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A synthesis of graphene/Co_3O_4 thin films for lithium ion battery anodes by coelectrodeposition

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ABSTRACT

We report on a facile strategy for the direct and uniform deposition of a graphene/Co_3O_4 thin film onto stainless steel substrate (SS) through cathodic deposition. Graphene oxides (GOs) were treated with poly(ethyleneimine) (PEI) which acted as a stabilizer and binder between GOs and cationic metal precursor. For the formation of PEI-modified GOs (PEI-GOs) and Co^{2+} complexes, the PEI-GOs dispersion was mixed with aqueous phase of $Co(NO_3)_2$, then, the solution was used as the plating bath for coelectrodeposition. Results showed that the PEI-GOs and cobalt oxides were uniformly distributed on the surface of SS evidenced by field emission scanning electron microscopy. The prepared graphene/Co_3O_4 film was employed as an anode material for lithium ion batteries, and it exhibited not only an enhanced cycleability but also high electronic conductivity.

1. Introduction

Graphene with a two-dimensional structure represents a promising material for use in lithium ion batteries (LIBs) due to its superior electronic conductivity, high surface area, and theoretical capacity (744 $mAhg^{-1}$) [1,2]. However, 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 nanocomposites was initially proposed, in an attempt to minimize the agglomeration of graphene sheets [3,4]. Although graphene-metal nanocomposites have been successfully prepared by the chemical or thermal reduction of metallic precursors in graphene oxides (GOs) dispersions, most of the currently proposed methods involve multiple steps.

A simple and rapid method for the direct electrodeposition of graphene-metal composites was recently developed [5,6]. Coelectrodeposited graphene-metal films are typically prepared by cyclic voltammetry because of the deposition voltage difference between graphene oxide and the metal. However, the above-mentioned method is limited to negatively charged metallic precursors because of the precipitation and agglomeration between GOs and the positively charged metal precursor. Cationic metallic precursors such as Co^{2+}, Ni^{2+} could presumably act as the cross-linkers due to their tendency to bind readily to the oxygen functional groups of GOs [5,7].

To expand this methodology to metal cationic precursors, we chemically modified GOs with poly(ethyleneimine) (PEI). Because it has been well known that PEI is an effective chelating agent due to the presence of a large number of amine groups [8,9], we expected that PEI on the surface of GOs (PEI-GOs) would provide ligand sites for complexation between the GOs and cationic precursor, which would facilitate the direct electrodeposition of the GOs/metal thin films.

The findings reported herein demonstrate the one-step coelectrodeposition of a graphene/Co_3O_4 composite, which is very simple compared to previously reported methods. The electrodeposited composite was employed as an anode for LIBs. We used the coelectrodeposition method for the synthesis of graphene/Co_3O_4 composite to address the following questions: (1) Can a graphene/Co_3O_4 composite be rapidly synthesized by eletrodeposition? (2) What are the roles of PEI in the electrodeposition process? (3) Does graphene improve the electrochemical properties of Co_3O_4?

2. Experimental

GOs were synthesized from commercially available graphite powder by a previously reported method [10]. A 0.3 g of as-synthesized GOs was dispersed in 200 ml of de-ionized (DI) water, and 0.1 g of PEI was then added to the solution. The mixed solution was stirred at 60 °C for 12 h. After cooling to room temperature, the resulting dispersion was centrifuged and washed with DI water to remove excess PEI. The resultant product was redispersed in DI water and 0.05 M of $Co(NO_3)_2$ and 0.075 M of $NaNO_3$ were added to the solution. The coelectrodeposition was performed potentiostatically at −1.0 V (vs Ag/AgCl) for 5 min at room temperature. A stainless steel foil (SS)

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was used as the substrate. Prior to the deposition, the stainless steel foil was cleaned. A Pt plate and Ag/AgCl were used as the counter electrode and reference electrode, respectively. After electrodeposition, the resulting films were rinsed with DI water and dried at room temperature. The as-prepared samples were calcined at 350 °C for 2 h under a nitrogen atmosphere. Co oxides films without GOs were prepared by a cathodic electrodeposition as a control sample.

The surface morphology and composition of the electrodeposited films were examined by scanning electron microscopy (SEM, Carl Zeiss., SUPRA 55VP) and energy dispersive spectrometer (EDS, Bruker, Xflash5030 detector). Zeta potential was determined using zeta-potential analyzer (Otsuka, ELS-Z). X-ray photoelectron spectroscopy (XPS, Thermo, K-Alpha), and X-ray diffractometer (XRD, Rigaku, D/max-2200) were used to examine the composite structure.

For the measurement of electrochemical properties, charge–discharge tests were carried out in a conventional coin cell (CR2032). A lithium foil and microporous polypropylenes were used as the negative electrode and separator, respectively. 1 M solution of $LiPF_6$ in a mixture of ethyl carbonate and diethyl carbonate (1:1 vol. ratio) was used as an electrolyte. Galvanostatic charge and discharge measurements were carried out with a constant current density of 700 mAg^{-1} in the voltage range of 0.01–3.0 V on a battery tester (WonA tech, WBCS3000). Electrochemical impedance spectroscopy was performed in a three electrode cell using a multi-potentiostat (VMP2, Princeton Applied Research).

3. Results and discussion

Typically, water-soluble PEI is reacted with GOs to be grafted onto the surface of GOs via the formation of amide bonds [9]. PEI is a cationic polymeric electrolyte that contains a large quantity of amine groups, and it can be immobilized on various surfaces due to the strong electrostatic interactions arising from these amine groups [8]. The modification of GOs surface with cationic PEI chain could result in well dispersed GOs-based materials. Positively charged (~46.8 mV) PEI-GOs can be protonated in aqueous solution when pH is lower than 10 due to a large amount of nitrogen atoms [9], which can coexist with cationic metallic precursors. Because PEI has excellent adsorption property for heavy-metal ions [8], PEI grafted onto GOs could act as a kind of trapping agent for Co^{2+}, which plays a key role in sequential complexation between GOs and Co^{2+}. Thus, a synthesis of graphene/Co_3O_4 films can be achieved by cathodic electrodeposition.

