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SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

One-step Template-free Solution Route for $Cu(OH)_2$ Nanowires[1]

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Abstract—$Cu(OH)_2$ nanowires with a diameter of 8-10 nm and lengths of tens of micrometers were fabricated in the basic solution by dropping simply NaOH solution into $CuCl_2$ solution at ambient temperature. The formation mechanism of nanowires was discussed. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD) were used to characterize the samples.

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For their novel and fascinating properties, and their potential applications in nanodevices, the considerable interest has been attracted to fabrication of one-dimensional (1D) nanomaterials, such as nanorods, nanowires, nanoribbons, and nanotubes [1]. Many methods have been developed for the fabrication of ID materials, including solvothermal methods [2], template-based methods [3, 4], VLS methods [5, 6], and so on. Among these methods, solution phase synthesis attracted increasing attention for its low cost, controllable synthesis [7, 8]. As a well-known layered material with orthorhombic structure, $Cu(OH)_2$ has received much attention in recent years. The magnetic properties of $Cu(OH)_2$ are remarkably sensitive to the intercalation of molecular anions, making the material a candidate for sensor applications [9–11]. Using $Cu(OH)_2$ nanowires as precursors, it is easy to prepare CuO, Cu_2O and Cu nanowires [12–14]. In previous works, copper (II) hydrous oxide solutions of various particle shapes and uniformity were obtained by aging copper salt solutions at different temperatures under controlled pH conditions [15, 16]. $Cu(OH)_2$ nanowires were synthesized mainly by two routes: precipitating cupric salt by the mixture of ammonia and NaOH solution [17–20] and oxidizing copper foil in the basic solution of ammonia [12, 21, 22]. Luo synthesized $Cu(OH)_2$ nanostrands by adding ammonia solution to $Cu(NO_3)_2$ solution [23]. $Cu(OH)_2$ nanofibers and nanotubes arrays were synthesized by oxidization of a copper foil in a basic solution electrically or chemically [24–26].

In this work, a simple and facile method was developed to synthesize $Cu(OH)_2$ nanowires by dropping NaOH solution into $CuCl_2$ solution at ambient temperature under controlled pH conditions. The formation mechanism of nanowires was discussed.

EXPERIMENTAL

1 mol/L NaOH (96.0%, Xi'an Chemicals Plant) solution was dropped into 150 mL 0.05 mol/L $CuCl_2$ solution under agitation at room temperature. The pH value of $CuCl_2$ solution was controlled by a pH meter of the PHS-3C type (2nd analytical instruments plant, Shanghai). When the pH value of solution reached 12.5, the pH value was maintained for 30 min by carefully dropping 1 mol/L NaOH solution or 1 mol/L HCl solution. After 1.5 h, agitation was stopped and the precipitate was aged for 1–3 days. The precipitate was washed with distilled water and absolute ethanol several times.

The products were characterized by JSM-5600LV scanning electron microscopy (SEM) (JEOL Ltd, Japan), X'Pert PRO X-ray diffractometer (XRD) (PANalytical, Holland), and Hitachi H-6000 transmission electron microscopy (TEM) (Hitachi, Japan). The X-ray diffraction analysis was performed at 40.0 KV and 30.0 mA with CuK_α radiation ($\lambda = 0.15406$ nm).

RESULTS AND DISCUSSION

Fig. 1 shows the XRD pattern of the as-synthesized $Cu(OH)_2$ a nanowires. All the peaks in Fig. 1 can be well indexed into the orthorhombic $Cu(OH)_2$ structure with lattice constants $a = 2.951$Å, $b = 10.59$ Å, and $n = 5.273$ Å (JCPDS 13-420). In the XRD pattern, the broadening peaks indicated the tiny size of crystals of as-synthesized products.

Fig. 2 are the scanning electron microscopy (SEM) images of $Cu(OH)_2$ nanowires. Two existing manners, bundle and nest in the $Cu(OH)_2$ nanowires, were observed from Fig. 2a,b. The bundle-like structure, which consisted of several or tens of single nanowires, was the dominant component. Fig. 2c shows the diameter of bundles was up to several hundred nanometers

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[1] This article was submitted by the authors in English.

