fold better remaining current percentage compared to Pt/C, even after an extended duration of 3600 s (Figure 2.15). Such durability improvement again affirms the weakened binding strength towards

poisoning intermediate species due to synergistic effects between Pt and NPGB. Our results jointly emphasize the high sustainability of strong Pt catalytic activities in our bimetallic system when NPGB is employed as co-catalyst platform. The superior durability of Pt-NPGB bimetallic catalytic platform therefore renders them immensely attractive for practical application in the field of energy harvesting and synthetic chemistry, where reproducible and sustainable catalytic properties are highly sought after.

Figure 2.15. Analysis plots of current remained at 600 s interval of chronoamperometric curves of Pt-NPGB samples with different Pt ratios and Pt/C in 0.5 M KOH + 2 M MeOH.

2.3 CONCLUSIONS

In summary, I demonstrate the wet-chemical synthesis of 0D Pt-NPGB bimetallic system with precise control over its d-band electronic structure arising from synergistic

intermetallic interaction for enhanced catalytic performance and durability. Variation of Pt content in the bimetallic catalyst directly modulates its d-band electronic structure, with the electronic energy of 1%Pt-NPGB (-4.24 eV) approximating that of chemically-resistance gold (-4.35 eV). Such lowering of d-band center is vital to weaken the binding strength between Pt active sites and intermediate poisoning species. Combining the synergistic effect with high Pt ECSA (17.1 mA/ μg_{Pt}) enabled by NPGB co-catalyst, Pt-NPGB hybrids excel over commercial Pt/C in MOR by 11-fold in catalytic activity, and also 227-fold in remaining current response even after an extended duration of 3600 s. This study is therefore the first demonstration on the exploitation of precisely-modulated synergistic effect at the electronic level to control and boost catalytic performance.

2.4 EXPERIMENTAL SECTION

Chemicals. Silver nitrate, hydroquinone (Hq), HAuCl_4 , ethylene glycol (EG), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, ascorbic acid (AA) and poly(vinylpyrrolidone) (PVP, average $M_w = 1300000$) were purchased from Sigma Aldrich. Potassium hydroxide and hydrochloric acid (37%) were purchased from Schedelco. Nitric acid (69%) was purchased from Honeywell. Methanol was purchased from J. T. Baker. Ammonium hydroxide (25% in water) was purchased from Sinopharm Chemical. Ethanol was purchased from Fisher Chemical. Pt/C with Pt weight ratio of 5% was purchased from Premetek Company. The chemicals were used without further purification. Milli-Q water (18.2 $\text{M}\Omega/\text{cm}$) was purified with a Sartorius arium® 611 UV ultrapure water system.

Synthesis of AgCl nanocubes. 0.4 g PVP and 0.4 g AgNO₃ were dissolved in 30 mL and 20 mL of cold EG correspondingly. After mixing PVP solution and AgNO₃ solution in RBF for 1 min at 500 rpm at room temperature, 1.23 mL of 37% HCl was added into the solution and kept stirring for 1 min. Then the solution was heated to 150 °C and kept stirring at 500 rpm for 20 min. After the reaction, the solution was naturally cooled down. 40 mL acetone was added to 10 mL resulting solution for sedimentation and centrifuged at 5000 rpm. After washing with water twice, the product was dispersed in 10 mL water to give a white suspension. This white suspension was used for future reactions.

Synthesis of AgCl / Au hybrid. 0.35 g PVP was dissolved in 50 mL water. 310 mg Hq was dissolved in 10 mL water freshly. HAuCl₄ was also dissolved in water to get 0.5 M solution. 4.52 mL AgCl nanocube solution (11.4 mg/mL) was first mixed with 45 mL PVP solution at 1300 rpm in RBF. After mixing for 1 min, 780 µL Hq solution was added followed by addition of 323 µL HAuCl₄ solution. After reaction for 1 min at 1300 rpm at room temperature, AgCl/Au hybrid was obtained. The solution was centrifuged at 3000 rpm for 3 min and washed twice with water. The product could be re-dispersed in water. After mixing AgCl/Au hybrid solution with 10 mL ammonia, the solution was centrifuged at 3000 rpm for 3 min and washed with water twice. Nanoporous gold bowls (NPGBs) aqueous solution could be obtained. The concentration of NPGb solution is determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

Synthesis of Pt-NPGB hybrid. Typically, 2.3 mL of NPGB solution (0.25 mg/mL) was added to a vial containing 5 mL water, then certain volume of H_2PtCl_6 solution (1 mM) was added. After stirring at 700 rpm for 1 h, calculated amount of ascorbic acid (0.2 M) was added into the vial under 700 rpm stirring, the volume ratio between H_2PtCl_6 solution and AA solution is fixed at 1:1. After mixing for 10 min, the vial was put into an oil bath of 50 °C for 14 h. Final product was sonicated, centrifuged and washed. Eventually the product was dispersed in ethanol. The concentration and composition of the solution were analyzed by ICP-OES.

Electrochemical measurement. Electrochemical measurements were performed in three-electrode electrochemical cell. Hg/HgO (0.5 M KOH) electrode was used as reference electrode, and all potential values were calibrated by referencing to normal hydrogen electrode (NHE). A 1 cm² platinum plate was used as counter electrode. For electrochemical active surface area evaluation, a glassy carbon electrode (GCE) with glassy carbon diameter of 5 mm was used. For other electrochemical measurements, GCE with glassy carbon diameter of 3 mm was used. Nanoparticle suspensions were dropped onto GCEs and dried in ambient environment, the modified electrodes were used for cyclic voltammetry (CV) and chronoamperometric tests. Electrolyte solution was bubbled with high purity argon gas for at least 30 min before tests.

Materials Characterization. Nanoparticles are drop cast on a clean silicon substrate for scanning electron microscopy (SEM) observation. SEM imaging was performed using a JEOL JSM 7600F microscope. Voltage was set at 5 kV. Nanoparticles are dropped on copper grids for transmission electron microscopy (TEM) observation. TEM images were performed on a JEOL-1400 model. Acceleration voltage was set at 100 kV. X-Ray photoelectron spectroscopy (XPS) spectra were measured using a Phoibos 100 spectrometer with a monochromatic Mg X-ray radiation source. 284.5 eV for C 1s binding energy peak was used for XPS calibration. Composition and concentration analysis of the obtained nanoparticle suspension were conducted using a Thermo Scientific iCAP 6500 model ICP-OES. Nanoparticle suspension was mixed with Aqua Regia, and then diluted with water prior to ICP-OES measurement. Electrochemical characterizations were performed using an Autolab PGSTAT128N electrochemical workstation.

ECSA determination. The equations for Pt and Au ECSA determination are:

$$\text{Pt ECSA} = Q_H / (210 \mu\text{C} / \text{cm}^2 * m_{\text{Pt}}) \quad (2.1);$$

$$\text{Au ECSA} = Q_{\text{Au-O}} / (450 \mu\text{C} / \text{cm}^2 * m_{\text{Au}}) \quad (2.2);$$

where m_{Pt} and m_{Au} are weight Pt and Au on working electrode, respectively.

Pt utilization calculation. Pt utilization is defined as the percentage of Pt atoms being exposed to the surface, which can be calculated using measured Pt ECSA divided by the theoretical surface area of 100% utilized Pt using the following equation:

$$U_{Pt} = 100\% * N_s / N_t; \quad (2.3);$$

where N_s stands for the number of Pt atoms that are exposed on surface, N_t stands for the total number of Pt atoms.

Based on the theory that hydrogen adsorption on Pt surface follows the atomic ratio of Pt:H = 1:1, N_s equals the number of hydrogen adsorbed on Pt surface (N_H). N_H could be calculated by the following equation:

$$N_H = Q_H / Q_e \quad (2.4);$$

where Q_e is the charge of an electron ($1.602 * 10^{-19}$ C).

Combining Equation 2.3 and 2.4:

$$\begin{aligned} U_{Pt} &= 100\% * N_s / N_t \\ &= 100\% * N_H / N_t \\ &= 100\% * (Q_H / Q_e) / (m_{Pt} * N_A / M_{Pt}) \\ &= 100\% * (Q_H * M_{Pt}) / (m_{Pt} * N_A * Q_e) \end{aligned} \quad (2.5);$$

N_A is Avogadro constant ($6.02 * 10^{23} \text{ mol}^{-1}$), M_{Pt} is the atomic weight of Pt (195 g / mol).

Combine Equation 2.1 and 2.5:

$$\begin{aligned} U_{Pt} &= 100\% * (Q_H * M_{Pt}) / (m_{Pt} * N_A * Q_e) \\ &= 100\% * (Pt \text{ ECSA} * 210 * m_{Pt} * M_{Pt}) / (m_{Pt} * N_A * Q_e) \\ &= 100\% * (Pt \text{ ECSA} * 210 * M_{Pt}) / (N_A * Q_e) \\ &= 100\% * Pt \text{ ECSA} / ((N_A * Q_e) / (210 \mu\text{C} / \text{cm}^2 * M_{Pt})) \\ &= 100\% * Pt \text{ ECSA} / (235.51 \text{ m}^2 / \text{g}_{Pt}) \end{aligned} \quad (2.6);$$

Therefore, Pt utilization can be determined by Equation 2.6 using corresponding Pt ECSA. For Pt-NPGB samples, the electro-active surface area of Pt on the NPGB

surfaces decreases from 136 to 82 m²/g_{Pt} with increasing Pt ratio from 1 to 5 %. These correspond to a decrease in Pt utilization from 58 to 35 %, respectively. Pt utilization reflects the percentage of surface exposed Pt atoms. Take 1%Pt-NPGB as example:

Percentage of Pt atoms with surface exposed = Pt utilization = 57.5%;

Percentage of Pt atoms not exposed = 100% - 57.5% = 42.5%;

Pt thickness calculation. Assume Pt islands are formed in a layer-by-layer fashion (for example, the third layer will only start formation after the second layer fully covers the first layer), the thickness of Pt islands in 1%Pt-NPGB can be estimated as follows:

$$\begin{aligned}\text{Thickness} &= (\text{number of unexposed Pt atoms} / \text{number of exposed Pt atoms}) + 1 \\ &= (42.5\% / 57.5\%) + 1 \\ &= \sim 1.7 \text{ atomic layers}\end{aligned}$$

Similarly, thickness of Pt islands in other samples can be calculated:

2%Pt-NPGB: ~ 2.1 atomic layers

3%Pt-NPGB: ~ 2.2 atomic layers

4%Pt-NPGB: ~ 2.4 atomic layers

5%Pt-NPGB: ~ 2.9 atomic layers

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Chapter 3

Harvesting Light by Different Shapes: Shape-dependent Photothermal Effect of Nanoporous Gold

ABSTRACT. In this chapter, I synthesize nanoporous gold (NPG) of three different shapes: nanoporous gold bowls (NPG-B), nanoporous gold tubes (NPG-T) and nanoporous gold plates (NPG-P). The photothermal temperature, heating speed and photothermal conversion efficiency of NPG with different shapes are compared. NPG-B is found to exhibit best photothermal conversion efficiency (88.9%) among all the shapes tested. I discuss the origin of the differences in the various shaped NPG using the experimentally determined laser penetration depth and light absorption cross section. The high photothermal conversion efficiency of NPG-B is attributed to its large absorption cross section and laser penetration depth. The controllability of the extent of the NPG-B photothermal effect is also demonstrated by adjusting the laser power. I exemplify the application of NPG-B photothermal effect using the photo-triggered deformation of NPG-B coated shape memory polymer (SMP). I also successfully demonstrate the potential in applying SMP / NPG-B as a remote-controlled photo-switch.

3.1 INTRODUCTION

Photothermal effect, which converts photon irradiation into heat via non-radiative decay after light absorption, has a wide range of applications such as localized killing of cancer cells, controlled drug release and enhancing reaction rate in catalysis.¹⁻⁷ Gold nanomaterials with surface plasmon resonance (SPR) have attracted much research interest in thermo-plasmonics light harvesting, because of the efficient light absorption promoted by SPR-enhanced electromagnetic (EM) fields, tunable absorption wavelength up to near infrared region and good biocompatibility for biological applications.⁸⁻¹¹ The SPR-enhanced EM field intensity of gold nanostructures is dependent on the shape, size and ensemble state of nanoparticles.^{12,13} This will in turn affect its light absorption ability, and hence photothermal effect. For example, the photothermal effect of individual gold nanospheres is found to be increasing with the decrease of gold nanosphere size.¹⁴ Shape-dependent studies of photothermal effect in individual gold nanoparticles have also been carried out, and nanocages are found to be more efficient than nanorods and hexapods.¹⁵ However, in contrast to shape and size of individual gold nanoparticles, the relationship between the shapes of gold nanostructure ensemble and photothermal effect, has not been reported. In particular, the shape of porous gold nanostructures, which is likely to influence photothermal effect through the laser penetration depth and light absorption cross-section apart from SPR, is yet to be investigated.

