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Shape-controlled synthesis of Prussian blue analogue $Co_3[Co(CN)_6]_2$ nanocrystals†

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Received (in Cambridge, UK) 6th January 2005, Accepted 21st February 2005
First published as an Advance Article on the web 14th March 2005
DOI: 10.1039/b500153f

Prussian blue analogue $Co_3[Co(CN)_6]_2$ nanostructures with morphologies of truncated nanocubes (polyhedra), cubes and rods, were synthesized in large quantities by a direct dissociation of the single-source precursor $K_3[Co(CN)_6]$ in a microemulsion system; the molar ratio of H_2O to surfactant and the concentration of $K_3[Co(CN)_6]$ both played important roles in determining the shape of the product.

Recently Prussian blue (PB) analogues have attracted renewed and growing interest in the field of molecule-based magnets because many unique properties have been found.[1–4] The mixed-valence cobalt(II) hexacyanocobaltate(III) compound, $Co_3[Co(CN)_6]_2\cdot xH_2O$, is a typical Prussian blue analogue. This compound contains two nitrogen-coordinated, two carbon-coordinated, and one interstitial cobalt atom as shown in Fig. 1 (inset),[5,6] in which the interstitial atoms are generally present to maintain electroneutrality of the Prussian blue analogue. Among Prussian blue and its analogues, the metals in the N-coordinated sites are generally in their high-spin state, but Co(III) is an exception. Currently research efforts mainly focus on Prussian blue,[7–10] and a little work on Prussian blue analogues.[11–13] Furthermore, the reported study is only limited to properties of bulk Prussian blue analogues. However, it was found that for a magnetic material, controlling shape and size both is of crucial importance to fine-tune the magnetic properties of the material. So it is a challenge to prepare Prussian blue analogues with different shapes at the nanoscale. In this communication, we report on the synthesis of single crystalline $Co_3[Co(CN)_6]_2$ nanostructures using a single-source precursor $K_3[Co(CN)_6]$ in a microemulsion system. By carefully controlling experimental conditions, $Co_3[Co(CN)_6]_2$ nanostructures with morphologies of truncated nanocubes (polyhedra), cubes and rods, can be efficiently achieved.

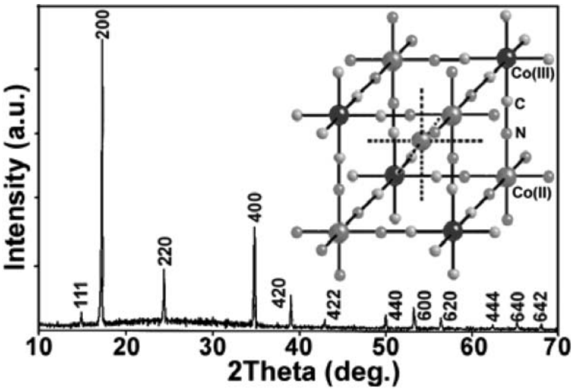

Fig. 1 An XRD pattern of the truncated nanocube sample, confirming the formation of pure fcc $Co_3[Co(CN)_6]_2$, the inset is the unit cell of $Co_3[Co(CN)_6]_2$.

For transition metal hexacyanometalates with the general composition $A^{m+}{}_i[B(CN)_6]^{n-}$, traditional synthesis is based on direct reaction of the A^{m+} cations and the $[B(CN)_6]^{n-}$ anions in an aqueous solution. For example, Mann's group[14,15] has recently prepared several PB analogue nanoparticles by means of the above reaction but confined to nanoscale water droplets formed in reverse microemulsions. In addition, they reported the synthesis of monodisperse hydrophobic PB nanoparticles by the photoreduction of $[Fe(C_2O_4)_3]^{3-}$ in the presence of $[Fe(CN)_6]^{3-}$ ions also in microemulsions.[16] In this paper, we report a novel and simple synthesis route to the formation of PB analogues $Co_3[Co(CN)_6]_2$ nanocrystals, in which $K_3[Co(CN)_6]$ was chosen as the only reactant. From its stability constant ($K_s = 1.0 \times 10^{65}$), we know the $[Co(CN)_6]^{3-}$ ions are very stable in aqueous solutions at room temperature, and almost no Co^{3+} ions can be detected. However, in our case (solvothermal conditions), it can be inferred that the growth of $Co_3[Co(CN)_6]_2$ nanocrystals within the restricted reaction field is controlled by a multistep process: firstly, $[Co(CN)_6]^{3-}$ ions partially dissociate slowly to produce Co^{3+} ions in water droplets; secondly, the Co^{3+} are immediately reduced to generate Co^{2+} as the Co^{3+} ions are very unstable in aqueous solutions; and finally, these Co^{2+} ions react with undissociated $[Co(CN)_6]^{3-}$ ions to form $Co_3[Co(CN)_6]_2$.

