

Research Article

Electrochemical Fabrication of Shape-Controlled Copper Hierarchical Structures Assisted by Surfactants

Huaping Dong,¹ Yajun Wang,² Feifei Tao,¹ and Linxia Wang¹

¹Department of Chemistry and Chemical Engineering, Shaoxing University, Shaoxing, Zhejiang 312000, China

²College of Biological and Environmental Engineering, Zhejiang University of Technology, Zhejiang 310014, China

Correspondence should be addressed to Feifei Tao, fingal.tao@gmail.com

Received 1 August 2011; Accepted 21 September 2011

Academic Editor: William W. Yu

Copyright © 2012 Huaping Dong et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Various copper hierarchical structures assisted by surfactants were successfully fabricated combined with the electrodeposition technique. To the best of our knowledge, it is the first report on the controlled synthesis of metal copper hierarchical structures. All of the products synthesized in the presence and absence of surfactants, such as cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), or polyvinylpyrrolidone (PVP), were face-centered cubic copper, characterized by X-ray diffraction (XRD), indicating the surfactant-independent crystal structure. However, supplementing surfactants is helpful to construct hierarchical structures and exerts an important influence on copper morphologies. The absence of surfactants led to the formation of the nubby structures, while the use of surfactants resulted in the synthesis of the flower, dendrite, and sphere-like hierarchical morphologies. The effect of deposition time on the copper morphologies was investigated by scanning electron microscopy (SEM), and the possible formation mechanism of the copper hierarchical structures with various morphologies was discussed.

1. Introduction

In recent years, nanostructured materials with special morphologies have attracted considerable research interests for their unique magnetic, optical, and electronic properties, and potential applications [1–4]. Hierarchical materials constructed by nanostructures have been the research hotspots due to their size, or shaped-dependent properties, which are mainly determined by their composition, crystallinity, size, and morphology [5]. Therefore, in order to obtain prominent performance, much effort has been made on the composition, size, and morphology control of various materials. In the current stage, metallic hierarchical structures with various morphologies [6, 7] have been attracting extensive attention because of their potential applications in nanoscale devices, sensors, nonlinear optics, and magnetic storage media. So far, many synthetic methods including solvothermal reduction, electrodeposition, and template growth have been developed to prepare metallic hierarchical materials [8–10]. Among them, electrodeposition has received extensive attention due to the rich variation of

growth morphologies and the simplicity of the experimental setup [11–13].

The importance of metal copper for the next-generation on-chip interconnection has been well established since the first discovery that copper wiring has advantages of lower resistance, higher allowable current density, and increased scalability compared with the Ti/Au (Cu) wiring. Increasing efforts have been devoted to the fabrication of metal copper nanostructures with various morphologies in recent years due to the potential applications in biomimetic design [14], sensor [15], and catalysis [16]. However, there are few of the works on the preparation of metal copper nanostructures [14, 16], especially self-assembled hierarchical structures [17]. The lack of a facile method to selectively fabricate copper hierarchical structures assembled by nanomaterials with different morphologies still remains a huge obstacle to the material researchers.

In this paper, we reported a novel and simple method to successfully fabricate the copper hierarchical structures with morphological variety, such as flower-like structures self-assembled by nanosheets, dendrite-like crystals constructed

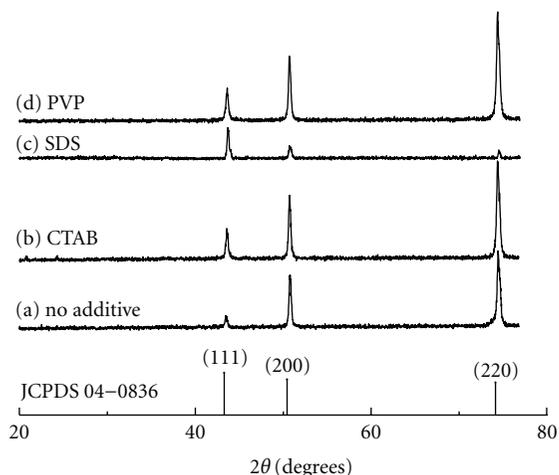


FIGURE 1: XRD patterns of the products fabricated with no additive (a), CTAB (b), SDS (c) and PVP (d) in the electrolyte.

by 1D nanostructures, and the large congeries built by sphere-like structures, by using the electrochemical deposition technology at room temperature. The metal copper materials with self-assembled structures can be selectively fabricated in the presence of surfactants. To the best of our knowledge, it is the first report on the controlled synthesis of various metal copper self-assemblies. This method is very facile, rapid, and effective for preparing the metal copper hierarchical structures with high yields.

