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Hollow TiO₂ nanocages with rubik-like structure for high-performance photocatalysts

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ABSTRACT

Hollow TiO_2 nanocages with rubik-like structure were synthesized via a combined hydrolysis/ hydrothermal method. Firstly, highly uniform Cu_2O nanocubes covered by TiO_2 layer were prepared by hydrothermal hydrolysis of $(NH_4)_2 TiF_6$ following by reducing copper-citrate complex with ascorbic acid. The Cu_2O core templates could be easily removed in dilute HCl solution to form a hollow rubik-like structure. The obtained TiO_2 nanocages show promising efficiency in the photocatalytic degradation of phenol pollutions.

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1. Introduction

 TiO_2 possesses a wide band gap ($E_g=3.2 \text{ eV}$) and is an important inorganic functional material because of its interesting chemical and physical properties [1]. In order to improve its photocatalytic activities, TiO₂ structures with various morphologies, such as nanorods, nanoparticles, nanotubes and micro/nano spheres have been fabricated successfully [2-4]. Among these structures, hollow nanostructures have attracted tremendous attention from researchers compared with their solid counterparts because of their low density, high surface area, good surface permeability and large light-harvesting efficiency [5.6], which can be widely applied in various fields, such as photocatalytic, photovoltaic, electrochromic devices, hydrogen, sensing and so on [7-9]. Many methods have been developed for the synthesis of TiO₂ hollow nanostructures and the majority of them are template-base approaches [10]. For example, Wang et al. [11] reported to synthesize of hollow TiO₂ microspheres with a high percentage of exposed (ca. 60%) {001} facets by a one-step hydrothermal strategy in the presence of soft template. The products exhibited enhanced photocatalytic activities for degradation of methylene blue dye present in aqueous solution under ultraviolet light irradiation at ambient temperature. The hollow TiO₂ nanospheres also can be obtained using a polymer or inorganic particles as hard template. The core-shell structure was firstly formed by deposited titanium dioxide onto the template and then removal of template by calcination or acid etching approach. Gu et al. [12] further developed a microemulsion-based approach to prepare spherical multihollow (MH) TiO₂ nanostructures. Owing to this hierarchical hollow structure, photoanode films derived from MH TiO₂ nanosphere as light scattering layer exhibits an enhanced light harvesting efficiency, thus leading to a 43% increment of photovoltaic performance compared to that from P25 nanoparticle film. Although considerable progress has recently been made by a number of groups, the fabrication of TiO₂ hollow structures with hierarchical structure still remains a great challenge. In the present contribution, hollow TiO₂ nanocages with rubik-like structure were synthesized by a combined acid catalytic hydrolysis/hydrothermal method.

2. Results and discussion

The synthesis strategy of anisotropic TiO_2 nanocages is schematically depicted in Fig. 1A. Firstly, highly uniform Cu₂O cubic crystals with ~200 nm in edge length are prepared by reducing copper-citrate complex with ascorbic acid at room temperature [13,14]. Scanning electron microscopy (SEM) examination of the scales in different magnification reveals that the Cu₂O sample consists entirely of uniform cube without impurity particles (Fig. 1B). Then, TiO₂ precursor was deposited on the surface of cubic Cu₂O nanoparticles by the synergy of accelerated hydrothermal hydrolysis of (NH₄)₂TiF₆ and simultaneous slight etching of Cu₂O by HF released from the hydrolysis of

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Fig. 1. Schematic illustration for fabrication of hollow and rubik-like TiO₂ nanocages (A): (I) uniform coating of TiO₂ onto Cu₂O cubes; (II) Ostwald ripening process; (III) remove of Cu₂O cube templates. SEM images of pure Cu₂O cubes (B), Cu₂O@TiO₂ composites (C) and hollow TiO₂ nanocages with rubik-like structure (D). The insets show the SEM images with higher magnification.

 $(NH_4)_2 TiF_6$. The surface roughness of these cubes is increased and the edge length of these hybrid particles is around 250 nm (Fig. 1C). Because of the high reactivity of Cu₂O cores, the Cu₂O@TiO₂ structures can be easily converted to anisotropic TiO₂ nanocages with entirely hollow interiors by acidic etching. In spite of very fast dissolution of Cu₂O cores, the TiO₂ shells are robust enough to withstand the osmotic pressure associated with mass diffusion. Collapse of the structure is only occasionally observed for some nanocages, as shown in Fig. 1D, [14].

By transmission electron microscopy (TEM) characterization, the roughness cube particles with \sim 250 nm in edge length can be observed while the inner cores are clearly revealed by the sharp contrast between TiO₂ shells and solid interiors. While, the TiO₂ shells are consisted of many little cube-like nanoparticles with 35 nm in edge length. Despite the partial dissolution induced by interfacial reactions, the Cu₂O cores remain single crystalline and are still connected to TiO₂ shells with large interface. Further the high resolution TEM (HRTEM) images taken near the particle edges reveal distinct lattice fringes with *d* spacing of 0.24 nm and 0.35 nm, which correspond to lattice spacing of the (111) planes in Cu₂O and (101) planes in anatase TiO₂ [15]. On the other hand, the selected area electron diffraction (SAED) and HRTEM analyses further indicate the polycrystalline texture of Cu₂O@TiO₂ composites (Fig. 2A). Fig. 2B shows the TiO₂ hollow nanocages after removal of the Cu₂O template; the pale center together with the dark edge provides evidence of the hollow structure. The hollow structures are still retained and the cubic symmetry remains. The SAED and HRTEM analyses further indicate the single crystal of TiO₂ hollow nanocages. The crystallographic structure of as-prepared products is further determined by X-ray powder diffraction (XRD) (Fig. S1). The obtained samples contain both a very developed free surface as well as extremely high specific area (Fig. S2). The complete solubility of an impurity in a polycrystal increases with decreasing grain size and this effect is especially strong when the adsorption layers (or the grain boundary phases) are multilayer. The oxides in thin layers seem to exhibit a ferromagnetic behavior due to the presence of defects on the structure [16,17].

