Research Article

Influence of Au Nanoparticle Shape on Au@Cu₂O Heterostructures

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Synthesis of metal-semiconductor heterostructures may allow the combination of function of the corresponding components and/or the enhanced performance resulting from the interactions between all the components. In this paper, Au@Cu₂O core-shell heterostructures are prepared by a seed-growth method, using different-shaped Au nanocrystals as the seeds such as nanorods, octahedra, decahedra, dots, and nanocubes. The results revealed that the final structure of Au@Cu₂O was greatly influenced by the shape of the seeds used. Exposure of Cu₂O{111} and Cu₂O{001} favored when the overgrowth happened on Au{111} and Au{001} surface, respectively. The size of the product can also be tuned by the amount of the seeds. The results reported here provide a thinking clue to modulate the shape and size of core-shell nanocrystals, which is useful in developing new materials with desired performance.

1. Introduction

Heterostructures have attracted enormous interest in the past decades, and due to that they could show enhanced and/or novel functions and performance, which is ascribed to the synergistic interactions between various components of them [1–8]. Core-shell structure is a typical type. For instance, core-shell nanofibers are popularly used in the field of tissue engineering and cell biology [1]. Also, core-shell hybrid structures have proven especially useful in electrolyte membrane fuel cell electrodes, supercapacitor, and catalysts [2–5].

Cuprous oxide (Cu₂O) is a typical p-type semiconductor. Because of its narrow forbidden band, Cu₂O can absorb the visible light efficiently and has a high absorption coefficient [9]. Then, it has potential applications in solar energy conversion and photocatalysis. Meanwhile, it was also frequently used in electrode materials, catalysts, and sensors. In the past few years, a number of Cu₂O nanostructures, including nanoplates [10], nanocubes [11, 12], octahedra [13, 14], spherical particles [15], nanocages [16–20], and nanowires [21–23], have been synthesized. Additionally, metal nanocrystals

could be taken as the core to grow Cu₂O shell and form metal@Cu₂O structures. For example, Huang's group has done pioneer work and found that gold nanocrystals can well direct the growth of Au@Cu₂O [24–27]. Our group proved that gold nanorods could act as the matrix for the epitaxial growth of Cu₂O and then allow fine size-tuning of Au@Cu₂O [28]. As expected, the reported Au@Cu₂O heterostructures exhibit distinct optical properties [26–30], gas sensing [31, 32], and catalytic performance [28, 33].

Previous reports on the synthesis of Au@Cu₂O always focused on using Au seeds to control the final shape of Cu₂O shell. In our work presented here, we first explored approaches for the synthesis of different-shaped Cu₂O nanocrystals, including octahedra, cubes, and truncated octahedra. Then, five kinds of Au nanocrystals including nanorods, octahedra, decahedra, dots, and nanocubes were prepared, which were introduced in the crystal growth systems of the above-mentioned Cu₂O nanocrystals for investigating the influence of the shape of Au seeds on the structures of Au@Cu₂O. The results show that Au{111} and Au{001} surfaces often lead to the exposure of Cu₂O{111} and Cu₂O{001}, respectively.

2. Materials and Methods

2.1. Synthesis of Au Nanorods. All the water used in this work was ultrapure water (18 M Ω). Gold nanorods were prepared in an aqueous solution by using a seeded growth method [28]. Firstly, the seed solution was prepared by adding 0.25 mL of 0.01 M HAuCl₄ into a solution of 9.75 mL of 0.1 M hexadecyltrimethylammonium bromide (CTAB) which was stirred rapidly in a plastic tube at the room temperature. The formation of the particles was initiated by the rapid addition of 0.6 mL of freshly ice-cold NaBH₄ (0.01 M). Then, the mixture was stirred for another 5 s. The resultant seed solution was left undisturbed for 2 h at a temperature of 26°C before use. For the growth of Au nanorods, 0.4 mmol of CTAB and 40 mL of ultrapure water were sonicated until the CTAB was completely dissolved in a vial. Then, HAuCl₄ (2.0 mL 0.01 M), AgNO₃ (0.4 mL 0.01 M), dilute HCl (about 0.8 mL 1.0 M), and L-ascorbic acid (0.32 mL 0.1 M) were added into the vial under gentle stirring to keep the pH value as 2.0 at 26°C. Subsequently, 0.096 mL of Au seed was injected into the growth solution quickly. The mixture was left undisturbed for 12 h at 26°C after stirring for another 5 s. The resultant hydrosol was washed and subjected to centrifugation (8500 rpm for 25 min, 3 times) to remove excess reagents and then was redispersed in water.

