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A simple wet chemical route for large-scale synthesis of $Cu(OH)_2$ nanowires

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Abstract

Polycrystalline $Cu(OH)_2$ nanowires with an average diameter of ca. 8 nm and lengths of up to hundreds of micrometers were synthesized by using a simple chemical route at ambient temperature. The crystallity, purity, morphology, and structure features of the as-prepared $Cu(OH)_2$ nanowires were investigated by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM). The growth mechanism of the $Cu(OH)_2$ nanowires were studied in detail.

Developing a controlled-synthesis method of nanostructures at the mesoscopic level is one of the most challenging issues presently faced by materials scientists [1]. This is especially true of nanowires, which are one-dimensional (1D) objects, for which the control of growth at the molecular level seems particularly difficult [2–11]. Several methods have been used to grow nanowires, such as laser-assisted catalytic growth [2–5], solution–liquid–solid (SLS) method [6–8], templating method [9–13]. To the best of our knowledge, there are a few reports on the preparation of $Cu(OH)_2$ nanoparticles. For example, McFadyen and Matijevic [14] synthesized $Cu(OH)_2$ colloids particles by using a wet chemical method. There are no report on the synthesis of $Cu(OH)_2$ nanowires. Herein we demonstrate a new and simple wet chemical route for large-scale synthesis of the nested $Cu(OH)_2$ nanowires.

The synthesis of $Cu(OH)_2$ nanowires includes the following steps: 0.998 g $CuSO_4 \cdot 5H_2O$ was dissolved in 100 ml distilled water, which was stirred with a magnetic stirrer. This solution was stirred for 15 min to ensure that the $CuSO_4$ dissolved completely. Then 30 ml of 0.15 M NH_4OH was fast added into $CuSO_4$ solution, under constant stirring. After stirring for 15 min, 6 ml of 1.2

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M NaOH was added dropwise into the above solution, under constant stirring. A blue precipitate of $Cu(OH)_2$ was produced. After stirring for 15 min, the blue $Cu(OH)_2$ precipitate was washed with distilled water several times, filtered, and dried in an oven at 35 °C for 24 h.

The powder X-ray diffraction (XRD) analysis was performed using a Rigaku (Japan) D_{max} X-ray diffractometer with graphite monochromatized Cu K_α radiation ($\lambda = 0.154178$ nm). Transmission electron microscopy (TEM) images were obtained on a JEM-200 CX transmission electron microscope, using an accelerating voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL-2010 transmission electron microscope, using an accelerating voltage of 200 kV.

Fig. 1 show powder XRD pattern of the as-prepared $Cu(OH)_2$ nanowires. All of the reflections of the XRD pattern of the as-synthesized $Cu(OH)_2$ nanowires can be easily indexed to those of orthorhombic crystalline $Cu(OH)_2$ (JCPDS 13-420), indicating the formation of single-phase $Cu(OH)_2$. The $Cu(OH)_2$ lattice constants calculated from the XRD data are $a = 2.954$, $b = 10.386$ and $c = 5.270$ Å, consistent with those of bulk $Cu(OH)_2$ (JCPDS 13-420).In the XRD pattern, the peaks were not widened obviously due to the facts that it is normal to the same as bulk pattern. The following TEM images (Fig. 2) indicate that the diameters of these nanowires are very small, and the lengths are long. The as-synthesized nanowires aggregate together easily due to their small dimension. Thus the pattern of XRD may be the result of the same as bulk.

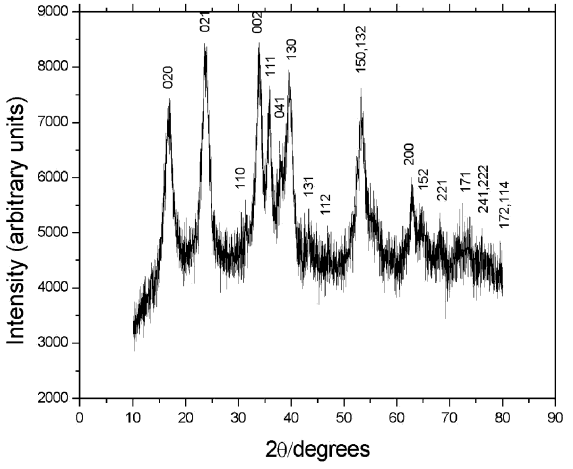


Fig. 1. The XRD pattern of the as-synthesized $Cu(OH)_2$ nanowires.

