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Facile synthesis of N-doped carbon-coated nickel oxide nanoparticles embedded in N-doped carbon sheets for reversible lithium storage

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ABSTRACT

In this work, we present a facile strategy for the synthesis of well-structured transition metal oxides based composites by the decomposition of nitrate and polyvinylpyrrolidone (PVP) followed by simple oxidation at a low temperature and using them as high performance materials for reversible lithium storage. As proofs of this simple strategy, three kinds of TMOs, namely NiO, Fe_2O_3 and Co_3O_4, based composites have been prepared with this simple strategy. The morphology and structure analyses indicate that TMOs nanoparticles with a size of 10 nm are tightly coated by the *in situ* formed graphene-like carbon shell and evenly dispersed in the microsized nitrogen-doped carbon sheets (C@TMOs@NCSs) derived from the PVP. As lithium storage materials, the as-prepared C@NiO@NCSs composites show excellent electrochemical performances in terms of cycle stability (651 mAh g^{-1} after 1500 cycles at 1 A g^{-1} and 518 mAh g^{-1} after 1400 cycles at 2 A g^{-1}) and rate capability (400 mAh g^{-1} at 4 A g^{-1}). Such superior electrochemical performance is attributed the well-structured composites with features of tight carbon coating layer, evenly dispersed TMOs nanoparticles and robust carbon supports.

1. Introduction

Lithium-ion batteries (LIBs) have been widely used in portable electronics and electric vehicles, owing to their high energy density and long lifespan [1–5]. Currently, one of the main research directions is searching for advanced electrode materials with enhanced lithium storage ability to improve the battery energy density [6–9]. Transition metal oxides (TMOs) have attracted considerable attention as their ability to uptake more than one lithium per transition metal, giving high theoretical specific capacities [10–17]. For example, the NiO and CuO can offer a high theoretical capacity of 718 and 674 mAh g^{-1}, respectively [17–21]. Despite TMOs anodes of high theoretical storage capacity, the fully achieving of their theoretical capacity still faces challenges [15,22]: First, the TMOs usually have an intrinsic low electron conductivity, leading to poor reactivity and reaction kinetics upon lithium [23]. Second, these materials suffer from drastic volume expansion during the Li^+ insertion-extraction processes, resulting in the pulverization of electroactive particles and then the fast capacity fading [19]. Finally, it is challenging to form a stable solid electrolyte interface (SEI) layer as the repeated volume change associated with repeated lithium insertion-extraction, leading to the limited cyclability and low Coulombic efficiency [24,25].

In response, tremendous efforts have been performed to optimize the electrochemical performance of TMOs anodes by enhancing their electrical conductivity and mitigating the adverse influences associated with large volume change. An effective strategy is to construct active/inactive composites with nanosized TMOs particles being evenly encapsulated into a conductive matrix (e.g., graphene, graphene oxides, carbon nanotubes and conductive polymers) [26–32]. In such design, carbon networks can enhance the electrical conductivity of the resulted hybrid materials, leading to the fasted electron transfer, the accelerated ionic diffusion across

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the electrolyte-electrode interface and the shortened diffusion pathway by confining the particles growth of TMOs during high temperature synthesis [33]. Simultaneously, the problem of volume expansion of the active material is tackled due to the physical buffer effect of the carbon matrix, leading to the prolonged lifetime [34]. Our recent study evidenced that well-designed nanocomposites with monodispersed carbon-coated electroactive particles can alleviate the large volume change upon cycling and provide excellent cycle stability and rate capability with high reversible capacity [35]. To synthesize the active/inactive composites, hydrothermal and solvothermal followed by calcining the resulted precursors at high temperature are the commonly used methods [15,19,23,36]. For example, Li et al. reported the high capacity composites of self-assembled porous CuO nanospheres decorated on reduced graphene oxide synthesized by solvothermal method [17]. Multi-yolk-shell copper oxide@carbon octahedral as high stability anode of LIBs has been synthesized by hydrothermal method [36]. And Mou et al. synthesized layer-cake-like Co_3O_4/C composites with hydrothermal technique [14]. In addition to the commonly used hydrothermal or solvothermal technique, developing of simple method with ability in large-scale production is greatly encouraged.

Herein, we report a facile strategy for the synthesis of TMOs based composites and using them as high-performance materials for reversible lithium storage. In the as-prepared composites, the *in situ* formed nitrogen-doped graphene-like carbon coated transition metal oxides nanoparticles evenly embed in the nitrogen-doped carbon sheets (C@TMOs@NCSs). The nitrogen-doped carbon derives from the decomposition of polyvinylpyrrolidone (PVP). This sample procedure can be expanded to synthesize different kinds of TMOs based composites: three kinds of TMOs, namely NiO, Fe_2O_3 and Co_3O_4, based composites have been synthesized. As anode materials for LIBs, the obtained composites show excellent reversible lithium storage ability and rate capability, due to the *in situ* formed N-doped carbon coating layer and carbon matrix significantly increasing the conductivity of the abstained TMOs composites and alleviating the pulverization of TMOs during repeated lithium insertion and extraction.