2.2. Synthesis of Au Nanocubes. The preparation of gold nanocubes was also using the seeded growth method introduced above. Specifically, when preparing the seed solution, the conditions were almost the same except that the aging time of the seed was 1 h. For the subsequent growth of Au nanocubes, a vial (100 mL) containing 0.4 mmol of CTAB and 40 mL of ultrapure water were sonicated until CTAB was completely dissolved. Then, 0.8 mL of 0.01 M HAuCl₄ and 3.8 mL of 0.1 M L-ascorbic acid were added into the vial. Subsequently, 0.02 mL of Au seed solution was injected into the growth mixture under vigorous stirring for 5 s. Finally, the flask stayed in a water bath at 26°C and was left undisturbed for 12 h. The resultant hydrosol was centrifugated for 25 minutes at 8000 rpm and then redispersed in water. This process was repeated three times to remove excess reagents.

2.3. Synthesis of Au Octahedral Nanocrystals. Au octahedral nanocrystals were prepared with a method reported by Li's group with some modifications [34]. In a typical synthesis, at the room temperature, 1.6 mL of polydimethyl diallyl ammonium chloride (PDDA) and 80 mL of diethylene glycol (DEG) were added into a three-neck flask with magnetic stirring for 5 min. Then, 20 mg of HAuCl₄ was put into the flask with stirring until it became homogeneous yellow. The reaction flask was immersed in an oil bath at 210°C for 30 min before it was cooled to room temperature. Then, the resultant hydrosol was added with 30 mL of ultrapure water followed by centrifugation at 12000 rpm for 20 min. The product was washed with ultrapure water three times to remove excess PDDA and DEG. Finally, the precipitate was redispersed in 60 mL of ultrapure water and stored at room temperature for further use.

2.4. Synthesis of Au Decahedral Nanoparticles. Au decahedral nanoparticles were synthesized according to a previous reported route [35]. Typically, 5.0 g of Polyvinylpyrrolidone (PVP) was dissolved by ultrasonication in 25.0 mL of diethylene glycol (DEG) at the room temperature, and this polymer solution was refluxed (245°C) for 5 min. Then, 2.0 mL DEG containing 20.0 mg HAuCl₄ was injected into the boiling solution, and the reaction mixture was allowed to reflux for 10 min. In this process, the color of solution changed from yellow to red. Subsequently, the mixture was cooled and diluted with 20 mL of ethanol. The precipitates were collected after centrifugation at 6000 rpm for 30 min and washed with ethanol thoroughly.

2.5. Synthesis of Au Dots. Firstly, hydrophobic Au nanoparticles were prepared according to a literature [36]. In a typical synthesis, under the protection of Ar, 0.5 mmol of HAuCl₄·4H₂O and 20 mL of oleylamine (OAm) were dissolved in 20 mL of tetralin at 25°C and stirred for about 10 min. Then, a solution of 1 mmol of tert-butylamine borane complex dissolved in 2 mL of tetralin and 2 mL of OAm was quickly injected into the above media. One hour later, the nanoparticles were precipitated by ethanol and collected by subsequent centrifugation. The precipitate was washed by ethanol and hexane three times. The final product was dispersed in 30 mL hexane for next use. 8 mL (0.0125 mmol) of Au nanoparticle dispersion, 0.144 g of SDS, and 30 mL of H₂O were emulsified together by intense ultrasound. After that, the emulsion was heated at 70°C for 2 h. The resulted dispersion was diluted to 50 mL by water for further use.

