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Preparation and characterization of $Cu(OH)_2$ and CuO nanowires by the coupling route of microemulsion with homogenous precipitation

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1. Introduction

One-dimensional (1D) inorganic nanomaterials, such as nanowires, nanorods, and nanotubes, have attracted considerable attention in recent years due to their potential applications in constructing nanoscale electronic devices, optoelectronic devices, and sensing devices [1–3]. Many methods have been used to prepare 1D nanomaterials, such as laser ablation [4], the plasma evaporation method [5], chemical vapor deposition (CVD) [6], solvothermal synthesis [7], hydrothermal synthesis [8], using microemulsions [9], sol-gel processing [10] and coprecipitation [11]. Of those methods, the microemulsion method has become popular for the synthesis of 1D nanostructures [12]. But this method is prone to cause a maldistribution of reactants: the size of the water droplets, and the stability of the water droplets and the grains change. The size distribution of particles thus becomes scattered. So, the coupling method of microemulsion with homogenous precipitation was proposed [13].

Layered materials, $Cu(OH)_2$ and basic Cu(II) salts with an orthorhombic structure have received much attention because of their potential applications in optoelectronic devices, catalysis,

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ABSTRACT

Using CuSO₄ and NH₃ · H₂O as raw materials, one-dimensional (1D) Cu(OH)₂ nanowires were prepared by the coupling route of microemulsion with homogenous precipitation. The morphology and structure of products were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results indicate that the as-prepared Cu(OH)₂ nanowires are of high purity and are single crystalline with orthorhombic structure. The diameter of Cu(OH)₂ nanowires ranges from 33 nm to 46 nm and the length ranges from 400 nm to 2000 nm. The effects of different conditions such as the molar ratio of water to surfactant (ω), reactant concentration and the aging time on the morphology and the size of the products were studied. 1D CuO nanowires could be simply obtained by the dehydration of Cu(OH)₂, while maintaining the wire-shaped architecture. The catalytic performances of CuO nanocrystals on the thermal decomposition of ammonium perchlorate (AP) were also studied.

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and superconductors [14,15]. The magnetic properties of $Cu(OH)_2$ are remarkably sensitive to the intercalation of molecular anions [16–18], making the material a candidate for sensor applications. More importantly, CuO can be obtained through the dehydration of $Cu(OH)_2$, and the original size and morphology of $Cu(OH)_2$ nanostructures can be retained. Copper(II) oxide (CuO) nanoparticles are an important inorganic semiconductor with a direct bandgap value of 1.85 eV [19]. This material has a great potential in different technological applications such as gas sensors, magnetic phase transitions, catalysts, superconductors, lithium ion electrode materials and field emission (FE) emitters [20–23]. Up to now, various methods have been developed for obtaining $Cu(OH)_2$ and CuO nanowires; however, no work has been published concerning the preparation of $Cu(OH)_2$ and CuO nanowires by the coupling method of homogenous precipitation with microemulsion.

In this work, $Cu(OH)_2$ and CuO nanowires were synthesized by the coupling route of microemulsion with homogeneous precipitation, and they characterized by TEM, SEM, XRD, TGA and FT-IR spectroscopy. The effects of the ω value, aging time, reactant concentration and the formation mechanism of $Cu(OH)_2$ nanowires were studied and discussed. The results show that the diameter of $Cu(OH)_2$ nanowires ranges from 33 nm to 46 nm and the length ranges from 400 nm to 2000 nm. 1D CuO nanowires could be simply obtained by the dehydration of $Cu(OH)_2$, while maintaining the wire-shaped architecture. The catalytic performances of CuO nanocrystals on the thermal decomposition of ammonium perchlorate were studied by DTA method.



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2. Experiments

2.1. Materials

The following chemicals were used: copper(II) sulfate pentahydrate (CuSO₄ \cdot 5H₂O), ammonia (NH₃ \cdot H₂O), NaOH, CTAB (Hexadecyl trimethyl ammonium bromide), *n*-butanol, and cyclohexane. All chemicals were analytical grade and used as received without further purification.

2.2. Preparation of Cu(OH)₂ and CuO nanocrystals

1 ml of 28 wt% ammonia was gradually added to 5 ml 0.2 mol/L aqueous solution of CuSO₄ with constant stirring, to prepare aqueous solution of Cu(NH₃)₄²⁺.