Nanoporous gold (NPG), with well-organized three-dimensionally interconnected gold ligament network, is ideal as a platform for the study of shape-dependent

photothermal effect in ensemble gold nanostructures.¹⁶⁻²⁰ In ensemble porous nanostructures of NPG, the different shapes of the ensemble structure affect the light absorption ability through the changes in EM fields, as well as the laser penetration depth. Therefore, it is of interest to investigate the shape-dependent photothermal effect of NPG. Conventionally, dealloyed free-standing or substrate based NPG particles could be synthesized by patterning of Au-Ag or Au-Cu alloy nanostructure using lithography, dewetting or Ar-plasma etching.¹⁹⁻²¹ The shape of NPG nanoparticles produced by dealloying method is limited to disk-like shapes due to lack of choices in templates and lithograph masks. As such, no shape-dependent NPG photothermal effect has been investigated yet. Recent work of our group reports that sacrificial-template wet chemical method provides plenty of opportunities for designing NPG nanoparticles of various shapes.²²⁻²⁴ Such synthetic strategy is advantageous over conventional dealloying method as it broadens the choices of NPG shapes for shape-dependent studies. By investigating the shape-dependent photothermal effect of NPGs, I will be able to pave the way of tuning the photothermal effect via altering the shapes of the gold porous nanostructures.

Herein, I develop shape-dependent NPG particles with tunable laser penetration depth and light absorption cross-section, investigate their photothermal properties, and design a proof-of-concept photo-switch utilizing the photothermal effect of NPG. The aim of this work is to obtain various NPG particle shapes using a template-assisted wet chemical method and optimize its photothermal conversion efficiency using different NPG particle shapes. I successfully synthesize nanoporous gold bowl (NPG-B), nanoporous gold tube (NPG-T) and nanoporous gold hexagonal plate (NPG-P) using

seeding templates of different shapes. For the first time, I discuss the relationship between NPG shape and photothermal effect. The origin of the differences in various shaped NPG is investigated from the perspectives of laser penetration depth and light absorption cross section. Using infrared (IR) camera for temperature determination, I compare the photothermal temperature, heating speed and photothermal conversion efficiency of NPG-B, NPG-T and NPG-P. I use x-z Raman scattering intensity distribution for the investigation of laser penetration depth of various shaped NPG. I also calculate the light absorption cross-section using experimental data. By analyzing its light absorption ability and laser penetration behaviors, I postulate the relationship between photothermal effect and the shape of NPG. I also achieve controllable photothermal heating of NPG with good repeatability by adjusting laser power and demonstrate the photothermal effect of NPG for light-induced unfolding polyurethane shape memory polymer rapid movement. I further demonstrate the application of this shape memory polymer / NPG material as a remote light-controlled switch. This shape-dependent study of NPG photothermal conversion efficiency initiates new structural design direction of NPG, and can be utilized into various photothermal applications such as localized heating biomedical devices and light-responsive movement for actuators.

3.2 Results and discussion

Morphology of different shape NPG

The synthesis of nanoporous gold (NPG) with various shapes offers great opportunities to investigate NPG's shape-dependent photothermal performance. To

achieve this, I employ a two-step template assisted method, which involves firstly the growing of nanoporous gold on AgCl nanocubes, AgCl nanowires, and AgBr nanoplates templates respectively, followed by the etching of Ag-based templates to obtain uniform nanoporous gold with bowl-like, tube-like, and plate-like shape, denoted as NPG-B, NPG-T, NPG-P respectively (Figure 3.1). All obtained gold structures consist of small pores (ranging from 4 - 30 nm) and interconnected ligaments with precisely controlled size (18 – 19 nm) (Figure 3.2). The as-synthesized NPG-B possess hemispherical and bowl-like shape with open cavity (diameter $0.7 \pm 0.1 \mu\text{m}$), whereas both NPG-T (length $6.1 \pm 2.3 \mu\text{m}$) and NPG-P (diameter $2.0 \pm 0.5 \mu\text{m}$) exhibit hollow structures (Figure 3.1). The chemical composition of as-prepared NPG is investigated by X-ray photoelectron spectroscopy (XPS) analysis and energy dispersive X-ray spectroscopy (EDS), which indicate the complete reduction of Au(III) to Au(0) in all three samples and almost full removal of Ag from NPG inner surface (Figure 3.3 and 3.4). Further quantitative elemental analysis by inductively coupled plasma optical emission spectrometry (ICP-OES) reveal that residual Ag atomic percentages in NPG-B, NPG-T and NPG-P are less than 3.4%, 3.8% and 5.7%, respectively. Moreover, all of the as-synthesized NPG samples exhibit broadband extinction spectrum over vis-NIR wavelength range due to the strong coupling between the interconnected gold nanoparticles in porous structure (Figure 3.5). Collectively, these results demonstrate the successful synthesis of shape controlled nanoporous gold structure and their prominent optical properties for further photothermal performance investigations.

Figure 3.1. Morphological characterization of as-synthesized nanoporous gold with various shapes. Scheme and SEM images of nanoporous gold bowl (NPG-B) (A, B, C), nanoporous gold tube (NPG-T) (D, E, F) and nanoporous gold plate (NPG-P) (G, H, I).

Figure 3.2. Magnified SEM images and corresponding ligament size distribution of NPG-B (A, B), NPG-T (C, D) and NPG-P (E, F).

Figure 3.3. XPS of Au in NPG-B (A), NPG-T (B) and NPG-P (C).

Figure 3.4. SEM images and relevant EDS mapping of (A) NPG-B, (B) NPG-T and (C) NPG-P.

Figure 3.5. UV-vis spectra of NPG-B, NPG-T and NPG-P.

Photothermal performance of NPG-B

The photothermal behavior of NPG upon laser (532 nm, 90 mW) irradiation is first studied by employing infrared (IR) camera to monitor the time and spatially resolved temperature maps in air ambient environment (Figure 3.6A). Typically, the NPG-B dispersion are manually dropcasted on thin layer chromatography (TLC) plate to form a spot (diameter 3.7 - 4.1 mm) composed of 16-17 layers of NPG-B (area density 7.55 $\mu\text{g}/\text{mm}^2$) (Figure 3.7). Prior to laser illumination, the NPG-B spot displays a homogenous surface temperature of 25 °C (Figure 3.6B). Upon laser irradiation, the surface temperature of NPG-B at the IR radiation center (distance = 0 mm) experiences an initial rapid increase to about 122 °C within 1 s, with a temperature increase rate $(dT/dt)_{\text{max}}$ of ca. 364 °C/s. Subsequently, the temperature gradually increases to reach thermal equilibrium at approximately 138 °C within 10 s and remains plateau throughout 25 s of laser irradiation (Figure 3.6C, 3.6D, Figure 3.8). Notably, our NPG-B exhibits 67 °C higher photothermal equilibrium temperature and 2.6-fold higher maximum temperature increasing rate than traditional random aggregation of Au nanoparticles with similar size to the ligament size of NPG-B (Figure 3.9). These results illustrate the superior photothermal performance of NPG with well-organized porous structure over randomly aggregated Au NPs.

I also observe a slower heat transfer from the irradiation center to the non-irradiated zone (distance > 1 mm) through the thermally conductive NPG-B spot compared to central irradiation zone, resulting in a gradual surface temperature

increase of non-irradiated NPG-B surface (distance = 2 mm) from 23 to 30 °C throughout 25 s of laser irradiation ($(dT/dt)_{\text{average}} \approx 1.4 \text{ }^{\circ}\text{C/s}$) (Figure 3.6C).

In general, such photothermal behaviors of NPG-B follow a two-step heating process. The initial drastic temperature rise is mainly attributed to the instant photothermalization of light by NPG-B. The interconnected gold nanoligaments and unique network of NPG-B generate abundant localized plasmonic “hot spots” after laser irradiation, leading to the significant temperature rise.

A subsequent slower temperature increment to steady state is attribute to a balance process between heat generation and heat dissipation through thermal transfer from irradiated NPG-B area to the areas surrounding the NPG-B, the substrate and the environment. Correspondingly, the cooling behavior of NPG-B spot after switching off the laser also follows a two-step process, with the temperature at central irradiation region decreasing rapidly from 138 to 33 °C within 1s, followed by a gradual temperature dropping down to the original temperature of approximately 25 °C (Figure 3.10). These results further highlight the excellent photothermal performance of NPG-B and its heat conductivity to achieve rapid temperature modulation.

Figure 3.6. Photothermal effect of NPG with various shapes. (A) Scheme of experimental setup composed of a laser beam irradiating on NPG surface and an IR camera to record the time and spatial temperature profile of the irradiated NPG surface. (B) Heating thermogram of NPG-B upon laser irradiation. Laser power = 90 mW. Scale bar, 4 mm. (C) Spatial temperature profiles of NPG-B as indicated in (B). (D) Time temperature profiles of NPG with various shapes.

Figure 3.7. Digital images of NPG-B (A), NPG-T (B), and NPG-P (C) deposited on TLC substrates.

Figure 3.8. (A) Heating speed and (B) maximum heating speed of NPG-B, NPG-T and NPG-P under irradiation of 90 mW laser.

Figure 3.9. (A) Temperature-time profile of the central irradiated zone of Au nanoparticles deposited on TLC plate when the irradiation laser is switched on. (B) 1st derivative temperature-time profile of the heating process, representing the temperature changing rate of the central irradiated zone of Au nanoparticles.

Figure 3.10. (A) Temperature-time profiles of the central irradiated zone of NPG-B, NPG-T and NPG-P, respectively, when the irradiation laser is switched off. (B) 1st

derivative temperature-time profiles of the cooling process, representing the cooling speed of the central irradiated zone of NPG-B, NPG-T, and NPG-P, respectively, and (C) their corresponding maximum cooling speed.

Shape-dependent photothermal performance

Next, I investigate the shape-dependent photothermal effect of NPG by comparing the heating behavior of NPG-B with NPG-T and NPG-P under the same experimental conditions.

The time and spatially dependent surface temperature profiles of irradiated NPG-T and NPG-P central zone display an almost similar behavior with that observed in NPG-B, but with different temperature changing rate and maximum equilibrium temperature (Figure 3.6D and 3.11). Within 1 s of laser irradiation, the surface temperature of NPG-T and NPG-P increase to 98 °C ($((dT/dt)_{\max} \approx 343 \text{ }^{\circ}\text{C/s})$) and 91 °C ($((dT/dt)_{\max} \approx 301 \text{ }^{\circ}\text{C/s})$), respectively, which is $> 24 \text{ }^{\circ}\text{C}$ lower than that achieved by NPG-B (Figure 3.8 and 3.12). Moreover, the equilibrium surface temperature of irradiated NPG-T and NPG-P central zone throughout 25 s of laser irradiation are approximately 125 and 112 °C respectively, whereas equilibrium surface temperature for NPG-B reaches 138 °C, corresponding to a 13% and 30% temperature increment over NPG-T and NPG-P. Consequently, the photothermal conversion efficiency, defined as the ratio of heat generated and the laser energy input from the experiment setup, is estimated as follows.

Figure 3.11. Thermograms and corresponding spatial temperature profiles of NPG-T (A, C) and NPG-P (B, D) when the irradiation laser is switched on.

Figure 3.12. Spatial temperature profiles of NPG-B, NPG-T and NPG-P within 1 s of laser irradiation.

Apparent photothermal conversion efficiency (η) is calculated based the on ratio of energy output and energy input:

$$\eta = \frac{\text{Thermal energy produced}}{\text{Laser energy used}} * 100\% \quad (3.1)$$

Energy output can be calculated based on the mass, heat capacity and temperature increase of gold and its surrounding substrate; energy input can be calculated based on the power of laser and the time of irradiation:

$$\eta = \frac{C_{Au} * m_{Au} * \Delta T + C_{silica\ gel} * m_{silica\ gel} * \Delta T}{P * \Delta t} \quad (3.2)$$

where C_{Au} refers to heat capacity of gold ($0.126 \text{ J g}^{-1} \text{ K}^{-1}$)¹⁹, $C_{silica\ gel}$ denotes heat capacity of silica gel ($0.921 \text{ J g}^{-1} \text{ K}^{-1}$)²⁵, m_{Au} refers to mass of gold in the central irradiated area, $m_{silica\ gel}$ refers to mass of silica gel in the central irradiated area, ΔT indicates the temperature increment, P is the power of laser, Δt refers to the heating time for temperature increment.

Equation (3.2) can be further expressed as equation (3.3).

$$\eta = \frac{C_{Au} * m_{Au} + C_{silica\ gel} * m_{silica\ gel}}{P} * \frac{\Delta T}{\Delta t} \quad (3.3)$$

In our case, C_{Au} , $C_{silica\ gel}$ and P are known, and m_{Au} , $m_{silica\ gel}$ and ΔT can be determined experimentally. Δt can be estimated according to the 1st derivative temperature-time profiles of the heating process. Generally, the temperature increment corresponds to when the heating speed (dT/dt) is larger than zero, whereas the heating speed tends to zero as the temperature reaches equilibrium. Therefore, the peak width of heating speed-time profile corresponds to the heating time for temperature increment. I here use an assumption of Gaussian distribution to estimate the width of peak. In a Gaussian peak, peak width equals 4σ (σ is the standard deviation in Gaussian distribution) and full width at half maximum (FWHM) equals 2.354σ .²⁶ Hence, the width of heating speed peak is 1.699 times the FWHM of heating speed peak.