In our reaction system, copper chloride is used as copper source, and cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS) or polyvinylpyrrolidone (PVP) as the shape-controllers that could effectively adjust the morphologies of metal copper hierarchical structures. And the copper structures with different morphologies were in detail investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Based on the experimental data, the possible formation process of metal copper hierarchical structures with various morphologies was discussed.

2. Experimental Sections

2.1. Chemical Reagents. Copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), sulfuric acid (H_2SO_4), cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), and polyvinylpyrrolidone (PVP) were purchased from Sino-pharm Chemical Reagent Co., Ltd. All chemicals were of analytical grade and used without any further purification. All solutions were prepared using deionized water.

2.2. Preparation of Metal Copper Hierarchical Structures. The electrodeposition solution consisted of CuCl_2 ($0.1 \text{ mol} \cdot \text{L}^{-1}$), H_2SO_4 ($0.1 \text{ mol} \cdot \text{L}^{-1}$), various additives at the same concentration of $40 \text{ g} \cdot \text{L}^{-1}$, such as CTAB, SDS, and PVP, and deionized water. Electrodeposition was carried out in a two-electrode electrochemical cell. Both the anode electrode and cathode electrode were composed of the copper foils with the diameter of 0.8 cm, the length of 1.5 cm, and the thickness

of 0.1 cm. The two electrodes were placed parallel to each other and perpendicularly inserted into the electrodeposition solution. The potentiostatic electrodeposition was carried out at the electric potential of 1.0 V for varying deposition time without heating or stirring.

2.3. Sample Characterization. After reacted for several minutes, the cathode as the working electrode was taken out, and carefully rinsed with deionized water more than five times, then allowed to air-dry before characterization. The samples for scanning electron microscopy (SEM) were directly fixed to a SEM stub and were sputtered with a 5 nm layer of platinum. Images were obtained with a JEOL JSM-5610 LV SEM operating at an accelerating voltage of 15 kV. The specimens for structural characterization were carefully peeled from the foils and subjected to X-ray diffraction (XRD) using a D/Max-RA diffractometer with $\text{Cu K}\alpha$ radiation.

3. Results and Discussion

3.1. XRD of Metal Copper Materials. Figure 1 shows the XRD patterns of the products fabricated at the electric potential of 1.0 V for 10 min in the absence of surfactant and in the presence of CTAB, SDS, and PVP in the electrolyte, respectively. The diffraction peaks in the range of $20^\circ < 2\theta < 80^\circ$ can be indexed as the face-centered cubic (fcc) directions of Cu (111), (200), and (220), in good agreement with Joint Committee on Powder Diffraction Standards (JCPDS) no. 04-0836. No peaks from other phases were found, suggesting the high purity was obtained. Besides, it is further indicated that supplementing surfactants does not change the crystal structure of the products but obviously affects the peak intensities of metal copper materials. Compared with the peak intensity ratio of 100:46:20 in JCPDS no. 04-0836, the ratios of (111), (200), and (220) peak intensities of various copper materials assisted by no additive, CTAB, SDS, and PVP were 100:416:600, 100:210:320, 100:42:29, and 100:195:329, respectively. On the other hand, for the as-prepared product in the presence of SDS (curve c in Figure 1), the diffraction peak strength at about 43° was obviously higher than those at about 50° and 74° , similar to that of JCPDS no. 04-0836. However, these phenomena did not happen on the products fabricated without additive or with other surfactants, attributing to the different growth rate of various directions of metal copper crystals. In contrast with the crystal structure of the products, supplementing surfactants has a notable effect on the growth rate of different direction of the as-prepared products.