2. Experimental

2.1. Chemicals

Copper foil (25 μm), Polyvinylpyrrolidone (PVP) ($M_W = 55000$, AR), $Ni(NO_3)_2 \cdot 6H_2O$ (98%), $Co(NO_3)_2 \cdot 6H_2O$ (97.7%) and $Fe(NO_3)_3 \cdot 9H_2O$ (98%) were purchased from Alfa Aesar. All of the chemicals were used directly as received.

2.2. Synthesis of the C@TMOs@NCSs composites

$Ni(NO_3)_2 \cdot 6H_2O$ (0.05 g) and PVP (0.1 g) were dissolved in 2 mL of ethanol by ultrasound for 5 min at room temperature. After forming homogeneous solution, it was evenly coated on the Cu foil substrate (20 cm × 20 cm squares) by tape casting. Then the obtained $Ni(NO_3)_2 \cdot 6H_2O$-PVP/Cu film was heated to 100 °C for 15 min to remove the ethanol solvent. The dried film was rolled up into a tube with the dimeter of 1 inch and then the obtained tube was wrapped by using a new copper strip. After that, the wrapped tube was annealed at 850 °C for 30 min under the H_2 (50 sccm) and Ar (500 sccm) flow to get the composite of C@Ni@NCSs, with the total pressure < 50 Torr. After fast cooled down to room temperature by opening the heating furnace without changing the gas flow, the obtained C@Ni@NCSs composites were scraped from Cu foil using a plastic knife. Finally, the C@NiO@NCSs composites were prepared by directly oxidized the as-synthesized C@Ni@NCSs powders in air at 300 °C for 60 min, with a ramp-rate of 5 °C min^{-1}. C@Fe_2O_3@NCSs and C@Co_3O_4@NCSs were synthesized by following the same procedures with the use of their corresponding nitrate precursor.

2.3. Synthesis of NCSs

The NCSs were obtained by removing the metal from C@Ni@NCSs composites by acid etching (2 M HCl for 24 h).

2.4. Synthesis of the NiO nanopartials (NiO NPs)

The NiO NPs were obtained by directly heating the as-synthesized C@NiO@NCSs powders in air to 600 °C and holding for 60 min to remove the carbon species.

2.5. Materials characterization

Powder XRD was conducted on a Bruker D2 Phase X-ray diffractometer using Cu Kα radiation at a scanning rate of 4° min^{-1} in the 2θ range of 10°–70°. SEM observation was carried out on a field emission scanning electron microscope (FEI, Magellan 400) operated at 20 kV. The transmission electron microscopy, high-resolution TEM, and elemental mappings were collected on a JEOL-2100 instrument. Raman spectra was recorded in a JY HR-800 Raman spectrometer (Horiba Jobin Yvon) with an excitation laser beam wavelength of 633 nm. The contents of C were determined using a NETZSCH STA 449C thermogravimetry analyzer (Diamond PE) under an air atmosphere with a heating rate of 10 °C min^{-1} from room temperature to 600 °C. The surface compositions of the composites were analyzed by X-ray photoelectron spectroscopy (XPS, ESCAlab-250) with an Al anode source. Nitrogen adsorption-desorption isotherms was measured on a Micrometitics Tristar 3000 system.

2.6. Electrochemical measurements

The working electrodes were prepared by coating the slurry of the as-prepared C@NiO@NCSs composites, Super P, and poly(vinyl difluoride) (5 wt%) binder in a weight ratio of 85:5:10 onto the Cu foil, which were then dried in a vacuum oven at 80 °C overnight. The active material loading of each electrode was about 1 mg cm^{-2}. The CR2032-type coin cells were assembled in a high-purity argon-filled glovebox (M-Braun) using 1 M $LiPF_6$ dissolved in a 1:1 (wt%) mixture of ethylene carbonate and diethyl carbonate with 1 wt% additive of vinyl carbonate as the electrolytes and Glass-fiber (Whatman, GF/A) as the separators. The cells were galvanostatically cycled at room temperature using a program-controlled test system (LAND CT2001A). The lithium storage capacity is calculated based on the total weight of the C@NiO@NCSs composites. The cyclic voltammetry (CV) measurements were carried out on an Autolab Electrochemical Workstation (PGSTAT302N) in the potential range of 0.001–3.0 V at a scan rate of 0.1 mV s^{-1}. The above-mentioned measurements were all carried out at room temperature (25 °C).

3. Results and discussion

The synthesis of the composites of nitrogen-doped carbon coated nickel oxide nanoparticles embedded in nitrogen-doped carbon sheets (C@NiO@NCSs) is schematically illustrated in Scheme 1. First, the nitrate precursor slurry was evenly coated on the Cu foil substrate by tape casting. In the second step, the polyvinylpyrrolidone (PVP) carbonized into the nitrogen-doped carbon, and the metal nitrates decomposed into metal oxides. Part of the *in*