Ag microtubes with novel pentagon pores templated by fivefold symmetric Cu microrods

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Abstract

In this work, we report a green, simple and fast method to fabricate novel Cu@Ag core@shell and Ag microstructures. According to galvanic replacement, the novel pentagon-shaped pores of Ag can form from the shape memory effect of fivefold symmetric Cu template. Additionally, the Ag and Cu@Ag crystals with different microstructures can be controlled by changing the complexing agent,

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solvent, as well as the ion concentration and source of silver. This work suggests that a shape memory of template can be used for micro/nanostructure control.

KEYWORDS: A. metals; B. chemical synthesis; C. electron microscopy; D. X-ray diffraction

1. Introduction

Recently, silver materials have caused great attention due to its wide applications in the fields of catalysis [1], optoelectronic device [2] and Raman spectroscopy [3,4]. As is known, silver with various morphologies can be used in different fields due to its diverse physical and chemical properties. For example, silver nanowires and nanoshells can be used as conductive electrodes in solar cell [5,6] and magneto-optical material [7] in high technology areas, respectively. Up to now, various morphologies of Ag such as nanowires [1,5], nanoplates [6,8], nanoshells [7,9], nanobelts [6], nanodisks and dendrites [6,8] have been fabricated. Meanwhile, various methods have been used to design silver structure. Among them, galvanic replacement is a popular method to design metal materials. For example, Hong *et al.* [10] have reported that a galvanic reaction will be occurred immediately when metallic Ag is mixed with HAuCl_4 in an aqueous solution system. Hence, it is still a challenge to design the metal core@shell structure.

Herein, we will report a simple, green and rapid method to synthesize ultralong (about 20 μm) silver microtube with pentagon pores for the first time. Besides, the thickness of Ag shell of Cu@Ag microtube also can be controlled by increasing the amount of AgNO_3 added into the solution during the transformation from Cu to Ag. Moreover, Ag nanoplates and nanospheres also can be obtained by adjusting other experimental parameters, including complexing or dispersing agents, pH and silver ion species.

2. Experimental

2.1. Materials and preparation

All of the chemical reagents used in this experiment were analytical grade.

Synthesis of fivefold symmetric copper. In a typical experiment, 0.01 mol disodium ethylenediamine tetraacetate (EDTA- Na_2), 0.01 mol CuSO_4 , 0.01 mol hexamethylenetetramine (HMT) and 0.8 g cetyl-trimethyl ammonium bromide (CTAB) was added into 30 mL distilled water successively, with magnetic stirring. After the solution became limpid, the mixture of precursor suspension was transferred into a Teflon-lined stainless steel autoclave and maintained at 150 °C for 5 days. When the reaction was over, the autoclave was cooled down to room temperature naturally, and the as-obtained samples were separated by centrifugation, washed with water and absolute alcohol several times, and then dried at 60 °C for 12h.

Synthesis of silver with pentagon pore. The silver microtube with pentagon pore samples was synthesized by a simple galvanic displacement reaction. Typically, 0.05 g of the as-prepared fivefold symmetric copper powders was added to the distilled water, then, 0.8 g of polyvinyl pyrrolidone (PVP) was added into above solution under magnetically stirred for 30 min. Then, 10 mL of AgNO_3 (3.16 g) was added into the suspension. After several seconds, the as-obtained sample was washed with distilled water several times and dried at 60 °C for 5h. In order to investigate the effect of PVP added on silver structure, we prepared Ag with x g ($x = 0, 0.2, 0.4, 1.2, 1.6$ g) PVP added while the other conditions remained the same.

Synthesis of Cu@Ag core@shell. Typically, 0.05 g of the as-prepared fivefold symmetric copper powders was added to the distilled water, then, 0.8 g of polyvinyl pyrrolidone (PVP) was added into above solution under magnetically stirred for 30 min. Then, x g ($x = 0.2, 0.4, 0.8, 1.2$ and 1.6 g) of AgNO_3 was added into above solution. After several seconds, the as-obtained sample was washed with distilled water several times and dried at 60°C for 5h.

Synthesis of silver nanospheres. Simply, using 0.01 mol vitamin C (Vc) to instead of PVP while the other conditions are keep consent with silver microtube.