In a typical experimental procedure, 2 g CTAB and 3 g *n*-butanol were added to 18 ml cyclohexane; after that 1.2 ml 0.2 mol/L $Cu(NH_3)_4^{2+}$ aqueous solution was injected into this mixture, which was stirred until a transparent microemulsion was obtained. Then, the procedure was followed by gradually dropping 0.3 ml 2 mol/L NaOH aqueous solution into the microemulsions; the solution instantly turned blue, which implied that nanometer $Cu(OH)_2$ particles had been produced. Then the mixture was constantly stirred for 30 min and rested for 8 h at room temperature. The resulting precipitate was obtained by centrifugation and washed with ethanol and distilled water, respectively. After being dried at 60 °C for 3 h, $Cu(OH)_2$ nanowires were obtained. The $Cu(OH)_2$ was calcined at 400 °C for 2 h to produce CuO nanowires. The procedure described above was repeated with different molar ratios (ω) of water to surfactant and different salt concentration.

2.3. Catalytic performance on thermal decomposition of ammonium perchlorate (AP)

0.02 g CuO was blended with 0.98 g AP (2:98) in an agate mortar; thermogravimetric analysis (TGA) of the mixture was performed with a Beijing Optical Instrument Factory WCT-2A TG-DTA apparatus under an atmosphere with a heating rate of 15 °C/min from room temperature to 600 °C.

2.4. Characterization

The composition and phase purity of the as-prepared products were characterized by X-ray diffraction(XRD) on a D/Max-3B X-ray diffractometer with monochromatized Cu K α radiation ($\lambda = 0.15405$ nm), at a scanning rate of 8 °min⁻¹ in a range from 10° to 70°; scanning electron microscopy (SEM) images were taken on a MX2600FE microscope at an accelerating voltage of 10 kV; transmission electron microscopy (TEM) was performed on a JEM 2100 microscope with an accelerating voltage of 200 kV; thermogravimetric analysis (TGA) was carried out with a Beijing Optical Instrument Factory WCT-2A TG-DTA apparatus with a heating rate of 15 °C/min in an atmosphere from room temperature to 600 °C. Fourier transform infrared (FT-IR) spectra were recorded on the diluted samples in KBr pellets using a Perkin Elmer spectrum 100 FT-IR spectrophotometer in the range 4000–400 cm⁻¹.

3. Results and discussion

3.1. TEM analysis

The TEM image shown in Fig. 1 reveals the general morphology of the as-produced Cu(OH)₂ nanowires for a reactant concentration of 0.3 mol/L, $\omega = 15$, and an aging time of 8 h. It can be seen that the uniform nanowires have a narrow size distribution. Most of the nanowires have fairly uniform diameters of around 37 nm and lengths up to 2000 nm.



Fig. 1. TEM image of Cu(OH)₂ nanowires.

3.2. TGA and FTIR analysis

The TGA test of the $Cu(OH)_2$ was conducted simultaneously at a heating rate of 15 °C/min between room temperature and 500 °C, and the result is shown in Fig. 2(a). According to the result, the major mass loss occurs in the temperature range of 140 °C to 190 °C, which is due to the hydroxide decomposition to give CuO. The second mass loss occurs in the temperature range from 190 °C to 400 °C, which may be attributed to decomposition of the residual absorbed organic compounds. Thus 400 °C is considered as an appropriate calcination temperature for the CuO precursor.

The samples were further examined by FT-IR analysis. As seen in Fig. 2(b), the FTIR spectrum indicated the existence of CTAB and cyclohexane molecules in the Cu(OH)₂ nanowires. The bands at 3573.3, 1385.2 and 939.7 cm⁻¹ can be assigned to the stretching mode of the hydroxyl, C–H, and C–C of pure CTAB. The band at 687.1 cm⁻¹ can be assigned to the C–H deformation vibration of cyclohexane. The bands at 3309.4 and 1631.2 cm⁻¹ correspond to the stretching and bending modes of the hydroxyls of adsorbed water. The band at 423.3 cm⁻¹ can be assigned to Cu–O stretching mode and may prove that Cu(OH)₂ is formed. The CuO precursor was obtained by calcining Cu(OH)₂ at 400 °C for 2 h. As can be seen from the FT-IR spectrum, except for the bands at 594.3 and 537.1, which can be assigned to Cu–O stretching mode, all bands corresponding to the CTAB and cyclohexane impurities disappear, clearly demonstrating that the impurities have been removed.

3.3. XRD analysis

It is well known that orthorhombic $Cu(OH)_2$ can be easily transformed to monoclinic CuO upon heat treatment [14]. According to the TGA analysis, the CuO nanowires were obtained by calcining $Cu(OH)_2$ at 400 °C for 2 h; the corresponding XRD patterns of the precursor $Cu(OH)_2$ nanowires and the final product, CuO nanowires, are shown in Fig. 3. Fig. 3(a) is the XRD pattern of the precursor $Cu(OH)_2$, in which all of the diffraction peaks can be indexed to orthorhombic $Cu(OH)_2$ (JCPDS 13-0420). The XRD pattern shown in Fig. 3(b) suggests that the as-prepared final product is pure monoclinic CuO (JCPDS 48-1548). No characteristic XRD peaks arising from possible impurity such as $Cu(OH)_2$, CTAB and cyclohexane are detected, indicating the complete transformation from $Cu(OH)_2$ to CuO.

