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NiO-Co_3O_4 nanoplate composite as efficient anode in Li-ion battery

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ABSTRACT

Nanocomposites rationally designed in structure and component are highly desirable for the development of electrodes in lithium-ion battery application for that they can take full advantages of different structures and components to achieve superior electrochemical properties. A nanocomposite with the two-dimension (2D) NiO nanoplate of a hexagonal structure and zero-dimension (0D) Co_3O_4 nanoparticles was synthesized by the hydrothermal method. Scanning electron microscopy, high-resolution transmission electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy were employed to characterize the composition, morphology, microstructure and chemical state of the nanocomposite, respectively. As an anode material of lithium-ion battery, the nanocomposite exhibits greatly improved specific capacities and stable cyclability of 633 mA h g^{-1} at a current density of 100 mA g^{-1} up to 70 cycles, much higher than the corresponding building block alone. The outstanding performance of the NiO/Co_3O_4 nanocomposite is attributed to the hybrid structure and the synergistic effect of different components. This large-scale and cost-efficient synthesis can be extended for the design and synthesis of transition metal oxides composite for high-performance electrochemical energy storage.

1. Introduction

Rechargeable lithium ion battery (LIB) is one of the potential power sources for electrical energy.[1–4] To meet the increasing demands for high energy and power density, the transition-metal oxides have been greatly exploited as the alternative anode materials for LIBs because of their higher theoretical specific capacities (e.g. > 600 mA h g^{-1}) than that of conventional graphite anode (e.g. 372 mA h g^{-1}). [5–9] However, like other metal oxides, poor capacity retention arisen from the poor electrical conductivity and the large volume expansion upon cycling limit their applications.[10–12] To overcome these drawbacks, several approaches have been applied, such as unique nanostructures/microstructure,[13–17] combining carbonaceous materials [18–21] and hybridzation of materials etc. [22,23] Especially, rational design of nanocomposites in structure and component has attracted increasing attention in which structural features and electroactivities of each component are fully manifested to achieve superior electrochemical properties.[23–26] For example, Luo and co-workers[27] reported a synthesis of TiO_2/Fe_2O_3 nanorods on a carbon cloth with a reversible capacity of 480 mA h g^{-1} at 120 mA g^{-1} after 150 cycles, much higher than those of TiO_2 nanorods on a carbon cloth. Gu et al.[28] synthesized porous α-Fe_2O_3 branches on β-MnO_2 nanorods, presenting a reversible capacity of 1028 mA h g^{-1} at 1000 mA g^{-1} after 200 cycles, much higher than the building blocks alone. Sun et al.[29] fabricated hierarchical $ZnCo_2O_4$/NiO core/shell nanowire arrays, which delivered a capacity of 357 mA h g^{-1} at 100 mA g^{-1} after 50 cycles. On the contrary, $ZnCo_2O_4$ nanowires only have the capacity of 152 mA h g^{-1}.

NiO and Co_3O_4 have also been selected to construct the hybrid nanocomposite,[30–33] due to their high theoretical capacities (718 mA h g^{-1} for NiO, and 890 mA h g^{-1} for Co_3O_4), [34–38] high abundance and low cost. For example, Li et al. synthesized NiO/Co_3O_4 composite nanosheets *via* a chemical solution method at low temperature, which exhibited a capacity of ~600 mA h g^{-1} at 400 mA g^{-1} after 15 cycles, much higher than pure Co_3O_4 nanosheets (~150 mA h g^{-1}). [30] Huang and co-worker reported a synthesis of aligned nickel-cobalt oxide nanosheet arrays on nickel foam substrates by means of chemical bath deposition technique, which delivered a capacity of 480 mA h g^{-1} and 430 mA h g^{-1} at 0.5 A g^{-1} and 1.0 A g^{-1} after 50 cycles, respectively.[31] The same group also synthesized ternary core/shell nanowire arrays of

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Co_3O_4/NiO/C on the nickel foam *via* a three-step solution method. [32] The Co_3O_4/NiO/C core/shell nanowire arrays exhibited specific capacity of 1053 mA h g^{-1}at 0.5 C, which is higher than that of the pure Co_3O_4 nanowire array film (724 mA h g^{-1}) and NiO nanoflake film (454 mA h g^{-1}). In this work, we develop a simple hydrothermal method to synthesize the 2D/0D (NiO/Co_3O_4) hybrid nanocomposite. 2D/0D (NiO/Co_3O_4) hybrid nanostructure could improve the electrochemical properties due to the following aspects. On the one hand, 2D hexagonal NiO nanoplates have several merits: (1) the huge surface area provides more space for the Li ions interaction and enhances the contact between electrolyte and active materials; (2) shorter diffusion length among the nanoblocks makes Li ions diffuse much easier; (3) the big interior space among nanoplates can accommodate the volume variation much better.[39–42] On the other hand, 0D Co_3O_4 nanoparticles can efficiently prevent the aggregation of the nanoplates and contribute the capacity as well. The as-obtained nanocomposites exhibit better Li ion storage properties with high capacity and stable cyclability compared with only pristine NiO nanoplate and pure Co_3O_4 nanoparticles.[43,44]

