



Facile fabrication of two-dimensional reduced graphene oxide/CoAl-layered double hydroxides nanocomposites for lithium-oxygen battery with improved electrochemical performance

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ABSTRACT

Hybrids of layered double hydroxides (LDHs) and graphene-based nanocomposites have invoked a great deal of interest due to the unique and highly tunable composition and properties. Herein, CoAl-LDHs nanosheets were *in-situ* incorporated with reduced graphene oxide (rGO) via a simple one-step reflux method to improve the electrochemical performance of lithium-oxygen (Li–O₂) battery. The obtained nanocomposites tended to decrease the particle size of CoAl-LDHs nanosheets and endowed more catalytic active sites. Benefiting from the synergistic effect, the fabricated rGO/CoAl-LDHs nanocomposites enhanced the charge transfer process and the first discharge specific capacity up to 300% higher than the pristine rGO under the same condition. In addition, the battery showed excellent cycling stability with no capacity loss over 30 cycles, as well as markedly lower recharge voltage. The results provide a facile way to prepare two-dimensional cathode material for Li–O₂ battery.

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1. Introduction

Due to the excessive depletion of traditional non-renewable fossil fuels and the serious environment pollution, there has been an increasing demand for green and sustainable energy resources [1,2]. Secondary batteries are promising electrochemical storage systems because of their ability to convert chemical energy into electrical energy by the reversible electrochemical oxidation/reduction reactions [3,4]. Among the reported advanced batteries, lithium-oxygen (Li–O₂) battery has attracted significant interest due to its ultrahigh theoretical energy density (~3505 Wh kg⁻¹), and the energy density can reach 800 Wh kg⁻¹ even take into account the packaging, remarkably larger than that of a Li-ion battery [5–7]. However, the present Li–O₂ battery is confined in laboratory stage due to the sluggish kinetics of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) during the discharge/charge

processes. Developing high-efficient catalysts is one of the effective methods to improve the electrochemical performance of Li–O₂ battery [8–10].

Up to now, various catalysts, such as noble metals, transition metal oxides, perovskite and so on have been investigated in Li–O₂ battery [11–14], among them, transition-metal-based catalysts have been extensively explored owing to the high natural abundance and low cost. Two-dimensional (2D) layered compounds have been designed as promising electrocatalysts because of their unique structural features and properties [15]. Layered double hydroxides (LDHs), a kind of 2D nanosheets, have been intensively studied recently in various applications such as catalyst, supercapacitor, anion exchange and so on [16,17]. As an alternative to precious metal-based catalysts, transition-metal-based LDHs have been identified as efficient and stable catalysts with additional advantages, including composition flexibility, low cost, ease of preparation and light weight [18,19]. NiFe-LDHs and CoCu-LDHs have been investigated in Li–O₂ battery and exhibited excellent catalytic activity with improved discharge capacity, decreased overpotential and improved cycling life [20,21]. In general, for the purpose of amelioration of the charge transport kinetics, a carbon

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material is usually needed to support the catalyst and the electrocatalytic activity of a catalyst is strongly dependent on the degree of the dispersion of the catalyst on carbon support. Among the various carbon-supporting materials, graphene or reduced graphene oxide (rGO) has attracted extensive attention due to its excellent electrical conductivity, large surface area, and high chemical tolerance. Incorporating rGO and LDHs is considered to be a promising nanomaterial because of its unique and wide composition-structure-property variability [22,23].

Herein, hybrid rGO/CoAl-LDHs nanocomposites were fabricated using *in-situ* method and then used as air cathode with three potential advantages: (1) rGO and CoAl-LDHs could be uniformly dispersed, minimizing the problem of agglomeration; (2) Providing sufficient pathways for oxygen/electrolyte/electron transports and enough space for the deposition of discharge products; (3) Supplying a large number of uniformly distributed catalytic sites for catalyzing discharge products formation and decomposition. The electrochemical performances of the rGO/CoAl-LDHs nanocomposites in Li–O₂ battery were investigated and the batteries exhibited improved energy output, high coulombic efficiency and long cycle stability due to the combination of the advantages of rGO and CoAl-LDHs.

2. Experimental

All the chemical agents used in this work were of analytical grade and used without further purification.

2.1. Materials synthesis

Synthesis of rGO nanosheets: GO was synthesized via a modified Hummer's method as reported elsewhere [24]. In order to obtain rGO sample, 40 mg dry GO powder was dispersed in 100 mL deionized water and ultrasonicated for 2 h, then ammonia solution was used to adjust the pH value to 9.0–10.0 to promote the colloidal stability of the GO nanosheets through electrostatic repulsion, and 1.0 g L-ascorbic acid was added into the mixture. Then the temperature was heated to 95 °C and kept for 2 h under magnetic stirring. After cooling to room temperature, the final products were washed with deionized water to remove the residual L-ascorbic acid and ammonia, followed by centrifuging at 9000 rpm for 15 min and finally freeze-dried for 48 h to obtain rGO sample.

