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Rational construction of Au–Ag bimetallic island-shaped nanoplates for electrocatalysis

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Abstract

Active electrocatalysts are the key to water splitting for hydrogen production through the electrolysis. In this paper, 50 nm silver nanoplates were used as templates for synthesis of Au–Ag island-shaped nanoplates by controlling the surface chemistry. The guiding mechanism of polyvinylpyrrolidone (PVP, Mw = 40 000) to Au–Ag island-shaped nanoplates crystal was also further investigated. It is found that the surface energy of Ag nanoplates between (100) and (111) crystal planes can be regulated by varying the amount of PVP in the system. Then a uniform Au–Ag triangular island nanostructure was obtained. Compared with the Ag nanoplates catalysts, the Au–Ag island nanoplates catalysts show the superior catalytic performances in hydrogen evolution electrocatalysis (HER). These results demonstrate a new surface chemistry modification by PVP and a galvanic displacement reaction for designing the active electrocatalysts. More importantly, the Au–Ag island-shaped nanoplates show an unconventional growth mode of preserving the original Ag nano-triangular crystal structure. The enhanced performance in electrocatalysis can be mainly attributed to Au–Ag alloy structure, which allows the appearance of synergistic effects. The present work demonstrates the crucial roles of surface chemistry in catalysts synthesis, which may guide the design of active bimetallic catalysts.

1. Introduction

Bimetallic materials have attracted the extensive attention due to their several advantageous properties, which make them ideal electrocatalytic materials [1–3], such as appropriate free energy of adsorption for reactive intermediates, high stability and high electrical conductivity, etc [4, 5]. The core–shell structure [6, 7], alloy structure [8–10] and island structure [11] are the main bimetallic structures being studied. Among these selective bimetallic structures, Au–Ag nanoalloys exhibit the unique surface activity, chemical stability [12, 13], and biocompatibility due to its unique atomic and electronic structure, and quantum confinement effects, making catalytic properties of this system particularly unique, and therefore attract more and more researchers’ attentions [14]. The formation of the alloy is usually prepared by reduction in the presence of both precursor solutions [15, 16]. Generally, high temperature annealing is a major method to prepare the alloys [17–19]. It is usually achieved by using lattice mismatch between island phase and base [20]. Feng-Ru Fan et al first synthesized gold cubes, then epitaxially grown palladium on the gold cubes, and finally synthesized epitaxially grown island-like composite structures using lattice mismatch of gold and palladium nanocrystals (4.71%). However, the lattice constants of gold and silver are almost the same (suitability: 0.1%) [21]. Etching, dealloying corrosion kirkendall effect and pitting processes have been widely studied in high lattice match Au–Ag nanoalloys materials [22–24].
these processes destroy the old morphology and built defect at the atomic level. Chemistry modification of nanoparticles is usually controlled by using the surface active agent to regulate the forces among nanoparticles. PVP is one of the most common surfactants for the synthesis of metal nanomaterials. Huang used the PVP and iodide ions to synthesize highly dispersed rod-like nano palladium structures. Different morphologies can be synthesized by controlling the amount of PVP [25]. Xia et al. reported that the PVP was employed as a protective agent to prepare regular linear, triangular and cubic silver nanomaterials. It is pointed out that the PVP plays an important role in these systems [26]. And the ratio of PVP in the reaction solution determines the morphology and size of the product [27, 28]. Zeng et al. found that Ag nanoparticles could grow in (100) faces or (111) faces mode depending on the PVP or NaAC. Finally, the results proved the PVP has more affinity towards (100) faces than (111) facets [29]. This result provides a versatile way for the preparation of Ag nanocrystals with controllable size and shape for various applications. In this work, we have revisited and combined silver nanoparticles form Au–Ag alloy island nanoparticles at the nanoscale. The guiding mechanism of polyvinylpyrrolidone (PVP, $M_w = 40,000$) to Au–Ag island-shaped nanoparticles is an important factor based on chemistry modification. It is also proved that the surface energy of silver nanoparticles (100) and (111) crystal planes can be regulated by varying the amount of PVP in the system. PVP not only provide the approaching surface energy between lateral faces of the product [27, 28], which are converted according to Nernst equation, such as $\Delta G = -RT \ln K = -RT \ln \frac{[1]}{[2]}$.

