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Selective Growth of Ag Nanodewdrop on Au Nanostructure: A New Type of Bimetallic Heterostructure

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Abstract

A new type of bimetallic Au-Ag heterostructured material was prepared by a selective growing strategy of Ag nanodewdrop on the petal tip of Au flower using electrochemical method. The whole process was strictly controlled by forming the reactive tip of flower petal and passivating the facet along the body of metal petal using poly(vinyl pyrrolidone)(PVP) coating film. The formed Au-Ag HSFs were observed to be about 2 μm in diameter and have the Ag particles of about 50 nm settled on the tips of Au petals. The Au-Ag HSFs were found to display the superior properties on the surface-enhanced Raman scattering (SERS). The presence of Ag nanodewdrops could also facilitate the oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ complex in electrogenerated chemiluminescence (ECL) measurements and dramatically enhance the emission intensity. The features of Au-Ag HSFs can promise a new type of heterogeneous bimetallic alloy material for the potential applications in chemical and biological sensors.

Keywords

Au-Ag heterostructured flower (HSF); electrodeposition; electron migration; surface-enhanced Raman scattering (SERS); electrogenerated chemiluminescence (ECL)

1. Introduction

Heterostructured metal, oxide, or semiconductor nanocrystals containing multiple components are becoming attractive due to the multifunctional properties and new features arising from the effective coupling of their different domains.¹⁻³ Recently, a new generation of hybrid nanocrystal accommodating with two or more different components on the same particle has appeared.^{4,5} Prototype structures of them are observed to have typical spherical shapes and double-domain components including semiconductor/semiconductor,^{2,4,5} metal/semiconductor,^{3,6-9} metal or metal oxide/magnetic oxide,¹⁰⁻¹³ semiconductor/oxide,¹⁴ and metal/metal^{15,16} interfaces.

The two components of hybrid nanocrystals can be built up in many structures. It is interesting to notice from a recent publication by Banin that the metal nanostructure can be controlled to grow as the second component on the preferred tip of semiconductor nanorod.⁷ This type of

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Supporting Information Available: SERS spectra of Au-Ag HSFs, band structures of Ag and Au, and ECL emission on Au-Ag HSF decorated electrode. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

metal-semiconductor heterostructure was determined to have the combined properties with two component materials and yield unique new optoelectronic properties and functionalities. So far, various technologies, e.g. chemical reduction, physical deposition, and photochemistry have been reported to control the selective growth of metal structure on the semiconductor rod, tetrapod, and prism, etc. It is also noticed from the publications that a wide range of metal-semiconductor materials have been studied including Au on CdSe,^{3,6} Au on CdS,⁷ Au or Ag on ZnO,^{17, 18} Co and Au on TiO₂, etc.^{19, 20, 21} Different from metal-semiconductor nanostructures, the metal-metal heterostructures are typically generated on the hard templates such as anodic aluminum oxides by in turn electrochemical depositions of different metals.^{1-3, 21-27} Without the templates, the synthesis of metal-metal heterostructures have to face a challenge owing to the distinct reduction rates and lattice mismatches from the different metal components. Even though the metal materials with the similar lattice constants are strictly selected, the reaction conditions are needed to precisely tune in the formations of multimetallic nanostructures. Thus, the preparations of metal-metal interfaced materials are regarded to be much more difficult. To our knowledge, only few reports appeared on this area.²² Recently, Song, et al., successfully generated the Au-Ag-Au heterometallic nanorod through a directed overgrowth of silver structure on a gold decahedron rod by electrochemical reduction of silver salt in the presence of poly(vinyl pyrrolidone) (PVP),²⁸ which provides a new strategy to generate the metal-metal heterostructures. In this paper, this method was employed and modified to prepare the Au-Ag bimetallic nanostructures.

In general, the heterostructured materials can be directionally constructed by controlling the growth conditions. For instance, in the formations of metal-semiconductor heterostructured materials, the second metal structures are prefer to grow on the tips of semiconductor rods due to several possible factors: surface defects, differences in the passivation degree between chemically different facets of the same nanocrystals, lattice mismatches, and minimizations of interfacial energies between the different materials.¹⁻⁷ We intend to prepare the metal-metal heterostructures with the directional growths in this research. A simple but low-cost electrochemical route was employed to synthesize the diameter-controlled hierarchical flowerlike gold structures, which have “clean” surfaces and triangular-shaped Au petals to build the blocks without any template or surfactant usages.²⁹ With the activated and sharpened tips on the Au petals, the second metal structures of silver were directionally constructed on the Au flowers to generate the subsequent Au-Ag bimetallic heterostructured flowers (HSFs), in which the dewdrop-like Ag nanoparticles were selectively settled on the petal tips of the Au flowers. These special structure features are believed to cause a remarkable interfacial change of bimetallic components and furthermore lead to a change of physical properties such as surface-enhanced Raman scattering (SERS). In this research, the Rhodamine molecules were conjugated on the metal structures of bare Au and Au-Ag HSF structures respectively to investigate the influences from the interfaces of bimetallic heterostructured materials to the Raman scattering properties.