According to equation (3.3), the experimental parameters and the correspondingly calculated apparent photothermal efficiency of NPG with three different shapes are listed in Table 3.1.

Table 3.1. The involved experimental parameters in equation (3.3) and the correspondingly calculated photothermal efficiency.

	m_{Au} (μg)	m_{silica} gel (mg)	ΔT ($^{\circ}C$)	FWHM of heating speed peak (s)	Δt (s)	Laser power (mW)	Efficiency
NPG-B	23.7	0.267	113	0.185	0.314	89.1	88.9%
NPG-T	23.4	0.267	100	0.187	0.318	88.8	78.2%
NPG-P	23.3	0.267	87	0.187	0.318	88.2	68.5%

From the results above, photothermal conversion efficiency is calculated to be 88.9% for NPG-B, whereas for NPG-T and NPG-P, the photothermal efficiency are 78.2% and 68.5%, respectively. These results collectively illustrate that the bowl-like NPG-B possess the superior photothermal effect and achieves the fastest heating speed, highest thermal equilibrium temperature, and photothermal efficiency over NPG-T and NPG-P. Such remarkable photothermal heating ability of NPG-B is of great importance for both functional research and technological innovations.

Insights into the shape-determined photothermal performance

To further elucidate the shape-induced photothermal performance improvement of bowl-like NPG-B over NPG-T and NPG-P, I investigate several fundamental factors that affect the heat generation at the surface of NPG according to the equation (3.4)¹⁴,

$$Q = C_{abs} * V * N * I * t = C_{abs} * A * d * N * I * t = C_{abs} * d * N * P * t \quad (3.4)$$

Where Q is the heat (J) generated from the laser photothermal heating, C_{abs} is the absorption cross section of the NPG (m^2/g), V is the effective laser irradiated sample volume (m^3), N is the apparent density of nanoporous gold (g/m^3), I is the laser intensity (W/m^2), A is the laser spot size (m^2), d is the depth of sample that laser travels through (m), P is the laser power (W), t is time (s). In accordance with the equation, the heat generated from different NPG samples upon laser illumination is mainly determined by laser penetration depth (d), the apparent density of NPG (N), and the absorption cross section of NPG (C_{abs}), since same laser power are used for all samples.

Firstly, the laser penetration depths (d) in various samples are evaluated by high-resolution surface-enhanced Raman scattering imaging technique, which determines how deep laser can travel in NPG layers (Figure 3.13). Due to the plasmonic effect of NPG, enhanced Raman scattering signal of 4-methylbenzenethiol (4-MBT) could be obtained when laser is irradiated onto NPG. x-z imaging is able to reveal the relationship between Raman signal and depth. Full width at half maximum (FWHM) of Raman peak in the line profile of z direction implies the depth of NPG with SERS signal, which is a direct indication of laser penetration depth. Typically, I measure the SERS spectra of 4-MBT on NPG surface and analyze x-z SERS imaging line profile of Raman intensity at 1078 cm^{-1} , a distinct and characteristic band of 4-MBT (Figure 3.14).²⁷ It is noted that NPG-B exhibits FWHM of the peaks of $12.1\text{ }\mu\text{m}$, higher than

that obtained using NPG-T (11.7 μm) and NPG-P (11.5 μm). The z-axis optical resolution of our Raman spectra collecting system (Nanophoton) is measured to be $8.5 \pm 1.5 \mu\text{m}$ using 100 nm fluorescent particles.²⁸ Therefore, FWHM of the actual x-z SERS intensity distribution peak should be calculated by deducting 8.5 μm from experimentally obtained FWHM. Laser penetration depth in our case can thus be estimated using the width of real x-z SERS intensity distribution peak (Table 3.2), which is 1.699 times of the corresponding FWHM as demonstrated previously. Therefore, considering the resolution of x-z imaging and the relationship between peak width and FWHM, the penetration depth of NPG-B is calculated to be 6.1 μm , which is 11% and 20% higher than those of NPG-T (5.5 μm) and NPG-P (5.1 μm) (see supporting notes 2 in supporting information). This result indicates that the laser (532 nm) can penetrate deeper in NPG-B layer and thus increase effective laser excitation volume.

Figure 3.13. (A-C) x-z SERS image of NPG with various shapes using 4-MBT as probe. The white dotted line denotes the location at which the intensity line profile is

obtained, from the upside to the underside of NPG layer. (D-F) SERS intensity profiling along the white dotted line of (A-C), respectively.

Figure 3.14. (A) SERS spectrum of 4-MBT modified NPG-B. The characteristic Raman peaks at 1078 cm⁻¹ is utilized as reference for (B) comparison of signal intensity obtained from NPG-B, NPG-T, NPG-P and Au NP, respectively.

Table 3.2. Laser penetration depth when irradiating NPG-B, NPG-T, and NPGP layers.

	FWHM from experiment (μm)	Actual FWHM (μm)	Laser penetration depth (μm)
NPG-B	12.1	3.6	6.1
NPG-T	11.7	3.2	5.5
NPG-P	11.5	3.0	5.1

Secondly, using the area density (NPG-B 7.55 μg/mm², NPG-T 7.44 μg/mm² and NPG-P 7.43 μg/mm²) and the height of aggregates (NPG-B 12.1 μm, NPG-T 12.0 μm

and NPG-P 12.1 μm , Figure 3.15), I calculate the apparent density of NPG-B, NPG-T and NPG-P to be 623.97 $\mu\text{g}/\text{mm}^3$, 620.00 $\mu\text{g}/\text{mm}^3$ and 614.05 $\mu\text{g}/\text{mm}^3$, respectively. Hence, the apparent density of NPG-B, NPG-T and NPG-P are almost the same, and is unlikely to attribute to the differences in photothermal effect.

Figure 3.15. Cross sectional SEM images and corresponding thickness analysis of (A) NPG-B, (B) NPG-T and (C) NPG-P.

Thirdly, the absorption cross section (C_{abs}) of NPG samples, which directly determines the heat generation capability of plasmonic nanoparticles, are calculated. Considering the fact of all NPG samples are composed of gold ligament with almost similar size (18-19 nm), the absorption of individual gold ligament component is the same. The photothermal difference is thus mainly arising from the absorption cross section from single NPG with various geometric shapes, which can be indirectly determined by the following equation¹⁴:

$$C_{\text{abs}} = Q / (d \cdot N \cdot P \cdot t) \quad (3.5).$$

Q can be determined using the capacity and temperature increase of gold and substrate.

Parameters d , N , P and t can also be experimentally determined.

Q equals the generated heat for heating both NPG and the underlying substrate and thus can be expressed as equation (3.6),

$$Q = C_{Au} * m_{Au} * \Delta T + C_{silica\ gel} * m_{silica\ gel} * \Delta T \quad (3.6)$$

where C_{Au} refers to heat capacity of gold ($0.126 \text{ J g}^{-1} \text{ K}^{-1}$), $C_{silica\ gel}$ denotes heat capacity of silica gel ($0.921 \text{ J g}^{-1} \text{ K}^{-1}$), m_{Au} refers to mass of gold in the central irradiated area, $m_{silica\ gel}$ refers to mass of silica gel in the central irradiated area, ΔT indicates the temperature increment.

According to equation (3.6), I can calculate Q generated when laser irradiation on NPG-B, NPG-T, and NPG-P (Table 3.3). Consequently, the absorption cross section can be calculated according to equation (3.5) (Table 3.4).

Table 3.3. Heat generated from laser irradiation on NPG-B, NPG-T, and NPG-P, respectively.

	$m_{Au} (\mu\text{g})$	$m_{silica\ gel} (\text{mg})$	$\Delta T (^{\circ}\text{C})$	Q (J)
NPG-B	23.7	0.236	113	0.0249
NPG-T	23.4	0.236	100	0.0221
NPG-P	23.3	0.236	87	0.0192

Table 3.4. The absorption cross section of NPG-B, NPG-T, and NPG-P, respectively.

		Laser	Apparent	Laser power		C_{abs}
	Q (J)	penetration	density		Δt (s)	
		depth (μm)	(μg/mm³)	(mW)		(m²/g)
NPG-B	0.0249	6.1	623.97	89.1	0.314	0.234
NPG-T	0.0221	5.5	620.00	88.8	0.318	0.229
NPG-P	0.0192	5.1	614.05	88.2	0.318	0.220

I found that NPG-B has the highest C_{abs} (0.234 m²/g), which is 2.2% and 6.4% higher than those of NPG-T (0.229 m²/g) and NPG-P (0.220 m²/g). Such improved absorption cross section of NPGB is further supported by the highest SERS enhancing ability when compared the SERS intensity of 4-MBT with that obtained from NPG-T and NPG-P (Figure 3.14B).

These results indicate that NPG with bowl-like shape provides the strongest surface plasmonic coupling and intensified localized electromagnetic field, which greatly increases the absorption cross section. Therefore, NPG-B exhibits the largest absorption cross section and laser penetration depth, thus resulting in the highest photothermal heat generation and photothermal conversion efficiency. These results also demonstrate the shape-mediated photothermal performance, which provide great insights for function-directed material design.

Comparison with other plasmonic nanomaterials

The significance of unique porous, well-organized structure of NPG material on the superior photothermal performance is further demonstrated by investigating the

heat generation and photothermal conversion efficiency of smooth Au nanoplates and randomly aggregated Au nanospheres as well as other Ag-based plasmonic nanostructures (Figure 3.16). Using the same laser power and irradiation time, the maximum equilibrium temperature of NPG-P surface is 71 °C higher than that on smooth gold nanoplate surface. Correspondingly, the photothermal conversion efficiency of NPG-P is estimated to be 68.5 %, which is 6-fold higher than that of smooth gold nanoplate surface (11.4%).

Figure 3.16. Maximum equilibrium temperature and photothermal conversion efficiency of various metal nanostructures.

Furthermore, we observe that all nanoporous gold samples (NPG-B, 88.9%; NPG-T, 78.2% and NPG-P, 68.5%) exhibit at least 2-fold higher conversion efficiency than randomly aggregated Au NPs of similar size as the NPG ligament (32.8%) (Figure 3.17). Meanwhile, the superior photothermal conversion efficiency of our NPG-B (~90%) is further highlighted by comparing with previously reported gold nanoshells (25%)²⁹, gold nanorods (50%)²⁹, NPG nanodisks (56%)¹⁹ and gold nanomatryoshkas (63%)³⁰. Such profound improvement of photothermal performance from our NPG-B

is mainly attributed to the rough surface, unique shapes, and interconnected porous gold nanoparticles framework, which induce stronger light trapping and abundant “hot spots”.

Additionally, I also investigate the photothermal behavior of silver nanocubes and nanooctahedral which are known to have strong localized surface plasmon. The results shows that all three kinds of NPG well surpass silver based nanoparticles in photothermal temperature (Ag nanocubes 48 °C and Ag nano-octahedra 62 °C) and conversion efficiency (Ag nanocubes 12.6% and Ag nano-octahedra 24.8%), again highlighting the superiority of NPG for photothermal effect.

Figure 3.17. SEM image of randomly aggregated Au nanoparticles.

Controllable Photothermal effect of NPG, using NPG-B as example

The controllability and repeatability of photothermal effect is of vital importance in real applications. Therefore, I test the tunability and repeating performance using NPG-B as a model structure. By tuning the laser power from 25 to 90 mW, modulated steady temperature (at 25 s) of irradiated NPG-B surface from 33 to 138 °C are achieved

(Figure 3.18A). After switching off the laser, the surface temperature decreases to the original state with temperature of around 25 °C (Figure 3.18B). Notably, the temperature increment and decrement in heating and cooling process are all positively correlated to laser power (Figure 3.18C), implying that the surface temperature can be precisely manipulated by laser power. Correspondingly, both maximum heating speed and cooling speed can be tuned from 31 °C/s to 364 °C/s, and from 32 °C/s to 479 °C/s when the laser power is changed from 25 mW to 90 mW (Figure 3.18D-E and 3.19). Moreover, the excellent repeatability of photothermal heating is observed by subjecting the NPG-B nanoparticles to continuous photothermal heating/cooling cycles using laser power of 90 mW. The steady surface temperature of irradiated central zone changes between 25 °C and 138 °C over 5 cycles, reflects the high repeatability of the photothermal heating of NPG-B (Figure 3.18F). Thus, NPG-B demonstrates precise and instantaneous surface temperature control which is important for practical plasmonic application.

Figure 3.18. Mediated photothermal behaviors of NPG-B. Temperature-time profiles of NPG-B surface when the laser irradiation is switched on (A) and off (B). The laser power is tuned from 25 to 90 mW. (C) Temperature changes of the NPG-B surface with laser power. (D) Heating and (E) cooling speed of NPG-B with different laser powers. (F) Repeatability of NPG-B photothermal heating/cooling cycles.