In a typical synthesis, 0.5 ml of 0.5 M $K_3[Co(CN)_6]$ aqueous solution was added in a dropwise manner to a solution containing 60 ml of cyclohexane, 3 ml of *n*-pentanol, and 6 mmol of cetyltrimethylammonium bromide (CTAB). After vigorous stirring, the optically transparent microemulsion solution was transferred into an 80 ml stainless Teflon-lined autoclave, kept at 140 °C for 48 h, and then cooled to room temperature naturally. The product was filtered and washed several times with distilled water and absolute ethanol, and finally dried in a vacuum oven at 25 °C for 12 h. The composition of the as-synthesized product was determined from the X-ray diffraction pattern (Fig. 1). All the reflections can be readily indexed as a pure face-centered cubic (fcc) phase of $Co_3[Co(CN)_6]_2$ [space group: *Fm*3*m* (no. 225)] with lattice constant a = 10.2 Å, which is in good agreement with the standard values for bulk cubic $Co_3[Co(CN)_6]_2$ (JCPDS 77-1161).

Large numbers of experiments indicated that the morphology of the product had a strong dependence on the reaction conditions. When the concentration of $K_3[Co(CN)_6]$ was kept at 0.75 M, the

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† Electronic supplementary information (ESI) available: SEM images of samples synthesized with reaction temperature increased to 160 and 180 °C, respectively. See http://www.rsc.org/suppdata/cc/b5/b500153f/

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molar ratio of H_2O to CTAB at 5, and the reaction temperature at 140 °C, $Co_3[Co(CN)_6]_2$ truncated nanocubes (polyhedra) were formed. Fig. 2a and b show scanning electron microscope (SEM) images of a typical sample of $Co_3[Co(CN)_6]_2$ polyhedra and indicate the large quantity and relatively good uniformity that were achieved using this method. Their surfaces were extremely smooth. A high-magnification SEM image (Fig. 2b) indicates that the $Co_3[Co(CN)_6]_2$ product consists of four kinds of polyhedra, as shown in Fig. 3a–d, respectively. It is clear that the four kinds of polyhedra are all truncated cubes enclosed with {100} and {111} facets, but the degree to which the cube is truncated is different, and from Fig. 3a to f it gradually increases. Previously Wang's group[17] had reported that the formation of various different shapes of an fcc nanocrystal depends on the ratio (*R*) of the growth rate along <100> to that along <111>, and geometrical shapes of cubooctahedral nanocrystals as a function of the ratio *R* were illustrated accordingly. So, according to Wang's report, in the present work the *R* values of the four polyhedra should be 0.7, 0.87, 1.0, and 1.15, respectively. They are between the most stable octahedron with an *R* value of 1.73 and the less stable cube with an *R* value of 0.58. The crystallinity and structure of the four kinds of polyhedra were examined using select area electron diffraction (SAED). The SAED patterns recorded on one $Co_3[Co(CN)_6]_2$ polyhedron against any one of the two sets of facets, show the hexagonal and square symmetry, respectively, which can be attributed to [111] and [001] zone axis diffraction of fcc $Co_3[Co(CN)_6]_2$. This result suggested that each polyhedron is a well-crystalline single crystal. Further study suggested that the size of the polyhedra mainly depended on the reaction temperature. When the reaction temperature was increased to 160 and 180 °C, respectively, the size of the polyhedra increased accordingly (see ESI†). It was also found that increased reaction temperature favoured a broader size distribution, and the polyhedron surfaces were relatively rough with some nanoparticles adhering to them.

