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LETTER

Shape- and size-controlled synthesis of coordination polymer $\{[Cu(en)_2][KFe(CN)_6]\}_n$ nano/micro-crystals

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Introduction

In the last decade, chemists have devoted their efforts and enormous attention to coordination polymers (CP) with infinitely extended structures due to their intriguing properties and potential applications in catalysis [1], gas storage [2, 3], nonlinear optics [4], molecular magnet [5], and molecular recognition and separations [6, 7]. Recently, CP nanocrystals, nanosized coordination polymers with finite repeating units, have aroused a growing interest due to their special properties distinctive from conventional bulk CP [8]. Up to now, the CP nanocrystals of Prussian blue analogies [9–11] have been intensively studied and various nanocrystals including nanoparticles, nanocubes, nanorods, and nanotubes have been successfully synthesized. However, it still remains a key research challenge to fabricate CP nano/micro-crystals with controlled shape and size, although some works have been demonstrated by several groups [12–16] in the past 3 years. This new class of materials promises to advance nanoscience into the realm of coordination polymers and thereby circumvent the nominal composition limitations generally ascribed to nanoparticles [17].

The novel crystal structure of $\{[Cu(en)_2][KFe(CN)_6]\}_n$ using $[Cu(en)_2]^{2+}$ as a template and K^+ as a connecting unit was reported in previous studies [18]. We now present the morphology and size control on the nano- and micro-crystals of the complex, and the results may refer a new approach for the synthesis of CP with an organic ligand.

Experimental

All chemicals and solvents were reagent grade and were used without further purification. In a typical experiment, the blue solution of $[Cu(en)_2]^{2+}$ ions was synthesized by adding 0.6 mmol of ethylenediamine into 30 mL of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.15 mmol) aqueous solution. The irregular nanorods of the title compound were prepared as follows: the blue solution was mixed with 30 mL of $K_3[Fe(CN)_6]$ aqueous solution (0.2 mmol) at room temperature under rapid stirring. A large quantity of brown precipitate can be obtained within 5 min. The precipitate was collected by centrifugation and washed five times with ethanol, and then dried in a vacuum-oven at 50 °C for 24 h. The microcubes and micro-arrowheads with regular morphology and size were synthesized as follows: adding the surface-regulating polymer of PVP into the $K_3[Fe(CN)_6]$ aqueous solution for the case of microcubes, and adding PVP and assisting with ultrasonic radiation for micro-arrowheads.

The morphology and structure of the obtained products were characterized by SEM (JSM-6480), TEM (JEM-200CX and TECNAI 20 PHILIPS), and X-ray diffraction (Shimadzu XRD-6000) with Cu Kα radiation. Fourier-transform infrared (IR) spectra were recorded on a Nicolet FT-ATAVAR360 spectrometer with KBr pellets in the 4,000–400 cm^{-1} region. The chemical composition of the complex was determined by AAS (TAS-986, Beijing PGENERAL) and elemental analyses (Flash 1112A, Italy CE).

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Results and discussion

The information about crystal structure of the as-synthesized products was inspected using XRD. The XRD patterns of the powders synthesized in the "Experimental" section and the standard pattern simulated from the single crystal X-ray diffraction data [18] were shown in Fig. 1. It can be seen that all the diffraction peaks match well with the data in standard pattern, indicating that they are pure phase of $\{[Cu(en)_2][KFe(CN)_6]\}_n$. Elemental analyses calcd. for $C_{10}H_{16}N_{10}FeCuK$: C 27.62, H 3.71, N 32.22, Cu 14.62, Fe 12.84, K 8.99. Found: C 27.87, H 3.92, N 32.85, Cu 14.11, Fe 12.60, K 8.75. The FT-IR spectra of the samples exhibited three peaks at 2,129, 2,115, and 2,102 cm^{-1} attributed to the CN stretching in the K^+–CN–Fe^{3+} linkage of $\{[Cu(en)_2][KFe(CN)_6]\}_n$ [18].

The SEM images shown in Fig. 2 reveal the morphologies of $\{[Cu(en)_2][KFe(CN)_6]\}_n$ nano/microcrystals. The Fig. 2a shows the nanorods obtained from the direct reaction of two precursors solutions. The as-prepared nanorods are irregular and without uniform size. By adding PVP into the $K_3[Fe(CN)_6]$ aqueous solution, the morphologies of the nanocrystals can been changed from nanorods to microcubes. As shown in Fig. 2b, the sample synthesized at [PVP] = 20 mM shows large-scale regular microcubes with an average diameter of 700 nm. More interestingly, when the reaction was assisted by ultrasonic radiation at [PVP] = 30 mM, the regular micro-arrowheads were obtained (Fig. 2c), with a length of ca. 5 μm and a width of ca. 2.0 μm. The higher magnification SEM image of the micro-arrowheads (Fig. 2d) indicated an obvious hollow structure with smooth surfaces and sharp edges.