Electrogenerated chemiluminescence (ECL) is an emission from an excited molecule generated by an electrochemical redox reaction.³⁷ Because of its versatility, simplified optical setup, low emission background, and good temporal and spatial control, this technology has been applied in the flow injection analysis, high-performance liquid chromatography, capillary electrophoresis (CE), and microchip CE to detect amino acids, oxalate, NADH, alkylamines, and nucleic acids, etc,³⁸⁻⁴⁰ since it was first reported in 1980s. As a detection technology, it is of importance to increase the ECL signals for the improvement of sensitivity. Compared with the solution-phase, the ECL efficiency will be increased significantly on the solid electrode surface due to reducing the consumption of expensive reagent. In addition, the experimental design for ECL can be simplified on the solid electrode surface. Thus, the ECL response is supposed to be sensitive to the interfacial characteristics of heterostructured

material as the electrode. Therefore, the ECL properties of probes on the Au-Ag bimetallic HSFs were also measured to compare with those on the bare gold rods in the paper.

2. Experiment section

Materials

All chemicals including HAuCl_4 (Aldrich), AgNO_3 , poly(vinyl pyrrolidone)(PVP), alcohol, acetone(Beijing Chemical Factory, China) are analytical grades and used without further purification. Distilled water was used in all experiments.

Electrochemical Synthesis of Au-Ag HSFs

The Au-Ag HSFs were synthesized through a two-step strategy of electrodeposition. The Au flowers were first synthesized in electrochemical method.²⁹ Briefly, the tin-doped indium oxide on glass (ITO; Shenzhen Hivac Vacuum Photo-electronics Co. Ltd.) was cleaned by sonicating for 10 min sequentially in acetone, 10% NaOH in ethanol, and distilled water and then used as working electrode. A clean platinum wire and an Ag/AgCl (sat. KCl) electrode were used as counter and reference electrodes, respectively, in a three-electrode cell. The Au flowers were generated by electrochemical deposition using amperometric $i-t$ curve technique with a potential at 0.5V in 24.3 mM HAuCl_4 aqueous solution. The formed Au flowers on the ITO substrates were dipped in 0.1 mM PVP aqueous solution to cover the PVP films. The silver structures were controlled to deposit on the gold structures to create bimetallic heterostructured materials using the metal-deposited ITO as the working electrode, a platinum wire as counter, and an Ag/AgCl electrode as reference. The electrochemical deposition was carried out with a bias at -0.6 V in AgNO_3 (10 mM) aqueous solution with different deposition times of 2 and 10 min, respectively, to control the size of formed silver particle on the primary gold structure.

Characterization—The morphologies of samples on the ITO substrates were directly subjected to characterize with Hitachi S4800 scanning electron microscope (SEM). For the high-resolution transmission electron microscope (HRTEM, JEOL 2010F) measurements, the samples were scraped from the ITO substrates into ethanol, and then cast onto the copper grids by placing a drop of solution. Power X-ray diffraction (XRD) measurements were performed on a Shimadzu XRD-6000 using Cu $K\alpha$ radiation (1.5406 Å) of 40 kV and 20 mA. For the Raman spectral measurements, the samples were dipped into Rhodamine 6G (R6G) aqueous solution (1×10^{-6} M) with stirring for 10 min, rinsed with de-ionized water, and dried with high-purity flowing nitrogen. The resonant Raman spectra were recorded on a Jobin Yvon LabRAM HR 800UV micro-Raman spectrophotometer with a 633 nm line of a He-Ne laser and 514 nm line of a He-Cd laser as the excitation sources. Cyclic voltammetry (CV) and electrogenerated chemiluminescence (ECL) studies were performed using a Model MPI-E from ECL Analyzer Systems (Xi'An Remax Electronic Science & Technology Co. Ltd., China). In the experiment, the samples were dipped into the $\text{Ru}(\text{bpy})_3\text{Cl}_2$ aqueous solution (10^{-3} M) with stirring for 5h, rinsed with de-ionized water, and dried in air. A three-electrode system was employed in the electrochemical measurements, in which the $\text{Ru}(\text{bpy})_3^{2+}$ complex adsorbed metallic structures on the ITO glass was used as working electrode, a platinum wire as counter, and an Ag/AgCl as reference. The photomultiplier tube (PMT) was biased at 600 mV and the electrolyte was a phosphate buffered saline (PBS, pH 7.0) with 0.001 M $\text{H}_2\text{C}_2\text{O}_4$. The potential scans were cycled between 0 and 1.25 V at rate of $100 \text{ mV} \cdot \text{s}^{-1}$.