3.2. Effect of Surfactants on Metal Copper Hierarchical Structures. To get an insight into the formation process of metal copper hierarchical structures with different morphologies, time-dependent experiments were carried out and the products were inspected by SEM. Figure 2 shows the SEM images of the products with no additive at the varying deposition time. At the beginning of the deposition, the ruleless nubby structures with inconsistent size were first formed after reacted for 5 min (Figure 2(a)). The SEM image

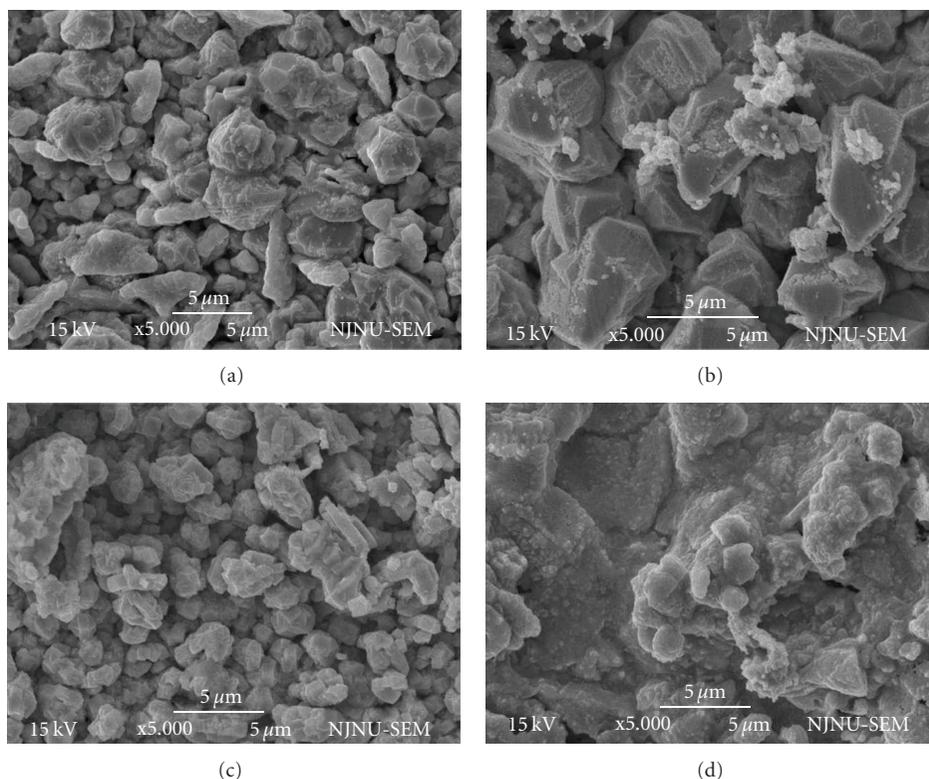


FIGURE 2: SEM images of the products with no additive in the electrolyte at the different deposition times of 5 min (a), 10 min (b), 20 min (c), and 30 min (d).

of the product formed at 10 min showed that the size of nubby structures increased with the increasing deposition time and came up to $5\text{--}8\ \mu\text{m}$ (Figure 2(b)). The crinkles on the surface of nubby structures indicated that the products were constructed by many small blocks. As the reaction time increased to 20 min (Figure 2(c)), the small nubby structures with the size of about $3\ \mu\text{m}$ were observed due to the further splitting of the former larger nubby structures. At the deposition time of 30 min, the ruleless nubby structures further grew up on the foil, piled up each other, and constructed the copper film (Figure 2(d)). The above experimental results show that in the absence of additive the similar growth rates in different directions lead to the formation of the ruleless nubby structures. With the prolonged deposition time, the nubby structures gradually grow up, and then split into many small blocks which further developed, and finally contribute to the formation of the copper film.

Figure 3 shows SEM images of the products by adding CTAB in the electrodeposition solution at varying deposition time. At the beginning of the deposition, the nanosheets with the thickness of about $50\ \text{nm}$ perpendicularly grew up on the foil and interwove each other, shown in Figure 3(a). With the increasing reaction time, taking the old nanosheets as the new growth points, the secondary sheet-like structures gradually matured, which caused the nanosheets with similar thickness to develop in number and to become bushier, forming the nanosheet arrays on the substrate (Figure 3(b)). After reacted for 30 min, the nanosheets further grew up and