2. Experimental

2.1. Material Synthesis

The scheme of the synthesis process of NiO-Co_3O_4 nanocomposite is shown in Fig. 1. The hydrothermal synthesis of NiO-Co_3O_4 hybrid structure was performed in two steps, in which the 2D NiO nanoplates were synthesized firstly and then the 0D Co_3O_4 nanoparticles were decorated on NiO nanoplates. The process is a very cost-effective and gram-scale route. First, the $Ni(OH)_2$ nanoplates were synthesized by a hydrothermal method. In a typical growth, 1 mmol $Ni(CH_3COO)_2{\cdot}2H_2O$ was dissolved in 30 ml de-ionized water and 1.5 mL $NH_3{\cdot}H_2O$ was added to form the precursor solution. Then the solution was transferred into a 50 ml Teflon-lined stainless steel autoclave and maintained at 150 °C for 3 h. After the reaction, the green product of $Ni(OH)_2$ nanoplates was collected by centrifugation, washed with de-ionized water and ethanol for several times and dried at 60 °C, respectively. The NiO nanoplates were obtained by annealing the $Ni(OH)_2$ nanoplates at 400 °C in air for 2 h. The hybrid NiO-Co_3O_4 nanostructure was prepared in a similar process. First, 1 mmol as-prepared NiO nanoplate powder was dispersed ultrasonically in 30 ml de-ionized water containing 1 g (PVP). Afterwards, 0.2 mmol Co $(CH_3COO){\cdot}2H_2O$ and 2 mL $NH_3{\cdot}H_2O$ were added to the above solution and the mixture was kept in the autoclave at 150 °C for 3 h. Then the product was collected by centrifugation, washed several times with de-ionized water and ethanol, respectively and further annealed in air at 400 °C for 2 h. The pure Co_3O_4 nanoparticles were also synthesized by the same procedure without the addition of NiO nanoplate for comparison.

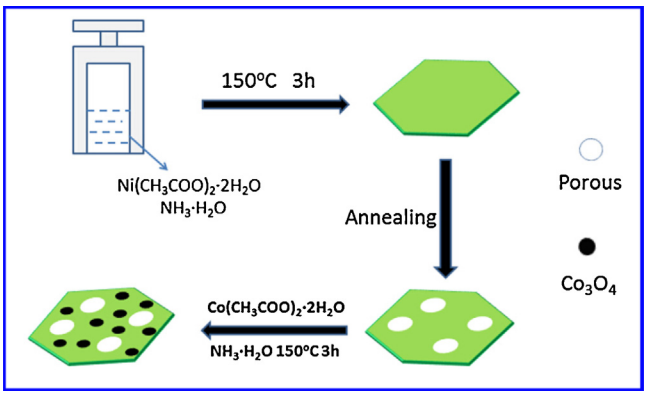

Fig.1. Schematic synthesis of NiO-Co_3O_4 nanocomposites.

2.2. Characterization

The crystallographic structures of the materials were studied by a powder X-ray diffraction (XRD) (Empyrean, PANalytical B.V.) equipped with Cu Kα radiation (λ=0.15406 nm). The morphology and microstructure of the products were observed by scanning electron microscope (SEM, FEI Quanta-200) and transmission electron microscopy (TEM, FEI Tecnai G2 F20 S-TIWN) with an accelerating voltage of 200 KV, respectively. The surface state and electronic structure of the composites were obtained by X-ray photoelectron spectroscopy (XPS) measurement (Kratos AXIS UltraDLD ultrahigh vacuum (UHV) surface analysis system), using Al Kα radiation (1486 eV) as a probe.

2.3. Electrochemical measurement

The electrochemical properties of the products were evaluated using CR2016-type coin cells. The working electrodes were made of the as-prepared product, acetylene black and polyvinylidene difluoride (PVDF) binder mixed at a weight ratio of 7:2:1 in N-methylpyrrolidone (NMP). The slurry was pasted on clean copper foil followed by drying in a vacuum at 70 °C for 12 h. The electrodes were assembled into half-cells in an Ar-filled glove box using Li foil as the counter electrode and polypropylene microporous film (Celgard 2300) as the separator. The electrolyte was 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 in volume). Cyclic voltammetry (CV) measurements were carried out at a scanning rate of 0.1 mVs^{-1} on a CHI660C workstation. The galvanostatic cycling tests were conducted in the range of 0.005-3 V versus Li^+/Li under a current density of 100 mA g^{-1}, using a multichannel battery test system (LAND CT2001A).

3. Results and discussion

XRD analysis was carried out to identify the crystal structure and composition of the products and the XRD patterns of NiO

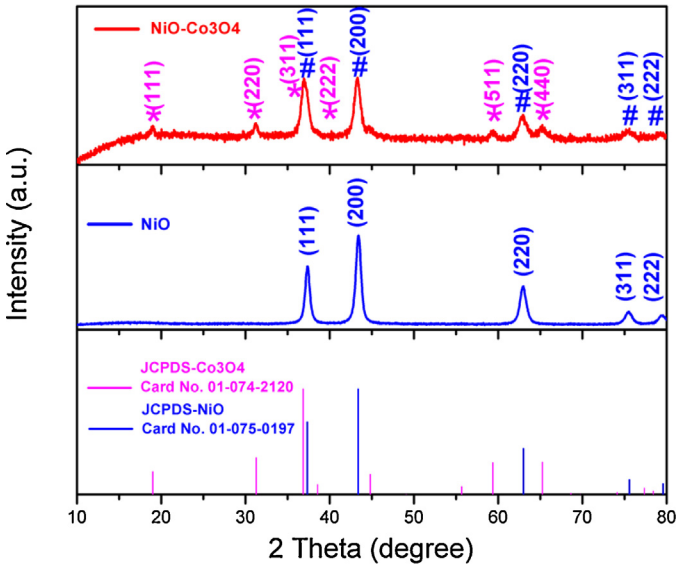

Fig.2. XRD patterns of NiO nanoplates and NiO-Co_3O_4 nanocomposite with the standard JCPDS files of pure NiO and Co_3O_4 crystals for comparison. The peaks of NiO and Co_3O_4 in the nanocomposite are highlighted as pounds and asterisks, respectively.