Figure 3.19. (A) Maximum heating speed and (B) maximum cooling speed of NPG-B achieved at laser powers ranging from 25 to 90 mW.

Light controlled shape memory material using NPG-B

The application of NPG-B as a remote heating platform is further demonstrated by the laser controlled movement of a thermo-responsive shape memory polymer (SMP) fully decorated with NPG-B nanoparticles. By heating the SMPs to a temperature higher than glass transition temperature (T_g) the polymer chain movement is initiated, which releases stress of material and triggers the movement of SMP.³¹⁻³⁴ Therefore, the SMP is capable of changing from a deformed temporary shape to its original shape in response to temperature change (Figure 3.20A). Prior to laser irradiation (532 nm, 100 mW), a flat SMP/NPG-B strip (length 5 mm, width 2 mm) is first fixed at its temporary shape. To achieve the temporary shape, I first heat up the SMP/NPG-B strip above its T_g and physically fold it to the desired temporary shape with an opening angle of $32^\circ (\pm 2^\circ)$. The strip is kept at this temporary shape and then cooled down to below T_g to fix the shape. After the temporary shape is fixed, laser is applied onto the SMP/NPG-B strip for the investigation of laser induced movement.

Figure 3.20. Application of NPG: controlled movement of SMP/NPG-B by 532 nm laser. (A) Scheme of substituting temperature-triggered to remote light-triggered movement of SMP strip after decorating with NPG-B. (B) A time series of digital photos displaying the movement of SMP/NPG-B strip when laser is irradiated on its surface. The black dotted circle indicates the area under laser irradiation. θ represents the opening angle of folded SMP. (C) Plots of the opening angle of folded SMP/NPG-B over laser irradiation time compared with SMP without NPG-B coatings. (D) Schematic showing the integration of SMP/NPG-B into electric circuit as an efficient

remote laser controlled kill switch to turn on the LED light. Digital images displaying (E) LED is off before laser irradiation and (F) LED is on after laser is switched on. Insets in (E) and (F) are magnified images of dotted rectangular region that highlight the folded and open state of SMP/NPG-B, respectively.

Within 1s of laser illumination, SMP/NPG-B strip initially opens up from 32° to 37° , followed by a rapid unfolding from 37° to 157° at 4 s and then slowing unfolding to reach a final steady state with angle of 169° (Figure 3.20B and 3.20C). On the contrary, a change of less than 2° in unfolding angle is observed as shining laser on SMP without the presence of NPG-B. The obvious movement of SMP is attributed to the heat produced from the photothermal effect of NPG-B. The slightly delayed temperature-sensitive mechanical behavior compared to the rapid photothermal behavior of NPG-B is due to the comparatively slow heat conduction process.³⁵ Hence, NPG-B clearly enables rapid and precise mechanical movement control of thermos-sensitive SMP through remotely manipulated laser irradiation.

Optically controlled light switch

The photo-triggered fast and responsive SMP deformation endowed by the photothermally heated NPG-B can potentially be further integrated into automatic electric, mechanical and aerospace systems. As a proof to demonstrate our concept, a remotely controlled LED light switch is investigated by adhering a conductive wire onto the SMP/NPG-B strip surface (Figure 3.20D-F).

Prior to laser irradiation, the angle of strip is 0° , the distance between copper wire attached on strip and the circuit is about 2 mm, and the LED light is switched off due

to the open circuit. Upon shining laser onto the SMP/NPG-B strip, then LED is lit within 2 s due to the unfolding of the SMP/NPG-B strip (up to around 60°, stopped by the hindrance of the connecting wire), allowing effective contact between the conductive wire and the LED and thus electricity current to pass through. The LED is therefore remotely switched on due to the laser-induced unfolding of the strip which swiftly connects the circuit. These results demonstrate that SMP/NPG-B is ideal for designing rapid and sensitive remote switches, which holds great potential in applications that require fast and remote control with no physical wire access. This also validates the superiority and immense potential of NPG-B for remotely temperature-controlled medical and biomimetic devices, actuators, sensors, and innovative delivery systems.

3.3 Conclusions

In this work, I synthesize NPG with bowl-like, tube-like and plate-like shapes, and compare their photothermal effect. Photothermal temperature and heating/cooling speed are found to be closely dependent on shapes. Bowl-like NPG-B is the best in photothermal conversion efficiency among all the shapes tested. The shape-dependent photothermal conversion efficiency is ascribed to the difference in gold excitation volume under laser irradiation. The photothermal effect of NPG-B is also found to be controllable by tuning the laser power. Application of NPG-B photothermal effect is exemplified by photo-triggered deformation of SMP/NPG-B and its potential as a remote photo-controlled switch is also demonstrated.

3.4 Experimental Section

Chemicals. Silver nitrate, hydroquinone (Hq), HAuCl_4 , ethylene glycol (EG) and poly(vinylpyrrolidone) (PVP, average $M_w = 1300000$) were purchased from Sigma Aldrich. Potassium hydroxide and hydrochloric acid (37%) were purchased from Schedelco. Nitric acid (69%) was purchased from Honeywell. Ammonium hydroxide (25% in water) was purchased from Merck. Ethanol and N,N-dimethylmethanamide (DMF) were purchased from Fisher Chemical. Polyurethane shape memory polymer (SMP MM-3520) was purchased from SMP Technologies Inc. The chemicals were used without further purification. Milli-Q water ($18.2 \text{ M}\Omega/\text{cm}$) was purified with a Sartorius arium® 611 UV ultrapure water system.

Synthesis of AgCl nanocubes, AgCl nanowires and AgBr nanoplates. AgCl nanocubes were prepared using the following method. 0.4 g PVP and 0.4 g AgNO_3 were dissolved in 30 mL and 20 mL of cold EG correspondingly. After mixing PVP solution and AgNO_3 solution in flask for 1 min at 500 rpm at room temperature, 1.23 mL of 37% HCl was added into the solution and kept stirring for 1 min. Then the solution was heated to 150°C and kept stirring at 500 rpm for 20 min. After the reaction, the solution was naturally cooled down. 40 mL acetone was added to 10 mL resulting solution for sedimentation and centrifuged at 5000 rpm. After washing with water twice, the product was dispersed in 10 mL water to give a white suspension. This white suspension was used for future reactions.

AgCl nanowires were synthesized using the method reported by Bi et al.³⁶ AgBr hexagonal nanoplates were prepared using the method reported by Wang et al.³⁷

Synthesis of NPG. 0.35 g PVP was dissolved in 50 mL water. 300 mg Hq was dissolved in 10 mL water freshly. H₂AuCl₄ was also dissolved in water to get 0.5 M solution. AgCl nanocube solution (containing 51 mg AgCl) was first mixed with 45 mL PVP solution at 1300 rpm in RBF. After mixing for 1 min, 780 μ L Hq solution was added followed by addition of 323 μ L H₂AuCl₄ solution. After reaction for 1 min at 1300 rpm at room temperature, AgCl/NPG-B hybrid was obtained. The solution was centrifuged at 3000 rpm for 3 min and washed twice with water. The product could be re-dispersed in water. After mixing AgCl/NPG-B hybrid solution with 10 mL ammonia, the solution was centrifuged at 3000 rpm for 3 min and washed with water twice. Nanoporous gold bowls (NPG-Bs) aqueous solution could be obtained. The concentration of NPG-B solution is determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Nanoporous gold tubes (NPG-Ts) and nanoporous gold plates (NPG-P) are synthesized using the same method, except for AgCl nanowires and AgBr nanoplates are used as sacrificial templates.

Synthesis of Au NPs, smooth Au plates, Ag nanocubes and Ag octahedral. Au NPs with same size as NPG ligaments were prepared by following the synthetic strategy reported by Sivaraman et al.³⁸ Smooth Au plates were prepared using the method reported by Jiu et al.³⁹ Ag nanocubes and Ag octahedral were prepared by following the experimental procedures reported by Yang et al. and Lee et al.^{40,41}

Preparation of shape memory polymer (SMP) / NPG-B. Typically, 500 mg of SMP pellets were dissolved in 15 mL DMF at 90 °C. The solution is poured into a glass petri dish. The solvent was slowly evaporated at 70 °C for 24 h to get SMP film. SMP was cut into 5*2 mm strips and NPG-B was dropcast onto SMP. The amount of NPG-B per area on SMP was controlled to be the same as previously prepared samples on TLC substrates.

Materials Characterization. Nanoparticles are drop cast onto a clean silicon substrate for scanning electron microscopy (SEM) observation. SEM imaging was performed using a JEOL JSM 7600F microscope. Voltage was set at 5 kV. FLIR SC7000 infrared (IR) camera (spatial resolution 0.05 mm, temporal resolution 0.08 s, temperature resolution 0.01 °C) was used to measure the photothermal temperature of NPG coated TLC substrates. Wavelength of laser used for photothermal temperature determination is 532 nm and its power was tuned by ND filters. X-Ray photoelectron spectroscopy (XPS) spectra were measured using a Phoibos 100 spectrometer with a monochromatic Mg X-ray radiation source. 284.5 eV for C 1s binding energy peak was used for XPS calibration. Composition and concentration analysis of the obtained nanoparticle suspension were conducted using a Thermo Scientific iCAP 6500 model ICP-OES. Nanoparticle suspension was mixed with Aqua Regia, and then diluted with water prior to ICP-OES measurement. x-z Raman imaging was acquired using Ramantouch microspectrometer (Nanophoton Inc, Osaka, Japan) with an excitation wavelength of 532 nm. A 532 nm laser attached in uRaman microscope is used for controlling the movement of SMP / NPG-B. The movement of SMP / NPG-B was recorded in the form of video and frames at certain time point were analyzed using ImageJ software.

3.5 References

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Chapter 4

Programmable Photo-mechanical Movements of Nanoporous Gold Coated Shape Memory Polymers.

ABSTRACT. In this chapter, I utilize the photothermal effect of nanoporous gold (NPG) to enable programmable movements of a shape memory polymer (SMP). Using a solution casting method, I prepared strips of SMP and coated them with NPG. By using a laser to induce heat, I compare the photo-mechanical unfolding of SMP/NPG strips with varying laser powers, NPG loading amounts and SMP thicknesses. I also study the photo-mechanical movement of SMP/NPG under different light source. In addition, photo-induced shape changes such as multi-stepped unfolding and untwisting in different SMP shape configurations are also successfully demonstrated. This systematic study of tunable photo-mechanical SMP/NPG movement demonstrates the potential of SMP/NPG in actuation applications that requires speed control and different shape changes.

4.1 INTRODUCTION

Stimuli-responsive materials have sparked enormous research interest owing to their capability to sense and react in a programmed manner under external stimuli such as heat, light irradiation or humidity.¹⁻¹¹ These materials have been successfully applied in various actuation applications, such as soft robotics, microelectromechanical systems, artificial muscles and sensors.^{4,12-15} Among all the sources of stimuli, light holds great potential in terms of controllability in actuation owing to its highly tunable monochromaticity, wavelength, intensity and polarization.¹⁵⁻¹⁸ Light-responsive actuator systems is also advantageous in remote manipulation because light can be controlled remotely and instantly with great precision.¹⁹⁻²²

There are two main strategies for the design of light-responsive actuation materials: photochemical actuation and photothermal actuation. Photochemical actuation involves molecular deformation based on photoactive groups, such as azobenzene, spiropyran, diarylethene and so on, which generally requires ultraviolet light and complicated molecular synthesis.^{13,23-25} On the contrary, photothermal actuation is achieved by utilizing the photothermal effect with the combination between thermal-responsive materials and materials with photothermal effect. Photothermal actuation materials are considered to possess better stability and working lifetime as compared to photochemical actuation materials, and hence endow them with greater potential for practical applications.¹⁵

The choice of thermal-responsive material is crucial for the performance of photothermal actuation materials. Volume-phase-transition gels, thermotropic liquid crystals, thermal expanding materials and shape memory polymers (SMPs) are most commonly used as thermal-responsive component. Amongst them, SMP is advantageous for photothermal actuation application due to its fast response to stimuli and can be easily combined with other functional materials. Generally, SMPs are able to display two states of shape; permanent and temporary shape, during the actuation cycle. The temporary shape of SMPs is achieved by mechanically shaping SMPs at temperatures above the phase-transition temperature (T_g (glass-transition temperature) or T_m (melting temperature)), followed by the freezing of the configuration at temperatures below phase-transition temperature. Owing to its entropic elasticity, the temporary shape of SMPs will be reverted back to their original permanent shape when the temperature is again heated above the phase-transition temperature. During this process, the mechanical energy stored in temporary shape is then released.

Nanoporous gold (NPG) is an ideal material for photothermal effect due to its strong surface plasmon resonance (SPR)-mediated light absorbing ability. In Chapter 3, I have demonstrated NPG's application in remotely controlled photothermal actuation using SMP/NPG. However, controllability of SMP/NPG actuators, which is of great importance in practical applications, has not been systematically investigated yet. Here in this chapter, I prepare a series of nanoporous gold bowls (NPGBs) coated on a polyurethane-based SMP and investigate their movement in response to light. I study the relationship between the photo-mechanical movement and laser power, NPG loading and the thickness of SMP. I also compare the difference in movement under

different light sources. I demonstrate that various folding shapes can be achieved using our SMP/NPG strategy. This chapter provides detailed studies of programmable photo-induced SMP/NPG movements which is essential for the future design of SMP/NPG photo-mechanical actuators.

