Journal of Colloid and Interface Science 468 (2016) 238–246

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Free-standing α-$Co(OH)_2$/graphene oxide thin films fabricated through delamination and reassembling of acetate anions intercalated α-$Co(OH)_2$ and graphene oxide in water

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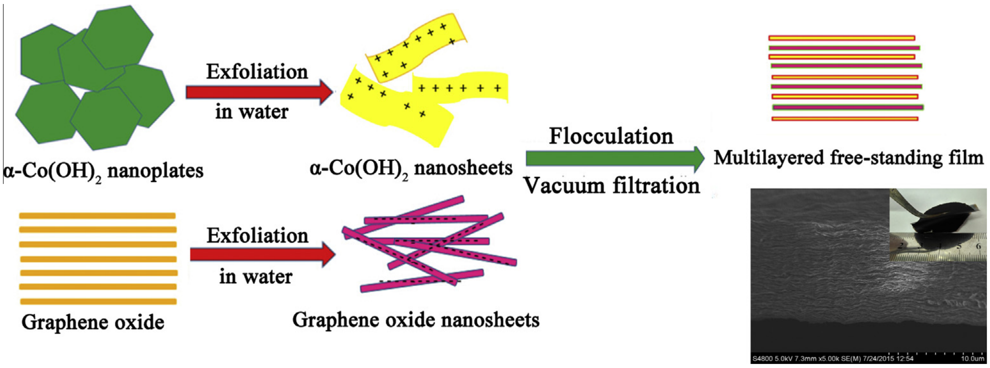
GRAPHICAL ABSTRACT

Free-standing α-$Co(OH)_2$/graphene oxide thin film was fabricated through delamination and reassembling of acetate anions intercalated α-$Co(OH)_2$ and graphene oxide in water.



ARTICLE INFO

Article history:
Received 21 November 2015
Revised 22 January 2016
Accepted 26 January 2016
Available online 27 January 2016

Keywords:
Acetate anions intercalated α-$Co(OH)_2$
Delamination in water
Free-standing film
Electrode material

ABSTRACT

A novel hydrothermal process is demonstrated to prepare acetate anions intercalated α-$Co(OH)_2$ that can be delaminated in water without any additional anion exchange processes. Positively charged $Co(OH)_2$ nanosheets with lateral size of hundreds of nanometers and thickness less than 2 nm can be obtained by dispersing the as-obtained α-$Co(OH)_2$ into water followed by sonication. The exfoliated $Co(OH)_2$ nanosheets can be restacked into its original structure with different interlayer *d*-spacings. A flexible free-standing film with stacking $Co(OH)_2$ nanosheets and graphene oxide (GO) layers can be obtained through flocculation of the $Co(OH)_2$ nanosheets with GO nanosheets suspensions followed by a vacuum filtration, but the content of $Co(OH)_2$ has to be kept under a low value so as to obtain films with flexible nature. Electrochemical tests show that this kind of film is not suitable to be used as electrode material for supercapacitor and lithium ion battery, because the content of active material is not high and the compacted junction between opposite charged nanosheets will prevent the electrolyte from diffusing into the interlayer space.

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http://dx.doi.org/10.1016/j.jcis.2016.01.058
0021-9797/

1. Introduction

Co-based materials have attracted considerable attention in the field of energy storage and conversion for both supercapacitors and lithium-ion batteries due to their high theoretical specific capacitance and lithium storage capacity [1–5]. For instance, α-Co(OH)$_2$ with a structure similar to layered double hydroxides (LDHs), has been widely studied as electrode materials for supercapacitors. Co_3O_4 has been regarded as one of promising electrode materials for lithium-ion batteries due to its high theoretical capacity. However, the volume expansion and particle aggregation resulted from ion insertion and extraction usually lead to the loss of reversible capacitance/capacity and poor cycling stability due to the structure collapse [6,7]. To overcome these drawbacks, various methods have been reported to synthesize nano-structured hybrid composites such as graphene sheet-wrapped $Co_2(OH)_3Cl$ [2] and Co_3O_4/graphene [8,9]. Because the hybrid composite materials have improved electron and ions transport and high capacitance/capacity that can be maintained for hundreds of cycles [8–10].

Multilayered free-standing film with two-dimensional structure has triggered tremendous interest in energy storage and conversion [11–15]. This kind of smart material usually enjoys unique properties such as increased active surface area, short transport pathways for electrons and accommodation for volume expansion. To date, various kinds of methods including chemical deposition, hydrothermal process and mechanical mixture have been applied to fabricate free-standing film electrodes composed of electroactive species and graphene nanosheets [12–14]. For instance, Wang et al. have reported flexible free-standing hollow Fe_3O_4/graphene film fabricated through vacuum filtration and thermal reduction processes for lithium-ion batteries [12]. Kong synthesized free-standing T-Nb_2O_5/graphene composite paper for lithium-ion intercalation pseudocapacitor [13]. Wang fabricated free-standing Co_3O_4/graphene film *via* mixing β-Co(OH)$_2$ dispersion with graphene followed by vacuum filtration and thermal treatment processes for lithium-ion battery electrode [14]. Recently, lamellar free-standing films composed of oppositely charged electrochemical active nanosheets and graphene oxide (GO) nanosheets have come into focus.