some sphere-like structures wrapped in the inner part of nanosheets were observed (Figure 3(c)). When the reaction time lasted for 1 h, there were some flower-like structures self-assembled by nanosheets in high yield with uniform size of about $15\ \mu\text{m}$, shown in Figure 3(d). The above experimental results clearly indicate the formation process of the flower-like hierarchical structures constructed by nanosheets. Assisted by CTAB, the different growth rates of metal copper in each direction promote vertical growth of the copper nanosheets with the uniform thickness on the substrate. With the rapid growth of nanosheets, the growth of the crystal nucleus of the inner part wrapped in nanosheets is easier to be affected by the electrolyte diffusion, leading to the lack of protection of CTAB in the growth process of metal copper. Therefore, the products further develop into the sphere-like structures with micrometer size and come up as shown in the inset of Figure 3(c), similar to the formation of crystal copper without additive. When the sphere-like particles emerged from the nanosheets come into contact with the electrolyte owing to the rapid growth rate, CTAB further promotes the appearance of the sheet-like structures and finally leads to the formation of the flower-like hierarchical structures self-assembled by nanosheets. Based on the above analysis, adjusting the electrodeposition time can effectively control the formation of nanosheet arrays and flower-like hierarchical structures.

Figure 4 shows the SEM images of the products assisted by SDS in the electrolyte at varying deposition time. At

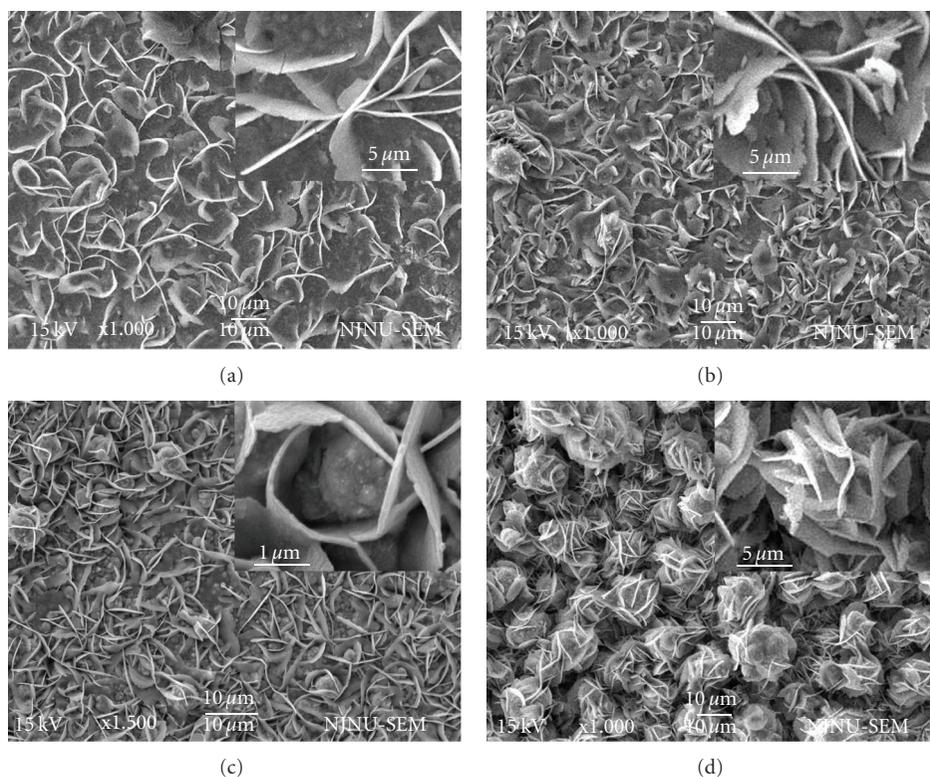


FIGURE 3: SEM images of the products by adding CTAB in the electrolyte at the different deposition times of 10 min (a), 20 min (b), 30 min (c), and 1 h (d). The insets in Figures 3(a)–3(d) show the magnification SEM images of the corresponding photos.

the beginning of the deposition, the prototype of dendrite-like structure with cross-linked branches was first formed and covered the whole substrate after being reacted for 1 min (Figure 4(a)). With the increasing deposition time, the branches of dendrite-like structure gradually developed and independently grew up (Figure 4(b)). The SEM images of the products reacted for 5 min (Figure 4(c)) which indicated that the trunks and branches of the dendrite-like structures further evolved and became thicker. And taking the old branches as the new growth points, the sub-dendrite-like structures occurred on the branches. After being reacted for 10 min, the sub-dendrite-like structures with the uniform length of about $2\ \mu\text{m}$ wove together (Figure 4(d)). The above experimental results clearly show that under the assistant role of SDS, the products first nucleate on the foil and grow at one-dimensional approach, and then the dendrite-like structures are gradually formed. With the increasing deposition time, the instability of the branches promotes the appearance of sub-dendrite-like structures with small size, which further evolve and interweave together, and finally construct the dendrite-like crystals constructed by 1D nanostructures. The formation of dendrite-like copper crystals is a nucleation-growth-regrowth process. It is an effective approach to rapidly fabricating the dendrite-like crystals.