2. Experimental section

2.1. Reagents

PVP ($M_w = 40,000$), Trisodium citrate (NaAC), Silver nitrate (AgNO$_3$), Sodium Borohydride (NaBH$_4$), ascorbic acid (AA), Chloroauric acid (HAuCl$_4$), and Hydrogen peroxide ($H_2O_2$) were purchased from Aladdin Industrial Corporation. All the chemical reagents were used without any further purification.

2.2. Synthesis of Ag nanoplates

Preparation of Ag nanoplates using double reducer method: 3 ml of 2 mM PVP solution was added to 50 ml of 0.1 mM AgNO$_3$ solution and stirred continuously at room temperature [28]. Then 3 ml of 30 mM trisodium citrate solution and 0.3 ml of 100 mM NaBH$_4$ solution was added successively. It can be observed that the color of solution immediately turns yellow. At this time, 0.24 ml of 30% hydrogen peroxide solution was added quickly and stirred continuously. After 10 min, the color of the solution turns from light yellow, yellow, red, purple and eventually to blue.

2.3. Synthesis of Au–Ag island-shaped nanoparticles

After magnetic stirring for 1 h, 2 ml of 2 mM PVP solution, 2 ml of 10 mM ascorbic acid, and 3 ml of 0.2 mM chloroauric acid solution was added to the solution quickly. Reaction time was 20 min at room temperature, centrifuged at 10,000 rpm for 10 min and dispersed in aqueous solution by ultrasound.

2.4. Morphological and structural analysis

Morphologies of the Ag nanoplates and Au–Ag island-shaped nanplates were tested by using a Transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) on a Philips CM10 instrument at an accelerating voltage of 160 kV.

2.5. Elemental analysis

The element in the near surface layers was determined with XPS, which was carried out with a Thermo scientific K-Alpa + system. Energy Dispersive x-ray (EDX) experiments were performed on JEOL JSM-6390LV instrument.

2.6. Electrochemical characterizations

The performance of electrocatalytic hydrogen evolution was carried out on Autolab (potentiostat PGSTAT-302 N) at 25 °C. Platinum wire electrode (1 cm$^2$) was used as counter electrode and Hg/HgO was used as reference electrode in 1 M KOH solution. All the electromotive forces mentioned in this paper are converted into reversible hydrogen electrodes (RHE), which are converted according to Nernst equation, such as $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 + 0.0591 \times pH$ (1) $E_{\text{RHE}}$ is the electrode potential, and $E_{\text{Hg/HgO}}$ is the potential measured with Hg/HgO as the reference electrode. Glass carbon electrode (GCE) is the working electrode.
2.7. The preparation of the catalyst

Typically, 20 ml Ag nanoplates or Au–Ag island-shaped nanoplates solution was centrifuged at 10 000 rpm for 10 min, and the supernatant was removed to obtain the precipitation. The product collected by centrifugation

Figure 1. The schematic illustration of PVP-guided synthesis of Au–Ag island-shaped nanoplates.

Figure 2. Characterization of Au–Ag island-shaped nanoplates. (a), (b) The transmission electron microscopy images of island-shaped structures; (c) The high resolution transmission electron microscopy image of the island-shaped structures; (d) The diffraction pattern of the island-shaped structures.

Mater. Res. Express 7 (2020) 025027 H Zhao et al
was dispersed in 2 ml ethanol. After fully mixing, 8 ml catalyst was dropped on the surface of glassy carbon electrode and dried naturally at room temperature. Finally, 2 ml ethanol was removed. The electrochemical hydrogen evolution performance was determined by wetting the electrodes with ultrapure water and then immersing them in the electrolyte.

