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Full Length Article

Assembly control of CoO/reduced graphene oxide composites for their enhanced lithium storage behavior

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ABSTRACT

We report on the strategy of controlling the morphology of CoO/reduced graphene oxide (rGO) composites through regulating the assembly of CoO nanoparticles in the CoO/rGO composites by using oleic acid (OA). With increasing of OA amount, the morphologies and structures of CoO/rGO composites display special changes. The OA was found to influence the assembly of CoO nanoparticles on the surface of rGO sheets. As the content of OA is 1 mL, the obtained CoO/rGO composites (S_1) shows 3-D network CoO anchored with rGO sheets structure. This 3-D CoO microstructure is composed of intertwined nanowires which assembled by tiny CoO nanoparticles. Moreover, S_1 exhibits superior cycle and rate capacitance. The reversible capacity of S_1 can reach 1309 mA h·g^{-1} after 100 cycles at 0.1 A·g^{-1}. Even at 2 A·g^{-1}, the reversible capacity of S_1 still maintains 550 mA h·g^{-1}. The excellent electrochemical performance of S_1 profits from its unique 3-D structure, accelerating the charge transfer rate in the conversion reaction in the lithiation/delithiation process. It believes that this work will inspire the variation of structural design in transition metal oxides (TMOs) and graphene composites as anode materials for LIBs.

1. Introduction

Lithium-ion batteries (LIBs) are the most promising candidates for energy storage devices, which have attracted research interest in the scientific and industrial fields because of the advantages of high energy density, power density and environmental friendliness [1–3]. Among various electrode materials, transition metal oxides (TMOs) have been extensively investigated as anode materials for LIBs [4–8]. Usually, TMOs use reversible redox reactions to achieve charge storage and therefore produce higher specific capacity than commercialized carbonaceous materials with electric double layer capacitance. As one of the promising TMOs, CoO has received much attention over the last decade due to its relatively low cost and high theoretical capacity (716 mA h·g^{-1}). Unfortunately, low electrical conductivity and large volume change during the charge-discharge processes have limited its applications [9–10]. To solve these problems, mixing the nanostructured CoO with conductive and stretchable carbonaceous materials is an efficient strategy [11–13]. Graphene owing to its high electrical conductivity, large specific surface area and good mechanical flexibility has been used widely for hosting active materials [14–20]. Indeed, according to the previous reports, most CoO/graphene composites exhibited various morphologies such as CoO nanoparticles, nanowires, nanorods or nanocubes loading on the graphene sheets, et. al. However, it is rarely reported that a kind of 3-D network CoO structure anchored with several graphene sheets rather than directly loading on graphene sheets, which might improve the utilization of graphene.

In this work, we used oleic acid (OA) as shape controller to adjust the assembly of CoO nanoparticles on the surface of rGO sheets through solvothermal technique followed by a heating treatment. Three totally different morphologies of CoO/rGO composites were obtained by changing the addition amount of OA in the synthesis process. When the content of OA was 1 mL, the obtained CoO/rGO composites presented three-dimensional (3-D) network CoO anchored with the rGO sheets structure (S_1). It presented enhanced electrochemical performance than other three contrast samples with different amount of OA in the initial solution. S_1 exhibited the high reversible capacity of 1309 mA h·g^{-1} after 100 cycles at 0.1 A·g^{-1}. Even at 2 A·g^{-1}, its reversible capacity was still kept at 550 mA h·g^{-1}, outperforming the previously reported hybrids of CoO and graphene composites [21–30].