4.2 RESULTS AND DISCUSSION

I employ the sacrificial-template method as in Chapter 3 for the synthesis of NPGBs. The size and ligament size of NPGBs are $715\text{ nm} \pm 84\text{ nm}$ and $19\text{ nm} \pm 2\text{ nm}$, respectively. Polyurethane SMP films are prepared by solution casting method in which N,N-dimethylmethanamide (DMF) solutions of SMP are poured into petri dishes. NPGBs are then dropcasted onto SMP strips with size of $5\text{ mm} * 2\text{ mm}$.

I first study the mechanism of the SMP/NPG unfolding via differential scanning calorimetry (DSC) test. As shown in Figure 4.1(A), the glass transition temperature (T_g) and melting temperature (T_m) of pure polyurethane SMP are at $35\text{ }^\circ\text{C}$ and $163\text{ }^\circ\text{C}$, respectively. Thus, the shape memory effect of SMP can be initiated when temperature is higher than $35\text{ }^\circ\text{C}$. Typically, the polymer chains of polyurethane SMP consist of hard segments that provide physical cross-linking points and soft segments which are able to undergo phase transition from glassy state to rubbery state when temperature surpasses T_g . Freezing the molecular motion of polyurethane SMP that is under constant deformation strain from temperature above T_g to temperature below T_g prevents the soft segment chains from regaining coil-shaped structures, and thus fixes the SMP at the desired ‘programmed’ temporary shapes. When the programmed SMP is heated to above T_g , the oriented soft segment chains are relaxed to form coiled

conformations, leading to the recovery of original shape (Figure 4.1(B)).²⁶ In the presence of NPG, the photothermal heat achieved by the NPG is able to heat the programmed SMP up to temperatures above T_g of 35 °C, leading to the light-controlled movement of SMP to revert from its temporary shape to its original shape.

Figure 4.1. (A) DSC curve of pure polyurethane shape memory polymer in the experiment. (B) Scheme of molecular chain structure during shape memory polymer programming cycles. Red thermometers represent that current temperature is higher than T_g . Blue thermometers represent that current temperature is lower than T_g . Process (1) indicates that soft segments are heated up to rubbery state. Process (2) indicates the deformation strain in molecular chains. Process (3) indicates the freezing of deformation strain energy by lowering the temperature to below T_g . Process (4) indicates the recovery of shape, which is the release of strain in molecular chains by

heating the temperature to above T_g . Process (5) indicates that removal of heat leads to the original state of SMP.

I then systematically study the relationship between the laser power and the light-induced SMP/NPG movement using a laser source with wavelength of 532 nm. Here, I utilize the unfolding of SMP/NPG strips to investigate their photo-mechanical behavior. The original shape of SMP/NPG strips is a flat strip with an opening angle of 180° , while the temporary shape of the SMP/NPG strips is set to be a folded shape with an opening angle of 30° . The temporary shape is fixed by folding the strips to 30° while the temperature is kept at 80°C , followed by cooling down of the strips using ice bath to maintain its configuration. Under irradiation of different laser powers, the SMP/NPG strips displays different unfold angles and unfolding speeds (Figure 4.2(A) and (B)). I observe that longer time is needed to reach the final opening angle as laser power decreases. The required irradiation time for SMP/NPG strips to unfold from 30° to 130° is prolonged from 2 s to 17 s when laser power decreases from 100 mW to 40 mW. In addition, higher laser power results in larger opening angle of SMP/NPG. Herein, I use the opening angle and the average unfolding speed at 5 s of irradiation as parameters to quantitatively compare the recovery ratio and recovery speed of SMP/NPG at the same irradiation time. Recovery ratio is defined as the ratio between the light-induced opening angle and the opening angle in original state (180°). Recovery speed is here defined as the average unfolding speed during the first 5 s of laser irradiation. The recovery ratios at 5 s are controlled to be between 43% and 90% under laser power between 40 mW and 100 mW, respectively. The average recovery

speed values during 5 s of irradiation are tuned from 9.3 °/s to 26.1 °/s when laser power is increased from 40 mW to 100 mW laser power (Table 4.1). Notably, when laser power increases from 40 mW to 100 mW, both recovery ratio and recovery speed at 5 s increases by more than two-folds. These results indicate that higher laser power results in faster and more complete SMP/NPG shape recovery during the initial irradiation of 5 s which is considered as the fastest and main shape-recovery stages in our experiment.

Figure 4.2. Relationship between laser power and SMP/NPG unfolding movement. (A) Digital images depicting the opening angles of SMP/NPG under various laser power at different times. (B) Time-dependent changes of opening angles for SMP/NPG under various 532 nm laser power irradiation. Thickness of SMP is fixed at 0.05 mm. Loading of NPG is 7.5 $\mu\text{g}_{\text{Au}}/\text{mm}^2$.

Table 4.1. Relationship between recovery ratio, recovery speed and laser power.

Laser power (mW)	40	60	80	100
Recovery ratio at 5 s	43%	69%	79%	90%
Recovery speed during 5 s (°/s)	9.3	18.3	22	26.1

I also examine the movement of SMP/NPG with different amounts of NPG loading under same laser power. As shown in Figure 4.3, the decrease of NPG loading leads to slower movement. The time needed for unfolding from 30° to 130° is extended by ~ 11-fold (from 2 s to 22 s) when NPG loading decreases from 7.5 $\mu\text{g}_{\text{Au}}/\text{mm}^2$ to 2.5 $\mu\text{g}_{\text{Au}}/\text{mm}^2$. The recovery ratios at 5 s decreases from 90% to 42% when NPG loading is decreased from 7.5 $\mu\text{g}_{\text{Au}}/\text{mm}^2$ to 2.5 $\mu\text{g}_{\text{Au}}/\text{mm}^2$. The average recovery speed values during 5 s of irradiation also gradually decreases, from 26.1 °/s to 8.6 °/s with the decrease of NPG loading from 7.5 $\mu\text{g}_{\text{Au}}/\text{mm}^2$ to 2.5 $\mu\text{g}_{\text{Au}}/\text{mm}^2$ (Table 4.2). This trend clearly indicates that with more NPG loading, the photothermal heat is generated at a faster rate, and this results in the increase of SMP/NPG movement speeds.

Figure 4.3. Time-dependent changes of opening angles for SMP/NPG with various NPG loading amounts. Thickness of SMP is fixed at 0.05 mm. Laser power is 100 mW.

Table 4.2. Relationship between recovery ratio, recovery speed and NPG loading.

NPG loading ($\mu\text{g}_{\text{Au}}/\text{mm}^2$)	2.5	5.0	6.0	7.5
Recovery ratio at 5 s	42%	68%	79%	90%
Recovery speed during 5 s (°/s)	8.6	17.9	22.5	26.1

To quantify the SMP thickness dependent movements of SMP/NPG, I prepared SMPs with different thicknesses ranging from 0.05 mm to 0.35 mm and coated them with the same amount of NPG. As shown in Figure 4.4, using laser power of 100 mW, thicker SMP exhibits slower photo-induced movement. The unfolding time from 30° to 110° is extended from less than 2 s to 58 s, when SMP thickness increases from 0.05 mm to 0.35 mm. The recovery ratios at 5 s are gradually tuned from 90% to 29% with the gradual increase of SMP thickness from 0.05 mm to 0.35 mm. The average recovery speed values during the first 5 s gradually decreases with SMP thickness, which drops from 26.1 °/s to 4.1 °/s when SMP thickness increases from 0.05 mm to 0.35 mm (Table 4.3). These results indicate both slower recovery and less complete recovery as the SMP strips becomes thicker. These trends can be explained by two thickness-dependent factors that influence the SMP/NPG movement. First, heat conduction is poorer in thicker SMP strips, thus leading to slower photo-induced movement.²⁷ Secondly, the strips are prepared with same amount of NPG loading, which therefore creates same amount of photothermal heat under same irradiation, resulting in lower average temperatures for thicker SMP/NPG strips, and consequently slower photo-mechanical movements.

Figure 4.4. Comparison of time-dependent changes of the opening angle relationship for SMP/NPG with SMP thicknesses. Loading of NPG is fixed at $7.5 \mu\text{g}_{\text{Au}}/\text{mm}^2$. Laser power is 100 mW.

Table 4.3. Relationship between recovery ratio, recovery speed and SMP thickness.

SMP thickness (mm)	0.05	0.15	0.25	0.35
Recovery ratio at 5 s	90%	76%	37%	29%
Recovery speed during 5 s (°/s)	26.1	20.8	7.0	4.1

I compare the unfolding behavior of SMP/NPG strips under different light sources: 100 mW 532 nm wavelength laser and 300 W Xe-lamp solar simulator. Faster movement of the SMP/NPG strips is observed under solar simulator irradiation than 532 nm laser. This can be attributed to the higher photo intensity of solar simulator ($19.0 \text{ W}/\text{cm}^2$) as compared to the laser used ($3.2 \text{ W}/\text{cm}^2$).

Figure 4.5. Comparison of time-dependent changes of the opening angle for SMP/NPG strips under different light source. SMP thickness is fixed at 0.05 mm. Loading of NPG is fixed at $7.5 \mu\text{g}_{\text{Au}}/\text{mm}^2$.

To showcase the versatility of our SMP/NPG strategy, I demonstrate the unfolding ability of SMP/NPG in various shapes configurations. Using SMP/NPG with double folded, multi-armed box-like and twisting shapes, all SMP/NPG structures exhibits fast movement upon laser irradiation, which highlights the unlimited potential in the type of configurations that can be tailored for different actuation-based applications.

Figure 4.6. Unfolding of SMP/NPG with various shapes under laser irradiation: (A) double folded shape, (B) multi-armed box-like shape and (C) twisting shape.

4.3 CONCLUSIONS

In this chapter, I investigate the tunable actuation of SMP/NPG under irradiation. I find that faster photo-mechanical movement of SMP/NPG can be achieved by increasing laser power, increasing NPG loading or decreasing the thickness of SMP. Photo-mechanical movement of SMP/NPG is also successfully initiated by other light

sources such as solar simulator. Faster unfolding of the SMP/NPG structures are observed under solar simulator irradiation than laser due to the high light intensity of solar simulator. Various photo-mechanical movement of multi-stepped unfolding and untwisting of SMP/NPG are also successfully achieved under laser irradiation. Controllable ranges of recovery speed and recovery ratio are very important in practical applications for the tuning of photo-mechanical movement for various application situations. SMP thickness offers the broadest range of recovery ratio (29% - 90%) and recovery speed (4.1 °/s – 26.1 °/s) among the all three factors within the tested experimental conditions. This chapter offers a systematic study of controllable photo-mechanical movement of SMP/NPG and is potentially applicable for photo-induced actuators.

4.4 EXPERIMENTAL SECTION

Chemicals. Silver nitrate, hydroquinone (Hq), HAuCl₄, ethylene glycol (EG) and poly(vinylpyrrolidone) (PVP, average M_w = 1300000) were purchased from Sigma Aldrich. Hydrochloric acid (37%) were purchased from Schedelco. Nitric acid (69%) was purchased from Honeywell. Ammonium hydroxide (25% in water) was purchased from Merck. Ethanol and N,N-dimethylmethanamide (DMF) were purchased from Fisher Chemical. Polyurethane shape memory polymer (SMP MM-3520) was purchased from SMP Technologies Inc. The chemicals were used without further purification. Milli-Q water (18.2 MΩ/cm) was purified with a Sartorius arium® 611 UV ultrapure water system.

Synthesis of AgCl nanocubes. 0.4 g PVP and 0.4 g AgNO₃ were dissolved in 30 mL and 20 mL of cold EG correspondingly. After mixing PVP solution and AgNO₃ solution in the flask at room temperature for 1 min at 500 rpm, 1.23 mL of 37% HCl was added into the solution and kept stirring for another 1 min. Then, the solution was heated to 150 °C and kept stirring for 20 min. After the reaction, the solution was left at room temperature to cool down. 40 mL acetone was added to 10 mL of the resulting solution for sedimentation and centrifuged at 5000 rpm. After washing with water twice, the product was dispersed in 10 mL water to give a white suspension. This white AgCl suspension was used for future reactions.