3. Results and discussion

Ag nanoplates were prepared by using the double reducer method [30]. The size of synthetic triangle is about 50 nm (figure S1, supporting information is available online at stacks.iop.org/MRX/7/025027/mmedia). The formation of Au–Ag island-shaped nanoplates is illustrated in figure 1. The PVP exhibit more affinities towards (100) facets than (111) facets [29, 31]. Firstly, the (100) crystal surface energy of net Ag nanoplates is higher than the (111) crystal surface. Then, by adding moderate amount of PVP, the PVP molecule selectively adsorbs on the (100) crystal surface, the (100) crystal surface energy is approximately equal to the (111) crystal surface. After, by adding moderate amount of ascorbic acid (AA) and chloroauric acid (HAuCl₄), a galvanic cell is formed between Au nanoplates on the (111) of Ag nanoplates as positive electrode and Ag nanoplates as negative electrode. Finally, Au–Ag island-shaped nanoplates were obtained. Figure 2 shows the typical TEM image, HRTEM image, and electron diffraction patterns of Au–Ag alloy island structure. The gold particles were deposited unevenly and the morphology of Ag nanoplates were reserved. The crystalline feature of the Au–Ag alloy island structure was further implemented to explore by High-resolution TEM (HRTEM). The high degree of crystallinity is proved by the distinct lattice fringes extended over the whole nanoplates. The d-spacings of 2.5 Å correspond to the crystal (111) faces is the same to Ag nanoplates (figure S1, supporting information). Typically, all the surfaces in the HRTEM image can be assigned to (111) faces (figure 2(c)), implying a good single-crystal characteristic.

![Figure 3](image-url)
In order to determine the Au–Ag alloy island structure and components of each element, EDX spectrum, XPS spectrum and TEM-EDX mapping of Au–Ag island nanoplates were carried out separately (figure 3). EDX spectrum was employed to determine the composition of Au–Ag island-shaped nanoplates, about 70% of Au elements, and small amount of Ag element is due to part of silver without replacement between Ag nanoplates and chloroauric acid. XPS were tested for Au–Ag island-shaped nanoplates to investigate the element distribution in the near surface layers (figures 3(a)–(c)). The atomic ratios of Au/Ag are lower than the EDX spectrum results (tables S1, S2, supporting information). The difference in atomic ratio between EDX spectrum and XPS results imply that Ag is rich in the near surface layers [15]. The binding energy peaks at about 373.4 and 367.4 eV are assigned to Ag 3d_{3/2} and Ag 3d_{5/2}, which can be ascribed to metallic Ag crystal face of Ag respectively. The binding energy peaks at about 86.9 and 83.3 eV are assigned to Au 4f_{5/2} and 4f_{7/2} crystal face of Au respectively. XPS analysis suggests that the product contains Au and Ag elements. And Ag is richer in the near surface layers than inner layer [32]. To gain more information of the Au–Ag island-shaped nanoplates nanostructure, TEM-EDX mapping was carried out and the signal mappings are shown in figure 3(e). Similar outlines between Au (green) and Ag (red) is demonstrated in signal mappings, demonstrating the formation of the bimetallic alloy and implying that Au and Ag are homogeneously distributed on the nanoplates surface. The overlapping of Ag and Au displays a mixed green profile, indicating the existence of Au-rich regions. However, the elemental mapping demonstrates a hollow interior among Ag (red) mapping and Au (green) mapping, which is confirmed partial dissolution of Ag nanoplates.

To better understand the forming mechanism of Au–Ag island-shaped nanoplates structure, we investigated the different parameter including reaction temperature, different concentration of PVP and chloroauric acid. The morphology evolution is shown in figure S2 at different reaction temperature. From the results we can observed that the Au–Ag island-shaped nanoplates is formed at room temperature. By varying the amount of PVP in the system, we try to investigate the formation of the Au–Ag island-shaped nanoplates. As shown in figure 4, there is a large number of disordered gold nanoparticles without PVP (figure 4(a)). By increasing the amount of PVP, complete and uniform island structure is obtained. Some surface active molecules are selective adsorbed on crystal surfaces. Once adsorbed on a crystal surface, the free energy of the crystal surface is reduced, thus reducing or limiting the epitaxial growth in the direction of the crystal surface [29, 31, 32]. It is speculated...
that the (100) crystal surface energy is greater than the (111) crystal by comparing the amount of PVP in figures 4(a)–(c), so gold particles are mainly deposited at (100), however the framework of the Ag nanoplates is destroyed because of the replacement between the chloroauric acid and Ag nanoplates, which leads to the deposition of gold particles without template deposition and dispersion in the aqueous solution. With the increase of PVP, the surface energy of (100) and (111) crystal is approximation, and the migration rate of $[\text{AuCl}_4^-]$ is slowed down, so that they aggregate to form an island structure on (111). The co-reduction of AgCl and $[\text{AuCl}_4^-]$ and the reduction rate of $[\text{AuCl}_4^-]$ is faster than that of AgCl, the reduction rate of $[\text{AuCl}_4^-]$ is slowed down as the $[\text{AuCl}_4^-]$ ion in the solution is consumed. Then Au-rich Au–Ag island-shaped nanoplates is obtained. As described in the literature [31], the Au nano-frame structure was reconstructed after Oswald mature, thus forming a nano-ring. In this work, by reducing the amount of chloroauric acid, a triangular ring structure can be directly prepared (figures S3, S4 and S5, supporting information).