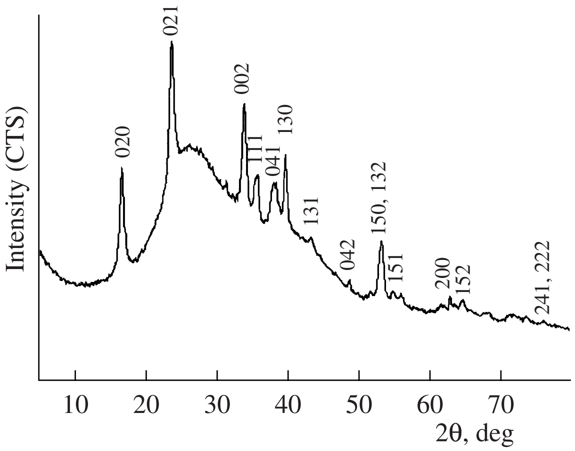

Fig. 1. The XRD pattern of the as-synthesized $Cu(OH)_2$ nanowires.

and length was about tens of micrometers. Fig. 2d shows the nest-like structures scattered among the bundles. They were constituted by short well-dispersed $Cu(OH)_2$ nanowires which interconnected to form a clew. The length of single $Cu(OH)_2$ nanowires in the nest-like structures was about 500–2 μm, which was much shorter than that of bundles. The bundle-like structures of $Cu(OH)_2$ nanowires were similar to that of $Cu(OH)_2$ nanowires synthesized by the KOH/NH_3 route, but in which nest-like structures were not be observed [17].

TEM images of as-synthesized $Cu(OH)_2$ nanowires are shown in Fig. 3. Though $Cu(OH)_2$ nanowires existed in two congregating manners, the diameter of single nanowires was relatively uniform. It ranged from 8 to 10 nm. The single nanowire was straight and its aspect ratio was up to several thousands. The bundle-like structures in Fig. 3a were composed of tens of single $Cu(OH)_2$ nanowires connecting closely side-by-side. The surface of bundles was full of holes, the diameters of which were about several nanometers. Fig. 3b are TEM images of nest-like structures in which well-dispersed thicker nanowires were composed of single or several $Cu(OH)_2$ nanowires. Among nest-like structures, holes were not found on the surface of single nanowires. It could be inferred that the holes were formed at the boundary between single nanowires during single nanowires connecting side-by-side.

In previous works, ammonia solution were used to prepare $Cu(OH)_2$ nanowires, in which NH_3 was considered to formed complex $[Cu(NH_3)_4]^{2+}$ with Cu^{2+} ion, played a transporter role of Cu^{2+} ion, and NH_3 adsorbed on the (010) surface of $Cu(OH)_2$ to prevent the formation of hydrogen bridges. Consequently, the packing of the (010) slices resulted in forming elongated particles and the preferential growth of planes [17, 18, 23]. In this work, we proposed that OH^- ions played an important role during the formation of $Cu(OH)_2$ nanowires, which replaced NH_3 of previous works to coordinate with Cu^{2+} ions to form $[Cu(OH)_4]^{2-}$ complexes which transported Cu^{2+} to the nanowires growing tips with

