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Shape-controlled synthesis of CuI Sub-microcrystalline under Solvothermal Condition

Chunxia Chai,[1] Peng Peng, [*1,3] Xinjun Wang,[2] Xinlei Zhang,[3] and Boshi Tian[3]

[*] [1]College of Chemistry and Chemical Engineering, Zhoukou Normal University, Zhoukou Henan, 466001, PR China

[2]College of Chemistry and Chemical Engeering, Henan Normal University, Xinxiang Henan, 453007 PR China

[3]Key Laboratory of Rare Earth Functional Materials and Application, Zhoukou Normal University, Zhoukou Henan, 466001, PR China

pengpeng@zknu.edu.cn

Abstract

The octahedral CuI microcrystals were synthesized in mixed solvent of water and ethanol at 180 °C for 20 h under solvothermal condition. The compared experiments were also carried out under various condition, and the optimum process was fixed. The results show that the suitable ripening process is helpful for growth of octahedral CuI microcrystals. The morphology of CuI microcrystals is mainly effected by polarity of solvent in these systems, and the growth mechanism of CuI microcrystals are also discussed.

Keywords: CuI microcrystals, octahedral, polarity

Introduction

Shape-controlled synthesis of inorganic micro- and nano-structures with well-defined morphology and uniform size plays an important role in uncovering their shape-dependent properties and fully achieving their potential practical applications. As a p-type semiconductor (direct band gap 3.1 eV) with unique optical, magnetic, γ-CuI (γ-cuprous iodide) is a perspective material with applications in solar energy conversion,[1-4] catalysis,[5-7] and solid electrolyte.[8] Different morphologies of CuI micro- and nanocrystals have been achieved by various methods in recent years. For example, Peng et al. have prepared CuI nanowires and nanorod via hydrothermal treatment.[9] Kozhummal and co-workers have prepared high-yield production of cuprous iodide (CuI) superstructures by antisolvent crystallization using acetonitrile/water as a solvent/antisolvent couple under ambient conditions.[10] Ma and co-workers have produced CuI nanoparticles by a new solution phase co-precipitation approach in the presence of both coordinating and noncoordinating solvents.[11] Tavakoli et al. synthesized CuI microstructures composed of trigonal nanostructures using pomegranate juice by a green and simple method.[12] Yan et al. have obtained CuI buffer layer by spraying method using acetonitrile as solvent.[13] Jiang et al. have fabricated cauliflower-like CuI nanostructures by an ampicillin-assisted clean, nontoxic, environmentally friendly synthesis strategy at room temperature.[14] However, as confirmed by plenty of recent studies, highly symmetric structures can exhibit physical and chemical properties that differ from other geometries because of their intrinsic architectural characteristics with regard to lattice symmetry and surface energy.[15] Another distinctive feature is their structural isotropy, which allows people to develop various architectural designs and superlattice organization using them as primary building blocks. Therefore, it is necessary to exploit a facile protocol for the shape-controlled synthesis of well-defined architectures with high symmetry. Herein, we prepared octahedron-shaped γ-cuprous iodide microcrystals with uniform size and morphology using a one-pot hydrothermal treatment of copper(II) acetate ($Cu(Ac)_2 \cdot H_2O$) and potassic iodide (KI) in the presence of a mixed solvent of ethanol and water.

Experiment Section

Synthesis of CuI

The reactants of $Cu(Ac)_2 \cdot H_2O$, CuI, and ethanol were all analytically pure and used as-received without further purification, water is deionized water. In a typical synthesis, 3 mmol of $Cu(Ac)_2 \cdot H_2O$ was dissolved in 50 mL of mixture composed of ethanol and water with 1:1 volume ratio, and then 6 mmol of KI was added under

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constant stirring. After 1.5 h, the mixture was transferred into a 60 mL Teflon-lined stainless autoclave and maintained at 180 °C for 20 h. The autoclave was cooled naturally to room temperature. Finally, the precipitates were filtered off, washed several times with distilled water and ethanol in turn, and the precipitates were dried in a vacuum environment. The compared experiments were also carried out under other condition.

Characterization

The powder X-ray diffraction (XRD) patterns of as-synthesized samples were recorded with a Bruker DX-8 X-ray diffractometer equipped with graphite monochromatized Cu K irradiation (λ = 0.15406 nm), employing a scanning rate of 0.06°s^{-1} in the 2θ range of 20-80°. A JEOL JSM-6700F field-emission scanning electron microanalyzer (FESEM) were used to obtain the images of products.