To investigate the electrocatalytic activity, Ag and Au–Ag island-shaped nanoplates were evaluated for hydrogen evolution (figure 5), the results were measured in N$_2$-saturated 1 M KOH solution using a typical three-electrode system. Measurements were performed on four duplicate samples which demonstrated the consistent activity, linear sweep voltammetry (LSV) curves of Ag and Au–Ag island nanoplates were studied as well. With the onset overpotentials necessary current density ranging from 196 to 168 mV. As shown in figure 5(a), the activity of the Au–Ag island-shaped nanoplates is compared with Ag nanoplates in the Tafel plot shown in figure 5(b). The figure 5(b) curve is based on the equation $h = b \log j + a$, $j$ is the current density and $b$ is the slope. The slope of Ag nanoplates and Au–Ag island-shaped nanoplates are 196 mV dec$^{-1}$ and 168 mV dec$^{-1}$ respectively. Literatures commented that Tafel slopes were 153 ± 15 mV dec$^{-1}$ and 180–200 mV dec$^{-1}$ at Au electrode and Ag electrode for the HER [33, 34]. By comparison, the Tafel curve value of the Au–Ag island-shaped nanoplates is lower than that of reported literatures under the similar testing conditions. This shows that the Au–Ag island-shaped nanoplates exhibit the higher activity which indicates that the kinetic speed of Au–Ag island-shaped nanoplates is faster in HER process. The electrochemical activity was evaluated by the linear slope of capacitive current to scanning rate as shown in figure 5(c). The performance data of HER catalysts were
obtained at different sweep speeds of 10 mV s\(^{-1}\), 20 mV s\(^{-1}\), 40 mV s\(^{-1}\), 80 mV s\(^{-1}\), 120 mV s\(^{-1}\) and 160 mV s\(^{-1}\) in the potential range of 0.22–0.33 V (versus RHE). It can be observed from figure 5(d) that the relationship between Ag nanoplates or Au–Ag island-shaped nanoplates and specific capacitance is linear at different sweep speeds. The electrochemical capacitance of Ag nanoplates and Au–Ag island-shaped nanoplates are 49.6\(\mu\)F cm\(^{-2}\) and 105.6\(\mu\)F cm\(^{-2}\) respectively. All above these data show that the Au–Ag island-shaped nanoplates bimetal with rough surface, large specific surface area, high density of active atoms and alloy synergistic effects. This unique characteristic can help to improve the performance of catalysts, as well as the active sites, and finally make Au–Ag island-shaped nanoplates better electrochemical performance.

4. Conclusions

In summary, Au–Ag island-shaped nanoplates with highly uniform size were successfully synthesized. The forming mechanism of Au–Ag island-shaped nanoplates crystal was also further studied, due to the Ag nanoplates (100) and (111) faces can be regulated by adding the moderate amount of PVP in the system. Using PVP guides and assembles the island structure of gold nanoparticles on the Ag nanoplates template. The Ag and Au–Ag island-shaped nanoplates were dispersed onto the glassy carbon electrode and the catalytic activity was determined toward HER in basic solution. The enhanced performances Au–Ag island-shaped nanoplates could be mainly ascribed to the rough surface of island structure and alloy synergistic effects. The present Au–Ag island-shaped nanoplates can be synthesized via a facile and rough one-pot procedure using Ag nanoplates template for the first time, which shows more advantages in mass production.

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