Synthesis of Nanoporous gold bowls (NPGBs). 0.35 g PVP was dissolved in 50 mL water. Aqueous Hq (30 mg/mL) was prepared freshly. HAuCl₄ was also dissolved in water to get 0.5 M solution. AgCl nanocube solution (containing 51 mg AgCl) was first mixed with 45 mL PVP solution at room temperature at 1300 rpm in a RBF. After mixing for 1 min, 780 µL Hq solution was added followed by 323 µL of HAuCl₄ solution. After reaction for another 1 min, AgCl/NPGB hybrid was obtained. The solution was centrifuged at 3000 rpm for 3 min and washed twice with water. The product is then re-dispersed in water. After mixing AgCl/NPGB hybrid solution with 10 mL ammonia, the solution was centrifuged at 3000 rpm for 3 min and washed with water twice. NPGBs solution is obtained. The concentration of NPGB solution is determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

Preparation of shape memory polymer (SMP) / NPG. Typically, 500 mg of SMP pellets were dissolved in 15 mL DMF at 90 °C. The solution is poured into a glass petri dish. The solvent was then slowly evaporated at 70 °C for 24 h to get SMP film. Thickness of SMP thin film was controlled by addition of different amounts of SMP solution. SMP was cut into 5*2 mm strips and NPGB was dropcast onto SMP. The amount of NPGB per area on SMP was controlled from 7.5 $\mu\text{g}_{\text{Au}}/\text{mm}^2$ to 2.5 $\mu\text{g}_{\text{Au}}/\text{mm}^2$.

Materials Characterization. DSC analysis was carried out at heating rate of 20 °C / min using TA Instruments Q100. Composition and concentration analysis of the obtained nanoparticle suspension were conducted using a Thermo Scientific iCAP 6500 model ICP-OES. Nanoparticle suspension was mixed with Aqua Regia, and then diluted with water prior to ICP-OES measurement. A 532 nm laser attached in uRaman microscope is used for controlling the movement of SMP / NPG. Xenon lamp based solar simulator (300 W, Newport Instruments, Model 66902) was also used for SMP/NPG photo-mechanical movement. IR filter is installed on solar simulator to eliminate the effect of solution heating by infrared light irradiation. The movement of SMP / NPG was recorded in the form of video and frames at certain time point were analyzed using ImageJ software.

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Chapter 5

Photothermal Synthesis of Molybdenum Sulfide Coated Nanoporous Gold and Its Application in Converting Electric Energy into Chemical Energy in Hydrogen.

ABSTRACT. Photothermal effect of nanoporous gold (NPG) is utilized in the direct synthesis of a NPG-based hybrid material. Upon solar simulator irradiation, the surface temperature of nanoporous gold bowls (NPGBs) increases to more than 230 °C, resulting in the successful localized deposition of amorphous molybdenum sulfide (MoS_x) onto NPGBs. By varying the concentration of precursor of MoS_x , the amount and size of amorphous MoS_x on NPGB can be controlled. The obtained MoS_x -NPG hybrids exhibit greatly enhanced catalytic activity in hydrogen evolution reaction (HER) as compared to pure amorphous MoS_x due to the abundance of active sites and better conductivity in the presence of NPG. The application in HER demonstrates the potential of NPG-based hybrid in converting electric energy into chemical energy, which holds great opportunities in the field of energy storage.

5.1 INTRODUCTION

Localized surface plasmon resonance (SPR)-mediated chemical reactions have shown extensive potential in constructing hybrid material structures, as well as other applications such as biomedical therapy and reaction kinetic tuning.¹⁻⁹ The enhancement of SPR-mediated chemical reactions is ascribed to the photothermal effect, which originates from the non-radiative decay after SPR electromagnetic field-enhanced light absorption.¹⁰⁻¹² Due to its ability to enable localized photothermal heating, controlled and precise local hybrid growth on materials with SPR-enhancement can be achieved.^{1,13-15} Moreover, the high surface temperature provides novel approaches towards the superheated liquid phase reactions, reaching temperature higher than 100 °C without using autoclaves.¹⁶ However, due to the comparatively low SPR enhancement of single nanoparticles, such SPR-mediated hybrid structure synthesis can only be achieved after the assembly of the particles onto substrates, which limits the possibility of functional nanostructure design.

Nanoporous gold (NPG), which consists of bi-continuous porous gold nanostructure, exhibits highly enhanced electromagnetic field due to the strongly enhanced localized SPR arising from the interconnected structure of gold nanoligaments.¹⁷⁻¹⁹ Thus, photothermal heating achieved by NPG is expected to surpass that of traditional smooth surface metal nanoparticles, making NPG ideal for SPR-mediated photothermal chemical reactions and hybrid structure growth.^{20,21} Moreover, NPG can be exploited for the formation of functional hybrid systems such as high-performance catalysts due to its large surface-to-volume ratio and easy mass

transport.²² As compared to two-dimensional (2D) NPG nanosheets, zero-dimensional (0D) NPG nanoparticles possess much higher surface-to-volume ratios and can be easily suspended in solution. Such properties enable the ability to perform SPR-mediated hybrid growth in solution-based synthesis methods.^{23,24}

Herein, I report the direct synthesis of a NPG-based hybrid nanostructure via a facile method of SPR-mediated photothermal heating. Using 0D nanoporous gold bowls (NPGBs) as a model system, I demonstrate the photothermal decomposition of aqueous $(\text{NH}_4)_2\text{MoS}_4$ upon solar irradiation, which results in the deposition of molybdenum sulfide (MoS_x) particles onto the NPGBs surface. By tuning the precursor concentration, the amount of MoS_x particles deposited can be systematically controlled. Transmission electronic microscopy (TEM) is used to confirm the morphology of deposited MoS_x particles. The structure of deposited MoS_x particles is characterized using X-ray photoelectron spectroscopy (XPS). In addition, quantitative element analysis of the obtained hybrid particles is carried out via inductively coupled plasma optical emission spectrometry (ICP-OES). Surface temperature of NPGBs is determined using the polymerization reaction of soybean oil and thermal decomposition reaction of $(\text{NH}_4)_2\text{MoS}_4$ as indicator reactions. Subsequently, I showcase the catalytic performance of our as-prepared MoS_x -NPG hybrid for enhanced hydrogen evolution (HER) reaction, which is an energy conversion process from electric energy into chemical energy as hydrogen. More importantly, this NPGB-based photothermal deposition strategy proceeds at mild reaction conditions with low energy cost and far surpasses that of traditional methods that requires harsh conditions

and high temperatures. This strategy is highly versatile and can be extended to synthesize various functional hybrid structures of different materials.

5.2 RESULTS AND DISCUSSION

Morphology of MoS_x-NPG

NPGBs are synthesized using sacrificial template method as reported previously.²⁴ Briefly, bowl-shape NPGs are grown at the corners of AgCl nanocubes which are removed by etching the AgCl nanocubes using aqueous ammonia solution. This results in homogeneously-sized NPGBs, with diameter of 678 ± 82 nm, and ligament and pore size as 18 ± 4 nm and 4 - 30 nm, respectively (Figure 5.1).

Figure 5.1. SEM images of as-prepared NPGBs under (A) low magnification and (B) high magnification. Distribution bar graphs of (C) diameter and (D) ligament size of NPGBs.

MoS_x-NPG hybrid is then achieved by irradiating an aqueous solution containing NPGBs and (NH₄)₂MoS₄ using solar simulator for 2 h. In order to investigate the

effects of precursor concentration on the overall hybrid nanostructure, I prepared MoS_x-NPG with starting precursors of different Mo/(Au+Mo) ratios of 0.5%, 1%, 1.5% and 2%. Herein, I denote these samples as 0.5%MoS_x-NPG, 1%MoS_x-NPG, 1.5%MoS_x-NPG and 2%MoS_x-NPG, respectively.

The resultant morphology of the MoS_x-NPG hybrids is characterized using Transmission electronic microscopy (TEM). Across all the different ratios, a layer of amorphous MoS_x is deposited on the surface of NPGBs (as indicated by the arrows of Figure 5.2). As the ratio between MoS_x and NPGBs increases from 0.5% to 2%, the thickness of the amorphous MoS_x increases gradually from 3 nm, 5 nm, 7 nm to 10 nm, respectively. Hence, this indicates that I am able to systematically vary the thickness of amorphous MoS_x by simply tuning the precursor concentrations.

Figure 5.2. Morphology of MoS_x-NPG. TEM images of (A) 0.5%MoS_x-NPG, (B) 1% MoS_x-NPG, (C) 1.5% MoS_x-NPG, (D) 2% MoS_x-NPG. Black arrows indicate amorphous MoS_x.

Structural and elemental analysis of MoS_x-NPG

In addition, I employ XPS to study the structure of deposited MoS_x on NPGB surface (Figure 5.3). I observe the Au 4f_{5/2} and 4f_{7/2} XPS peaks at binding energy values of 87.0 eV and 83.3 eV, indicating that the valence state of gold in NPGBs is metallic Au(0). Deconvolution of Mo high-resolution spectra shows that Mo 3d_{3/2} and 3d_{5/2} peaks are present at 231.9 eV and 228.7 eV, respectively. The position of Mo 3d peaks indicates that the valence state of Mo in MoS_x-NPG is Mo(IV).²⁵ A small broad multiple valence state S 2s peak can also be found beside the Mo 3d peaks. Deconvolution of S 2p high-resolution spectra results in two different kinds of S doublets. The peaks at 163.7 eV and 162.5 eV originates from the bridging S₂²⁻ and apical S²⁻ ligands of MoS_x, respectively. The other two peaks located at 162.2 eV and 161.0 eV are indexed to the unsaturated S and terminal S²⁻ and S₂²⁻ ligands.^{26,27} In contrast to the single doublet S 2p peaks in crystalline MoS₂, the various S ligands in the molybdenum sulfide deposited on NPGB surface affirms the formation of amorphous MoS_x in the photothermal deposition process.²⁸

Figure 5.3. XPS characterization of MoS_x-NPG. XPS curves of (A) Au 4f, (B) Mo 3d and (C) S 2p in 0.5% MoS_x-NPG. (D) Bar graph comparing the ratio values between S and Mo in different MoS_x-NPG samples and amorphous MoS_x sample.

Subsequently, the composition of amorphous MoS_x on NPGBs surface is analyzed using XPS peak area ratio of Mo and S. The S / Mo atomic ratio values are found to be 3.49, 3.29, 3.08 and 3.06 for 0.5%MoS_x-NPG, 1%MoS_x-NPG, 1.5%MoS_x-NPG and 2%MoS_x-NPG, respectively. Notably, these S / Mo ratios are all close to pure amorphous MoS_x (S / Mo ratio = 3.01) rather than crystalline MoS₂ (theoretical S / Mo ratio = 2), indicating the amorphous nature of MoS_x in MoS_x-NPG hybrids.

I also analyze the yield of amorphous MoS_x deposition after solar simulator irradiation. The actual Mo / (Mo + Au) percentage is calculated using the

concentrations of Mo and Au obtained from ICP-OES. As shown in Figure 5.4(A), actual Mo ratio values are very close to the theoretical Mo ratio, indicating the high yield of MoS_x deposited onto NPG. For 0.5%MoS_x-NPG and 1%MoS_x-NPG, the yields are 100%. In the case of 1.5%MoS_x-NPG and 2%MoS_x-NPG, the yields are as high as 94% and 95%, respectively. The high yield of MoS_x deposition therefore validates the effectiveness and localized photothermal deposition of MoS_x onto NPG in solution.

Figure 5.4. Mechanism of MoS_x deposition and composition study. (A) Comparison of actual and theoretical Mo atomic ratio in MoS_x-NPG hybrids using ICP-OES results. (B) Thermogravimetric analysis curve of (NH₄)₂MoS₄. (C) Raman spectra of soybean oil during irradiation when mixed with NPG. The spectra have been baseline-

subtracted and normalized using the intensity at 3016 cm⁻¹ for easier visual comparison.

(D) Relationship between irradiation time and peak ratio between aliphatic C-H (2856 cm⁻¹) and vinyl C-H (3016 cm⁻¹).

Surface temperature of NPG during irradiation

The mechanism of MoS_x photothermal deposition on NPGBs surface involves the photothermal heating of NPGBs followed by the thermal decomposition of (NH₄)₂MoS₄ induced by NPGB photothermal effect. The SPR-enhance electromagnetic field in NPG dramatically enhances the absorption of light, which results in non-radiative damping, creating abundant heat and thus raising the temperature of NPGB surfaces. In order to gauge the temperature achieved by NPGB, thermal decomposition process of (NH₄)₂MoS₄ is first investigated using thermogravimetric analysis (TGA). During the heating from 100 °C to 800 °C, two main stages of thermal decomposition occur (Figure 5.4(B)). Stage 1 involves the decomposition from (NH₄)₂MoS₄ to MoS_x, which occurs between temperature range from 200 °C to 250 °C. The second stage is the decomposition of MoS_x into MoS₂ within the temperature region between 300 °C to 450 °C.²⁹ The process of two stages can be written as:

The TGA evaluation indicates that the thermal decomposition of (NH₄)₂MoS₄ to MoS_x proceeds only at temperatures higher than 200 °C, which in turn suggests that

the minimum surface temperature achieved by NPGB is at least 200 °C for decomposition to occur. To further investigate the surface temperature of NPGB upon solar simulator irradiation, I carry out an indirect temperature determination using polymerization of soybean oil as probe reaction (Figure 5.4(C)). Soybean oil, which is a mixture of triglycerides, undergoes thermal polymerization when heated above 230 °C.³⁰ The polymerization process can be traced using Raman peaks of aliphatic C-H bonds (2856 cm⁻¹) and vinyl C-H bonds (3016 cm⁻¹).³¹ I dispersed the NPGBs in soybean oil and monitored the changes in Raman peak ratio of aliphatic C-H and vinyl C-H during irradiation. The ratio of aliphatic C-H / vinyl C-H gradually increases from 4.92 to 5.82 during 2 hours of irradiation, indicating the extent of soybean oil polymerization becomes higher during solar simulator irradiation (Figure 5.4(D)). This clearly indicates the NPGB photothermal effect successfully initiated the polymerization of soybean oil. This observation demonstrates that the surface temperature of NPGB is capable of reaching at least 230 °C under solar simulator irradiation.