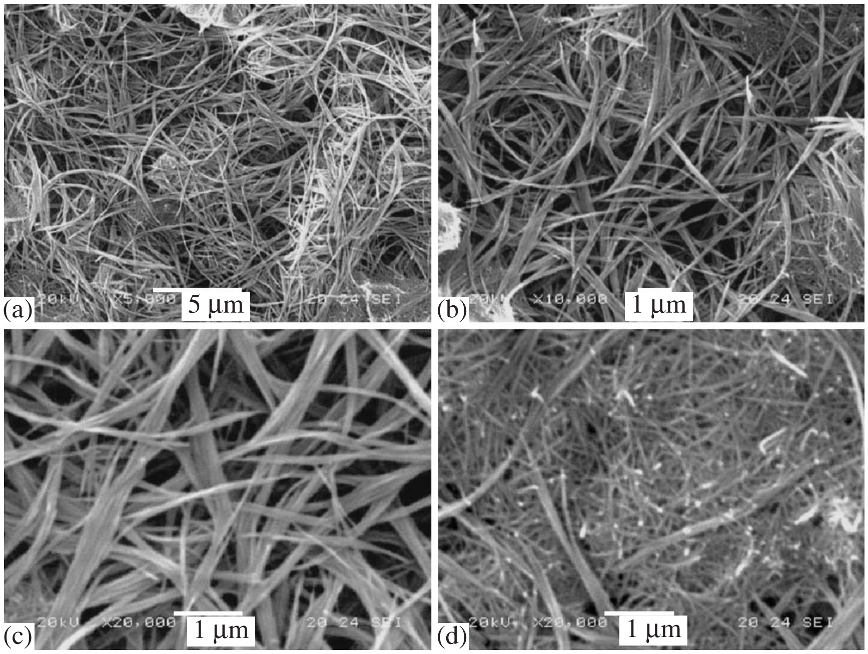

Fig. 2. SEM images of the as-synthesized $Cu(OH)_2$ nanowires.

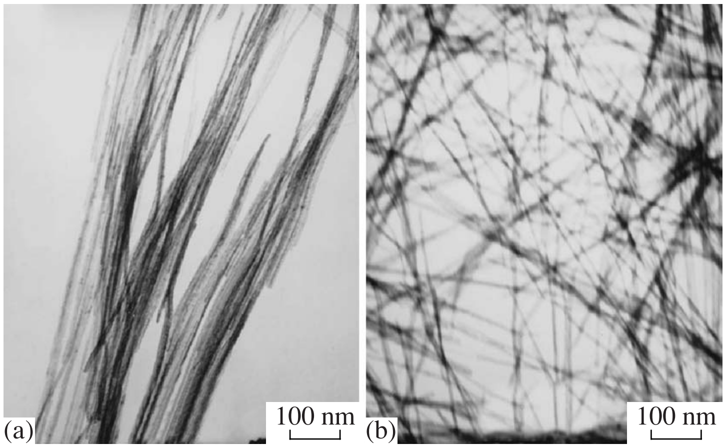

Fig. 3. TEM images of the as-synthesized $Cu(OH)_2$ nanowires.

OH^- ligands attached. $Cu(OH)_2$ strongly absorbed OH^- ions in the strong basic solution for its positively charging. It was well-known that the surface energy density of different crystal planes was varied drastically, which suggested that the different crystal planes of $Cu(OH)_2$ absorbed different amounts of OH^- ions. The crystal planes that absorbed more OH^- ions would repel the approach of $[Cu(OH)_4]^{2-}$ and growth of the crystal planes would be hindered. On the contrary, proper absorption would favor the growth of crystal planes. As a result, $Cu(OH)_2$ nanowires were fabricated. When the pH of solution was about 10, the precursor atacamite $Cu_2Cl(OH)_3$ was obtained, which was about 5–8 nm. The diameter of the atacamite nanoparticle was paralleled to the diameter of $Cu(OH)_2$ nanowires. It suggested that the atacamite nanoparticles played a template role at the beginning of the formation of $Cu(OH)_2$ nanowires. With the increasing of pH and the prolonging of aging time, the templates were dissolved by forming $[Cu(OH)_4]^{2-}$ ions, which reprecipitated by self-assembly to the growing tips of $Cu(OH)_2$ crystals. For the slow growth of side crystal planes of $Cu(OH)_2$ nanowires, the diameter of nanowires was increased to 8–10 nm. As for the single $Cu(OH)_2$ nanowires connecting side-by-side, the marginal hydrogen bonds in the nanowires reacted with OH^- ions in the strong basic solution to form hydrogen bond bridges between adjacent nanowires with aging. The driving dynamics was to form more stable bundle-like structure relative to the nanowires of 8–10 nm in diameter. As a result, single nanowires aggregated into bundles. Nest-like structures were the remnants of single nanowires slightly aggregated, which were not completely transformed into bundle-like structures.

In summary, $Cu(OH)_2$ nanowires were fabricated in a basic solution by a one-step wet-chemical method at room temperature. $Cu(OH)_2$ nanowires existed in two manners: bundle and nest. OH^- ions played an important role in transporting Cu^{2+} by forming the complex $[Cu(OH)_4]^{2-}$ and resulting in varying growth rates of crystal planes by absorption on the surfaces of $Cu(OH)_2$ crystals. This paper presented a facile and simple method to synthesize $Cu(OH)_2$ nanowires at ambient conditions without any surfactant. It may be extended to the synthesis of other hydroxides nanowires, such as $Ni(OH)_2$ and $Co(OH)_2$, which we are investigating.

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