Figure 5 shows the SEM images of the products with PVP in the electrolyte at the varying deposition time. At the beginning of the reaction, only a few protuberances of

approximately $1\ \mu\text{m}$ irregularly were arranged on the foil, shown in Figure 5(a). With the increasing reaction time, the protuberances further developed, and gradually wove together, then became the sphere-like structures with the diameter of about $2\ \mu\text{m}$ (Figure 5(b)). When the reaction time lasted for 20 min, the sphere-like structures assembled each other and became the larger congeries as shown in the inset of Figure 5(c). The above experimental results distinctly display that assisted by PVP, the same growth rates in all directions promote the formation of the sphere-like structures. With the further evolution, the sphere-like structures assemble each other and finally form the large congeries constructed by sphere-like structures.

Based on the above experimental results, it is clearly shown that the copper hierarchical structures with different morphologies, such as flower-like structures self-assembled by nanosheets, dendrite-like crystals constructed by 1D nanostructures, and the large congeries built by sphere-like structures, can be effectively fabricated by using the additives of CTAB, SDS, and PVP. The schematic presentation of the fabrication procedure of metal copper materials fabricated by the assistance of CTAB, SDS, and PVP was shown in Figure 6, clearly illustrating the evolution of various copper hierarchical structures. Due to some reasons, such as the interactions of copper ions and the additives and the selective adsorption of the surfactants on certain crystallographic planes, the difference of the additives has an important effect on the growth rate of the different orientation of

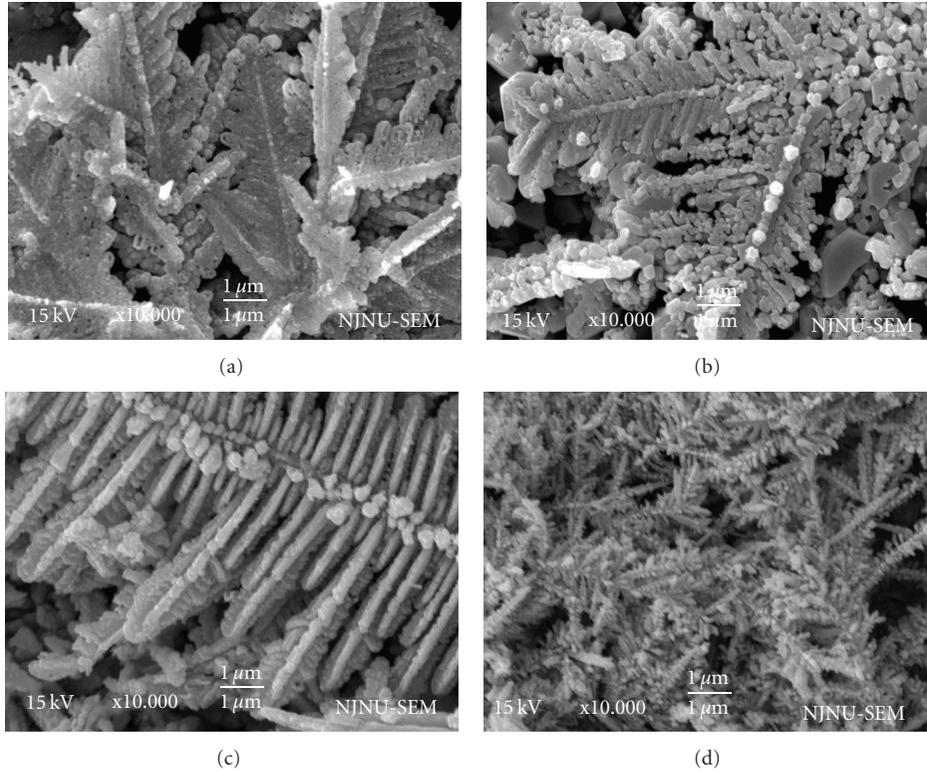


FIGURE 4: SEM images of the products by adding SDS in the electrolyte at the different deposition times of 1 min (a), 3 min (b), 5 min (c), and 10 min (d).

