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Controllable synthesis and growth mechanism of α-$Co(OH)_2$ nanorods and nanoplates by a facile solution-phase route

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ABSTRACT

A facile chemical precipitation route has been developed to control synthesis of α-cobalt hydroxide nanostructures with rod-like and plate-like morphologies. The α-$Co(OH)_2$ nanorods were achieved in large quantity when the experiments were carried out in the presence of a suitable shape-controlling reagent polyvinyl pyrrolidone (PVP), while the α-$Co(OH)_2$ nanoplates were obtained when the experiments were conducted in the absence of PVP, whilst keeping other experimental conditions constant. The chemical composition and morphologies of the as-prepared α-$Co(OH)_2$ nanoparticles were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The effect of polymer PVP on the morphologies of α-$Co(OH)_2$ nanoparticles were discussed in detail. The results indicated that PVP played a key role for the formation of α-$Co(OH)_2$ nanorods. The growth mechanism of the as-synthesized nanorods and nanoplates were discussed in detail based on the experimental results. A possible growth mechanism has been proposed to illustrate the growth of α-$Co(OH)_2$ nanorods.

1. Introduction

Recently, there are great growing interests for the controllable synthesis of low-dimensional nanoscale materials with well-controlled morphologies due to their novel optical, electronic, magnetic, and catalytic properties and potential applications in the fields of photonic, electronic magnetic devices and catalysts [1]. Much effort has therefore been focused on the design, synthesis, and characterization of nanoscale materials with different morphologies such as nanocubes, nanorods, nanowires, nanobelts, and nanotubes [2–7]. Till date, many methods have been employed to synthesize nanoscale materials such as nanoparticles, one-dimensional (1D) nanostructures and two-dimensional (2D) nanostructures. Among these synthetic methods, both hard and soft template methods are generally used to synthesize nanostructures with well-controlled shapes. In case of hard template method, the alumina, silica, block polymer, mica, and membranes are usually used as templates for the direct growth of nanostructures [8–10]. While in soft template process, surfactants are generally applied to stabilize the surface of nanonuclei and kinetically control the growth rates of various facets of nuclei, leading to the formation of nanostructures with well-controllable morphologies [11–13].

In recent years, cobalt hydroxide has attracted increasing attention because of its unique electric and catalytic properties for electrochemical, magnetic, and catalytic applications. It is well-known that cobalt hydroxide, a divalent transition-metal hydroxide, crystallizes in two polymorphs, the metastable α-type and the thermodynamically stable β-type [14,15]. The previous research works have reported that the thermodynamically stable β-type cobalt hydroxide is a stoichiometric phase of the composition $Co(OH)_2$ with brucite-like structure and consists of a hexagonal packing of hydroxyl ions with Co(II) occupying alternate rows of octahedral sites [16,17], while the metastable α-type cobalt hydroxide is reported to be isostructural with hydrotalcite-like compounds that consist of positively charged $Co(OH)_{2-x}(H_2O)_x$ layers and charge balancing anions in the interlayer gallery [18–21]. It has been reported that the α-type cobalt hydroxide shows superior electrochemical properties as compared to its β-type counterpart because of its poorly or turbostratically crystallized structure [15]. In addition, the α-type cobalt hydroxide intercalated organic anions show long-range magnetic ordering and are regarded as new candidates for organic magnetic materials [22,23]. The novel electrochemical and magnetic properties of α-type cobalt hydroxide triggered the recent great interest in shape-controlled synthesis of α-type cobalt hydroxide by the chemical or electrochemical process. However, it is difficult to synthesize α-type cobalt hydroxide because it is metastable and is easily transformed into the β-type cobalt hydroxide during the reaction or aging. Although few methods have been developed to

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synthesize α-type cobalt hydroxide nanostructures with mainly plate-like morphologies [24–26], there are a few reports on the synthesis of α-type cobalt hydroxide with rod-like morphology to the best of our knowledge. In the present work, we demonstrate a facile chemical precipitation route for controllable synthesis of α-type cobalt hydroxide nanorods and nanoplates for first time. The growth mechanism of nanorods and nanoplates were discussed in detail on the basis of experimental results and analysis. A possible growth mechanism has been proposed to illustrate the growth of α-$Co(OH)_2$ nanorods.

