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Electrochemical properties of WO_3-reduced graphene oxide composite powders prepared by one-pot spray pyrolysis process

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ABSTRACT

In this work, we report the preparation of WO_3-reduced graphene oxide (rGO) composite powders by spray pyrolysis process using a stable graphene oxide colloidal solution with ammonium tungstate. The ultrafine WO_3 nanocrystals below 10 nm in size are dispersed within the rGO matrix. The bare WO_3 powders prepared from the aqueous spray solution of ammonium tungstate are spherical and do not aggregate. The bare WO_3 and WO_3-rGO composite powders show monoclinic and cubic crystal structures, respectively. The initial discharge capacities of the bare WO_3 and WO_3-rGO composite powders at a current density of 100 mA g^{-1} are 771 and 941 mA h g^{-1}, respectively, and their initial Coulombic efficiencies are 67 and 65%, respectively. The discharge capacities of the bare WO_3 and WO_3-rGO composite powders at the 300th cycle are 282 and 546 mA h g^{-1}, respectively.

1. Introduction

Transition metal oxide materials have been researched as promising anode materials for lithium ion batteries (LIBs) because of their high energy densities [1–10]. Nanostructured and carbon composite materials have been mainly considered in the view of improving the electrochemical properties of the transition metal oxides [9–20]. Nanostructured tungsten oxide (WO_3) materials with various forms, such as nanorods, nanowires, and mesoporous structures have also been developed as anode materials for LIBs [21–29]. However, nanostructured WO_3 materials have typically shown low capacities and poor cycling performances because of the structural instability caused by repeated lithium insertion and extraction processes. WO_3-carbon composite materials have, however, been scarcely studied as anode materials for LIBs [30,31]. Yu et al. reported WO_3 nanowire-graphene nanocomposites prepared by a facile hydrothermal process, which exhibited a reversible lithium storage capacity of 656 mA h g^{-1} after 100 cycles at 100 mA g^{-1} [32].

Spray pyrolysis, a gas phase process, has successfully been applied to the production of metal oxide-reduced graphene oxide (rGO) composite materials [33–35]. Spray pyrolysis has been evaluated to be an efficient, simple, and continuous process for large-scale production of metal oxide-rGO composite materials without involving additional processes, such as thermal heating, pulverizing, and washing. Sphere-like fine metal oxide-rGO composite powders prepared by spray pyrolysis showed superior electrochemical properties, such as high capacity and fast rate capability and better cycling performances than bare metal oxides [36].

In this study, sphere-like WO_3-rGO composite powders were prepared by spray pyrolysis by using a stable GO colloidal solution with ammonium tungstate. Dense WO_3 powders were also prepared by spray pyrolysis under identical conditions without GO to compare the lithium ion storage properties.

2. Experimental

Bare WO_3 and WO_3-rGO composite powders were directly prepared by spray pyrolysis from spray solutions without and with graphene oxide nanosheets, respectively. The pyrolysis was carried out in a quartz reactor 1200 mm in length and 50 mm in diameter and the reactor temperature was maintained at 800 °C. Nitrogen was used as the carrier gas at a flow rate of 10 L min^{-1}. GO was synthesized from graphite flakes by a modified Hummers method, as described in the previous reports [33,37]. The as-obtained

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graphite oxide was redispersed in distilled water and then exfoliated to generate graphene oxide nanosheets by ultrasonication. Then, 500 mL of the exfoliated GO solution (0.2 mg mL^{-1}) was added to 14.2 g of ammonium tungstate.

The crystal structures of the powders were investigated by X-ray diffractometry (XRD, X'pert PRO MPD) using Cu-K_α radiation ($\lambda = 1.5418$ Å). Further, the morphological features of the powders were investigated using scanning electron microscopy (SEM, JEOL JSM-6060) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F) at an acceleration voltage of 200 kV. The specific surface areas of the powders were calculated by the Brunauer–Emmett–Teller (BET) analysis of nitrogen adsorption measurements (TriStar 3000). To determine the amount of rGO in the WO_3-rGO composite powders, thermogravimetric analysis (TGA, SDT Q600) was performed in air at a heating rate of 10 °C min^{-1}.

The capacities and cycling properties of all the powders were determined using a 2032-type coin cell. The cell electrode was prepared from a mixture containing active material (70 wt%), Super P (20 wt%), and sodium carboxymethyl cellulose (CMC) binder (10 wt%). Lithium metal and a microporous polypropylene film were used as the counter electrode and separator, respectively. The electrolyte was a solution of 1 M $LiPF_6$ in a 1:1 vol mixture of fluoroethylene carbonate/dimethyl carbonate (FEC/DMC). The charge/discharge characteristics of the samples were determined through cycling in the 0.001–3 V potential range at a fixed set of current densities. Cyclic voltammetry measurements were carried out at a scan rate of 0.07 mV s^{-1}.