2.6. Synthesis of Cu₂O Octahedra. A 50 mL round-bottom flask including 0.721 g of sodium dodecyl sulfate (SDS) and 20 mL of ultrapure water was sonicated until the SDS was completely dissolved. Then, 0.0604 g Cu(NO₃)₂·3H₂O was added into the flask and was sonicated until the solution became homogeneous blue. Whereafter, the flask was immersed into a water bath at 30°C with magnetic stirring, followed by dropwise addition of NaOH aqueous solution (0.40 g/5 mL). After 20 minutes of magnetic stirring, 0.1 mL of hydrazine hydrate diluted with 5 mL of H₂O was also dropwise added into the flask slowly. 40 min later, the reaction finished. The products were collected by centrifugation at 4000 rpm for 2 min and then washed with the mixture of water and ethanol three times to remove excess reagents.

2.7. Synthesis of Cu₂O Nanocubes. When preparing Cu₂O nanocubes, the conditions were almost the same as the synthesis of Cu₂O octahedral nanocrystals except that 0.721 g of SDS was replaced by 0.24 g of SDS, and glucose solution (0.27 g/5 mL H₂O) took the place of N₂H₄·H₂O (0.10 mL/5 mL H₂O).

2.8. Synthesis of Cu₂O Truncated Octahedra. For a standard synthesis, PVP (3.40 g), CuCl₂·2H₂O (0.1705 g), sodium citrate (0.10 g), and ultrapure water (100 mL) were mixed together in a 250 mL round-bottom flask. The flask was immersed in an oil bath at 55°C. Then, NaOH solution

FIGURE 1: SEM images of the Cu_2O nanocrystals with different shapes: (a) octahedron, (b) cube, and (c) truncated octahedron.

(0.80 g/10 mL) was dropwise added into the flask slowly and stirred for another 30 min. Subsequently, L-ascorbic acid (1.0578 g/10 mL) was also dropwise added into the flask slowly. After vigorous stirring 3 h, the reaction finished. Similar separation and purification steps were used.

2.9. Synthesis of $\text{Au@Cu}_2\text{O}$ Heterostructures. Au nanorods, Au octahedra, Au nanocubes, Au decanedra, and Au nanoparticles were diluted to 32 mL, respectively, to obtain the proper concentration of Au precursors. Then, the Au precursor was added into the synthetic systems of different Cu_2O nanocrystals introduced above, respectively, with other conditions unchanged. By this means, we obtained the $\text{Au@Cu}_2\text{O}$ heterostructures.

2.10. Characterization. Field emission scanning electron microscopy (FESEM) images were taken on a Nova NanoSEM 200 scanning electron microscope. TEM and HRTEM images were recorded on a JEOL JEM-1200EX transmission electron microscope and FEI TecnaiG2 F20 S-Twin working at 300 kV. The phase of the product was determined by a Bruker D8 Advance X-ray powder diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm).

3. Results and Discussion

Firstly, pure Cu_2O nanocrystals were synthesized with the method listed above. All the synthesis was based on a redox reaction. $\text{Cu}(\text{OH})_4^{2-}$ firstly formed after the addition of the excess NaOH. The reducing agent then reduced it to Cu_2O . With different reductants and surfactants, we obtained three kinds of different Cu_2O nanocrystals. The combination use of SDS and N_2H_4 has produced Cu_2O octahedra, as shown in Figure 1(a). When glucose was used as the reductant instead of N_2H_4 , Cu_2O cubes could be obtained. Figure 1(b) displays the scanning electron microscope (SEM) image of the corresponding sample. In addition to the reductant, N_2H_4 could also act as the ligand coordinating with Cu^{2+} . But glucose do not have this function in this synthetic system. So they would lead to different-shaped Cu_2O crystals. The coordination