2. Experimental procedure

All of the chemical reagents used in the experiments were of analytical grade as received without further purification. In a typical synthetic procedure of α-$Co(OH)_2$ nanorods, $CoCl_2 \cdot 6H_2O$ (0.48 g) and HMT (1.68 g) were dissolved in 200 mL of a 9:1 mixture of deionized water and ethanol to give the final concentrations of 10 and 60 mM, respectively. Then 0.20 g of polyvinyl pyrrolidone (PVP) ((K30, molecular weight of 58 000) was dissolved into the above solution. The reaction solution was then heated at 90 °C under magnetic stirring. After being heated for 1 h, a suspension containing green particles were resulted. The solid product was filtered and washed with deionized water and anhydrous ethanol several times, and finally air-dried at room temperature.

The synthetic procedure for α-$Co(OH)_2$ nanoplates is same as the above procedure for the synthesis of α-$Co(OH)_2$ nanorods, but no PVP was added in the whole experimental process.

The powder XRD analysis was performed using a Rigaku (Japan) Dmax X-ray diffractometer with graphite monochromatized Cu*K*α radiation (λ=0.154178 nm), employing a scanning rate of $0.02^o\,s^{-1}$ in the 2θ range from 10° to 90°. Transmission electron microscopy (TEM) images were taken with a Hitachi-7650 transmission electron microscope, with an accelerating voltage of 80 kV.

3. Results and discussion

The crystallinity and chemical composition of the as-prepared α-$Co(OH)_2$ nanorods was first characterized by XRD. Fig. 1 shows typical XRD pattern of α-$Co(OH)_2$ nanorods obtained by precipitation of $CoCl_2$ aqueous solution with HMT in the presence of PVP at 90 °C for 1 h. The peak assignment is made with reference to the previous report about the crystal structure of α-$Co(OH)_2$ [24–26]. According to the previous published works, five characteristic peaks located at 10.97°, 22.34°, 33.69°, 37.96°, and 58.94° that attributed to (003), (006), (012), (015), and (110) crystalline planes of α-$Co(OH)_2$ were observed. It was reported that typical low-crystalline α-type cobalt hydroxides generally showed broadened peaks of (003), (006), (100), and (110) planes in the XRD patterns [24]. In contrast, almost all the characteristic peaks of α-$Co(OH)_2$ are observed on the XRD pattern of the precipitates in the present study.

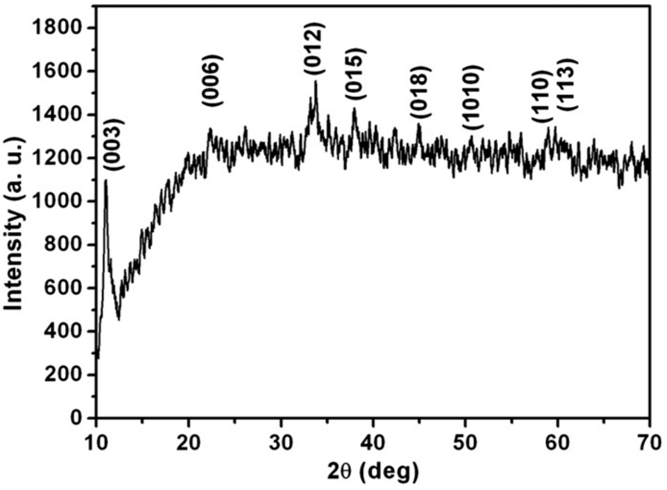

Fig. 1. A typical XRD pattern of α-$Co(OH)_2$ nanorods obtained by precipitation of $CoCl_2$ aqueous solution with HMT in the presence of shape-controlled reagent PVP at 90 °C for 1 h.