2. Experimental

2.1. Synthesis of CoO/rGO composites

All experimental reagents used in this work were analytical grade and used as raw materials without further purification. The CoO/rGO

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composites were synthesized via solvothermal method followed by a heating treatment. The graphene oxide (GO) was synthesized via modified Hummers' method [31]. In a typical synthesis, a certain amount of oil acid (OA) added into a mixture of 10 mL deionized water and 60 mL ethanol. Then the 0.582 g $Co(NO_3)_2{\cdot}6H_2O$, 0.6 g $CO(NH_2)_2$ and 0.07 g GO dispersed in this solution one after another under magnetic stirring. The resulting suspension was sonicated for 2 h. Subsequently, the suspension was transferred into a 100 mL Teflon lined stainless-steel autoclave and maintained at 120 °C for 5 h. After the reaction, the precipitate was washed several times by ethanol and then dried at 80 °C overnight. Finally, it was heated at 400 °C in Ar for 2 h to get the CoO/rGO composites. The samples were marked as S_x (x = 0, 0.5, 1, 1.5) where x represented the content of OA in the raw materials.

2.2. Characterization

The crystal structure of as-prepared samples was analyzed by X-ray diffraction (XRD, Rigaku, D/max-2200, Cu Kα radiation: λ = 0.15406 nm) at a scanning rate of 8°·min^{-1}, in the 2θ range from 10° to 70°. Raman spectra of the as-prepared samples were recorded on the Renishaw-invia with a 532 nm laser excitation. X-ray photoelectron spectroscopy (XPS) was obtained on Kratos Axis Ultra DLD. The morphology and microstructure were investigated by field-emission scanning electron microscopy (FESEM) system (Hitachi, S4800) and Transmission electron microscope (TEM, Tecnai G2 F20S). Thermogravimetry analysis (TG, Bruker, STA449 F3) was conducted in air from room temperature to 800 °C at the heating rate of 10°·min^{-1}. The specific surface area was examined by the Brunauer-Emmett-Teller (BET) measurement with Micromeritics (ASAP2460).

2.3. Electrochemical measurements

The electrochemical performance of the CoO/rGO composites was carried out using CR2032 coin cells. The test cells composed of Li metal foil as counter electrode, 1 M $LiPF_6$ in ethylene carbonate (EC)/ethyl methyl carbonate (EMC)/dimethyl carbonate (DMC) (1:1:1 in volume) as the electrolyte and which were assembled in an Argon atmosphere-filled glove box (Mbraun, LABSTAR, Germany). The working electrodes were comprised of active materials, acetylene black, and carboxy methyl cellulose sodium at a weight ratio of 8:1:1 dissolved in deionized water. Galvanostatic discharge-charge tests were performed between 0.005 and 3.0 V at different current density on Neware battery testing system. The electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) (0.005–3.0 V, vs Li^+/Li) were measured with use of an electrochemical workstation (CHI660C).

3. Results and discussion

The phase components and structure information of the prepared CoO/rGO composites were characterized by XRD. As shown in Fig. 1a, the diffraction peaks can be assigned to the (1 1 1), (2 0 0), (2 2 0) crystal plane of the face-centered cubic CoO (JCPDS No. 43-1004) [32–33]. The broad peak of composites near 24° is caused by reflection of the (0 0 2) facets of rGO sheets [34]. Compared with that of $S_{0.5}$, S_1 and $S_{1.5}$, the broad peak around 24° becomes gradually weaker and the diffraction peaks of CoO became gradually stronger with the increase of amount of OA. The probable reason why the crystallinity of products becomes higher with the increase of OA is that as the content of OA increased the interaction between OA moleculars is enhanced, which affects the nucleation and growth of crystals and then effect the crystallinity of products. The crystallite sizes of S_0, $S_{0.5}$, S_1 and $S_{1.5}$ calculated with Scherrer equation, are 12, 6, 8 and 11 nm, respectively. Fig. 1b shows the Raman spectroscopy of S_0, $S_{0.5}$, S_1 and $S_{1.5}$. The remarkable peaks at about 1350 cm^{-1} and 1590 cm^{-1} are attributed to D band (disorder carbon) and G band (graphitic carbon), respectively [35–36]. The intensity ratio of D band to G band (I_D/I_G) is a measure of the surface defects of rGO [37–39]. It can be seen that the intensity ratio (I_D/I_G) of S_1 is 1.36 which is higher than that of S_0 (1.06), $S_{0.5}$ (1.10) and $S_{1.5}$ (1.19). The relatively higher I_D/I_G of S_1 indicates the more defects or edge areas from rGO to CoO. It is beneficial to provide more active sites for electron storage as well as enhance binding energies with ions in the electrolyte.