3. Results and Discussion

The gold nanostructures were generated by electrochemical deposition on the ITO substrates. Figure 1a and b presented the SEM morphologies of bare gold structures obtained at different

deposition times. An individual gold nanoparticle was shown with many triangular-shaped petals and changeable diameters from the base to tips. These metal petals with the sharpened tips on the widened bases were connected to one center core to form the flower-like structures. The morphologies of flower-like gold structures were observed to rely on the deposition times. At a short deposition time of 2 min, an average diameter of Au flowers was about 2 μm (Figure 1a), on which a typical length of one petal was 400–500 nm and a thickness 50 nm. In addition, the diameters at the bases were ranged in 200–300 nm and the diameters of tips in 50–70 nm, respectively. With increasing the deposition time to 10 min, the flower-like Au structures were observed to significantly grow in the sizes (Figure 1b), accompanying with narrowing the petals as well as a sharpening and compacting the tips on the SEM morphologies.

In order to generate the bimetallic heterostructured Au-Ag materials, the Au flowers with the deposition time of 2 min were covered by the PVP films, and subsequently treated by the electrochemical deposition to grow the Ag nanoparticles on the Au structures. In a three-electrode system, the metal-deposited ITO was used as the working electrode, a platinum wire as counter, and an Ag/AgCl electrode as reference. The electrochemical deposition was carried out with a bias at -0.6 V in AgNO_3 (10 mM) aqueous solution with the different deposition times of 2 and 10 min, respectively, to control the growths of nanodewdrop-like silver particles on the gold structures. The morphologies of nanostructures were presented with only optimal conditions of Au and Ag concentrations in the electrodeposition solutions. In fact, we have investigated the concentration-dependent depositions of both formed bare Au flowers and Au-Ag HSFs in this research, showing that under other concentrations, the bare Au flowers were composed of many triangular-shaped petals and as a result the Ag nanoparticles could not be grown on the Au flowers as expected in the subsequent treatments.

Because of the lattice differences, the formed silver particles could be identified distinctly from the gold flowers. Most Ag particles (bright spot) were observed to grow on the tips of triangular-shaped Au petals (Figure 1c). A detail inspection to the image of Au-Ag heterostructured flowers (HSFs) was presented in Figure 1d, furthermore revealing that these dewdrops-like Ag nanoparticles with average diameter of about 50 nm were settled on the tips of petals of Au flowers. A low-magnification SEM image of Au-Ag HSF in Figure 1e expressed an analogous morphology. We also tested the Au structures, which were prepared with prolonging the electrodepositing time to 10 min, and then by the Ag deposition. Similar to the 2 min deposition samples, the SEM images of 10 min deposition samples (Figure 1f and g) also showed that the silver nanoparticles were selectively grown on the petal tips of Au flowers.

A representative TEM image of Au-Ag HSFs (Figure 2a) provided a direct observation to the distinct growths of Ag nanoparticles on the tip of petals on the Au flowers, consistent with the observation on the SEM image. The nanocrystalline nature of Ag nanodewdrop was clearly identified in the HRTEM image (Figure 2b), on which the lattice fringes of 0.237 nm could be indexed as the {111} crystal planes of metal Ag. Although we did try to make a HRTEM image measurement, a distinct of Au-Ag interface was not available in this paper because the petal of Au flower was too thick to penetrate through and get interface structure. In order to understand the orientation of Au petals on the precursor flowers, we recorded their X-ray diffraction (XRD) patterns (Figure 2c). All peaks were assigned to the diffractions from the (111), (200), (220), and (311) planes of Au structure, respectively. The estimated intensity ratio of the (111) to the (200) diffraction line in this case was 2.3 higher than that of the standard diffraction of Au powder (1.9), indicating that the metal structures were grew on the surface sites that were dominated by the lowest energy {111} facets.³⁰