To build such kind of Co-based lamellar free-standing films, an important strategy must be concerned on preparing ultrathin α-Co(OH)$_2$ nanosheets to be used as building blocks. The preparation process for dispersed α-Co(OH)$_2$ nanosheets with thickness of approximately nanometer from its corresponding bulk material is usually called delamination or exfoliation [16]. α-Co(OH)$_2$ is usually stable in nature due to the forces between neighboring host layers including van-der-Waals force, hydrogen bonding, and the affinity of anions to host layers that are sufficient to keep the layers stacked together [17–19]. The exfoliation of α-Co(OH)$_2$ is a breakdown process of the force between adjacent layers. It has been found that α-Co(OH)$_2$ nanosheets can be obtained in formamide and this method has been widely applied to prepare α-Co(OH)$_2$ colloidal nanosheets until now [17,20,21]. But this method which usually involves additional anion exchange process is somewhat complex and not environment friendly [22–24]. Thus, new ecologically friendly and easy Co(OH)$_2$ delamination methods are eagerly desired. As one of the most common and non-toxic solvents, water has been tried to be explored as a possible candidate to exfoliate α-Co(OH)$_2$. Up to now, many studies have showed that some LDHs intercalated with special anions, such as lactate ions [19,25], 2-hydroxyethane sulfonate anions [26] and zwitterions [27], could be delaminated in water. For instance, Hibino found that lactate intercalated LDH could be exfoliated in water due to the formation of hydrogen-bonds between the lactate anions and water molecules [25]. Nethravathi reported the delamination of p-aminobenzoate ion intercalated a-hydroxides of nickel and cobalt in water [27]. All these reports showed that the delamination of α-Co(OH)$_2$ in water could be accomplished by using specific intercalation anions. It is well known that the intercalated anions should be large in size, having a lower affinity to host layers and good miscibility with water.

In this work, we report a facile method to prepare acetate anions intercalated α-Co(OH)$_2$ that can be delaminated in water without any additional anion exchange processes. Compared with previous methods, our process is easier because the synthesis process can be accomplished within one step and the anion exchange process is not necessary at all. Flexible free-standing film can be gained by flocculation of Co(OH)$_2$ nanosheets and GO nanosheets suspensions assisted by vacuum filtration. The obtained film was tested as electrode material for energy storage. But electrochemical results show that this kind of free-standing film with compact layered structure may not be suitable for capacitor and Li-ion battery electrode materials.

2. Experimental section

2.1. Synthesis of Co(OH)$_2$ and GO

The synthesis of acetate anions intercalated α-Co(OH)$_2$ (denoted as Co(OH)$_2$–Ac) that can be delaminated in water without anion exchange process is performed *via* a simple hydrothermal process. Briefly, 500 mg cobalt acetate ($Co(CH_3COO)_2 \cdot 4H_2O$) was dissolved into a mixture solution of 40 mL N,N-Dimethylformamide (DMF) and 10 mL deionized water (which had been boiled to remove possible CO_2) under stirring to form a clear solution. Subsequently, it was transferred into a 70 mL Teflon-lined stainless-steel autoclave. The autoclave was sealed, heated and kept at 120 °C for 2 h, then cooled down to room temperature naturally. The cobalt hydroxide product was collected by centrifugation and washed with alcohol repeatedly (Supporting Information S-Fig. 1). The weight of the harvested product was about 40 mg after being dried at 80 °C.

GO was prepared via the method reported by Hummers and Offeman with some changes [28]. Briefly, 1 g of worm-like expanded graphite powder was added into 23 mL concentrated H_2SO_4 in a clean beaker which was submerged in a mixture of ice and water. Then, 3 g $KMnO_4$ was gradually added into it under stirring. After that, the mixture was stirred for more 30 min at 35 °C. About 46 mL of deionized water was slowly added into the system, at the same time the temperature began to rise. Subsequently, the mixture was maintained in a water bath at 95 °C for 10 min. The reaction was terminated by adding 140 mL of distilled water followed by the addition of 10 mL of 30% H_2O_2 solution [29]. The resulted product was separated by centrifugation, washed repeatedly with deionized water and alcohol subsequently. Finally, the product was dried in an oven at 80 °C overnight.

2.2. Delamination of Co(OH)$_2$–Ac and GO

The delamination of Co(OH)$_2$–Ac and GO were realized in water. For the delamination of Co(OH)$_2$–Ac, various amounts (10 mg, 12.5 mg, 25 mg and 50 mg) of Co(OH)$_2$–Ac powder were dispersed into 100 ml deionized water (which had been boiled with pour of N_2 to remove the O_2) by ultrasonic. Then different treatments were applied to corresponding samples according to Table 1. The delamination of GO was followed by the same route as Co(OH)$_2$–Ac treated under sonication.

2.3. Fabrication of free-standing α-Co(OH)$_2$/GO thin film

30 mg of the as-prepared Co(OH)$_2$–Ac and 20 mg GO were exfoliated in 100 mL water, respectively. Subsequently, the two