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Fabrication of 3D Co_3O_4 Homoarchitectures via a Novel Template-assisted Coprecipitation Process

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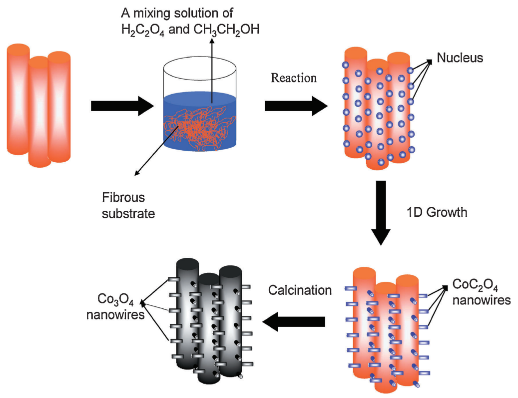
Three-dimensional hierarchical Co_3O_4 structures with high densities of secondary Co_3O_4 nanowires grown on primary Co_3O_4 fibers have been fabricated employing a coprecipitation growth on an electrospinning PVA/cobalt acetate nanofiber template followed by annealing in air. The structural analyses showed that as-prepared amorphous CoC_2O_4 nanowires converted into crystalline spinel Co_3O_4 after annealing. The morphology of the hierarchical Co_3O_4 structures could be further controlled by adjusting the mixing ratio of $H_2C_2O_4$ to CH_3CH_2OH.

In recent years, controllable synthesis of hierarchically structured materials via bottom-up techniques assembled by nanoscale building blocks has attracted intense attention, which is not only a useful tool for the realization of controllable synthesis technology but also expected to explore their potential application in optics, mechanics, magnetics, electronics, catalysis, and biology because of their optimized properties such as large surface-to-volume ratio, full of nanotips or nanoplates, and multifunctions.[1,2]

Co_3O_4 is a p-type semiconductor ceramic material with high Vickers hardness and fracture toughness.[3] It has great technological importance in diverse fields, including catalysis, lithium batteries, gas sensing, and electronics.[4] As we know, the properties of Co_3O_4 depend highly on its structure, including crystal sizes, orientations, and morphologies. Therefore, Co_3O_4 homoarchitectures with different structures will afford more opportunities for their application. Therefore, there is a growing interest to synthesize Co_3O_4 nanostructures with novel shape and unique size. Over the years, many studies have been made to produce hierarchical structures, such as Co_3O_4 nanocubes[5] and so forth. In addition, the improved performance of Co_3O_4 hierarchical structures in various potential applications, such as rechargeable batteries and electron field emission. On the other hand, only a few studies have focused on Co_3O_4 hierarchically structures.[6]

In this communication, we report an effective three-step route to synthesize Co_3O_4 hierarchical structure arrays on substrates, as schematically shown in Scheme 1. Step I: Employing an electrospinning technique[7–9] to generate PVA/cobalt acetate composite nanofibers which served as substrates to guide the growth of secondary cobalt oxalate (CoC_2O_4) nanowires. Step II: The electrospinning fibrous PVA/cobalt acetate film was put into a conical flask with stopper containing different mixing ratios of $H_2C_2O_4$–CH_3CH_2OH solution. The reaction was carried out at 50 °C for 12 h. The coprecipitation led to the formation of a CoC_2O_4 nucleus.[10] Due to the continuously proceeding reaction, the growing nuclei were beginning to impinge on other neighboring crystals and assemble along a specific orientation preferentially. The uniform CoC_2O_4 nanowires with novel 1D architecture can grow on the substrates. Step III: After annealing at 450 °C for 4 h in air, cobalt oxalate decomposed gradually, and black Co_3O_4 hierarchical nanostructured arrays on substrates were obtained.



Scheme 1. Schematic fabrication process for the direct-growth process of one-dimensional Co_3O_4 nanowires on the fibrous substrates.

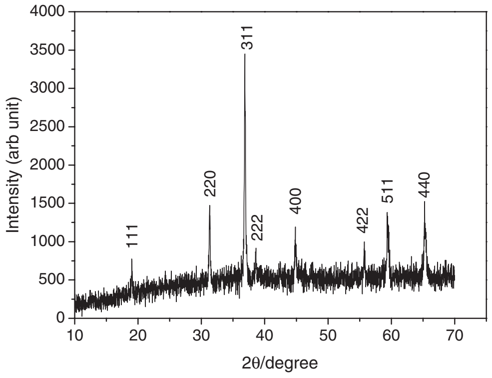


Figure 1. The XRD pattern of the Co_3O_4.