It is interesting to notice from the experiments that the structures of Au-Ag HSFs are controlled by two critical factors. The first is the extension of many triangular-shaped petals from the centers of Au flowers in three dimensions. These metal petals are found to display higher

reactivity at the tips than along the bodies due to the increase of surface energy that can lead to the preferential sites for the settlements of silver particles. The other is the blocking effect of PVP coating film. It has been reported that the PVP coated film tends to passivate the Au rod side surfaces, {100} and {110} facets through the chemical interactions with the oxygen (and / or nitrogen) atoms of their units, in while the interaction with the {111} facets at the ends are much weaker so the {111} facets remain to be reactive.³¹ This can be understood that the bodies of Au petals were mostly covered by PVP, but the uncovered tips of metal petals remained to be reactive in the deposition of Ag nanodewdrops. In order to confirm the block effect of PVP coating film, the bare Au flowers without the PVP treatments were used to deposit the silver nanodewdrops. The results revealed that the Ag particles were unselectively grown on the either tips or falloff petals of the Au flowers without the directions as shown in Figure 3, indicating that the sites of silver particle growths were indeed controlled by the PVP films coated on the Au flowers in this case.

It is known that the bimetallic material can display the characteristic properties due to the energy or/and electron migrations on the interfaces. To evaluate the interface interactions between the Au flowers and Ag nanodewdrops in the current system, we took the surface-enhanced Raman scattering (SERS) spectrum measurements using the bare Au flowers as the control. The total SERS signals are considered to generate from both the resonance and pure SERS that can be investigated using the non-resonant vibrational probe. The Rhodamine 6G molecules were used as the probes to conjugate on the metal substrates. Although the Raman scattering spectra can be enhanced on the bare Au flowers owing to their radiative structures,^{29,32, 33} the experimental results in both Figure 4 and Figure S1 in the supporting information support that the bimetallic Au-Ag HSFs can create the additional enhanced-SERS signals. It is known from both theoretical and experimental studies that the SERS signal is primarily due to the electromagnetic excitation of strongly localized surface plasmon resonance on the noble metal substrate,³⁴ which arises from the metal nanostructure and relies on its size and shape as well as surrounding medium. For a star-shaped metal particle in this case, the local electromagnetic field is regarded to distribute heterogeneously around the metal structure: more intensive on the sharp tip but lower on the petal.³⁵ As a result, a stronger local electromagnetic field was formed at the interface between the Au flower and Ag nanodewdrop, and the SERS signal by the localized dye molecule hence was furthermore enhanced. On the other hand, the SERS signals on the Au-Ag HSFs were found to be much higher than that on the bare gold structure as shown in Figure 4, which was considered to arise from the bimetallic interfacial interaction that was due to their different work functions (Figure S2 in the supporting information).³⁶

We also noticed that the silver particles were grown as aggregates instead of individuals on the gold structures. To exclude the possibility that the intensification of SERS signals on the HSFs may be simply due to the silver hot spots rather than the formed silver-gold hot spots, the SERS measurements were also carried out upon excitation at 514 nm and the results were presented in Figure S1. Compared with the spectra upon the excitation at 633 nm in Figure 4, the spectra achieved upon excitation at 514 nm in Figure S1 expressed an analogous tendency but much lower enhancement efficiency indicating that the intensification of SERS signal on the bimetallic hybrid flowers should be attributed to the formations of Au-Ag hot spots. In addition, we also took the SERS spectral measurements on the non-selectively grown bimetallic structures (shown in Figure 3), and the Raman scattering signal was presented in Figure S1, showing a lower SERS signal (curve c in Figure S1) than that for the selectively grown Au-Ag HSF (curve b). It means that the interfacial properties of bimetallic Au-Ag HSFs may principally contribute to the additional enhancement of SERS.

Besides SERS measurement, we carried out the ECL measurement on the bimetallic structures to investigate the interfacial effect in this paper. The ECL-potential scanning curves by the Ru

(bpy)₃²⁺ complex on the either Au-Ag HSF decorated electrode or pure Au flower decorated electrode in 0.1 M phosphate buffered saline (PBS, pH 7.0) containing 1.0 mM H₂C₂O₄ were present in Figure 5. The ECL onset voltage on the Au-Ag HSF decorated electrode is 0.69 V, 0.07 V more negative than that on the Au flower decorated electrode (0.76 V). In addition, the ECL intensity on the former is about 6-fold higher than that on the pure Au flowers, indicating a significant increase of ECL signal on the Au-Ag HSF decorated electrode. This superiority of Au-Ag HSFs is believed to associate with the electronic structure caused by the join of Ag nanoparticles on the Au structures. Thus, it is of importance to interpret the experiment result from the ECL mechanism. The whole ECL process is expressed in equations (1) ~ (5) that starts with the lose of one electron of Ru(bpy)₃²⁺, and then follows by the reaction with the coreactant H₂C₂O₄ to produce the excited state of Ru(bpy)₃²⁺, which can give off light during falling back to the ground state.