The morphology and size of the as-prepared α-$Co(OH)_2$ nanorods have been characterized by TEM. Fig. 2 shows typical TEM images of α-$Co(OH)_2$ nanorods prepared by a facile chemical precipitation route, in which precipitation of $CoCl_2$ was used as Co^{2+} source, HMT was used as precipitation reagent, and PVP was used as structure-directing reagent. The low-magnification TEM image (Fig. 2a) shows that the as-prepared α-$Co(OH)_2$ nanoparticles exhibit a rod-like morphology in large quantity. Medium-magnification TEM image clearly indicates that the as-prepared α-$Co(OH)_2$ nanoparticles have perfect rod-like shape with an average diameter of about 10 nm and length of up to 1000 nm

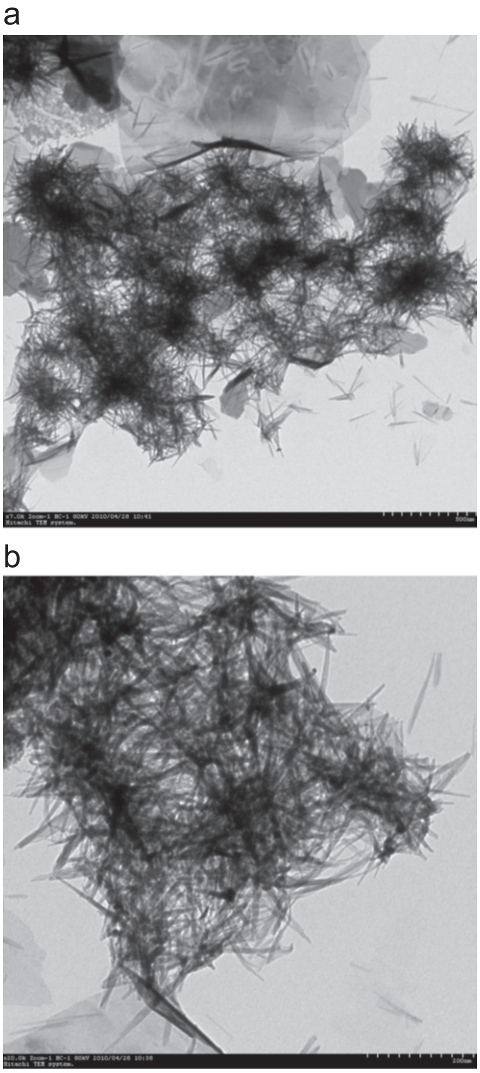

Fig. 2. Typical TEM images of α-$Co(OH)_2$ nanorods obtained by precipitation of $CoCl_2$ aqueous solution with HMT in the presence of shape-controlled reagent PVP at 90 °C for 1 h.

as presented in Fig. 2b. An aspect ratio obtained from TEM images is more than 100.

A comparative experiment has been carried out to understand the role of PVP in the formation of α-Co(OH)$_2$ nanorods and the formation mechanism of α-Co(OH)$_2$ nanorods. Fig. 3 shows a typical XRD pattern of nanoparticles obtained in the absence of PVP, whilst keeping other experimental conditions constant. One can find that three characteristic peaks of (003), (012), (015) crystalline planes of α-Co(OH)$_2$ located at 10.97°, 33.46°, and 37.84° are observed, indicating that α-Co(OH)$_2$ can also be synthesized in the absence of structure-directing reagent PVP.

Fig. 4 shows typical TEM images of α-Co(OH)$_2$ nanoparticles obtained in the absence of PVP, whilst keeping other experimental conditions constant. TEM images clearly show that plate-like α-Co(OH)$_2$ nanoparticles were achieved in large quantity. Careful examinations indicate that some nanoplates exhibit hexagonal morphology as indicated by arrows in Fig. 4a. One also can find that the as-prepared nanoplates are very thin and some nanoplates are crimped as shown by arrows in Fig. 4b.

The above experimental results clearly demonstrated that PVP played a key role for the formation of α-Co(OH)$_2$ nanorods. Before we discuss the role of PVP in the formation of α-Co(OH)$_2$ nanorods, we first discuss about the structure, properties of PVP and its application in controlling synthesis of nanocrystals. It is known that the growth morphology of the crystals is often determined by the surface free energies under thermal equilibrium. However, in the nanometer scale, crystal growth is usually far from the thermal equilibrium; thus, the shape of the crystals is not characterized by minimizing the surface energy, but rather the growth rate of each face as determined by the kinetics [27]. Meanwhile, it has been reported that PVP has the structure of polyvinyl skeleton with strong polar group (pyrrolidone ring), so it has an affinity toward many chemicals to form coordinative compounds. The polar groups, such as the $>$C$=$O groups of PVP chain, can interact with metal ions and form coordinating complex. For example, the previous published works have demonstrated the orientating role of PVP in the formation of Ag nanowires because of the interaction between the Ag$^+$ and the PVP chains to form Ag$^+$–PVP coordinating complex, in which Ag$^+$ ions can be reduced to Ag^0 to form PVP–Ag coordination complex compound containing extremely fine Ag embryos. The PVP–Ag coordination compound arranges in a one-dimensional (1D) manner because silver ions coordinate along the long chain of PVP as discussed above. Thus linear Ag embryos with a longer size could be formed. Accordingly, the linear Ag embryos would continue to grow becoming silver nanowires with the reduction reaction going [28].

