Controlled synthesis of nanorods/nanorings of a novel Co–Cu complex in microemulsion at room temperature†

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Novel Co–Cu complex nanorods with diameters of 100–200 nm and nanorings with a ring-diameter of 80 nm were synthesized *via* a microemulsion method at room temperature. Using this method, the addition of $Co(NH_3)_6^{3+}$ to aqueous solutions of Cu(II) in excessive carbonate promotes the assembly of a new highly charged carbonato-copper(II) anion, $[Cu_4(OH)(CO_3)_8]^{9-}$.

Over the past few years, low-dimensional nanoscale building blocks such as nanorods, nanowires, nanotubes and nanorings have attracted intensive interest due to their importance in fundamental research areas and potential wide-ranging applications.[1–4] Utilizing various methods, different types of nanostructured materials including metals,[5] metal oxides,[6] metal sulfides,[7] metal nitrides and phosphides,[8,9] as well as metal oxysalts[10] have been fabricated because of their extraordinary specialities. However, to the best of our knowledge, until now, there have been few reports on metal complex nanostructured materials except nickel complex nanotubes synthesized recently by Guo's group.[11] During the past two years, our group have successfully reported the preparation of PbO_2/Pb_3O_4 nanorods, BaF_2 nanowhiskers, $Cu/Cu_2O/CuO$ nanotubes, and hydroxyapatite nanofibers *via* a cetyltrimethylammonium bromide (CTAB) assisted method.[12–15] Studies have shown that the key to fabricate a one-dimensional (1D) nanostructure is the way by which atoms or other building blocks are rationally assembled into structures with nanometer-sized diameters but much higher lengths.[1] Microemulsion systems have been widely used as ideal media to prepare nanoparticles.[16–18] A water-in-oil (w/o) microemulsion is a transparent and isotropic liquid medium with nanosized water pools dispersed in a continuous phase and can be stabilized by surfactant and cosurfactant molecules at the water–oil interface. These water pools offer ideal microreactors for the formation of nanoparticles. However, it can also be used to prepare some 1D nanostructures under certain conditions.[12–15] In this communication, we report the synthesis of novel Co–Cu complex ($[Co(NH_3)_6]_3[Cu_4(OH)(CO_3)_8]\cdot 2H_2O$) nanorods with diameters of 100–200 nm and nanorings with a ring-diameter of 80 nm through a simple microemulsion method at room temperature. Furthermore, we speculate that these nanomaterials may exhibit outstanding magnetic properties due to their nanostructure, and might have potential applications in radar absorption.[19,20]

The experimental procedure can be summarized as follows: a quaternary microemulsion, CTAB–water–cyclohexane–n-pentanol, was employed for this study. As a typical synthesis, firstly, two identical solutions were prepared by dissolving CTAB (2 g) in 50 ml of cyclohexane and 2 ml of n-pentanol. The mixed solution was stirred for at least 30 min until it became transparent. Secondly, 0.5 g (2.1 mmol) of $Cu(NO_3)_2\cdot 6H_2O$ was dissolved in an aqueous saturated solution of $K_2CO_3/KHCO_3$ (2.4 and 1.25 M respectively, 10 ml), and then this solution was added to one of the two microemulsions prepared during the first step with stirring. Thirdly, 0.4 g (1.55 mmol) of $Co(NH_3)_6Cl_3$ was dissolved in water (8 ml), and the solution thus formed was added to the other microemulsion with stirring. After substantial stirring, the two optically transparent microemulsion solutions were mixed to form a glaucous suspension which was then stirred for 1–24 h at room temperature. Laurel-green nanostructured materials of the Co–Cu complex began to form. Centrifugation was used to separate the precipitate, which was rinsed with distilled water and absolute ethanol several times. Finally, the volatile solvent was evaporated *in vacuo* at 40 °C and a loose laurel-green powder was obtained. The as-prepared product was used for characterization.

The overall crystallinity and purity of the as-synthesized sample were examined by X-ray diffraction (XRD) measurements performed on a SHIMADZU X-ray diffractometer with Cu Kα radiation. Since the compound was reported very recently,[21] its standard XRD data cannot be found. We simulated the XRD data through calculating the single crystal data (CCDC 228199). The comparison of the two XRD patterns (Figs. 1a and 1b) indicates that all the diffraction peaks of the nanorods (Fig. 1a) are in good agreement with those of the bulk material synthesized by

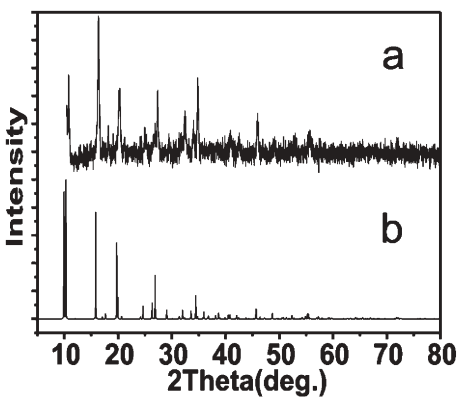

Fig. 1 XRD patterns of (a) Co–Cu complex nanorods and (b) bulk Co–Cu complex (the latter was simulated through calculating the single crystal data CCDC 228199[21]).