For investigation the formation process of cubic TiO₂ on Cu₂O templates, the shape evolution of the heterostructures was regularly checked over time during the reaction. The formation process of the hollow spheres went through the hydrolysis of the poor-crystallized TiO₂ nanoparticles and their aggregation to solid spheres, as well as the following Ostwald ripening and surface reconstruction processes (Fig. S3).

To demonstrate the potential application of the as-prepared Ti₂O nanocages, we investigated the photocatalytic activity of Ti₂O nanocages for the photodegradation of toxic phenol. P25 as a commercially available photocatalyst was used as the reference. As shown in Fig. 3A, the phenol concentration almost has no changed without a catalyst under UV irradiation for 3 h. Using P25 as a catalyst, \sim 75% of phenol was degraded after the phenol solution was irradiated by UV light for 3 h, while 99.9% was decomposed using hollow TiO₂ nanocages as the catalyst. In addition to efficiency, the durability of the photocatalyst is also very important for its practical application [18]. As a result, the recycling degradation tests were applied to evaluate the durability of hollow TiO₂ nanocages photocatalyst. As shown in Fig. 3B, the phenol molecules even can be completely degraded after 6 runs (3 h for each run), indicating this photocatalyst can be reused several times without obvious change in catalytic activity and displays good durability.

3. Conclusion

In summary, well-dispersed hollow TiO₂ nanocages with rubik-like structure were prepared using a simple template method. The formation process of the hollow spheres went through the hydrolysis of the poor-crystallized TiO₂ nanoparticles and their aggregation to solid spheres, as well as the following Ostwald ripening and surface reconstruction processes, and then to remove the Cu₂O residue completely to form hollow structure. The as-prepared hollow nanostructures showed superior photocatalytic activity on the degradation of phenol compared to Degussa P25.



Fig. 2. A: TEM images (a and b) and high resolution TEM (HRTEM) image of Cu₂O@TiO₂ composites (c), and the selected area electron diffraction (SAED) image. B: TEM images (a and b) and high resolution TEM (HRTEM) image of hollow TiO₂ nanocages (c), and the selected area electron diffraction (SAED) image.



Fig. 3. Photocatalytic degradation of phenol over P-25 and hollow TiO₂ nanocages with UV light irradiation (A) and cycling runs for the photodegradation of phenol over as-prepared hollow TiO₂ nanocages (B).

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2012. 08.092.

References

- [1] Zhang Q, Li W, Liu S. Powder Technol 2011;212:145-50.
- [2] Chen Z, Liu J, Qiu S, Dawson G, Chen W. Catal Commun 2012;21:1-4.

- [3] Jiang G, Zheng X, Wang Y, Li T, Sun X. Powder Technol 2011;207:465-9.
- [4] Zhang Q, Li W, Liu S. Powder Technol 2011;212:145-50.
- [5] An K, Hyeon T. Nano Today 2009;4:359–73.
- [6] Xu J, Tang YB, Zhang W, Lee CS, Yang Z, Lee S. Cryst Growth Des 2009;9:4524–8.
- [7] Pan H, Qian J, Cui Y, Xie H, Zhou XJ. Mater Chem 2012;22:6002-9.
- [8] Moon HG, Shim YS, Su D, Park HH, Yoon SJ, Jang HW. J Phys Chem C 2011;115:9993-9.
- [9] Kong L, Lu X, Bian X, Zhang W, Wang CJ. Solid State Chem 2010;183:2421–5. [10] Sun XM, Liu JF, Li YD. Chem Eur J 2006;12:2039–47.
- [11] Wang X, He H, Chen Y, Zhao J, Zhang X. Appl Surf Sci 2012;258:5863-8.
- [12] Jiang J, Gu F, Shao W, Li C. Ind Eng Chem Res 2012;51:2838–45.
- [13] Zhang WX, Chen ZX, Yang ZH. Phys Chem Chem Phys 2009;11:6263-8.
- [14] Wang Z, Lou XW. Adv Mater 2012;24:4124-9.
- [15] Li Z, Liu J, Wang D, Gao Y, Shen J. Int J Hydrogen Energy 2012;37:6431-7.
- [16] Straumal BB, Protasova SG, Mazilkin AA, Myatiev AA, Straumal PB, Schütz G, et al. J Appl Phys 2010;108:073923.
- [17] Straumal BB, Myatiev AA, Straumal PB, Mazilkin AA, Protasova SG, Goering E, et al. JETP Lett 2010;92 396–400.
- [18] Wang R, Jiang G, Wang X, Hu R, Xi X, Zhou Y, et al. Powder Technol 2012;228:258–63.