3. Results and discussion

The morphologies of the WO_3-rGO composite powders prepared by spray pyrolysis under nitrogen atmosphere are shown in Fig. 1. The SEM and TEM images revealed the crumpled structure of the WO_3-rGO composite powders. The graphene oxide nanosheets dispersed in the droplet distorted the spherical morphology of the powders during the formation of the WO_3-rGO composite. The ultrafine WO_3 nanocrystals below 10 nm in size were dispersed within the rGO matrix, as shown in the HRTEM image in Fig. 1d. The rGO nanosheets minimized the crystal growth of the WO_3 nanocrystals. rGO layers with a few layers were observed in the HRTEM image, as shown by the arrows in Fig. 1d. The clear lattice fringes shown in Fig. 1d separated by 0.36 nm could be assigned to the (020) crystal plane of cubic WO_3 phase. The elemental mapping images shown in Fig. 1e showed the uniform distribution of rGO throughout the WO_3-rGO composite powder. The morphologies of the bare WO_3 powders prepared by spray pyrolysis are shown in Fig. 2. The bare WO_3 powders were completely spherical and did not aggregate. The TEM images shown in Fig. 2c and d revealed the filled structure of the bare WO_3 powders. Hollow metal oxide powders are generally formed during spray pyrolysis because of the high drying rate of droplets inside the reactor, which is usually maintained at high temperatures [38]. In this study, ammonium tungstate powders with hollow structures could have been formed because of the high drying rate of the droplets. However, melting of ammonium tungstate before decomposition into WO_3 resulted in the formation of ammonium tungstate powders with a dense structure as an intermediate product in the front part of the reactor maintained at 800 °C. Therefore, the decomposition of ammonium tungstate powders with a dense structure resulted in the formation of bare WO_3 powders with filled structure. The mean size of the bare WO_3 powders measured from the low-resolution SEM images was 570 nm. The HRTEM image shown in Fig. 2d revealed well-developed WO_3 crystals with sizes of several tens of nanometers, as shown by circle. The clear lattice fringes separated by 0.37 nm

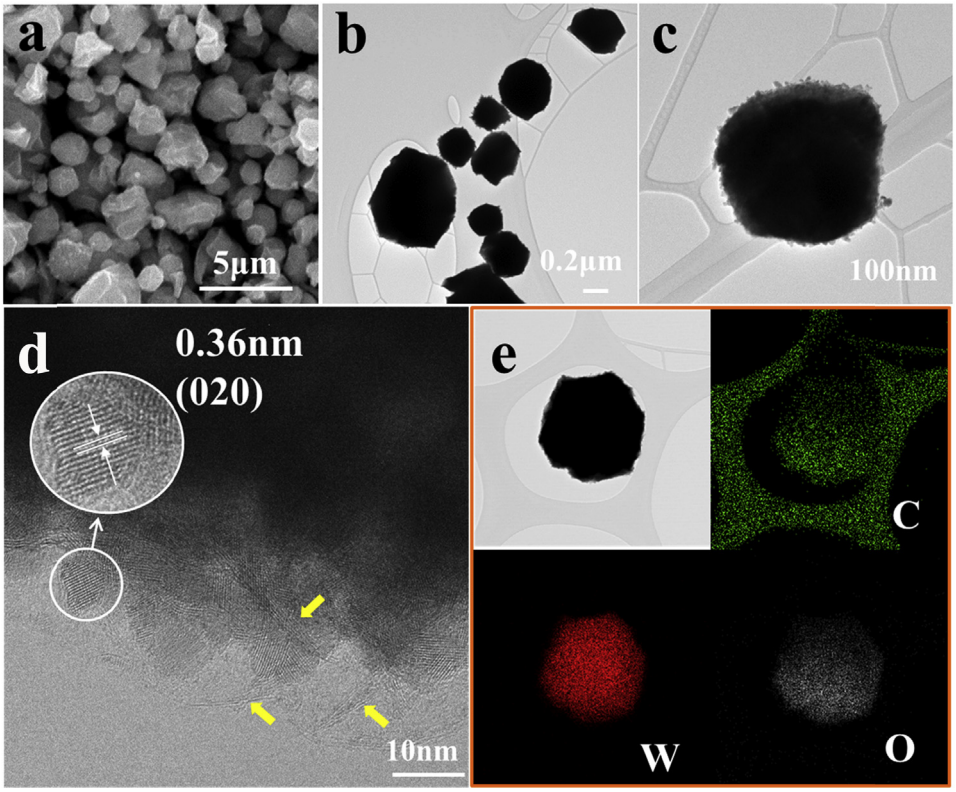

Fig. 1. Morphologies and elemental mapping images of WO_3–rGO composite powders prepared by spray pyrolysis: (a) SEM image, (b) and (c) TEM images, (d) high resolution TEM image, and (e) elemental mapping images.