3.4. Effect of the molar ratio (ω) of water to surfactant

Fig. 4 shows the morphology and the size distribution of $Cu(OH)_2$ nanocrystals with different molar ratio (ω) of water to surfactant, for a reactant concentration of 0.2 mol/L and an aging time of 8 h. As can be seen from these images, when the ω value



Fig. 2. TGA and FT-IR curves of Cu(OH)₂ nanowires to CuO nanowires.



Fig. 3. XRD patterns of Cu(OH)₂ nanowires (a) and CuO nanowires (b).

is 5 (Fig. 4(a)), the majority of Cu(OH)₂ nanoparticles have a small size of 30-40 nm (mean size 35 nm) with sphere-like shape and a narrow size distribution. When the ω value increases to 10 (Fig. 4(b)), 15 (Fig. 4(c)), and 20 (Fig. 4(d)), the morphology of Cu(OH)₂ changes to nanowires: the average diameter is 33, 40, and 46 nm, respectively, and the average length is 400, 1000, and 1650 nm, respectively. This indicates that the morphology of droplets in the microemulsion is sphere-like when the ω value is low; with the increase of the ω value, the morphology of droplets in the microemulsion becomes wire-like and both the diameter and the length of the nanowires increase simultaneously. When the sizes of the nanowires reach that of the droplets, the surfactants absorb on the surface of the nanowires and restrict their growth further. Therefore, by changing the ω value, the microemulsion method can effectively control the size and morphology of the product.

3.5. Effect of precursor salt concentration

Figs. 5 and 4(c) show the morphology and the size distribution of the Cu(OH)₂ nanowires with different concentrations; the ω

value is 15 and the aging time is 8 h. As can be seen from these images, when the reactant concentration is 0.1, 0.2, and 0.3 mol/L, the average length is 1400, 1650, and 2000 nm, respectively; however the diameter shows no remarkable change.

As we know, when the ω value is fixed, the size and morphology of the droplets do not change, but the number of particles that take part in the reaction will increase when the concentration of reactant increases: the formation rate of Cu(OH)₂ crystal nuclei becomes rapid and the size of the Cu(OH)₂ nanowires increases. In this work, the length of the nanowires changes obviously, but the diameter shows no remarkable change. Chen et al. [24] also observed similar phenomena in the synthesis of barium strontium titanate nanorods in reverse microemulsion. They suggested that the crystal nucleus forms and starts to grow along the droplet morphology to form nanorods after the molecules of the anion penetrate in the droplet. The transverse growth of the crystal is prone to end quickly because the diameter of droplets is much shorter. But it is difficult for the length of the nanorods to reach that of the droplet, because the length of droplets is much longer and there are not sufficient reactants to afford the longitudinal growth of the crystal. This can explain why the length of nanowires changes obviously, but the diameter does not when the concentration of reactant increase.

3.6. Effect of aging time

Fig. 6 shows the morphology and the size distribution of the $Cu(OH)_2$ nanocrystals aged for 16 h; the other experimental conditions are the same as those in Fig. 4(c). In contrast to the nanowires shown in Fig. 4(c), there is no obvious change in diameter and length. This shows that there is no significant effect on the size of $Cu(OH)_2$ nanowires on increasing the aging time.

3.7. Morphology analysis of CuO nanocrystals

The CuO nanocrystals were obtained by calcining $Cu(OH)_2$ at 400 °C for 2 h, Fig. 7(a) shows the morphology and the size



Fig. 4. SEM images of products for different ω values: (a) 5, (b) 10, (c) 15, (d) 20; c = 0.2 mol/L; t = 8 h.



Fig. 5. SEM images of products at different reactant concentrations: (a)0.1 mol/L, (b)0.3 mol/L; $\omega = 20$; t = 8 h.



Fig. 6. SEM images of products aged for 16 h. $\omega = 20$; c = 0.1 mol/L.



Fig. 7. SEM image of CuO nanowires.

distribution of the CuO nanoparticles when the other experimental conditions are the same as those in Fig. 4(a). Compared with Fig. 4(a), no obvious change is observed in the morphology and the size distribution. Fig. 7(b) shows the morphology and the size distribution of the CuO nanowires when the other experimental conditions are the same as those in Fig. 4(d). In contrast to the samples without calcination (Fig. 4(d)), the wire-shaped architecture was still maintained; the morphology and the size show no remarkable change. This means the Cu(OH)₂ has a high thermal stability and is stable even after calcination at 400 °C.