According to the different Fermi energy levels of Au and Ag, we believe that more positive-charged Ru(bpy)₃²⁺ complexes were absorbed on the bimetallic Au-Ag HSFs relative to on the bare Au structures. The increased amounts of Ru(bpy)₃²⁺ and Ru(bpy)₃^{2+*} complexes adsorbed on the bimetallic Au-Ag structures can result in more complexes involving in the ECL reaction on the electrode surface thus lead to an enhanced photo efficiency in the ECL process. In addition, the improvement of ECL photo efficiency on the Au-Ag HSFs can be also attributed to the orientation connection between the Au and Ag components, which provides an electron “highways” for the rapid electron migrations through the bimetallic interfaces. The rapid electron migrations through the bimetallic interfaces can cause a decrease of potential barrier in equation (1) that leads to a significant negative-shift of ECL onset voltage and an enhancement of the photo efficiency. It also facilitates the diffusion of C₂O₄²⁻ into the electrode and accelerates the reactions between the coreactant (C₂O₄²⁻ and CO₂^{·-}) and Ru(bpy)₃³⁺ to generate the excited state Ru(bpy)₃^{2+*} in equations (2) and (4). In order to support this viewpoint, under the same conditions, the ECL measurements were also carried out on the non-directional Au-Ag HSF sample as shown in Figure 3. The results in Figure 6 showed that the ECL intensity on the directional Au-Ag HSFs was much higher than that on the non-directional Au-Ag HSFs, implying that the interfacial feature on the bimetallic HSFs is an important factor to influence the ECL behavior.

We also determined the ECL stability on the Au-Ag HSF decorated electrode in the paper. It was shown that the Au-Ag HSF decorated electrode could be consecutively and repeatedly scanned at least 10 cycles from 0 to 1.25 V in PBS (pH 7.0) with 1 mM H₂C₂O₄ (Figure S3 in the supporting information), representing its good ECL stability. Based on the excellent ECL behaviors, we suggest that the Au-Ag HSFs modified ITO substrate can be potentially developed as the electrodes in highly sensitive electrochemical sensors.

4. Conclusions

In this paper, we reported the successful preparation of a novel bimetallic heterostructured material, Au-Ag heterostructured flower (HSF), in which the dewdrop-like Ag particles are site-specially and directionally grown on the petal tips of the Au flower. This route is developed based on the special morphology of bare Au flower and the selective facets covered by the PVP film. The developed Au-Ag HSFs were observed to display the interesting optical-electronic properties including SERS and ECL. The ECL properties is particularly attractive when considering that the emission intensity of Ru(bpy)₃²⁺ complex on the Au-Ag HSF decorated ITO electrode can be enhanced to almost 6-fold than that on the pure Au flower in the ECL reaction and the ECL onset voltage is negative-shifted significantly. The Au-Ag HSF decorated electrode thus can be used in the development of sensitive ECL sensor. Owing to the straightforward and controllability in the operations, the electrochemical deposition technique developed in this paper can be considered to apply in the preparations of other heterostructured materials in large-scale and low-cost for the potential applications in future.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

SEM images of bare Au flowers (a, b) and Au-Ag HSFs (c-g). The deposition times for (a) and (b) are 2 min and 10 min, respectively. (c): Au-Ag HSF with (a) as the building block, (d): a detailed Au-Ag heterostructure of (c), (e): large-scale Au-Ag HSFs. (f): Au-Ag HSF with (b) as the building block, and (g): a detailed Au-Ag heterostructure of (f).

Figure 2.

(a) TEM images of a petal of Au-Ag HSF, (b) HRTEM image of Ag component in Au-Ag HSF, (c) XRD pattern of Au flowers.

Figure 3. SEM image of Au-Ag heterostructured flower formed without using any surfactant (a) and an enlarged part of this heterostructured flower (b).

Figure 4. SERS spectra (a 633 nm line of a He-Ne laser as the excitation source) of R6G molecules absorbed onto the Au-Ag HSFs (a) and bare Au flowers (b).

Figure 5. ECL potential scanning curves of Au-Ag HSF decorated electrode (a) and pure Au flower decorated electrode (b) in 0.1 M PBS (pH 7.0) with 1 mM $\text{H}_2\text{C}_2\text{O}_4$ in solution at scan rate = 100 mV s^{-1} .

Figure 6.

ECL emission on the orientated Au-Ag HSFs (red line) and non orientated Au-Ag HSFs from Figure 3 (black line) in 0.1 M PBS (pH 7.0) with 1 mM $\text{H}_2\text{C}_2\text{O}_4$ in solution at scan rate = 100 mV s^{-1} .