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Hydrothermal preparation of Co_3O_4/graphene composite as anode material for lithium-ion batteries

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ABSTRACT

We report a facile hydrothermal strategy to synthesize the Co_3O_4/graphene composite as anode material for high-performance lithium-ion batteries. The polyhedral Co_3O_4 particles are homogeneously anchored on graphene sheets, and the growth mechanism has been discussed. The obtained Co_3O_4/graphene composite displays large reversible capacity (~840 mAh/g after 50 cycles), excellent cyclic stability, and good rate capability in comparison to pure Co_3O_4 nanoparticles. The flexible structure of graphene sheets and the strong interaction between graphene and Co_3O_4 particles are beneficial for providing excellent electronic conductivity, short transportation length for Li^+ ions, and elastomeric space to accommodate volume varies upon Li^+ insertion/extraction.

1. Introduction

With impending energy crisis and increasing concerns about the environment, advanced energy storage materials and devices with high performance are urgently called for. Graphene represents a promising material for application in lithium ion batteries (LIBs) due to its superior electronic conductivity, high surface area, and large theoretical capacity [1]. The practical applications of graphene have been limited by its irreversible aggregation during the reduction process, leading to changes in intrinsic chemical and physical properties. The synthesis of graphene-metal composites was initially proposed, in an attempt to minimize the agglomeration of graphene sheets [2,3].

A large number of studies have demonstrated that transition metal oxides (e.g. Co_3O_4 [4,5], NiO [6], Fe_2O_3 [7], CuO [8]) are promising anode materials of LIBs. However, pure metal oxides have been hampered by poor capacity retention upon cycling caused by large volume expansion. The metal oxides loaded onto graphene can act as spacers to prevent the re-stacking of graphene and the incorporation can generate a porous network, providing excellent electron-conducting and ion-transporting pathways [9,10]. Recently, graphene-based composites become an intriguing strategy to improve the electrochemical performance of transitional metal oxides.

Co_3O_4 is a promising anode for LIBs with theoretical capacity of 890 mAh/g. Porous Co_3O_4 [5] and Co_3O_4/graphene [9] have been prepared to improve the electrochemical performance. The Co_3O_4/graphene composites with different morphologies have been reported. Co_3O_4 nanoparticles of 10–30 nm were homogeneously grown on graphene by chemical deposition [11] and solution-based method [12]. Co_3O_4 nanoparticles could also be deposited on graphene sheets by hydrothermal synthesis followed by calcinations [13], which is a two-step method. Co_3O_4 nanorods/graphene composites have been obtained through a one-spot solvothermal method [14]. In this paper, we report a simple one-step hydrothermal synthesis of Co_3O_4/graphene composites, which consist of well-dispersed polyhedral Co_3O_4 particles on graphene sheets, and exhibit super electrochemical performance.

2. Experimental

Graphene oxide (GO) was synthesized from natural graphite powder by the modified Hummers method [15]. In a typical preparation process of Co_3O_4/graphene composite, 0.29 g of $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in 20 mL ethanol solution. 20 mg of GO was dispersed in 20 mL alcohol solution by ultrasonic stirring. Subsequently the prepared two solutions was mixed under stirring and 4 mL of ammonia solution ($NH_3 \cdot H_2O$, 25%) was slowly added. The as-obtained mixture was transferred into a Teflon-lined stainless steel autoclave and heated at 190 °C for 24 h. After the reaction was complete, the precipitates were centrifuged and collected. For comparison, pure Co_3O_4 was also prepared as described above without the addition of GO.

The electrochemical properties of the products were evaluated using CR2025-type coin cells. The electrode slurry was made by

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mixing the Co_3O_4/graphene, acetylene black, and polyvinylidene fluoride in a weight ratio of 75:15:10 in N-methyl pyrrolidone. Half cells were assembled with a Li metal counter electrode, a separator (Celgard 2300), and an electrolyte of 1 M $LiPF_6$ in a 1:1 mixture of ethylene carbonate and dimethyl carbonate in a glove box.

3. Results and discussion

The crystallographic structures of the as-prepared product were analyzed by XRD. As shown in Fig. 1(a), a few characteristic peaks were observed at 31.3°, 36.9°, 44.8°, 59.3° and 65.2°, and they can be assigned as (220), (311), (400), (511), and (440) planes of Co_3O_4, respectively. All the refraction peaks can be perfectly indexed to the cubic phase of Co_3O_4 (JCPDS No.78-1970). We cannot find obvious diffraction peak for graphene sheets because the content of graphene is low and the refraction of graphene is weaker than well-crystalline Co_3O_4. The morphology of the Co_3O_4/graphene composite was examined with SEM. A large number of uniform Co_3O_4 particles are homogeneously distributed on graphene sheets as shown in Fig. 1(b–d). These Co_3O_4 particles are around 100-250 nm in size with regular polyhedral morphology. The Co_3O_4 particles can prevent the graphene sheets from aggregating in the synthesis process, and vice versa, which is beneficial for the electrochemical performance in LIBs. Here, we conclude that the obtained products are Co_3O_4/graphene composite from XRD and SEM analysis.