Results and discussion

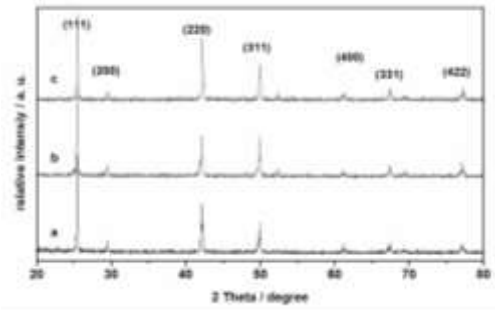

Fig. 1 XRD pattern of CuI particles as-prepared in (a) ethanol/water mixture (the volume ratio of ethanol to water is 1:1), (b) water and (c) ethanol at 180 °C for 20 h.

Fig. 1 shows the typical XRD patterns of as-prepared CuI samples at 180 °C for 20 h in different solvent of mixture (Fig. 1a), deionized water (Fig. 1b), and ethanol (Fig. 1c). All of the diffraction peaks of sample a, b and c can be well indexed to cubic CuI (JCPDS No. 06-0246). The results indicate there is little effect on the CuI product phase when the solvent was changed in our experiments. No other diffraction peaks arising from possible impurities such as Cu_2O and CuO are detected, indicating that pure cubic CuI is obtained in the three kind of solvents. The relative intensity of the diffraction peaks of the products shows good crystallinity, and the higher intensity of the (111) diffraction peak suggests that the {111} facets are dominantly exposed in obtained grains.

Chemical reactions occurring in this experiment are as follows:

$$2Cu^{2+} + 2I^- = 2Cu^+ + I_2 \quad (1)$$

$$Cu^+ + I^- = CuI\ (s) \quad (2)$$

In solution, Cu^{2+} and I^- firstly react with each other by following a procedure of redox reaction (denoted by equation 1). And then, CuI embryos were precipitated from solution (denoted by equation 2). The ripening process finally facilitated the growth of CuI grains at 180 °C for 20 h. Obviously, I^- is not only reducer but also precipitator in the system.

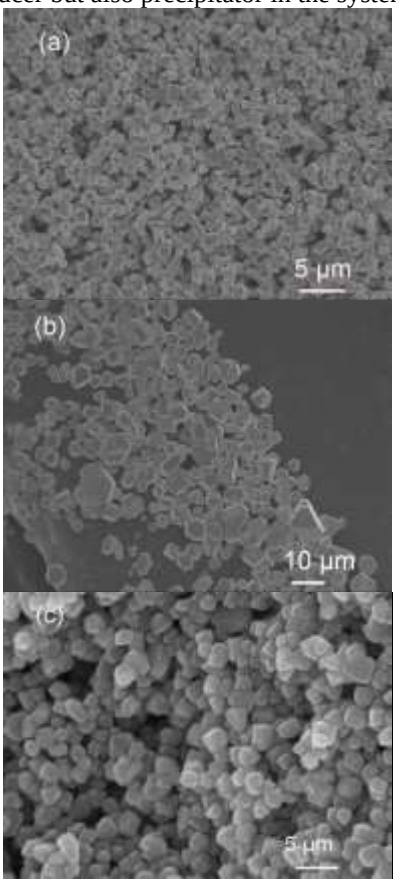

Fig. 2 SEM image of CuI particles as-prepared in (a) ethanol/water mixture (the volume ratio of ethanol to water is 1:1), (b) water and (c) ethanol at 180 °C for 20 h.

Fig.2 is SEM images of CuI as-prepared in ethanol/water mixture (Fig. 2a), water (Fig. 2b) and ethanol (Fig. 2c) at 180 °C for 20 h. Monodispersed octahedral CuI microcrystals can be seen in Fig. 2a with diameter of *ca*. 500 nm. Both morphology and size of the CuI microcrystals are relatively uniform. Fig. 2b shows that the CuI microcrystals obtained in water are irregular polyhedrons with diameter of 1-10 μm. The SEM image of CuI microcrystals obtained in ethanol is listed in Fig. 2c. The CuI microcrystals are also polyhedral morphology with diameter of 3-10 μm, similar to microcrystals from water. However, these polyhedrons are truncated octahedrons after closer observation, suggesting incomplete growth of CuI grains in ethanol. In our experiment, the filtrate was also collected and examined. More precipitated