Synthesis of silver nanoplates. Typically, using 30 mL absolute ethyl alcohol (EtOH) to instead of distilled water while the other conditions are keep consent with preparation of silver microtube.

Synthesis of the other silver micro/nanostructures. The typical process is keep consent with preparation of silver microtube, while the detail changes are listed in the corresponding figures.

2.2. Characterization

The crystal structures of the samples were determined by X-ray powder polycrystalline diffractometer (Rigaku D/max-2550VB), using graphite monochromatized Cu K_α radiation ($\lambda = 0.154$ nm), operating at 40 kV and 50 mA. The XRD patterns were obtained in the range of $20 - 80^\circ$ (2θ) at a scanning rate of 7° min^{-1} . The samples were characterized on a scanning electron microscope (SEM, Hitachi SU-1510) with an acceleration voltage of 15 keV.

3. Results and discussion

3.1 Effect of the PVP amount added

The effect of PVP amount added on the samples was investigated firstly. Fig. 1 shows the scanning electron microscopy (SEM) images of Ag micro-structure. At lower concentration of PVP (0 and 0.2 g), the as-prepared samples display irregular morphology (Fig.s S1a and S1b, seeing electronic supporting information (ESI[†])). With increasing the amount of PVP added on the samples (0.4 g), the Ag microtubes have formed, but there are still some irregular particles (Fig. S1c, ESI[†]). Further increasing the added amounts of PVP (0.8, 1.2 and 1.6 g), it is clear that most of the morphologies are microtubes shown in Fig.s 1a, 1b and 1c. The XRD patterns of silver microtube synthesized in PVP (0.8 g) system is shown in Fig. 1d, which confirms the phase-pure silver was obtained. Fig.s S2a and S2b show the TEM images of the Ag sample, confirming the formation of the Ag microtubes. The selected-area electron diffraction (SAED) patterns reveal the single-crystalline nature of the Ag microtubes (Fig. S2c). Additionally, the lattice fringe spacing of 0.24 nm agrees well with the (111) plane of cubic Ag (Fig. S2d). Interestingly, the silver microtubes with pentagon pores have completely inherited the structure of fivefold copper. The above results indicate that the amount of PVP added plays a key role in the formation of Ag microtube with pentagon pore, which will be explained in the following section.

It is well known that the polyvinyl pyrrolidone (PVP) is an excellent dispersant which is used by many other researchers. Zhang *et al.* [11] and Qiao *et al.* [12] have

reported that PVP can form a mixture with silver ion, which can strongly absorb in Ag surfaces and protect the silver particles from growing and agglomerating. Zheng *et al.* [13] and Xia *et al.* [14] have reported that PVP preferentially absorbs on the {100} facets of Ag due to its higher surface energy. But, the influences of PVP used in our system have some differences with them. Firstly, mixing up the fivefold Cu with a certain amount of PVP to form a uniform solution, and then silver ion was added into the above solution. The purpose of this is to make the Cu micro-wires dispersing in PVP solution more uniformly, and then PVP absorbed in the surfaces of Cu to suppress the reaction between Cu and Ag ion. Another, as we know that PVP can easily coordinate with Ag ion and compound with Ag [12]. Therefore, the reaction rate between Cu and Ag ion can be controlled well by PVP. As a result, the pentagon structure can be restrained well during the transformation from Cu to Ag.

3.2 Effect of AgNO₃ amount added

Furthermore, the added amount of AgNO₃ was varied from 0 to 3.16 g to investigate the effect of the added amount of silver ion while the other conditions were kept constant. It is obvious that with increasing the amount of Ag ion, the more particles of Ag occurred in the surface of Cu and the diameter of Cu micro-wire decreased gradually (Fig.s 2a-2e), meanwhile, the Cu@Ag core@shell structure formed. The XRD patterns of phase-pure copper and Cu@Ag core@shell sample (AgNO₃ = 1 mL) are shown in Fig. S3 (ESI[†]) and Fig. 2f, respectively. At the amount of AgNO₃ = 3.16 g, the Cu metal is completely despaired and Ag microtube with pentagon pore formed shown in Fig. 2e. Further increasing the amount of silver nitrate, there is no further changing in morphology and size of Ag metal (Fig. S4, ESI[†]).