To analyze the electronic structure and chemical composition of the CoO/rGO composites, the XPS spectrum of S_1 were carried out. In Fig. 2a, the peaks of Co (Co 2s, Co$2p_{1/2}$, Co $2p_{3/2}$, Co LMM, Co 3s, Co 3p) and O (O 1s, O KLL) in the survey XPS spectrum for S_1 are assigned to CoO. The peak of C 1s is attributed to rGO [32]. Fig. 2b shows the XPS spectrum of the Co 2p, two main peaks at binding energies of 780.2 eV for Co $2p_{3/2}$ and 796.2 eV for Co $2p_{1/2}$, indicating the characteristic of Co^{2+} [25]. In addition, two satellite peaks at 786.3 eV and 802.7 eV suggests the domination of CoO phase. As for C 1s high-resolution spectrum (Fig. 2c), it splits into four major components centered at 284.5, 285.3, 286.8 and 289.1 eV, which are assigned to C═C, C−O, C═O and O−C═O functional groups, respectively. The stronger C 1s peak at a binding energy of 284.5 eV indicates the deoxygenation procedure accompanying the reduction of GO, which is consistent with the reported results [40,41]. The spectrum of O 1s (Fig. 2d) shows three independent peaks. The peak at 528.5 eV is assigned to oxygen species in CoO, and the peak at 532.2 eV is attributed to C−OH or C−O−C groups. Particularly, the peak at 531.1 eV can be ascribed to C═O or Co−O−C linkages in the composites [42–43]. For all we know, the strong chemical combination between the M_xO_y and rGO via the oxygen bonding (M−O−C) would be helpful for interfacial charge transfer and decrease the loss of active materials, which can enhance electrochemical property of the M_xO_y/rGO composites [42,44,45].

The morphology of CoO/rGO composites obtained from different addition content of OA were characterized by SEM (Fig. 3). As shown in Fig. 3a, the CoO/rGO composites without the addition of OA (i.e. S_0)

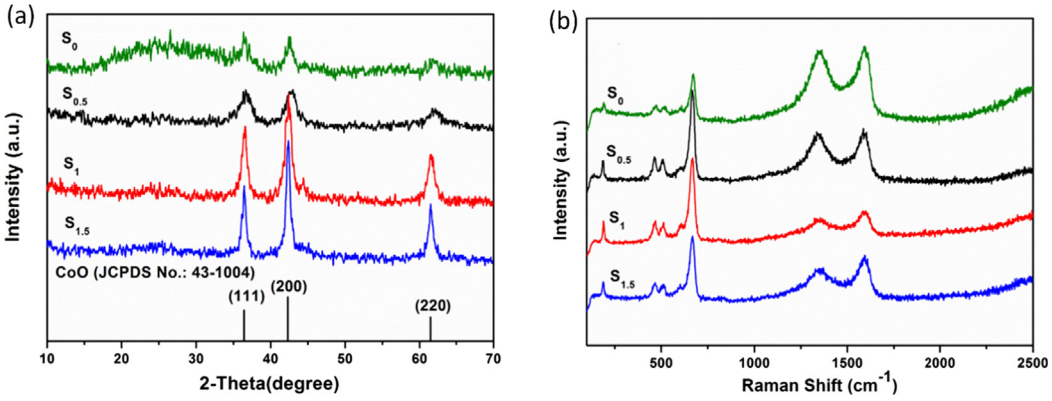

Fig. 1. (a) XRD patterns and (b) Raman spectra of CoO/rGO composites with different content of oleic acid (OA) (S_0, $S_{0.5}$, S_1 and $S_{1.5}$).