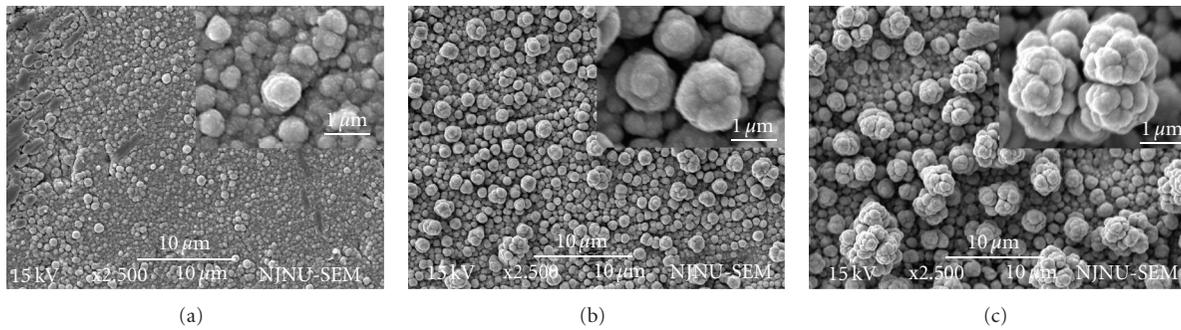


FIGURE 5: SEM images of the products by adding PVP in the electrolyte at the different deposition times of 5 min (a), 10 min (b), and 20 min (c). The insets in Figures 5(a)–5(c) show the magnification SEM images of the corresponding photos.

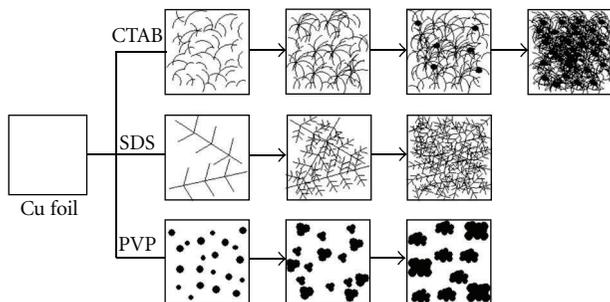


FIGURE 6: Schematic presentation of the process involved in the preparation of various metal copper hierarchical structures assisted by CTAB, SDS, and PVP.

metal copper during the electrodeposition, resulting in the formation of metal copper self-assemblies with various morphologies. The exact role of the additives in the formation of copper hierarchical structures is not clear at this moment and further studies are needed.

4. Conclusion

In this paper, we developed the controlled fabrication of copper hierarchical structures with different morphologies by using the additives, such as CTAB, SDS, and PVP, combined with the electrodeposition technology. The outstanding features of this template-free method are its simplicity, convenience, and effectiveness. It is the first time that the

shape-controlled synthesis of metal copper self-assemblies is reported. All of the products were face-centered cubic copper, and the crystal structure was surfactant independent. In the absence of additives, only ruleless nubby structures are observed; in contrast, in the presence of CTAB, the flower-like hierarchical structures self-assembled by nanosheets with the uniform size are formed. Adjusting the deposition time was efficient to control the formation of the nanosheet arrays and the flower-like hierarchical structures. When the electrolyte was supplemented with SDS, the dendrite-like copper crystals constructed by 1D nanostructures are rapidly synthesized. When the electrolyte was added by PVP, the large congeries built by sphere-like structures was revealed. In summary, a simple and novel way to selectively control the formation of copper hierarchical structures with different morphologies is established by using the different additives.

Acknowledgments

The authors acknowledge financial supports from Foundation of Zhejiang Educational Committee of China (Grant no. Y200805544), Natural Scientific Foundation of Zhejiang (Grant no. Y4090605), the National Science Foundation for Young Scientists of China (Grant no. 20901051), and 973 Program (no. 2011CB710800).