Figure 1 shows the XRD patterns of Co_3O_4. The sample remained as a single phase, both of which can be perfectly indexed to the pure cubic phase of the spinel Co_3O_4 with the lattice constant $a = 8.083$ Å, which is consistent with the value in the standard card (JCPDS Card No. 42-1467). No additional peaks could be observed in the diffraction patterns.

Figure 2a presents an SEM image of the PVA/cobalt acetate nanofibers. The fibers, 826 nm in diameter, interweave to form a nonwoven nanofibrous film. It can be clearly seen that the PVA/cobalt acetate composite nanofibers are of relative smooth surface without secondary structures. The template-assisted coprecipitation reaction was carried out at 50 °C in a mixed solution with a 2.0:3.0 molar ratio of $H_2C_2O_4$ to CH_3CH_2OH, long CoC_2O_4 nanowire arrays with a relatively high density were obtained on the fibrous substrates as shown in

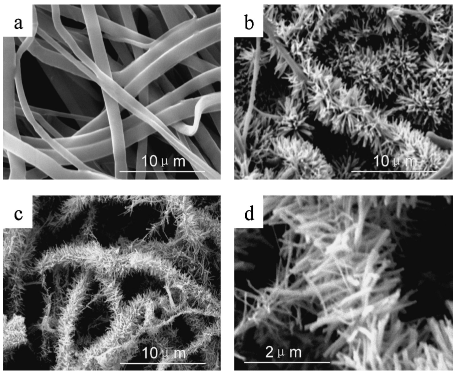


Figure 2. SEM images of (a) PVA/cobalt acetate composite fibers, (b) hierarchical cobalt oxalate nanowires before the annealing, and (c) low and (d) high-magnification hierarchical Co_3O_4 structures after the annealing.[11]

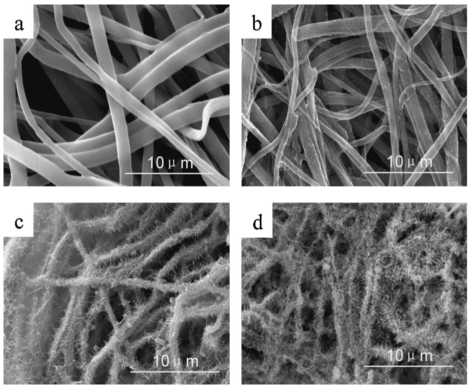


Figure 3. SEM images of the products obtained at different reaction times: (a) 0, (b) 0.5, (b) 4, and (d) 10 h.

Figure 2b. Upon calcination at 450 °C, because of the decomposition of CoC_2O_4 and PVA, the secondary Co_3O_4 nanowires were attained on the primary Co_3O_4 nanofiber substrates (Figure 2c). The magnified SEM image in Figure 2d reveals that the thermal decomposition generated Co_3O_4 nanowires are of lengths ranging from 300 to 750 nm and have diameters ranging from 47 to 142 nm.

In order to investigate the formation of the hierarchy, detailed time-dependent experiments were carried out at 50 °C. From the SEM images of these products shown in Figure 3. Figures 3a–3c, the morphology evolution of the hierarchical Co_3O_4 nanostructure is observed clearly. From the time-dependent experiments, we found that the as-synthesized nanofibers (0 min, Figure 3a) gradually changed morphology during the reaction. At the beginning, when the reaction time was 0.5 h (Figure 3b), some nanoparticles (CoC_2O_4 nucleus) on the nanofibers surfaces could be observed. When the reaction time is increased to 4 h, the nanoparticles gradually diminish while the nanowires gradually increase in length and diameter. The main products are the nanowires on the fiber surfaces. After prolonging the reaction time to 10 h, as shown in Figure 3d, the hierarchical nanowires become more uniform and perfect, as well as the final products.

The effects of the initial ratio of $[H_2C_2O_4]/[CH_3CH_2OH]$ in solution on the end products were examined. Figure 3 shows the SEM micrographs of the samples obtained with adding different amount of $H_2C_2O_4$. When the molar ratio of $H_2C_2O_4$ to CH_3CH_2OH is 1.0:1.0, the fibrous surface was covered by a scaffold organization of Co_3O_4 nanowires 114 nm in diameter (Figure 4a). While the molar ratio of $H_2C_2O_4$ to CH_3CH_2OH was increased to 2.0:1.0, as manifested in Figure 4b, large-scale uniform Co_3O_4 nanowire arrays with a smaller diameter of 86 nm can be observed. Meanwhile, compared to the Co_3O_4 nanowire arrays on the Co_3O_4 nanofiber substrate in Figure 4a and Figure 2b, we observed that the Co_3O_4 nanofiber substrate becomes unnoticeable. It indicates that, when the concentration of $H_2C_2O_4$ in the as-prepared reactant solution increased, the further reaction led to the disappearance of cobalt acetate nanofibers to form Co_3O_4 nanowires. So in order to obtain Co_3O_4 with hierarchical structure, the molar ratio of $H_2C_2O_4$ to CH_3CH_2OH should be lower than 1.0:1.0.