Synthesis of 2D rGO/CoAl-LDHs nanocomposites: Certain amount of GO powder (20, 40 and 60 mg) was dispersed in 100 mL deionized water and ultrasonicated for 2 h to obtain GO suspension, respectively. Then 1.164 g Co(NO₃)₂·6H₂O and 0.75 g Al(NO₃)₃·9H₂O was added to the suspension and ultrasonically treated for 30 min to allow metal cations adsorb on the GO surface via electrostatic interaction. Subsequently, 0.74 g urea was added and the temperature was heated to 100 °C and kept for 5 h under magnetic stirring. At the end of reaction, the resulting slurry was washed thoroughly with deionized water, the obtained products were then transferred to a flask to reduce GO with the same experiment condition with L-ascorbic acid and ammonia, yielding 2D rGO/CoAl-LDHs nanocomposites, the products were finally freeze-dried for 48 h and denoted as 20rGO/CoAl-LDHs, 40rGO/CoAl-LDHs and 60rGO/CoAl-LDHs, respectively.

Synthesis of CoAl-LDHs nanosheets: CoAl-LDHs nanosheets were synthesized via the process similar to that of rGO/CoAl-LDHs nanocomposites without adding GO powder, and the product was finally dried at room temperature in a vacuum drying oven at 60 °C for 12 h.

2.2. Battery assembly and electrochemical measurement

The air cathodes were prepared by pasting the slurry mixture of 90 wt% rGO (rGO/CoAl-LDHs or CoAl-LDHs) and 10 wt% polyvinylidene (PVDF) on a nickel foam current collector and drying at 110 °C overnight to remove the solvent (NMP). A swagelok-type Li–O₂ battery was assembled inside an Ar-filled glove box, and the concentrations of H₂O and O₂ were controlled to below 0.5 ppm. In each battery, a Li foil (14 mm in diameter) was used as the anode and rGO or rGO/CoAl-LDHs electrode (14 mm in diameter) was used as the cathode, a Celgard 2500 membrane was used to separate the anode and cathode, and the electrolyte was 100 μL 0.9 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME). After standing for 2 h, the galvanostatic discharge-charge cycles were tested by Neware battery tester at room temperature under pure O₂ atmosphere (1 atm). The capacities and current densities were calculated based on the weight of rGO, the potential range was from 2.0 to 4.5 V (vs Li⁺/Li). The linear scan voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) measurements were carried out using CHI660E electrochemical workstation, the scan rate was 0.5 mV s⁻¹ and the frequency was from 100 kHz to 10 mHz.

2.3. Characterization

The crystalline phase was determined using an X-ray diffractometer (XRD-D/max2200pc, Japan) with Cu Kα radiation. The morphology and elemental mapping of the samples were confirmed by scanning electron microscopy (SEM) using Rigaku S4800. Thermo gravimetric analysis (TGA) data were collected on a thermal analysis instrument STA409PC Diamond TG-DTA thermal analyzer under air atmosphere from ambient temperature to 600 °C with a heating rate of 10 °C min⁻¹. Raman spectra were measured at room temperature on an InVia confocal Raman microscope system equipped with a 532 nm laser excitation. X-ray photoelectron spectroscopy (XPS) measurements were performed with an AXIS SUPRA X-ray photoelectron spectrometer.

3. Results and discussion

Fig. 1a shows the XRD patterns of the obtained CoAl-LDHs nanosheets and three kinds of rGO/CoAl-LDHs nanocomposites. The diffraction peaks of the pristine CoAl-LDHs nanosheets could be indexed to a rhombohedral structure of typical Co-Al hydroxalite is (JCPDS: 51-0045) [25], the peaks at 2θ values of 11.5°, 23.2° and 34.5° correspond to the (003), (006) and (012) planes, respectively, and no impure phase could be found, indicating CoAl-LDHs nanosheets were successfully prepared by one-step reflux method [26,27]. All diffraction peaks observed in 20rGO/CoAl-LDHs, 40rGO/CoAl-LDHs and 60rGO/CoAl-LDHs nanocomposites in good accordance with those of CoAl-LDHs nanosheets, indicating that the addition of rGO did not impede the growth of LDHs nanosheets, while no typical characteristic peaks of rGO could be observed in the composites, one possible reason is that rGO was highly dispersed in hydroxalite structure, in other words, the *in-situ* growth of CoAl-LDHs on rGO via a simple one-step reflux method effectively reduced the agglomeration of rGO nanosheets and avoided the CoAl-LDHs stacking together. In addition, the XRD patterns of the rGO/CoAl-LDHs nanocomposites showed an increase intensity of (012) and (015) peaks, indicating the introduction of rGO affected the crystal orientation of the CoAl-LDHs, which should be further investigated in detail in the future. However, the XRD pattern of the nanocomposites showed a decreased intensity of (003) peak compared with CoAl-LDHs nanosheets, maybe the presence of rGO brought down the crystallinity of the rGO/CoAl-

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