References

- [1] T. Thurn-Albrecht, J. Schotter, G. A. Kastle et al., "Ultrahigh-density nanowire arrays grown in self-assembled diblock copolymer templates," *Science*, vol. 290, no. 5499, pp. 2126–2129, 2000.
- [2] E. C. Lin, J. J. Cole, and H. O. Jacobs, "Gas phase electrodeposition: a programmable multimaterial deposition method for combinatorial nanostructured device discovery," *Nano Letters*, vol. 10, no. 11, pp. 4494–4500, 2010.
- [3] R. Brayner, R. Iglesias, S. Truong et al., "Surface-enhanced Raman scattering on Silver nanostructured films prepared by spray-deposition," *Langmuir*, vol. 26, no. 22, pp. 17465–17469, 2010.
- [4] A. Frömsdorf, A. Kornowski, S. Pütter, H. Stillrich, and L. T. Lee, "Highly ordered nanostructured surfaces obtained with silica-filled diblock-copolymer micelles as templates," *Small*, vol. 3, no. 5, pp. 880–889, 2007.
- [5] Y. Sun and Y. Xia, "Shape-controlled synthesis of gold and silver nanoparticles," *Science*, vol. 298, no. 5601, pp. 2176–2179, 2002.
- [6] Y. Zhao, T. Topping, J. F. Bingert et al., "High tensile ductility and strength in bulk nanostructured nickel," *Advanced Materials*, vol. 20, no. 16, pp. 3028–3033, 2008.
- [7] D. Wei, W. Qian, Y. Shi, S. Ding, and Y. Xia, "Mass synthesis of single-crystal gold nanosheets based on chitosan," *Carbohydrate Research*, vol. 342, no. 16, pp. 2494–2499, 2007.
- [8] M. P. Zach, K. H. Ng, and R. M. Penner, "Molybdenum nanowires by electrodeposition," *Science*, vol. 290, no. 5499, pp. 2120–2123, 2000.
- [9] Y. L. Hou and S. Gao, "Solvochemical reduction synthesis and magnetic properties of polymer protected iron and nickel nanocrystals," *Journal of Alloys and Compounds*, vol. 365, no. 1–2, pp. 112–116, 2004.
- [10] D. Li, R. S. Thompson, G. Bergmann, and J. G. Lu, "Template-based synthesis and magnetic properties of cobalt nanotube arrays," *Advanced Materials*, vol. 20, no. 23, pp. 4575–4578, 2008.
- [11] G. She, W. Shi, X. Zhang, T. Wong, Y. Cai, and N. Wang, "Template-free electrodeposition of one-dimensional nanostructures of tellurium," *Crystal Growth & Design*, vol. 9, no. 2, pp. 663–666, 2009.
- [12] N. Tian, Z. Y. Zhou, N. F. Yu, L. Y. Wang, and S. G. Sun, "Direct electrodeposition of tetrahedral Pd nanocrystals with high-index facets and high catalytic activity for ethanol electrooxidation," *Journal of the American Chemical Society*, vol. 132, no. 22, pp. 7580–7581, 2010.
- [13] B. Zhang, Y. Y. Weng, X. P. Huang et al., "Creating in-plane metallic-nanowire arrays by corner-mediated electrodeposition," *Advanced Materials*, vol. 21, no. 35, pp. 3576–3580, 2009.
- [14] C. R. Kothapalli and A. Ramamurthi, "Copper nanoparticle cues for biomimetic cellular assembly of crosslinked elastin fibers," *Acta Biomaterialia*, vol. 5, no. 2, pp. 541–553, 2009.
- [15] T. R. L. C. Paixão and M. Bertotti, "Development of a breath alcohol sensor using a copper electrode in an alkaline medium," *Journal of Electroanalytical Chemistry*, vol. 571, no. 1, pp. 101–109, 2004.
- [16] E. A. Karakhanov, A. L. Maximov, Y. S. Kardasheva et al., "Copper nanoparticles as active catalysts in hydroxylation of phenol by hydrogen peroxide," *Applied Catalysis A*, vol. 385, no. 1–2, pp. 62–72, 2010.
- [17] C. Jiang, W. Zhang, Y. Liu, and Y. Qian, "Self-assembled copper nanowalls into microstructures with different shapes: a facile aqueous approach," *Crystal Growth & Design*, vol. 6, no. 11, pp. 2603–2606, 2006.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