† Electronic Supplementary Information (ESI) available: the FT-IR and thermal analyses of the Co–Cu complex nano-materials. See http://www.rsc.org/suppdata/cc/b4/b416222f/

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the general method (Fig. 1b). So it can be considered that the product is pure $[Co(NH_3)_6]_3[Cu_4(OH)(CO_3)_8]\cdot 2H_2O$ and no other impurities were measured in the product to a detection limit. This result was further confirmed by elemental analysis of the product. C, H, and N were analyzed on an Elementar Vario Germany Elemental analyzer, and the contents of cobalt and copper were determined by ICP-Echelle analysis. The elemental analysis found C 7.4%, H 4.6%, N 19.5%, Co 13.7%, and Cu 19.8%, which were consistent with the calculated values for $[Co(NH_3)_6]_3[Cu_4(OH)(CO_3)_8]\cdot 2H_2O$ (C 7.5%; H 4.6%; N 19.8%; Co 13.9%; Cu 20.0%). In addition, FT-IR spectra and TG-DTA curves of the product have also proved the composition of the Co–Cu complex (Figs. S1 and S2,‡, ESI†).

By simply adjusting the reaction time, different morphologies of this complex can be obtained. When the reaction time was at least 24 h, the product consisted mainly of nanorods. The low magnification transmission electron microscope (TEM) images of the synthesized product (Figs. 2a and 2b) show a one-dimensional rod-like structure. From these two figures, we observe that the diameters of the Co–Cu complex nanorods are about 100 nm with lengths ranging from hundreds of nanometers to several micrometers. Moreover, it was found that under long-time bombardment of the electron beam the Co–Cu complex nanorod (Fig. 2b) began curving, which implies the complex might be partly decomposing. When the reaction time was no more than 1 h, we obtained ring-like nanostructures in the product in large-scale yields (Figs. 2c and 2d). As shown, the Co–Cu complex rings have an outer diameter of about 250 nm and an inner diameter of about 90 nm. Further, the SAED patterns in Figs. 2e and 2f confirm that in this region both nanorods and nanorings possess single crystal structures.

To explain the mechanism of the reaction, different conditions which are important factors on the morphology were explored such as the $[H_2O]$/[surfactant] molar ratio (w), the reaction time (t) and the instance with the absence of microemulsion. The results are shown in Figs. S3, S4, S5† and Fig. 3.

As described above, when the reaction time was changed, the nanorods and nanorings of the Co–Cu complex were obtained. In succession, the $[H_2O]$/[surfactant] molar ratio (w) was adjusted to w = 35, 40 and 50 respectively, but with a constant CTAB concentration of 0.1 M. The TEM images of five as-synthesized products are shown in Figs. S3–S5 in the ESI.† When w = 35 and t = 24 h, only nanoparticles were obtained and their diameters are about 50 nm (Fig. S3). When w = 50 and t = 24 h, however, the nanorods we obtained have some defects with low-grade crystallization (Fig. S5). When w = 40 and t = 1, 12, and 24 h, products with different morphologies were observed (Fig. S4): Fig. S4a (t = 1 h) shows the morphology is spherical; Fig. S4b (t = 12 h) indicates a short needle-like morphology with a diameter of 80 nm and a length of 500 nm; from Fig. S4c (t = 24 h) nanorods can be observed which are 100 nm in diameter and 2–3 μm in length. In the absence of microemulsion, only a bulk Co–Cu complex with regular hexagonal and tetragonal structures was obtained (Fig. 3). The diameters of the two structures are both about 1 μm. In addition, the latter structure is hollow and consistent with the tetragonal crystal structure of $[Co(NH_3)_6]_3[Cu_4(OH)(CO_3)_8]\cdot 2H_2O$.[21]

To our best knowledge, the microemulsion can result in different shaped microreactors such as rod-like and spherical structures under different conditions.[11–15] In this case, based on the above discussion, we speculate the formation mechanism as follows: the microemulsion with a certain concentration forms circular microreactors firstly and then the crystals of the Co–Cu complex nucleate and grow with the reaction proceeding. The microemulsion plays an important role as a "soft" template in the formation of the nanostructural materials. However, due to the existence of the cationic surfactant, there is one layer of inorganic anions encircling the aqueous nucleus. And the crystal should first nucleate and grow in the outermost layer, and then gradually grow toward the center of the aqueous nucleus. If the reaction time is short, the compound will form a ring-like structure. When the time is prolonged enough, the rodlike structure is formed gradually.