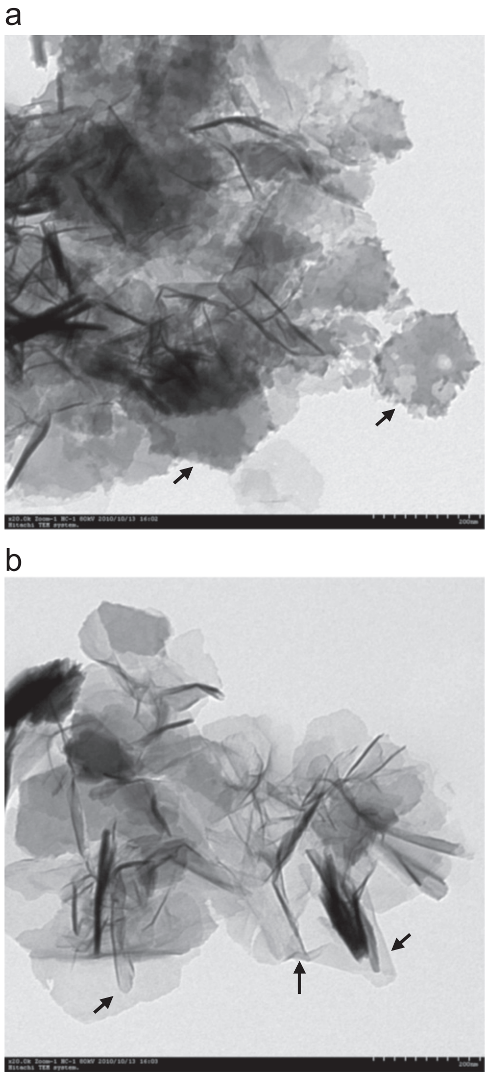

Fig. 4. Typical TEM images of α-Co(OH)$_2$ nanoplates obtained by precipitation of CoCl$_2$ aqueous solution with HMT in the absence of shape-controlled reagent PVP at 90 °C for 1 h.

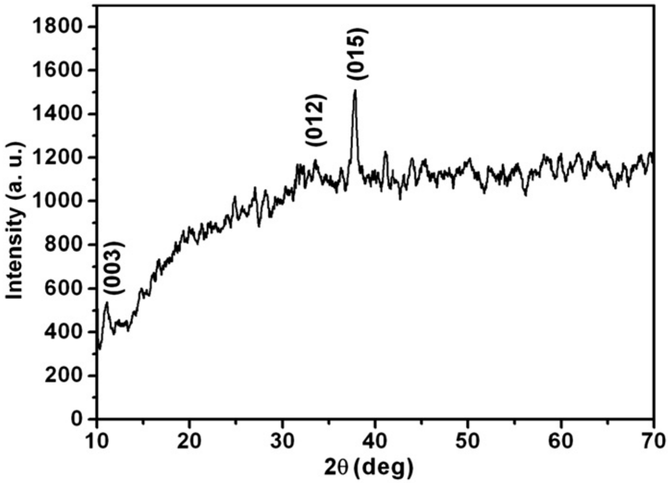

Fig. 3. A typical XRD pattern of α-Co(OH)$_2$ nanoplates obtained by precipitation of CoCl$_2$ aqueous solution with HMT in the absence of shape-controlled reagent PVP at 90 °C for 1 h.