To understand the role of the GO in the synthesis, a pure Co_3O_4 sample was prepared with similar procedure while GO was not added. As revealed by XRD in Fig. 2(a), the obtained sample shows the same crystal phase of Co_3O_4. Fig. 2(b–d) show the SEM and TEM images of the pure Co_3O_4, revealing that the product is an aggregation of many Co_3O_4 nanoparticles around 20 nm. The sizes of Co_3O_4 aggregates are around 0.6–1 μm. Therefore, the GO can prevent Co_3O_4 from aggregating during growth, and reduce the powder size. In the preparation of composite, Co_3O_4 nucleus were firstly formed on the GO nanosheets through the hydrothermal reaction between $Co(NO_3)_2$ and $NH_3 \cdot H_2O$. According to the previous report [16], there are many surface groups on the GO nanosheets. The possible linkage between these groups of GO and Co_3O_4 nuclei might be helpful to stabilize the particles. So well-dispersed Co_3O_4 particles were anchored on graphene sheets.

Cyclic voltammogram (CV) measurements were performed to understand the electrochemical process of Co_3O_4/graphene composite in LIBs. Fig. 3(a) shows the CV curves of Co_3O_4/graphene electrode. In the first cycle, a strong cathodic peak was observed at 0.65 V, corresponding to a multistep electrochemical reduction reaction of Co_3O_4 with Li. Two anodic peaks appear at around 1.6 and 2.2 V, which are ascribed to the oxidation reaction of Co atoms. In the following cycles, the CV curves exhibit two broad reduction peaks at 0.8 and 1.1 V in the cathodic process and two broad oxidation peaks at 1.75 and 2.25 V in the anodic process. The CV results demonstrate an irreversible reaction present in the first electrochemical cycle due to the electrolyte decomposition and SEI layer formation [17], which accounts for the capacity loss of the anode materials in the first cycle. The electrochemical reaction mechanism of Co_3O_4 is different from the classical reversible insertion/deinsertion of Li^+ in layered materials. It involves the formation and decomposition of Li_2O, accompanied by the reduction of Co_3O_4 to Co and the oxidation of Co to Co_3O_4 through an intermediate of CoO [18]. This multiple electron process can be represented by Eqs. (1) and (2).

$$Co_3O_4+2Li^++2e^-\leftrightarrow Li_2O+3CoO \quad (1)$$

$$3CoO+6Li^++6e^-\leftrightarrow 3Li_2O+3Co \quad (2)$$

The electrochemical performances of the Co_3O_4/graphene composite were evaluated by galvanostatic charge/discharge cycling at a current density of 100 mA/g (Fig. 3b). The charge/discharge profile of the composite in the first cycle is different from that in the following cycles due to the irreversible reaction revealed in the CV analysis. The shapes of the profiles are not significantly altered after the first cycle, indicating a good stability of the composite as anode in LIBs. In discharge, the plateaus at 1.0–1.3 V correspond to the formation of Li_2O and the reduction of metal oxide. In addition, the capacity below 1.0 V can be attributed to lithiation of graphene and/or a reversible polymerization of the electrolyte. In charging state, the reactions are reversed.

Fig. 3(c) depicts the cycling performance of the Co_3O_4/graphene electrode. A discharge capacity of 1236 mAh/g was obtained in the

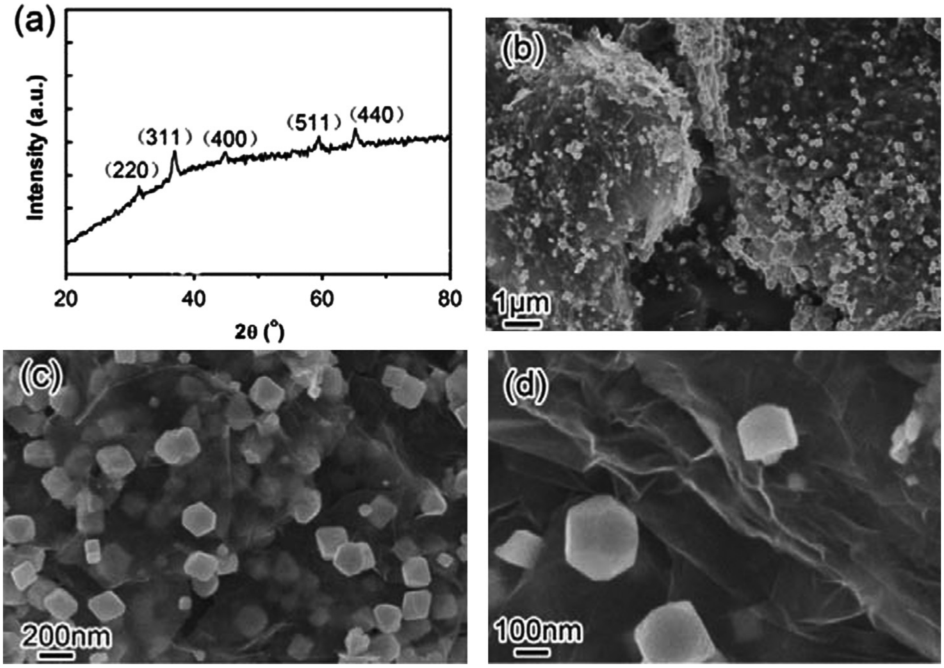

Fig. 1. (a) XRD pattern and (b–d) SEM images of the Co_3O_4/graphene composite.