In addition, owing to the existence of the Co(III) ions and the single bond between Cu atoms[21] this compound may possess interesting magnetic specialities,[19,20] and research into the metal complex nanomaterials is still in progress.

In summary, we selected a quaternary microemulsion, CTAB–water–cyclohexane–n-pentanol, for the preparation of the Co–Cu complex nanomaterials at room temperature. By changing the conditions of the reaction, we can obtain different morphologies such as nanorods and nanorings. The powder XRD pattern, FTIR

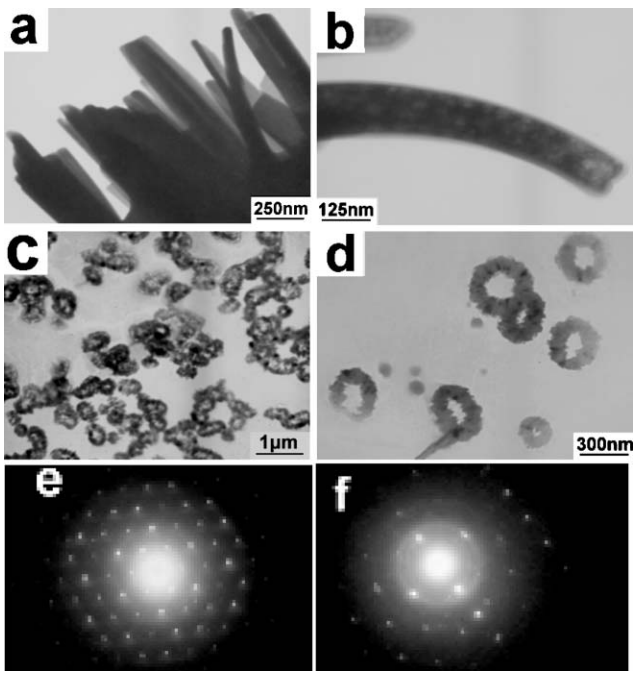

Fig. 2 Different magnified TEM images of (a), (b) the as-synthesized nanorods; (c), (d) the nanorings; and the SAED patterns of (e) the nanorings and f) the nanorods.

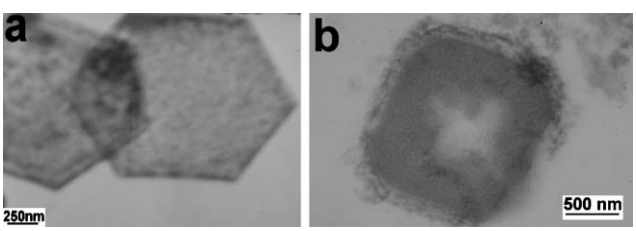

Fig. 3 The TEM images of two different structures of the products obtained in the absence of microemulsion.

spectra, TG-DTA curves and elemental analysis of the product were utilized to confirm the Co–Cu complex composition. Meanwhile, studies of the magnetic specialities of these novel complex nanorods and nanorings are underway.§

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Notes and references

‡ Characterization of materials: a) powder XRD was performed on a SHIMADZU XRD6000 with Cu Kα radiation operated at 40 kV voltage and 50 mA current and XRD patterns were recorded from 15° to 80° (2θ) with a scanning step of 0.02° at room temperature. b) FTIR spectra were recorded on a Nicolet MAGNA-IR 560 spectrometer with a wide-band MCT liquid nitrogen-cooled detector and a KBr beam splitter. c) TG-DTA was recorded on TA2000 with a calefactive speed of 5 °C min^{-1}. d) C, H, and N element analyses were performed on an Elementar Vario Germany Elemental analyzer, and the content of cobalt and copper were determined by ICP-Echelle analysis with emissive power 1.1 kW, velocity of cooling gas flow 18 L min^{-1}, assistant gas 0.5 L min^{-1}, pulverization gas 50 psi and pump speed 0.6 mL min^{-1}. e) Transmission electron micrographs were taken with a Hitachi H-8100 microscope operated at a voltage of 200 kV. § The FT-IR and thermal analyses of the Co–Cu complex nano-materials are discussed in the ESI.†

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