On the basis of above experimental results and analysis, we now discuss the role of PVP in the formation α-Co(OH)$_2$ nanorods and growth mechanism of α-Co(OH)$_2$ nanorods. In our present case, we think that PVP will not only prevent the agglomeration of the formed α-Co(OH)$_2$ nuclei at the initial stage but also orientate their subsequent development to form α-Co(OH)$_2$ nanorods. A possible growth process of α-Co(OH)$_2$ nanorods may mainly comprise three processes: (1) formation of α-Co(OH)$_2$ crystal nuclei, (2) formation of linear α-Co(OH)$_2$ embryos with longer size by arranging of PVP–Co^{2+} coordination compound [29], and (3) subsequent crystal growth from these linear α-Co(OH)$_2$ embryos to form α-Co(OH)$_2$ nanorods. In the first growth process, Co^{2+} in aqueous solution first reacts with PVP to form a relatively stable PVP–Co^{2+} coordination complex because of strong affinity of PVP to Co^{2+} [29]. Afterwards, the PVP–Co^{2+} coordination complex reacts with OH$^-$ mainly coming from HMT to form α-Co(OH)$_2$ crystal nuclei as shown in Fig. 5a. In the second growth process, the newly formed α-Co(OH)$_2$ crystal nuclei, which are fixed by PVP molecules, coalesce with adjacent ones, decreasing their surface energy and enhancing the formation of linear

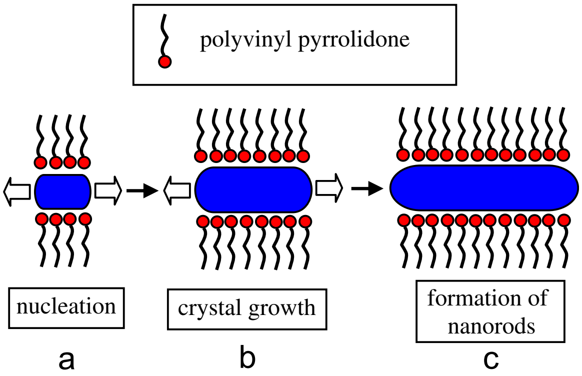

Fig. 5. Schematic illustration for the formation of α-$Co(OH)_2$ nanorods.

α-$Co(OH)_2$ embryos by arranging of PVP–Co^{2+} coordination compound as presented in Fig. 5b. In the third growth process, the linear α-$Co(OH)_2$ embryos continue to grow into nanorods with the reaction going as presented in Fig. 5c. The growth mechanism of α-$Co(OH)_2$ nanorods is similar to formation process of Ag nanowires [28]. The growth mechanism discussed above can be demonstrated by a schematic illustration as shown in Fig. 5.

As for the formation mechanism of α-$Co(OH)_2$ nanoplates, a possible mechanism of forming such α-$Co(OH)_2$ nanoplates may be due to its anisotropic structure. As we discussed above, hydroxides of cobalt are well-known to crystallize in α and β-polymorphic forms. The β-polymorph is a stoichiometric phase of $Co(OH)_2$ with brucite-like structure, while the α-cobalt hydroxides are hydrotalcite-like compounds consisting of positively charged hydroxide layers and charge balancing in the interlayer gallery between hydroxide layers. This intrinsic crystal property may dominate the shape of the primary α-$Co(OH)_2$ particles (i.e., platelet seed), resulting in the formation of plate-like crystals, which is similar to the formation of Sb_2Te_3 and Bi_2Te_3 nanoplates [13,30].

4. Conclusion

In summary, we have described a facile chemical precipitation route to control synthesis of α-type cobalt hydroxide nanostructures with rod-like and plate-like morphologies. When the experiments were conducted in the presence of a suitable shape-controlling reagent PVP, α-$Co(OH)_2$ nanorods were achieved in large quantity. While the α-$Co(OH)_2$ nanoplates were obtained when the experiments were carried out in the absence of PVP, whilst keeping other experimental conditions constant. XRD and TEM were used to characterize chemical composition and morphologies of the as-prepared α-$Co(OH)_2$ nanoparticles. The effect of polymer PVP on the morphology of α-$Co(OH)_2$ nanoparticles were discussed in detail. The results indicated that PVP played a key role in the formation of α-$Co(OH)_2$ nanorods. The growth mechanism of the as-synthesized nanorods and nanoplates were discussed in detail based on the experimental results. On the basis of the experimental results and analysis, a possible growth mechanism has been proposed to illustrate the growth of α-$Co(OH)_2$ nanorods.

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