SEM images of electrodeposited thin films before heat treatment are shown in Figs. 1a, and b. The as-synthesized PEI-GOs/$Co(OH)_2$ thin film is comprised of a very uniform layer, and GOs appears to be well dispersed within the hierarchical structure of the electrodeposited $Co(OH)_2$. Fig. 1c shows the graphene/Co_3O_4 film after calcination, and it was confirmed that the thin graphene layers are anchored on the surface of electrodeposited Co_3O_4. It should be emphasized that, in the absence of a PEI treatment, the addition of Co^{2+} ions led to agglomeration with GOs and precipitation in the electrolyte [5]. This strongly indicates that PEI plays a significant role in the formation of uniformly dispersed films. After heat treatment, the elemental distribution of cobalt and carbon in the graphene/Co_3O_4 films was examined by EDS, shown in Figs. 1d, e, and f. Both cobalt and carbon are very uniformly distributed on the electrode surface. The average ratio of carbon-cobalt is about 23.8:76.2 at.%, respectively. The above results confirm that a graphene/Co_3O_4 composite with a very high uniformity was successfully prepared by the electrodeposition method.

The as-deposited films (after drying at room temperature) were confirmed to be amorphous (data not shown), and the XRD patterns of the electrodeposited Co_3O_4 and graphene/Co_3O_4 thin films on SS substrates after calcination at 350 °C are shown in Fig. 2a. For both films, the major diffraction lines can be assigned as Co_3O_4 (JCPDS CARD No. 42–1467). Fig. 2b shows the N1s XPS spectra of coelectrodeposited graphene/Co_3O_4 films before and after calcination. As shown in Fig. 2b, the disappearance of the N1s peak in the XPS after the heat treatment clearly indicates that the PEI chains were completely eliminated from the resulting composite.

The electrochemical performances of the electrodeposited pure Co_3O_4 and graphene/Co_3O_4 thin films were evaluated using a coin cell. Fig. 3a and b show the first and second charge/discharge behavior of pure Co_3O_4 and the graphene/Co_3O_4 films in the voltage range between 0.01 and 3.0 vs Li/Li^+ at 700 mAg^{-1}. As shown in Fig. 3a and b, the first discharge (1342 $mAhg^{-1}$) and charge capacities (1042 $mAhg^{-1}$) of the graphene/Co_3O_4 were much higher than those of the pure Co_3O_4 film (1209 and 899 $mAhg^{-1}$, respectively). In the potential range of 1.0–1.2 V, both samples show voltage plateaus that correspond to the formation of Li_2O, indicative of the typical characteristics of the voltage profile for Co_3O_4 electrodes. The

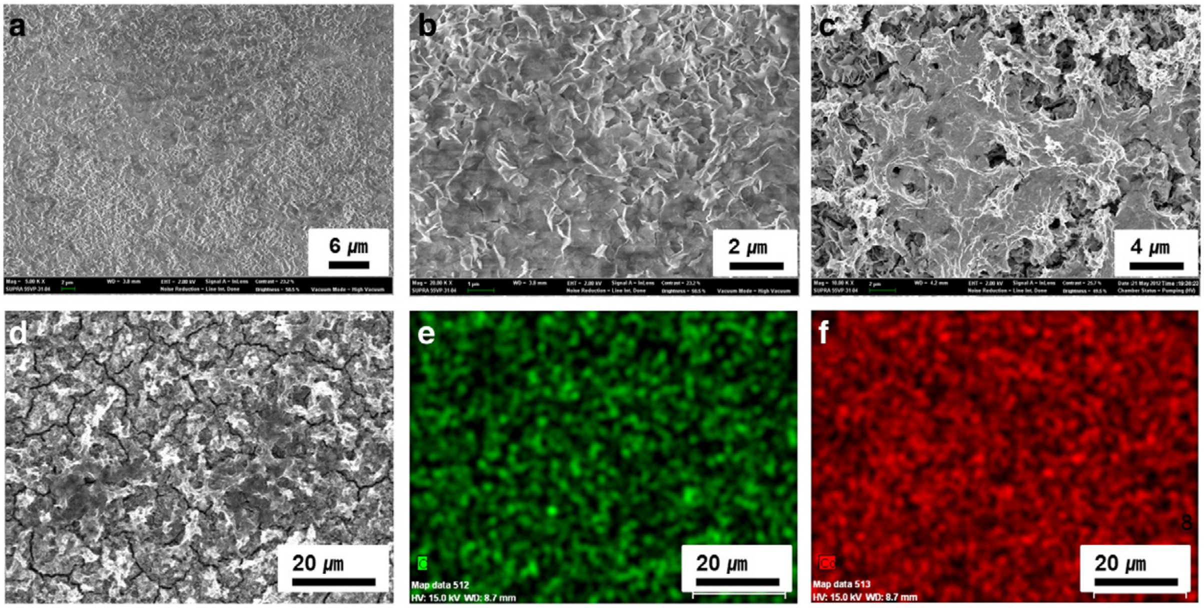

Fig. 1. SEM images of electrodeposited thin films; (a and b) PEI-GOs/$Co(OH)_2$, (c) graphene/Co_3O_4. EDS atomic analysis results of graphene/Co_3O_4 film; (d) SEM image of thin film, (e) carbon, and (f) cobalt.