Figure 3 displays the TEM images of the $\{[Cu(en)_2][KFe(CN)_6]\}_n$ products. As shown in Fig. 3a, the edges of the microcubes are obvious lighter than the centers, indicating that the center of the cube is thicker than its edges, in other words, the morphology of the cubes are less regular with a trapeziform section. Figure 3b reveals that the micro-arrowheads are highly uniform and monodisperse with smooth facets of a mean edge length of 5 μm. However, the hollow structure cannot be observed in this TEM image because the micro-arrowheads are too thick.

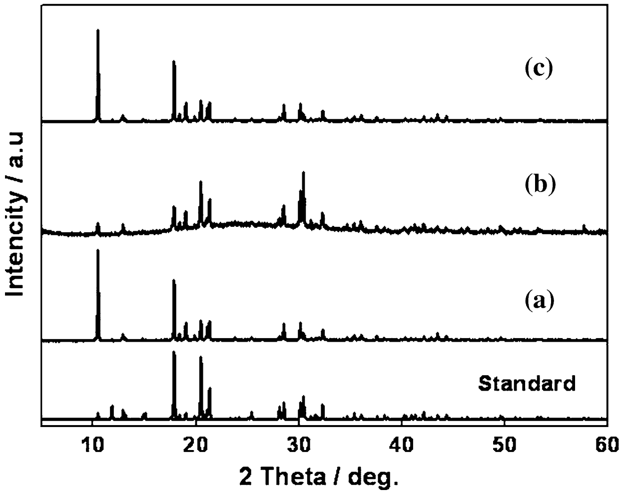

Fig. 1 XRD patterns of the products with different morphologies: (*a*) nanorods; (*b*) microcubes; (*c*) micro-arrowheads

As shown in Fig. 4, with the increase of the amount of PVP, the mean size of the micro-arrowheads becomes larger. When micro-arrowheads are prepared with [PVP] = 5 mM, the average size of the irregular trigonal-crystals is 800 nm (Fig. 4a). Increasing the concentration of PVP to 10 mM (Fig. 4b), the average size of the arrowheads is up to 1 μm and the shapes become more regular. The SEM images of the samples synthesis at [PVP] = 20, 30, and 40 mM were shown in Figs. 4c, 2c, and 4d, respectively. From these images, an obvious size increase (2.5, 5, and 10 μm, respectively) and more obvious hollow structures can be observed. The result indicated the remarkable effect of PVP on the crystallization of $\{[Cu(en)_2][KFe(CN)_6]\}_n$ micro-arrowhead.

This phenomenon is interesting because the conventional route for size tuning of crystals usually exhibits an opposite behavior: higher concentrations of additives yield smaller crystals such as nanoparticles due to effective suppression of crystal growth [19, 20]. In supramolecular crystal growth system, crystals can grow until the reversible reaction between monomeric precursor and solid crystal reaches equilibrium. Thus, control over the nucleation process in the preparation of CP should strongly affect the size of the final crystals [21]. In the classical nucleation theory: this polymer forms stable polymer complexes with Cu^{2+}, which precedes the nucleation stage [22]. The supersaturation of the precipitation ions (Cu^{2+}) was decreased, which resulted in a decrease in the parameter $\Delta\mu$ (the difference in chemical potential of the solid and the liquid) [23]. Hence, the addition of PVP to the reaction mixture leads to a slow rate of nucleation (fewer nuclei) and consequently provides larger crystals. Moreover, the corners and edges of these micro-arrowheads became sharper with increasing the molar ratio of PVP to $K_3[Fe(CN)_6]$ from 5 to 40. We believe that the PVP also plays a surface-regulating role in the synthesis.

Conclusion

In conclusion, a variety of low-dimensional nano- and micro-scale coordination polymer materials of $\{[Cu(en)_2][KFe(CN)_6]\}_n$ including short nanorods, nanocube, and hollow micro-arrowhead have been prepared by a simple self-assembly method in aqueous solution. It is suggested