The morphology of the nanowires was observed by TEM. TEM images of the as-synthesized $Cu(OH)_2$ nanowires are shown in Fig. 2. Bulk quantities of the nested $Cu(OH)_2$ nanowires were fabricated with relatively uniform diameters. The nanowires are relatively straight and long, resulting in a large aspect ratio. The diameters of nanowires range from 4 to 12 nm. It can be seen that most nanowires have diameters of ca. 8 nm, and the lengths of up to hundreds of micrometers; but nanowires with diameters of less than 5 nm were also found. The average diameter of nanowires is ca. 8 nm estimated from the TEM images. Due to the small diameters and aggregated together of nanowires, it is very difficult to accurately give the size distribution of diameters.

A typical HRTEM image of a single nanowire with a diameter of ca. 8 nm is shown in Fig. 3a. The visible lattice fringes illustrate that the nanowire is a polycrystalline rather than a single crystal within the lateral dimension, as shown. The interplanar spacing is about 0.2625 nm, which corresponds to the {0 0 2} planes of orthorhombic $Cu(OH)_2$. This result reveals that the growth plane of the nanowires is one of the {0 0 2} planes in the area shown. The two-dimensional lattice image

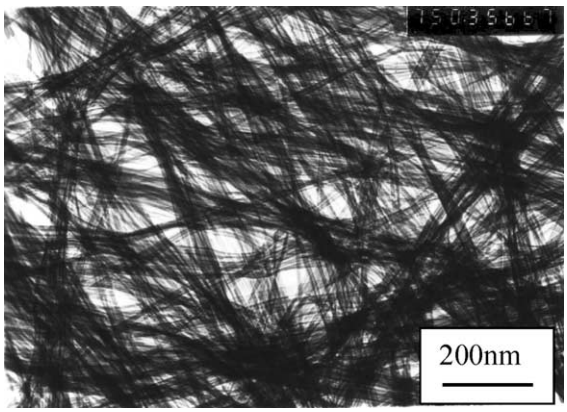


Fig. 2. TEM images of the as-prepared $Cu(OH)_2$ nanowires.

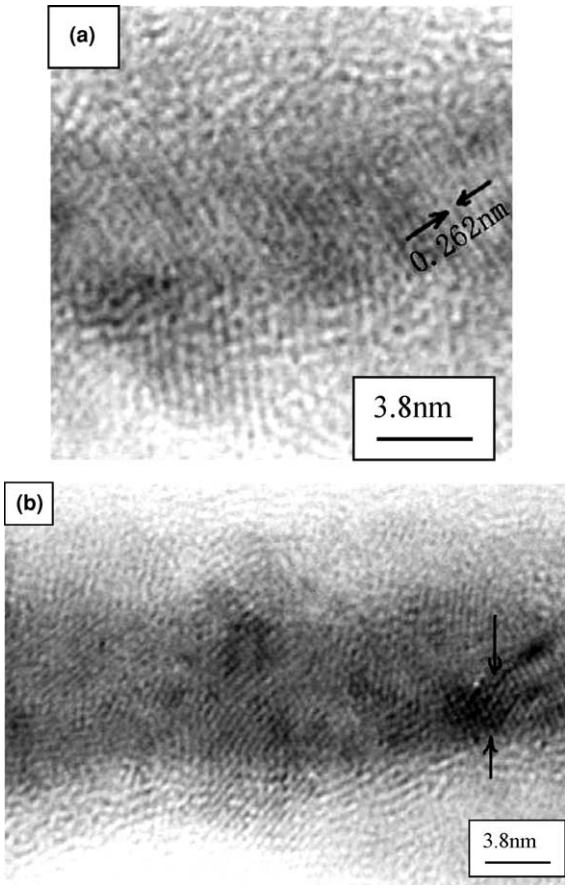


Fig. 3. (a) and (b) HRTEM images of a ca. 8 nm $Cu(OH)_2$ nanowire.

pointed by the arrowheads (Fig. 3b) also indicates that the $Cu(OH)_2$ nanowires are polycrystalline.

This work has shown that both ammonia and sodium hydroxide are needed in order to obtain the $Cu(OH)_2$ nanowires. In the present case, it is well known that Cu^{2+} ion forms complex with anions and ligands present in the precipitating solutions, the bond strength of which follows the order $OH^- > NH_3 > SO_4^{2-}$. At the pH of interest (before the addition of NaOH), stability constants [15] indicate the most stable species to be the square-planar amino complex $[Cu(NH_3)_4^{2+}]$. A rise in the pH on addition of NaOH causes a decrease in the stability of this complex, resulting in the precipitation of $Cu(OH)_2$. The chemical reactions we employed for the synthesis of $Cu(OH)_2$ nanowires can be formulated as