of N_2H_4 may accelerate the growth rate of $\{001\}$ faces and then induced the exposure of $\{111\}$ planes. In addition, PVP could tune the ratio between $\{001\}$ and $\{111\}$ facets [37]. Accordingly, with the assistant of proper amount of PVP, the exposure of both $\{001\}$ and $\{111\}$ faces could be realized. As shown in Figure 1(c), truncated octahedra formed when L-ascorbic acid and PVP were utilized as the reducer and surfactant, respectively. From the images, we can see that most of the particles are regular in shape and the size of them is within micrometer scale.

Then, we introduced different-shaped Au nanocrystals into the above reaction mixtures for the synthesis of $\text{Au@Cu}_2\text{O}$. Figure 2(a) shows the SEM image of as-prepared Au nanorods. When they were added into the system of preparing Cu_2O octahedra, the final $\text{Au@Cu}_2\text{O}$ was still octahedral (Figure 2(b)), showing epitaxial growth over Au rods. And the size of them decreased obviously. If the rods were put into the media of preparing Cu_2O cubes, the produced $\text{Au@Cu}_2\text{O}$ was also in cubic shape (Figure 2(c)), indicating that Au nanorods could well satisfy the formation of both $\{001\}$ and $\{111\}$ facets of Cu_2O . So when the rods were used as seeds in the growth mixture of Cu_2O truncated octahedra, the competition of the formation of $\{001\}$ and $\{111\}$ facets can disturb the homogeneous growth of the truncated octahedral, leading to some irregular polycrystals exposing several $\{001\}$ and $\{111\}$ facets (Figure 2(d)). The values of interplanar spacing of Au(111) and Au(002) are 0.2355 nm and 0.2039 nm, respectively, which are rather close to that of Cu_2O (111) and Cu_2O (002) (0.2427 nm and 0.2120 nm, resp.). Then the lattice mismatch is small enough for the epitaxial growth.

X-ray diffraction (XRD) patterns (Figure 3) reveal that the main species in $\text{Au@Cu}_2\text{O}$ octahedra, cubes, and truncated octahedra were Cu_2O . Because a small amount of Au seeds was used, the reflections of Au in the XRD profiles can hardly be recognized. Only a weak peak at 38.2° in Figure 3(c) can be found.

Au octahedra were also prepared as the seeds, using the method developed by Li and coworkers [34] with some modifications. Uniform octahedra were obtained and the typical

FIGURE 2: (a) SEM image of the typical as synthesized Au nanorods. (b) SEM image of Au rod@Cu₂O octahedron. (c) SEM image of Au rod@Cu₂O cube. (d) SEM image of Au rod@Cu₂O truncated octahedron.

FIGURE 3: (a) Typical XRD patterns of different samples: (a) Au rod@Cu₂O octahedra; (b) Au rod@Cu₂O truncated octahedra; (c) Au rod@Cu₂O cube.

FIGURE 4: (a) SEM image of as-synthesized Au octahedron. (b) SEM image of Au octahedron@Cu₂O octahedron. (c) TEM image of Au octahedron@Cu₂O cube.

SEM image is shown in Figure 4(a). When Au octahedra solution was added into the Cu₂O octahedron synthetic system, the morphology of Cu₂O has nearly unchanged (Figure 4(b)). Typical high-resolution transmission electron microscope (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of the Au@Cu₂O octahedra are shown in Figure 4(c) and Figure S1a (see Supplementary Material available online at <http://dx.doi.org/10.1155/2015/389790>). Obvious contrast in the Au@Cu₂O octahedra clearly reveals the core-shell structure and shows that one octahedron captures one gold seed. Compositional line profiles across a single Au@Cu₂O probed by EDS line scanning (Figure S1b, Supporting Information) further distinctly identify that the core is Au seed and the shell is Cu₂O. The gold octahedron loads in the center of the octahedron without any change of morphology. Both Au seeds and Cu₂O are enclosed by {111} faces, so the epitaxial growth is easy to realize. However, when Au octahedra were introduced into the synthetic mixture of Cu₂O cubes which expose {001} planes, the resulting core-shell structure became irregular. As shown in Figure 4(d), one core-shell particle