To further validate the effect of NPGB photothermal effect in MoS_x deposition, control experiment using (NH₄)₂MoS₄ solution of same concentration without NPGBs was performed. After irradiating the (NH₄)₂MoS₄ solution for 2 h, there is no sign of color change in solution (Figure 5.5), and no formation of MoS_x particles due to the absence of sediment after centrifuging the irradiated solution. Hence, this highlights the importance of NPGB in attaining high and localized temperatures for photothermal deposition to occur.

Figure 5.5. Digital photo of $(\text{NH}_4)_2\text{MoS}_4$ solution in absence of NPGB (a) before solar simulator irradiation and (b) after solar simulator irradiation.

Catalytic activity of MoS_x -NPG in hydrogen evolution reaction

I demonstrate the potential application of our MoS_x -NPG hybrid as an electrocatalyst using hydrogen evolution reaction (HER) as model reaction. The HER catalytic activity of MoS_x -NPG hybrid is tested in 0.5 M H_2SO_4 aqueous solution using a typical three-electrode setup (Figure 5.6(A)). Linear sweep voltammetry (LSV) measurements imply that 0.5% MoS_x -NPG hybrid shows the lowest onset overpotential of 193 mV. Onset potential values of 1% MoS_x -NPG, 1.5% MoS_x -NPG and 2% MoS_x -NPG are 201 mV, 222 mV and 227 mV, respectively. In contrast, pure amorphous MoS_x exhibits inferior onset overpotential of 232 mV. Another method to evaluate HER performance is the cathodic current density. In order to drive a cathodic current density of 200 $\text{mA}/\text{cm}^2 \cdot \text{mg}_{\text{Mo}}$, 0.5% MoS_x -NPG hybrid requires an overpotential of

only 234 mV, which is lower than those of 1%MoS_x-NPG (244 mV), 1.5%MoS_x-NPG (275 mV) and 2%MoS_x-NPG (286 mV). In contrast, control experiment using pure MoS_x requires much higher overpotential (304 mV) to reach cathodic current density of 200 mA/cm²*mg_{Mo}. These results clearly indicate that MoS_x-NPG hybrids exhibit much better HER performance than pure amorphous MoS_x.

To clarify the importance of hybridization between MoS_x and NPGB, I carried out a control experiment using physical mixture of NPGB and 0.5% amorphous MoS_x particles. For the physical mixture of two components, HER current density at 200 mA/cm²*mg_{Mo} requires an overpotential of 294 mV, which is 60 mV higher than that of 0.5%MoS_x-NPG hybrid. This implies that the coalescence of amorphous MoS_x with NPGB affects the HER performance. Hybridizing MoS_x with NPGB platform offers a much higher HER activity than simply mixing them physically.

To investigate which component is catalytically active in MoS_x-NPG hybrids, I compare the current density per area per unit metal mass of pure MoS_x and NPGB (Figure 5.6(B)). I observe that MoS_x (1020 mA/cm²*μg_{metal}) exhibits more than 2100 times current density than NPGB (0.47 mA/cm²*μg_{metal}) at overpotential of 0.4 V. Even though the amount of gold is 49 – 199 times higher than Mo in MoS_x-NPG hybrids with 0.5 – 2 % MoS_x, the contribution of NPGB in HER catalysis is relatively negligible. This comparison of HER performance in pure MoS_x and NPGB implies that the catalytic activity is mainly due to MoS_x. LSV results indicate MoS_x-NPG hybrids exhibit much better HER performance than pure amorphous MoS_x. Therefore,

the improved HER activity of MoS_x-NPG hybrids is attributed to the enhanced MoS_x catalytic activity that is promoted by NPGs which acts as a cocatalyst.

Figure 5.6. (A) LSV polarization curves of MoS_x-based samples with, and without NPG, at scan rate 2 mV/s, electrolyte solution: 0.5 M H₂SO₄ aqueous solution saturated with Ar. (B) LSV polarization curves of NPG at the same experimental condition. (C) Corresponding Tafel plots derived from the samples in (A). (D) Chronoamperometric curve for 0.5% MoS_x-NPG.

To obtain deeper insights into their HER performance, I analyze the Tafel plots of HER results using Tafel equation ($\eta = b \log j + a$), where η stands for overpotential, j is current density, b is the Tafel slope, and a is the intercept relative to exchange current density. Linear regions of Tafel plots of different samples are shown in Figure 5.6(C). The Tafel slope (mV/dec) reflects the overpotential required to increase HER

reaction rate ten times, lower Tafel slope indicates better HER activity. 0.5%MoS_x-NPG exhibits the lowest Tafel slope out of all samples (50 mV/dec). Besides 0.5%MoS_x-NPG, 1%MoS_x-NPG (53 mV/dec), 1.5%MoS_x-NPG (60 mV/dec) and 2%MoS_x-NPG (68 mV/dec) all display much lower Tafel slope values than pure MoS_x (87 mV/dec) (Table 5.1). This demonstrates the presence of NPGB cocatalyst platform greatly enhance HER catalytic performance of MoS_x. The Tafel slope of physical mixture of NPGB and MoS_x is 73 mV/dec, more than 40% higher than that of 0.5%MoS_x-NPG. This again shows the importance of using NPGB as cocatalyst platform.

Table 5.1. Comparison of Tafel slope values of different samples.

Sample	Tafel slope (mV/dec)
0.5%MoS _x -NPG	50
1%MoS _x -NPG	53
1.5%MoS _x -NPG	60
2%MoS _x -NPG	68
0.5% MoS _x mixed with NPGB	73
MoS _x	87
NPGB	93
Pt/C	29

Furthermore, the stability of HER performance of MoS_x-NPG hybrids is demonstrated using 0.5%MoS_x-NPG as an example (Figure 5.6(D)). No appreciable current decay is observed in the time-dependent current density curve at 225 mV of overpotential after 8 h, demonstrating the outstanding catalytic stability of MoS_x-NPG hybrids.

I carried out detailed structural study and electrochemical impedance spectroscopy (EIS) study in order to further understand the mechanism of how NPGB promotes the catalytic activity of MoS_x in MoS_x-NPG hybrids.

I hypothesize that the increased catalytic activity is due to the additional active S atoms present in our hybrid structures. Using the XPS S 2p spectra of MoS_x-NPG (Figure 5.3(C) and Figure 5.7). The S 2p XPS peaks can be deconvoluted into the doublets of bridging S₂²⁻ / apical S²⁻ ligands as well as unsaturated S and terminal S²⁻ / S₂²⁻ ligands. It has been reported that the bridging S₂²⁻ and apical S²⁻ ligands are more catalytic active for HER reaction (Figure 5.8).^{27,32} I compare the ratio between bridging S₂²⁻ / apical S²⁻ ligands and other S ligands to analyze the ratio of highly active S atoms in MoS_x-NPG hybrids. I observe that 0.5% MoS_x-NPG exhibits the highest ratio of bridging S₂²⁻ / apical S²⁻ ligands, and the ratio of bridging S₂²⁻ / apical S²⁻ ligands decreases with the increase of MoS_x amount in hybrids. All MoS_x-NPG hybrids exhibit higher bridging S₂²⁻ / apical S²⁻ ligands ratio than pure amorphous MoS_x. This trend coincides with the trend of HER catalytic activity. Thus, I ascribe the enhanced HER performance to the increased ratio of active bridging and apical S atoms.

Figure 5.7. High-resolution S 2p XPS curves of (A) 1%MoS_x-NPG, (B) 1.5%MoS_x-NPG and (C) 2% MoS_x-NPG. (D) Bar graph comparing the ratio values between the peak area sum of bridging S₂²⁻ and apical S²⁻ ligands and the peak area sum of terminal S²⁻ and S₂²⁻ in different samples.

Figure 5.8. Proposed structures for amorphous MoS_x : bridging S₂²⁻ (green), apical S²⁻ (blue), unsaturated S²⁻ (red), and terminal S₂²⁻ (yellow).

In addition, I utilize EIS to determine the conductivity of MoS_x-based catalysts (Figure 5.9). Though amorphous MoS_x is found to possess abundant active sites, the poor conductivity of amorphous MoS_x restricts its application in electrochemical catalysis.^{33,34} Using Nyquist plots from EIS results, the electrochemical system can be simulated as circuit models. In the case of MoS_x-NPG hybrids, the system can be simulated as a circuit model composed of solution spreading resistance (R_s), charge-transfer resistance (R_{ct}) and capacitor (CPE) (inset of Figure 5.8 (A)). The conductivity is determined by charge-transfer resistance which can be calculated from the radius of the semicircle of Nyquist plots. EIS results reveal that the radius of semicircle is dramatically reduced when amorphous MoS_x is hybridized with NPGBs. By simulating the Nyquist plots using the circuit model indicated in Figure 5.8(A), the charge-transfer resistance of 0.5%MoS_x-NPG (29.6 Ω) is less than 10% of amorphous MoS_x (313 Ω). Besides 0.5%MoS_x-NPG, 1%MoS_x-NPG (32.2 Ω), 1.5%MoS_x-NPG (34.1 Ω) and 2%MoS_x-NPG (37.8 Ω) all exhibit much lower charge-transfer resistance than amorphous MoS_x. The dramatically improved conductivity is ascribed to the conductive NPGB cocatalyst platform. I also compare the charge-transfer resistance of 0.5%MoS_x-NPG and physically mixing NPG with 0.5% MoS_x (63.0 Ω). Using NPGBs as cocatalyst exhibits less than 50% that of the physical mixture (63.0 Ω), demonstrating the importance of using NPGB as cocatalyst platform in increasing conductivity. Therefore, based on these results, I envisage the increased conductivity to be responsible for the enhanced HER activity in MoS_x-NPG hybrids.

Figure 5.9. (A) EIS Nyquist plots of different samples and the corresponding equivalent circuit model for simulation. (B) Magnified image of the dotted rectangular region in (A).

5.3 CONCLUSION

In summary, I have successfully demonstrated the SPR-mediated photothermal hybridization of NPG using MoS_x-NPG hybrids as an example. MoS_x is deposited on NPG surface under solar simulator irradiation. The amount and thickness of amorphous MoS_x on NPG can be tuned by changing the initial concentrations of the precursors. The surface temperature of NPGs during photothermal deposition is determined to be higher than 230 °C using TGA and soybean oil Raman spectra results. The potential application of NPG-based hybrid materials is then demonstrated using HER reaction as the model reaction. MoS_x-NPG hybrids exhibit much lower overpotential and smaller Tafel slopes values than pure amorphous MoS_x. The enhanced catalytic activity of MoS_x-NPG hybrids is attributed to the abundance of unsaturated S active sites and better conductivity in presence of NPG cocatalyst

platform. This work offers a new synthetic strategy for the preparation of energy-conversion functional hybrid by employing the photothermal effect of NPG. Our new strategy features mild preparation conditions, low cost and abundant active sites, which can be exploited for future novel functional materials.

5.4 MATERIALS AND METHODS

Chemicals. Silver nitrate, hydroquinone (Hq), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, ethylene glycol (EG), poly(vinylpyrrolidone) (PVP, average $M_w = 1300000$), $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, CH_3CSNH_2 , soybean oil and $(\text{NH}_4)_2\text{MoS}_4$ were purchased from Sigma Aldrich. Potassium hydroxide and hydrochloric acid (37%) were purchased from Schedelco. Nitric acid (69%) was purchased from Honeywell. Ammonium hydroxide (25% in water) was purchased from Merck. Ethanol was purchased from Fisher Chemical. Pt loaded on carbon black was purchased from Premetek. The chemicals were used without further purification. Milli-Q water ($18.2 \text{ M}\Omega/\text{cm}$) was purified with a Sartorius arium® 611 UV ultrapure water system.

Synthesis of AgCl nanocubes. 0.4 g PVP and 0.4 g AgNO_3 were dissolved in 30 mL and 20 mL of cold EG correspondingly. After mixing PVP and AgNO_3 solution in the flask for 1 min at 500 rpm at room temperature, 1.23 mL of 37% HCl was added into the solution and kept stirring for 1 min. Then, the solution was heated to 150°C and kept stirring at 500 rpm for 20 min. After the reaction, the solution was naturally cooled down. 40 mL acetone was added to 10 mL resulting solution for sedimentation and

centrifuged at 5000 rpm. After washing with water twice, the product was dispersed in 10 mL water to give a white suspension. This white suspension was used for future reactions.