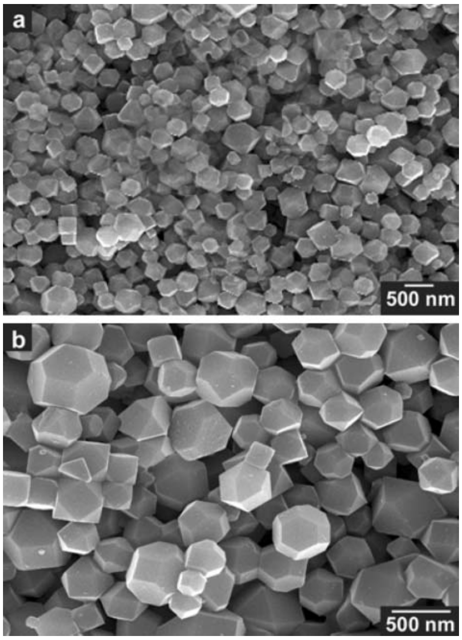

Fig. 2 (a) SEM image of the as-prepared $Co_3[Co(CN)_6]_2$ polyhedra at a low magnification. (b) SEM image of the same sample as in (a) but with a higher magnification.

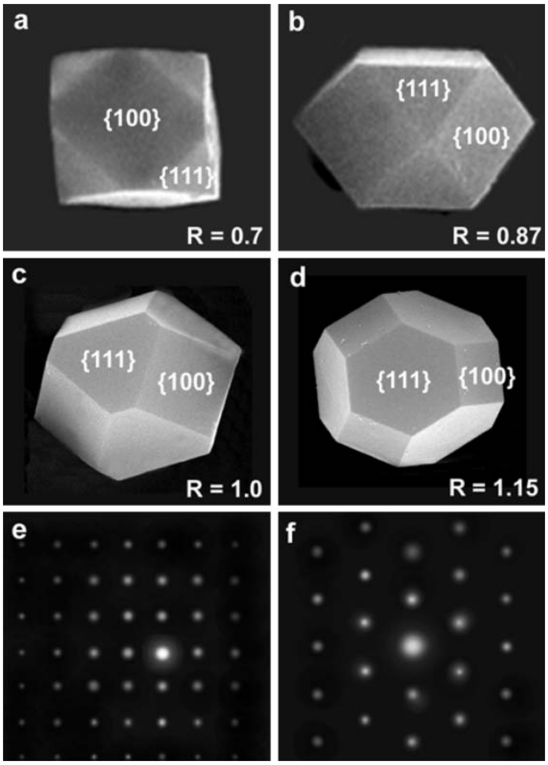

Fig. 3 (a–d) SEM images of the four $Co_3[Co(CN)_6]_2$ polyhedra. (e and f) SAED image of two polyhedra with their square and triangular facets oriented perpendicular to the electron beam, respectively.

When the concentration of $K_3[Co(CN)_6]$ was reduced to 0.5 M, and the molar ratio of $[H_2O]$: [CTAB] was increased to 10, an obvious shape evolution of $Co_3[Co(CN)_6]_2$ nanocrystals from polyhedra to nanorods was observed. Fig. 4a shows the TEM

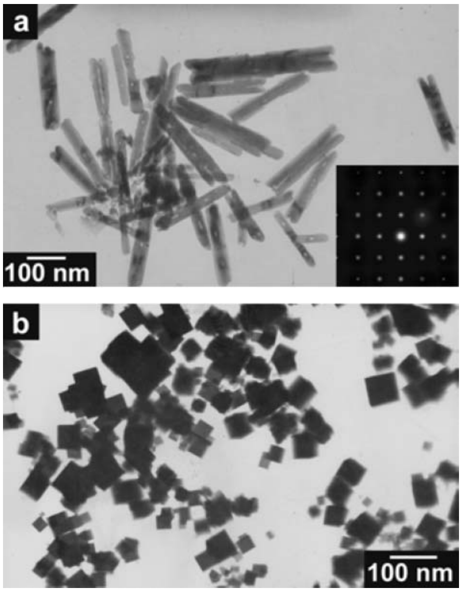

Fig. 4 (a) TEM image of $Co_3[Co(CN)_6]_2$ nanorods, the inset is an SAED image of a single nanorod. (b) TEM image of $Co_3[Co(CN)_6]_2$ nanocubes.