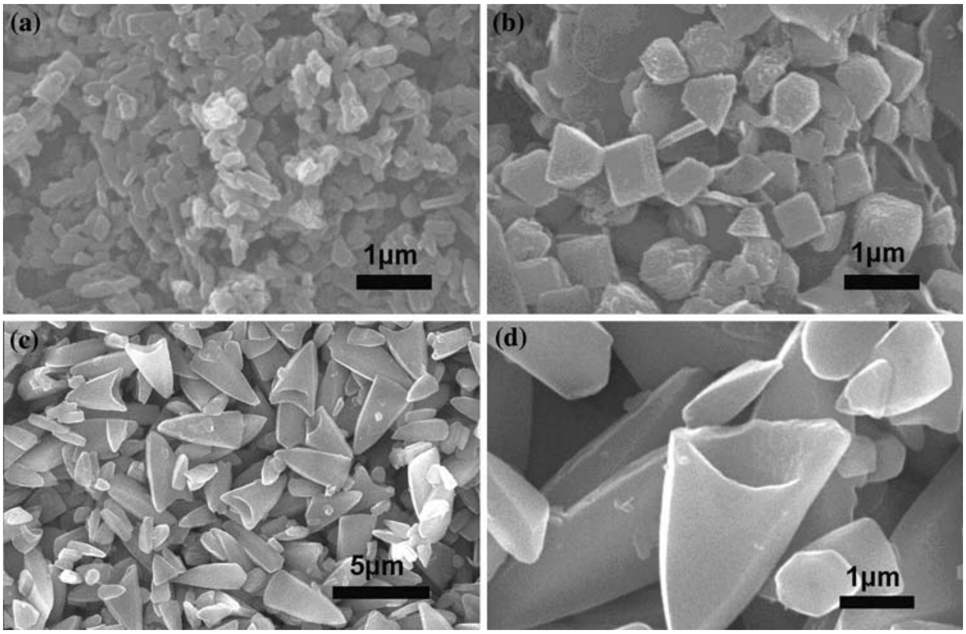

Fig. 2 SEM images of the samples synthesized via a typical procedure described in the "Experimental" section: **a** nanorods; **b** microcubes; **c** and **d** micro-arrowheads

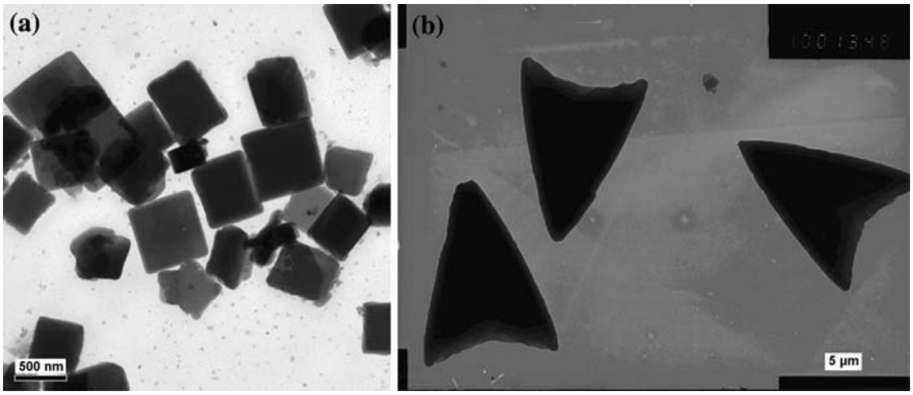

Fig. 3 TEM images of **a** microcubes and **b** micro-arrowheads

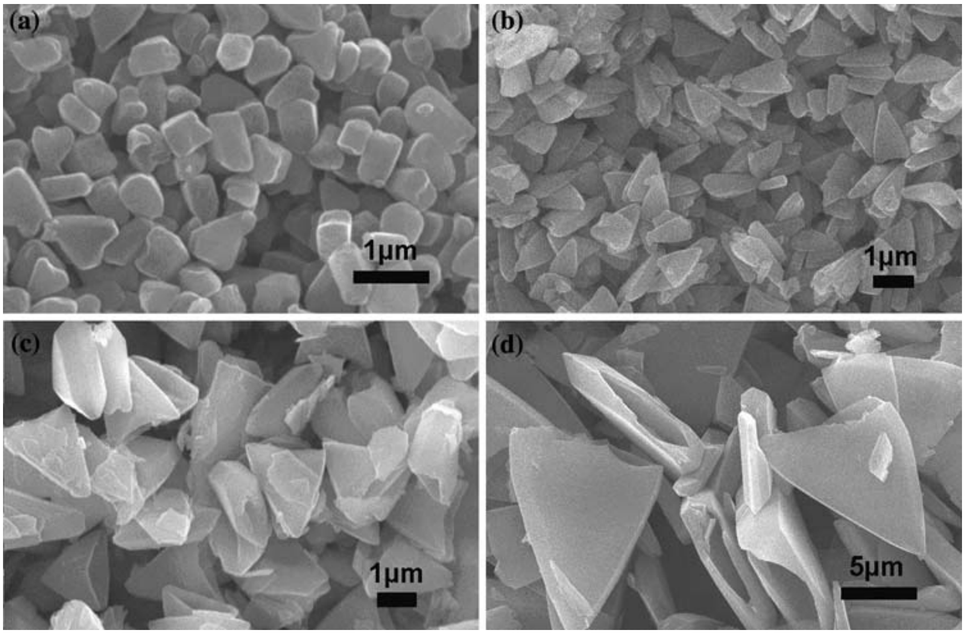

Fig. 4 The influence of PVP concentration on the sizes of micro-arrowheads: **a** [PVP] = 5 mM; **b** [PVP] = 10 mM; **c** [PVP] = 20 mM; **d** [PVP] = 40 mM

that PVP and ultrasonic radiation played a key role in the morphology development of the nano/micro-crystals. PVP acts not only as a stabilizer but also as a shape and size controller. It is expected that this work can refer some experience for the future works in the field of coordination polymer nanomaterials.

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