3.8. Catalytic effect

The catalytic performances of CuO nanoparticles and nanowires on thermal decomposition of ammonium perchlorate were studied by the DTA method. Fig. 8 shows the DTA curves of AP decomposition in the absence and presence of CuO nanoparticles and nanowires. It can be seen that the decomposition of pure AP mainly consists of three steps: the endothermic peak at a maximum peak temperature of 243.6 °C is due to the transition of AP crystals from the orthorhombic form to cubic form [25], the low-temperature exothermic peak at 337 °C can be attributed to



Fig. 8. DTA curves for the decomposition of the AP catalyzed by different morphologic CuO catalyst: (a) pure AP, (b) AP + CuO nanowires, (c) AP + CuO nanoparticles.

the partial decomposition of AP and the formation of some intermediate NH₃ and HClO₄ by dissociation and sublimation, and the high-temperature exothermic peak at 437 °C is caused by the complete decomposition to volatile products [26]. It is found that CuO nanocrystals have no obviously effect on the both endothermic peak and low-temperature exothermic peak. But all of the hightemperature exothermic peaks of AP in the presence of different CuO nanocrystals shift somewhat to lower temperatures; the decomposition heat is obviously increased when CuO nanocrystals are mixed with the AP, which indicates that CuO can promote the thermal decomposition of AP. For nanowires and nanoparticles of CuO, the temperature shifts for the high-temperature exothermic peaks of AP are 114.4 °C and 129.8 °C. respectively. In this work. the CuO nanoparticles exhibit better catalytic activity than CuO nanowires. However, in many important fields such as constructing nanoscale electronic devices, the CuO nanowires exhibit better potential application than CuO nanoparticles.

3.9. Formation mechanism of the $Cu(OH)_2$ nanowires

Most researchers consider that the formation of 1D nanostructures is closely related to the molar ratio (ω) of water to surfactant. When the ω value is low, the droplets are small. There is lots of surfactant on the interfaces of the droplets, the boundary strength of the droplets is higher, the morphology of droplets is spherelike in shape, so nanoparticles are obtained. With the increase of ω value, the volume of droplet increases, the sphere-like shape of the droplets easily changes to a rod-like shape, and the 1D nanostructure can be obtained.

In theory, without the assistance of an additive, the crystallization of $Cu(NH_3)_4^{2+}$ and OH^- as source materials also shows a tendency toward 1D nanostructures (Fig. 9(a)). Cu^{2+} prefers square-planar coordination by OH^- . When OH^- is added, OH^- replaces NH_3 in the[Cu(NH_3)₄]²⁺ complex to form square-planar [Cu(OH)₄]²⁻ units and a coordination self-assembly of > Cu(OH)₂ \cdots Cu(OH)₂Cu < chains takes place quickly [14].

In this work, we put Cu(NH₃)₄²⁺ into the microemulsion; the process of homogenous precipitation occurred in microemulsion. Fig. 9(b) gives the reaction process that we suggest. At a lower ω value ($\omega = 5$), only particles are obtained. The reason may be that the interfacial intensity of spherical droplets is higher, the sphere-like morphology of droplets is hard to metamorphose, so nanoparticles are obtained. When the ω value increases to 10–20, the bulk of droplet becomes larger, the sphere-like morphology of droplets becomes lower. As OH⁻ is added into microemulsion, OH⁻ replaces NH₃ in the [Cu(NH₃)₄]²⁺ complex to form square-planar [Cu(OH)₄]²⁻ units. At the same time, the square-planar [Cu(OH)₄]²⁻ will be absorbed to the surface of CTA⁺ and arrange with the spatial location of CTAB to



Fig. 9. The formation process of Cu(OH)₂ nanowires.

form > $Cu(OH)_2 \cdots Cu(OH)_2Cu$ < chains. The transverse growth of the crystal is prone to end quickly because the diameter of the droplets is much shorter. But the longitudinal growth is difficult to end because the length of the droplets is much longer. The special properties of the droplets controls the necessary anisotropy of enriching water molecules to generate the 1D nanostructured inorganic morphology.

4. Conclusion

Cu(OH)₂ nanowires were successfully synthesized by the coupling method of microemulsion with homogenous precipitation. The characterized results of TGA, FT-IR, XRD, TEM, and SEM investigation confirmed that the products were single-crystalline orthorhombic Cu(OH)₂ nanowires. The size and morphology of the nanowires can be controlled by changing the ω value and precursor salt concentration. The formation mechanism was also discussed. 1D CuO nanowires could be simply obtained by the dehydration of Cu(OH)₂, while maintaining the wire-shaped architecture. The prepared CuO nanocrystals showed high catalytic performance for the decomposition of AP: the decomposition temperature of the AP was significantly decreased.

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