image of nanorods, which clearly revealed the effect of the reaction conditions on the shape of the product. The nanorods had a mean diameter of 50 nm and a length of 500 nm. The SAED pattern (inset in Fig. 4a) recorded on a single nanorod confirms the $Co_3[Co(CN)_6]_2$ nanorod to be single crystalline. When the concentration of $K_3[Co(CN)_6]$ continued to be reduced to 0.1 M, and the molar ratio of $[H_2O]$: [CTAB] was increased to 30, the product mainly consisted of perfect nanocubes as shown in Fig. 4b. These nanocubes had a mean edge length of 50 nm. All corners and edges of these nanocubes were not truncated. The nanocube should be bounded by the less stable {100} planes with an *R* value of 0.58 as described by Wang.[17]

From the above experiment results, it can be seen that the morphologies of the final products were strongly dependent on the molar ratio of H_2O to CTAB and the concentration of $K_3[Co(CN)_6]$. CTAB used as a cationic surfactant has proved to be an effective template for the synthesis of mesoporous and nanometre materials, also confirmed by previous work of our group,[18–21] and in the water-in-oil microemulsions it can self-assemble into sphere-like, cylinder-like, flat sheet, and bicontinuous droplet microstructures under appropriate reaction conditions.[22] In our case, when the molar ratio of H_2O to CTAB was kept at as low as 5 (low water content), the formed droplets may have a spherical microstructure with a smaller size as the size of the droplets increases linearly with the amount of water added to the system.[23] After $Co_3[Co(CN)_6]_2$ nucleation within the smaller spherical droplet microstructures, it is believed that the selective interaction between CTAB and various crystallographic planes of fcc $Co_3[Co(CN)_6]_2$ could greatly reduce the growth rate along the <100> direction and enhance the growth rate along the <111> direction, resulting in the formation of truncated nanocubes (polyhedra). Thus the *R* value reduces from 1.73 to 1.15–0.7. On increasing the molar ratio of $[H_2O]$: [CTAB], the shape of the droplets may change from spheres to cylinders.[24] The CTAB molecules of the side of the cylindrical droplet microstructures will preferentially adsorb on the growing surfaces parallel to a certain axis of the $Co_3[Co(CN)_6]_2$ nuclei, resulting in the growth of anisotropic primary particles. Then these primary particles can attach to each other side-by-side and end-by-end, resulting in rodlike $Co_3[Co(CN)_6]_2$ nanocrystals. As the molar ratio of $[H_2O]$: [CTAB] continues to increase, more water may induce a new phase transition, and the surfactants may self-organize into interconnected cylinders,[25] which may be responsible for the formation of the nanocubes. In fact, the final nanocrystal size is larger than the microemulsion drops, so continued growth must occur through solution transport outside of the microemulsion.

In conclusion, $Co_3[Co(CN)_6]_2$ nanocrystals with controllable morphologies were synthesized *via* the dissociation reaction of the single precursor $K_3[Co(CN)_6]_2$ in a microemulsion system. A higher concentration of $K_3[Co(CN)_6]_2$ and a lower molar ratio of H_2O to surfactant favours polyhedron formation, whereas a lower concentration and a higher molar ratio generally leads to rod or cube formation. The shape-controlled synthesis of $Co_3[Co(CN)_6]_2$ nanocystals can be explained in terms of selective ion adsorption on facets during the crystal growth. The $Co_3[Co(CN)_6]_2$ nanostructures with different morphologies may have interesting magnetic properties as molecule-based magnets, and studies on the magnetic properties of these $Co_3[Co(CN)_6]_2$ nanostructures are in progress. This work offers not only a novel and convenient route to the synthesis of $Co_3[Co(CN)_6]_2$ nanocrystals but also an attractive strategy for the fabrication of nanostructures with different morphologies.

This work was supported by the Natural Science Fund Council of China (NSFC, No. 20331010, 20271007, 90406002 and 20401005) and Specialized Research Fund for the Doctoral Program of Higher Education (SRFDP, No. 20030007014). This work was also supported by Jilin Distinguished Young Scholars Program and the Natural Science Young Foundation of Northeast Normal University.

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