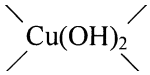
$$2CuSO_4 + 2NH_3 \cdot H_2O \rightarrow Cu_2(OH)_2SO_4 + (NH_4)_2SO_4 \quad (1)$$

$$Cu_2(OH)_2SO_4 + 8NH_3 \rightarrow 2[Cu(NH_3)_4]^{2+} + SO_4^{2-} + 2OH^- \quad (2)$$

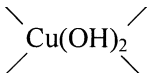
$$[Cu(NH_3)_4]^{2+} \rightarrow Cu^{2+} + 4NH_3 \quad (3)$$

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \quad (4)$$

We can give a reasonable explanation for wire formation of $Cu(OH)_2$ according to $Cu(OH)_2$ structure feature and specific interaction of constituent Cu^{2+} ions with ligands forming solutes in the mother solutions. Oswald et al. [16] have determined that the $Cu(OH)_2$ structure consists of oblate chains



in the planes (0 0 1), oriented along [1 0 0], with characteristic of the square planar coordinated Cu^{2+} ion and $\sigma_{x^2-y^2}$ strong bonds. This strong



olated chain is parallel with the shortest lattice parameter, and acts as a structure-making factor, around which another set of stronger bound chains is created through olation/oxolation bridges connected with the first one by the OH^- or O^{2-} anions. This bond structure leads to a two-dimensional or quasi-one-dimensional framework packed together by hydrogen bridges, yielding the formation of wire-like $Cu(OH)_2$. On the other hand, Matijevic and co-workers [15] applied the periodic bond chains (PBC) theory, which is based on the existence of strong bonds in the particle of a given morphology, to the $Cu(OH)_2$ structure. They concluded that the {0 1 0} is very important face of morphological significance. Based on these results, we can make another rational explanation for the formation of $Cu(OH)_2$ wire particles. The formation of the $Cu(OH)_2$ nanowires could be due

to the adsorption of solutes on the crystal faces. This process should be related to the bond strength of such species to Cu^{2+}; thus, the strong bonds in the planar coordination of copper will always be occupied by OH^-. However, NH_3 may adsorb on (0 1 0) surface, thus preventing the formation of hydrogen bridges and, consequently, the packing of the (0 1 0) slices; as a result elongated particles are formed. This explanation is corroborated by the presence of NH_3 in the $Cu(OH)_2$ particles, detected by infrared spectroscopy (not shown here) of the $Cu(OH)_2$.

In order to investigate the effects on the $Cu(OH)_2$ particle size and shape of PH, NH_3 and SO_4^{2-} at different concentration, several comparative experiments were made. Keeping other conditions the same, the concentration of $NH_3 \cdot H_2O$ is between 0.05 and 0.15 M, $Cu(OH)_2$ nanowires can be successfully synthesized. Because higher concentration of $NH_3 \cdot H_2O$ may cause a decrease in the stability of complex $[Cu(NH_3)_4^{2+}]$, resulting in the formation of particles, and lower concentration could not produce enough stabile complex $[Cu(NH_3)_4^{2+}]$ to form nanowires. The pH of solution also has effects on the size and shape of $Cu(OH)_2$ particles. During the experiment, we found that at the pH of interest (>8), a large number of nuclei are formed instantaneously, that grow to reasonably uniform nanowires, but if the concentration of NaOH is above 4 M, only large particle formed because the formation of cuprate ions at high pH lead to lower supersaturation and a smaller number of nuclei that grow to large $Cu(OH)_2$ particles. According to reaction (2), the concentration of SO_4^{2-} also affects the stability of complex $[Cu(NH_3)_4^{2+}]$. Lower concentration of SO_4^{2-}, i.e. lower concentration of Cu^{2+}, controls the number of nuclei of $Cu(OH)_2$, resulting in the formation of large $Cu(OH)_2$ particles, instead of nanowires, but if the concentration of SO_4^{2-} is higher, this could not produce enough stabile complex $[Cu(NH_3)_4^{2+}]$ to form nanowires. In our experiments, the nanowires are successfully fabricated in the concentration of $CuSO_4$ range from 0.005 to 0.15 M.

In conclusion, a new and simple synthetic approach has been successfully developed to synthesize the nested $Cu(OH)_2$ crystalline nanowires with an average diameter of ca. 8 nm and the lengths of up to hundreds of micrometers. This method requires neither complex apparatus and sophisticated techniques nor metal catalysts and surfactants. The process is carried out at ambient temperature and the yield of the final $Cu(OH)_2$ nanowires is bulk. From these points of view, this method has potential for industrial-scale application.

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