Herein, by adjusting the added amount of AgNO_3 , we can control the thickness of Ag shell of Cu@Ag .

3.3 Effects of complexing agent and silver source

Moreover, the synergistic effect of PVP and other complexing agent on silver structure was also studied in this work. The SEM images of as-obtained samples are shown in Fig. 3. With the acetic acid and trisodium citrate added into system, the surface of Ag microtube becomes smooth and uniform (Fig. 3a and 3c). Additionally, with tetrahydrofuran (THF) added into solution, no silver microtube obtained (Fig. 3b). What is more, both microtubes and micro-rods can be observed in Fig. 3d and 3e, which are synthesized in trisodium citrate and ethylenediamine (EDA) system without PVP, respectively. Some other complexing agents with and without PVP have also been discussed (Fig. S5 and S6, ESI[†]). It is obvious that triethanolamine, ethylene glycol and Vc acting with PVP have a negative effect on the morphology of Ag microtube structure (Fig.s S5c-S5e, ESI[†]). But the mechanism is not clear. From Fig. S5b (ESI[†]), we can see that the microtubes were self-assembled of nanosheets uniformly. If without PVP, both the irregular particles and nanosheets will be obtained, but cannot assemble to microtubes shown in Fig. S6b (ESI[†]). Herein, we concluded that the function of PVP was to control the reaction rate and the microtube structure. Meanwhile, the function of HTM is to control the formation of Ag nanosheets. So, the Ag microtube assembled by nanosheets is an emergent property resulting from interactions among the two factors. But the specific interaction mechanism between PVP, HTM, copper and silver still need further study.

In addition, the influence of silver source was further investigated. The SEM images of the as-obtained samples are shown in Fig. 4. It is clear that the surfaces of microtubes obtained in $C_2AgF_3O_2$ and $Ag(NH_3)_2OH$ systems are smoother than that in $AgNO_3$ system. It may due to the releasing rate of silver ion in $C_2AgF_3O_2$ and $Ag(NH_3)_2OH$ system are slower than that in $AgNO_3$ system. What is more, the influence of solvents and HNO_3 amounts added on the morphology of Ag crystal during the transformation from Cu to Ag was also investigated in this work, which is stated in supporting information (Fig. S7 and S8, ESI[†]).

4. Conclusions

The new pentagon-shaped pores of Ag microtubes form from the shape memory effect of fivefold symmetric Cu template. Further, we can control the Ag shell thickness of Cu@Ag core-shell structure by adjusting the amount of $AgNO_3$ added into the solution. Our further work will concern on the formation mechanism of various morphologies and its applications.

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[†] Electronic supplementary information (ESI)

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Figure List

Fig. 1

Fig. 1. Effects of the PVP amount added on the morphology of Ag: (a) 0.8g; (b) 1.2g; (c) 1.6g; (d) XRD of Ag microtube synthesized in PVP (0.8 g) system.

Fig. 2

Fig. 2. SEM images of the samples prepared at different AgNO_3 (1.86 mol/L) added: (a) 0 mL; (b) 250 μL (0.08 g); (c) 500 μL (0.16 g); (d) 8 mL (2.53 g); (e) 10 mL (3.16 g); (f) XRD of Cu@Ag with core@shell synthesized in 8 mL of AgNO_3 and 0.8 g PVP system.

Fig. 3

Fig. 3. SEM images of the samples synthesized at different additives in the presence of PVP (0.8 g): (a) acetic acid (0.01 mol); (b) THF (0.01 mol); (c) trisodium citrate (0.01 mol). SEM images of complexing agent without PVP of samples; (d) trisodium citrate (0.01 mol); (e) ethylenediamine (EDA, 1 mL); (f) and (g) are the magnifying images of (e).

Fig. 4

Fig. 4. Effect of silver source on the sample: (a) AgNO_3 ; (b) silver trifluoroacetate ($\text{C}_2\text{AgF}_3\text{O}_2$); (c) $\text{Ag}(\text{NH}_3)_2\text{OH}$ solution.

Graphic Abstract

Ag microtubes with interesting pentagon pores form via a simple displacement reaction by using fivefold symmetric Cu as template