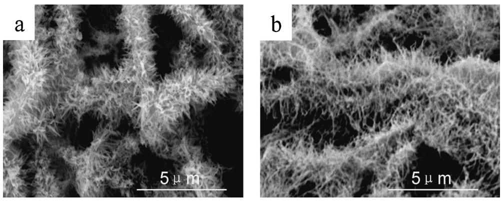


Figure 4. SEM images of Co_3O_4 hierarchical structures synthesized with different molar ratios of $H_2C_2O_4$ to CH_3CH_2OH: (a) 1.0:1.0 and (b) 2.0:1.0.

In summary, we have successfully synthesized 3D Co_3O_4 homojunctions with novel hierarchical architectures via a template-assisted coprecipitation method. Moreover, the morphologies of hierarchical Co_3O_4 structures could be facilely tuned by adjusting the mixing ratios of $H_2C_2O_4$ and CH_3CH_2OH. We believe this methodology provides a new avenue that offers a relatively mild and environmentally benign approach for large-scale preparation of various one-, two-, and three-dimensional homojunctions with structural complexity and thus enable various functions. These special homojunctions possess great potential for applications in photocatalysts, photovoltaics, and supercapacitors.

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References and Notes

1 a) M. Li, H. Schnablegger, S. Mann, *Nature* **1999**, *402*, 393. b) J. Q. Hu, Y. Bando, J. H. Zhan, X. L. Yuan, T. Sekiguchi, D. Golberg, *Adv. Mater.* **2005**, *17*, 971.

2 R. Ostermann, D. Li, Y. D. Yin, J. T. McCann, Y. N. Xia, *Nano Lett.* **2006**, *6*, 1297.

3 S. Sakamoto, M. Yoshinaka, K. Hirota, O. Yamaguchi, *J. Am. Ceram. Soc.* **1997**, *80*, 267.

4 a) P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.-M. Tarascon, *Nature* **2000**, *407*, 496. b) X. W. Lou, D. Deng, J. Y. Lee, L. A. Archer, *J. Mater. Chem.* **2008**, *18*, 4397. c) L. Ren, P. P. Wang, Y. S. Han, C. W. Hu, B. Q. Wei, *Chem. Phys. Lett.* **2009**, *476*, 78.

5 a) T. He, D. R. Chen, X. L. Jiao, Y. L. Wang, *Adv. Mater.* **2006**, *18*, 1078. b) J. Jiang, J. P. Liu, X. T. Huang, Y. Y. Li, R. M. Ding, X. X. Ji, Y. Y. Hu, Q. B. Chi, Z. H. Zhu, *Cryst. Growth Des.* **2010**, *10*, 70.

6 A.-M. Cao, J.-S. Hu, H.-P. Liang, W.-G. Song, L.-J. Wan, X.-L. He, X.-G. Gao, S.-H. Xia, *J. Phys. Chem. B* **2006**, *110*, 15858.

7 D. Li, Y. N. Xia, *Adv. Mater.* **2004**, *16*, 1151.

8 a) C. Pan, L.-Q. Ge, Z.-Z. Gu, *Compos. Sci. Technol.* **2007**, *67*, 3271. b) Z.-Z. Gu, H.-M. Wei, R.-Q. Zhang, G.-Z. Han, C. Pan, H. Zhang, X.-J. Tian, Z.-M. Chen, *Appl. Phys. Lett.* **2005**, *86*, 201915. c) Y. F. Yao, Z.-Z. Gu, J. Z. Zhang, C. Pan, Y. Y. Zhang, H. M. Wei, *Adv. Mater.* **2007**, *19*, 3707.

9 R. Ostermann, D. Li, Y. D. Yin, J. T. McCann, Y. N. Xia, *Nano Lett.* **2006**, *6*, 1297.

10 C. K. Xu, Y. K. Liu, G. D. Xu, G. H. Wang, *Chem. Phys. Lett.* **2002**, *366*, 567.

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