Synthesis of Nanoporous gold bowls (NPGBs). 0.35 g PVP was dissolved in 50 mL water. Aqueous Hq (30 mg/mL) was prepared freshly. HAuCl_4 was also dissolved in water to get 0.5 M solution. AgCl nanocube solution (containing 51 mg AgCl) was first mixed with 45 mL PVP solution at 1300 rpm in RBF at room temperature. After mixing for 1 min, 780 μL Hq solution was added followed by addition of 323 μL HAuCl_4 solution. AgCl/NPGB hybrid was obtained after stirring for an additional 1 min. The solution was centrifuged at 3000 rpm for 3 min and washed twice with water and then re-dispersed in water. After mixing AgCl/NPGB hybrid solution with 10 mL ammonia, the solution was centrifuged at 3000 rpm for 3 min and washed twice with water to obtain the NPGBs. The concentration of NPGBs solution is determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

Preparation of molybdenum sulfide coated NPGB (MoS_x -NPG) hybrid. Typically, 13.0 mg $(\text{NH}_4)_2\text{MoS}_4$ is dissolved in 10 mL H_2O to get freshly prepared 5 mM $(\text{NH}_4)_2\text{MoS}_4$ solution. 10 mL solution containing 5 μmol Au and corresponding ratio of Mo is prepared by mixing NPGBs solution and 5 mM $(\text{NH}_4)_2\text{MoS}_4$ solution. The theoretical ratio of Mo / (Mo + Au) is designed to be 0.5%, 1%, 1.5% and 2% in this

work. The mixed solution is irradiated under Xenon lamp based solar simulator (300 W, Newport Instruments, Model 66902). IR filter is installed on solar simulator to eliminate the effect of solution heating by infrared light irradiation. After 2 h of irradiation, the MoS_x-NPG product can be obtained by centrifuging and washing with water and ethanol twice. The concentration of Mo and Au in MoS_x-NPG is determined by ICP-OES.

Preparation of amorphous molybdenum sulfide. Amorphous MoS_x particles were prepared for control experiments via a previously reported method.³⁵ Typically, 150 mL solution containing 1.8 g Na₂MoO₄·2H₂O and 2.4 g CH₃CSNH₂ was heated up to 80 °C, followed by quick addition of 10 mL 3.6 M H₂SO₄ solution. Brownish precipitation was observed after vigorous stirring for several minutes. Amorphous MoS_x can be obtained after centrifuging and washing the precipitate using ultrapure water several times and drying at 100 °C overnight.

Materials Characterization. Scanning electron microscopy (SEM) imaging was performed using a JEOL JSM 7600F microscope under 5 kV voltage. MoS_x-NPG hybrids are dropcast on Cu grids for transmission electron microscopy (TEM) observation. TEM images were taken on a JEOL-1400 model with 100 kV acceleration voltage. X-Ray photoelectron spectroscopy (XPS) spectra were carried out using a Phoibos 100 model spectrometer equipped with monochromatic Mg X-ray radiation

source. XPS results were calibrated using 284.5 eV as standard for C 1s binding energy peak. Thermo Scientific iCAP 6500 ICP-OES machine was used for composition and concentration analysis for NPGB and MoS_x-NPG hybrids. Prior to ICP-OES tests, NPGB or MoS_x-NPG hybrids solution was mixed with Aqua Regia for metal dissolution, followed by quantitative dilution with ultrapure water. Thermogravimetric analysis (TGA) of (NH₄)₂MoS₄ precursor is measured using TA Q500 model machine. The sample was tested with heating rate of 20 °C/min under air flow. Raman spectra were carried out using uRaman microscope (Technospex PTE LTD) using laser of 532 nm wavelength.

Electrochemical measurements. Electrochemical measurements were performed in three-electrode electrochemical cell. Saturated calomel electrode (SCE) electrode was used as reference electrode, and all potential values were calibrated by referencing to a reversible hydrogen electrode (RHE). A pure graphite rod was used as counter electrode. Glassy carbon electrodes (GCE) with glassy carbon diameter of 3 mm were used as working electrodes. For linear sweep voltammetry (LSV) measurements, a scan rate of 2 mV/s was used. To obtain a chronoamperometric curve for 0.5% MoS_x-NPG, an overpotential of 205 mV was applied. Electrochemical impedance spectroscopy (EIS) was collected from the frequency from 0.5 MHz to 0.1 Hz with 10 mV amplitude under 300 mV overpotential. Electrolyte solution was bubbled with high-purity argon gas for at least 30 min before tests.

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Chapter 6

Summary and Outlook

6.1 SUMMARY

In this thesis, I design nanoporous gold (NPG) based nanostructures with tailored functions and exploit these nanostructures in the applications of energy conversion.

This thesis aims to find out the mechanism of synergistic effects and shape-dependent photothermal effect of NPG nanostructures and enhancing their performance in energy conversion applications. The objectives stated in the first chapter have been achieved in this thesis.

(1) The mechanism of synergistic effects in NPG-based hybrids has been studied in detail in both chapter 2 and chapter 5. In chapter 2, the synergistic effects of Pt-nanoporous gold bowl (Pt-NPGB) bimetallic hybrid is found to be from the lowering of d-band center which is attributed to the presence of NPGB co-catalyst platform. Such synergistic effects result in the weakened binding strength towards intermediate poisoning species in methanol oxidation, thus significantly enhancing the catalytic efficiency of the Pt-NPGB bimetallic catalysts. In chapter 5, the synergistic effects in molybdenum sulfide-nanoporous gold (MoS_x -NPG) hybrids originate from the higher ratio of catalytically active S sites and better conductivity. The abundance of catalytically active S sites offers higher activity towards hydrogen evolution reaction (HER) and better conductivity improves the charge transfer

efficiency during the electrochemical reaction. From the results of these two chapters, I can conclude that the excellent conductivity, good chemical stability, large surface area and ability in tuning electronic structure of NPG make it a promising platform for extensive design of novel hybrid catalysts in applications for energy conversion. This thesis has provided detailed mechanism study of the synergistic effects of NPG-based hybrid, thus paving the way of designing high-performance functional NPG hybrids.

(2) NPG with bowl-like, tube-like and plate-like shapes are synthesized using templates with different shapes, and the shape-dependent performance of NPG in photothermal effect has been studied in chapter 3 and chapter 4. Among all shapes tested, bowl-like NPGB exhibits highest photothermal conversion efficiency. The relationship between shape and photothermal effect is found to be related with their absorption cross section and laser penetration depth. Controllability of NPGB photothermal effect is also achieved by tuning laser power. I exploit the superior photothermal effect of NPGB in the application of photo-induced deformation of a shape memory polymer. Its potential in remote photo-controlled switch application is also demonstrated.

(3) Besides mechanism study, chapter 5 also provides a novel preparation method for constructing particle-based NPG hybrid nanostructure. Particle-based MoS_x -NPG hybrid nanostructures are prepared by utilizing the photothermal effect of zero-dimensional NPGB nanoparticles. Tunable amount and thickness of amorphous MoS_x on NPGB are achieved by changing the initial concentrations of the precursors. The surface temperature of NPGBs during photothermal deposition is found to be over 230 °C, which is determined by thermogravimetric analysis and soybean oil Raman spectra results. This work describes a

mild, low-cost and effective synthetic strategy for the preparation of electrical-to-chemical energy-conversion functional hybrid utilizing by employing the photothermal effect of NPG.

In conclusion, this thesis summarizes our fundamental studies of NPG-based nanostructure design, which bridges the relationship between structures and functions of NPG-based materials. This is a major contribution to the fabrication strategies of NPG-based functional materials, and is particularly relevant to applications involving energy conversion.

Figure 6.1. Scheme summarizing the conclusions of the thesis.

6.2 OUTLOOK

In this thesis, I have provided novel structural insights to boost the performance of NPG-based materials in energy conversion applications. Nevertheless, research efforts should be extended in further improving energy conversion efficiency as well as exploring other forms of energy conversion.

I demonstrate the synergistic effect of Pt-NPGB bimetallic catalysts in converting chemical energy in methanol molecules to electrical energy in Chapter 2. Inspired by the reported bimetallic catalysts based on gold nanoparticles and conventional 2D NPG sheets,

I envisage that 0D NPG particle co-catalyst platform is also favorable for converting chemical energy of other organic molecules to electrical energy, such as Pd-NPGB bimetallic catalysts for ethanol oxidation and formic acid oxidation.¹⁻³ The high surface area, synergistic effect and open-structure of NPGBs are highly promising for the design of high-performance bimetallic catalysts. I could also evaluate the flexibility of NPG-based bimetallic materials using wet chemistry synthesis method, such as reducing two noble metals at the same time in order to obtain homogeneously mixed porous bimetallic nanostructure. As various NPG-based nanomaterials are promising in enhancing catalytic performance in various interdisciplinary fields, I can try to develop bimetallic NPG hybrid with different structure, such as noble metal coated NPG and homogeneously mixed bimetallic NPG hybrid, and relate their catalytic performance with their structure.

I also look forward to the combination of synergistic effect and photothermal effect of NPG in enhancing catalytic performance of NPG-based hybrid catalysts. Temperature is an important factor for controlling catalytic reactions. Catalytic reactions enhanced by photothermal effect have been reported using hybrids based on gold nanorods and gold nanobipyramids.⁴⁻⁶ The abundance of ‘hot spots’ renders NPG with greater potential in enhancing catalytic reactions via photothermal effect. Therefore, NPG-based hybrid catalysts are highly promising in exploiting photothermal effect-enhanced reactions.

I have achieved photo-triggered movement of SMP by coating NPG particles. In the future, I shall further explore the effect of NPG dispersion on SMP photo-mechanical movement. For example, homogeneous dispersion of NPG inside SMP film is ideally favorable for photothermal heat conduction, which is expected to give rise to shorter photo-

mechanical response time. However, homogeneous dispersion of NPG in SMP/NPG nanocomposites requires much efforts in surface modification of NPG particles. By binding surface ligands with different polarities and chain lengths, I am able to investigate the relationship between NPG dispersion and photo-mechanical response of SMP.

Apart from the above-mentioned forms of energy conversion, I suggest that NPG-based hybrids should be exploited in converting more forms of energy. Photoacoustic effect, which is used as an important tool for biological imaging, is the creation of sound waves after the absorption of light. Photoacoustic effect is closely related to photothermal effect as the sound waves originate from the photothermal elastic expansion of the materials.⁷ Gold nanoparticles, with good biocompatibility and SPR-induced photothermal effect, have been applied in cancer cell detection utilizing photoacoustic effect.⁸ As strong photothermal effect has been demonstrated in NPG, I envisage that NPG is promising in providing strong signals in photoacoustic imaging applications.

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Chapter 7

List of Publications, Conferences and Awards

Publications:

- **Zhe Yang**, Srikanth Pedireddy, Hiang Kwee Lee, Yejing Liu, Weng Weei Tjiu, In Yee Phang, Xing Yi Ling*; Manipulating the d-Band Electronic Structure of Platinum-Functionalized Nanoporous Gold Bowls: Synergistic Intermetallic Interactions Enhance Catalysis, *Chem. Mater.*, **2016**, 28 (14), 5080-5086.
- Charlynn Sher Lin Koh, Hiang Kwee Lee, Gia Chuong Phan-Quang, Xuemei Han, Mian Rong Lee, **Zhe Yang**, Xing Yi Ling*; SERS- and Electrochemically-Active 3D Plasmonic Liquid Marble for Molecular-Level Spectroelectrochemical Investigation of Microliter Reaction, *Angew. Chem. Int. Ed.*, **2017**, 56 (30), 8813-8817.
- Wee Shern Chew, Srikanth Pedireddy, Yih Hong Lee, Weng Weei Tjiu, Yejing Liu, **Zhe Yang**, Xing Yi Ling*; Nanoporous Gold Nanoframes with Minimalistic Architectures: Lower Porosity Generates Stronger Surface-Enhanced Raman Scattering Capabilities, *Chem. Mater.*, **2015**, 27 (22), 7827-7834.

Conferences:

- Zhe Yang, Xing Yi Ling. “Manipulating the d-Band Electronic Structure of Platinum-Functionalized Nanoporous Gold Bowls: Synergistic Intermetallic

Interactions Enhance Catalysis” Oral presentation at 91st ACS Colloid & Surface Science Symposium, 2017, New York, USA.

- Zhe Yang, Xing Yi Ling. “Manipulating the d-Band Electronic Structure of Platinum-Functionalized Nanoporous Gold Bowls: Synergistic Intermetallic Interactions Enhance Catalysis” Poster presentation at 9th Asian Photochemistry Conference, 2016, Singapore
- Zhe Yang, Xing Yi Ling. “Synergistically Engineering Pt Catalytic Activity via Nanoporous Gold Bowls Co-catalyst Platform” Poster presentation at 2nd Workshop on the Chemistry of Energy Conversion: From Molecular Design to Advanced Materials, 2016, Singapore

Awards:

- NPG Asia Materials Poster Award at 9th Asian Photochemistry Conference, Singapore, 2016
- Best Teaching Assistant Award, Division of Chemistry and Biological Chemistry, Nanyang Technological University