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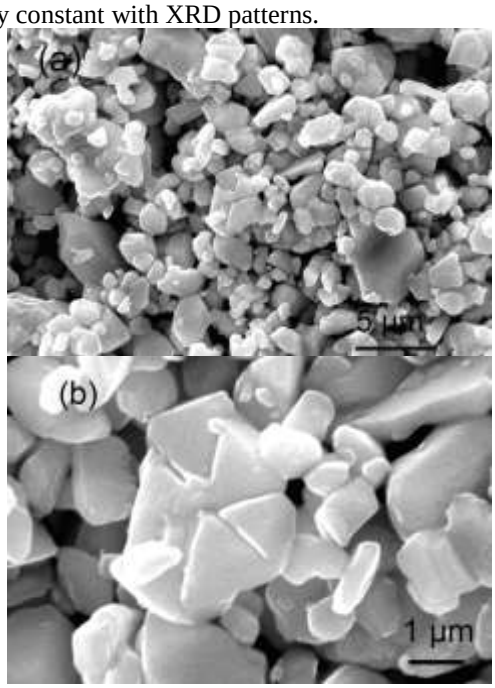
were generated when reaction of filtrate, only from ethanol solution, was prolonged. So, this proves that the reaction is not complete in ethanol.

Based on above results, mixture of water and ethanol favor the generation of octahedral CuI microcrystals with uniform particle size. The results suggest that the growth of cubic CuI microcrystals is mainly effected by solvent polarity. For ionic reactions, the reaction is faster in higher polarity solution. The CuI microcrystals grow faster in water and slower in ethanol than in mixture. The faster exhaustion of reactants in water result in irregular polyhedral CuI microcrystals. For cubic CuI, {100} facets are closely packed and grow faster than other low index facets.[16] Finally, slower growth of {111} facets are dominantly exposed and form octahedron. The octahedral morphology of CuI microcrystals is very constant with XRD patterns.



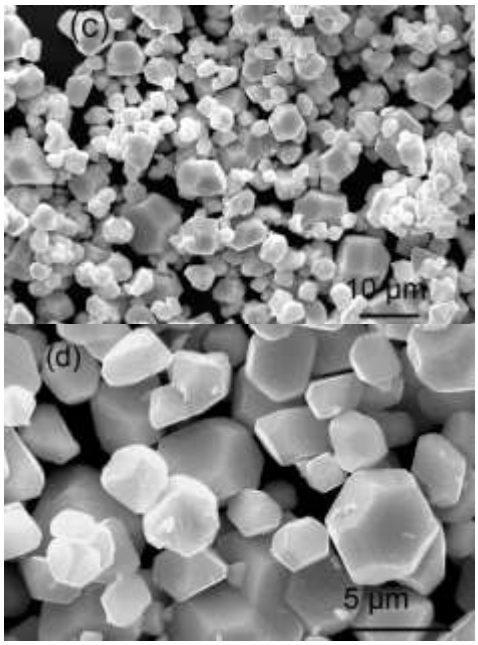


Figure 3 SEM images of CuI as-prepared: (a) and (b) with $CuSO_4$ as reactant at 180 °C for 20 h, (c) and (d) at 180 °C for 6 h.

More compared experiments to examine the effect of reaction condition were carried out. Fig. 3a and 3b are SEM images of CuI samples using copper sulfate and potassium iodide as reactants under the same conditions. Most of the particles are flakes and uneven particle size, which shows that anion has some effect on the morphology and size of CuI particles. Fig. 3c, 3d are SEM images of the CuI samples under conditions of 180 °C for 6 h. All the samples are polyhedron, and have the tendency to grow into octahedron. It suggests that elevated reaction temperature and prolonged reaction time are conducive to preparing octahedral shape CuI microcrystals.

Conclusion

The octahedral and polyhedral CuI microcrystals were prepared using $Cu(Ac)_2$ and KI as reactants by solvothermal method. The octahedral CuI microcrystals are readily precipitated in the mixed solvent with equal volume ratio of water to ethanol at 180 for 20 h. The obtained CuI microcrystals are regular octahedrons with diameter of *ca.* 500 nm. The irregular polyhedral CuI microcrystals and truncated octahedral CuI microcrystals are precipitated in water and ethanol, respectively. The products are mainly effected by polarity of solvent in our experiments. Finally, growth mechanism of CuI microcrystals are also promoted.

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Author Bibliography

	**Chunxia Chai** Accept her M. S of Henan Normal University in 2009, and has been working in Zhoukou Normal University as a lecture since 2002. Email: ccxy66@126.com
	**Peng Peng** Accept his Ph. D. of Nankai University in 2009, and has been working in Zhoukou Normal University as a assistant professor since 2010. Email: author@xxx.xxx