seems to be constructed by several cubes cross each other. Therefore, Au{111} is suitable for the epitaxial development of Cu₂O{111} but not Cu₂O{001}.

Gold decahedral nanoparticles which were also bounded by {111} facets have been synthesized as the seeds. The SEM image of them is given in Figure 5(a). It can be seen that the particles are not pure in shape. Some octahedra, truncated octahedra, and prisms also exist in the sample. When they were added into the synthetic system of Cu₂O nanocubes, similar results to Figure 4(d) were obtained, as displayed in Figure 5(b). Because of the impurity of the Au seeds, when they were introduced into the synthetic system of Cu₂O octahedra, the products are also not pure in shape, as shown in Figures 5(c) and 5(d). TEM images (Figures 5(e) and 5(f)) show two typical particles of the product. The bright/dark contrast in the pictures clearly reveals the core-shell structure. The projection of the core in Figure 5(e) describes that it is an octahedron, and then it leads to octahedral Au@Cu₂O. The projection of the core in Figure 5(f) reveals that it is a decahedron having five {111} surface planes. Although it is suitable for the formation of Cu₂O{111} facets, its twin

FIGURE 5: (a) SEM image of the as-synthesized Au decahedra. (b) SEM image of Au decahedron@Cu₂O cube. SEM images of Au decahedron@Cu₂O octahedron: (c) 1 mL of Au decahedra solution and (d) 8 mL of Au decahedra solution. (e) TEM image of Au octahedron@Cu₂O octahedron. (f) TEM image of Au decahedra@Cu₂O octahedron.

FIGURE 6: (a) SEM image of the as-synthesized Au dots. (b) SEM image of Au dot@Cu₂O octahedron. (c) SEM image of Au dot@Cu₂O cube. (d) SEM image of the typical as-synthesized Au cube. (e) SEM image of Au cube@Cu₂O octahedron. (f) SEM image of Au cube@Cu₂O cube.

structure caused the development of Cu₂O{111} toward five directions and led to Au@Cu₂O star structure with five corners (Figure 5(f)). The typical HAADF-STEM image of the sample and compositional line profile across a single Au@Cu₂O probed by EDS line scanning (Figure S2, Supporting Information) further proved the core-shell structure.

Finally, small gold dots and cubes were used as the seeds. Figure 6(a) is the TEM image of the gold dots, which are spherical and have narrow size distributions. Figure 6(d) depicts the SEM photograph of as-prepared Au cubes. Due to the small size (~3 nm) of the dots, their surface is more complicated. The exposed facets are not the usual planes,

which has led to irregular Au@Cu₂O structures when they act as the seeds in the synthetic media of Cu₂O cubes and octahedra (Figures 6(b) and 6(c)). Au cubes are larger, but some of them lost corners, making some of the Au@Cu₂O structures irregular (Figures 6(e) and 6(f)).

4. Conclusion

In conclusion, we have synthesized Au@Cu₂O core-shell heterostructures by use of Au nanorods, octahedra, decahedra, dots, and nanocubes as structure directing cores for the overgrowth of Cu₂O crystals. The shape of Au cores has great influence on the morphology of the shells. Au{111} and Au{001} surface is beneficial to the exposure of Cu₂O{111} and Cu₂O{001}, respectively. The size of Au@Cu₂O heterostructures can be diminished with respect to pure Cu₂O nanocrystals. These results are helpful for us to synthesize desired materials for scientific and technical applications.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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