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Preparation and performance of tubular nanoflaky (Ni, Co, Mn) oxides with hierarchical mesoporous structure

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ABSTRACT

The nickel cobalt manganese oxide (NCMO/CNT) with hierarchical tubular nanoflaky structure is intentionally designed and synthesized via a facile method by using carbon nanotube (CNT) as a backbone template, then the nickel cobalt manganese oxide with nanosheet-like nanotube structure (NCMONST) is synthesized after removed successfully the CNT templates. The morphology, structure and physicochemical properties of the NCMONST samples are characterized by field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and nitrogen adsorption–desorption isotherms. The results reveal that the NCMO shell with a thickness of 0.2 μm grows uniformly on the surface of the CNT with a diameter of 0.1 μm. After calcined NCMO/CNT in air, the mesoporous NCMONST is successfully obtained. The as-prepared NCMONST maintains the tubular and sheets-like structure of NCMO/CNT, and possesses a high specific surface area of 134.1 $m^2 g^{-1}$, large pore volume of 0.609 $cm^3 g^{-1}$ and broad pore-size distribution. The electrochemical results show that the NCMONST exhibits a high specific capacitance of 680 F g^{-1} at 1 A g^{-1}, excellent rate capability of 38% at 20 A g^{-1} and good capacity retention of 88% after 1000 cycles. Therefore, the transition metal oxide with porous structure is a promising electrode candidate for the application of supercapacitors.

1. Introduction

With the increasing demand in electric energy storage for electronic devices and electric vehicles, supercapacitors have received immense attention as one of the most promising energy storage devices because of their high power density and long cycle life [1,2]. Electrical double layer capacitors use electrode materials with high surface area to store electric charges, however, the stored charges simply stay on the very limited surface of the electrode material, which leads to the low specific capacitance. However, the pseudocapacitors not only use the high porous electrodes to maintain specific capacitance as supercapacitors, but also can possess much more specific capacitance through storing the charges within the electrode materials as the case of batteries [3]. Thus, to ensure the supercapacitors with high specific capacitance, extensive pseudocapacitor materials have been studied extensively. As one of promising electrode materials for pseudocapacitors, transition metal oxides/hydroxides have been widely investigated due to their variety of oxidation states which can be able to undergo reversible faradic reactions [4–7]. These properties make them possess much higher specific capacitances than the electrical double layer capacitors.

Among numerous transition metal oxides, Ni, Co, and Mn oxides have been extensively studied as promising candidate of electrode material for pseudocapacitors owing to their inherent advantages, including abundant resources and environmental friendliness [8,9]. However, it is still a challenge to achieve high energy density for supercapacitors due to the low conductivity and low diffusion coefficiency of inserted cations [10]. To address these problems, one common adopted strategy is to rationally design structure of transition metal composite with improved the electrochemical performances resulting from the synergistic effects of different components. For example, hybrid NiO/CO_3O_4 with flower-like architectures reported by Xu et al. shows a high specific capacitance (1190 F g^{-1} at a current density of 4 A g^{-1}) [11]. Besides, due to the poor conductivity of transition metal oxides, it is often in situ grown on conductive matrix such as Ni foam [12], carbon textile [13,14], carbon nanotubes [15] and graphene sheet [16,17]. Among those rational design methods, synthesizing transition metal oxides with high specific surface area, which can provide more sites for reaction between the active materials and electrolyte ions, are considered to be a most promising method for preparing pseudocapacitors electrode materials. Thus, several

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porous structures of transition metal oxides have been synthesized via hydrothermal method [18–22].

In our previous work, three kinds of hierarchical mesoporous structure transition metal oxides, which are composed of a β-MnO_2 nanorod core and one of three different nanosheet hybrid (Ni, Co, Mn) oxide shells, have been facilely synthesized via a novel *in situ* nucleation and growth of transition metal oxides on the surface of the β-MnO_2 nanorod [23]. The results reveal that the β-MnO_2@NCMO exhibits the best electrochemical performance than any others, indicating the shell of NCMO has advantage over the shell of NMO and CMO. Herein, in this paper, firstly we in situ grow the macroporous NCMO on the surface of CNT via a facile hydrothermal method. Then, the mesoporous NCMONST with a higher specific surface area is successfully obtained by calcining the macroporous NCMO/CNT in air. The as-prepared mesoporous NCMONST is used as the electrode material for supercapacitor. The structure, morphology and electrochemical properties of the as-prepared mesoporous NCMONST are discussed in details.

2. Experiment

2.1. Sample synthesis

All the reagents were analytical grade and used without further purification. NCMO/CNT nanocomposite was synthesized in a simple process, 0.1 g commercial multiwall CNT was dispersed in 75 ml of deionized water and ultrasonic treatment for 30 min, then the 0.5 g $KMnO_4$ was added to form a homogeneous purple solution followed by stirring for 2 h, and then designed amount of $CoSO_4{\cdot}7H_2O$ and $NiSO_4{\cdot}6H_2O$ were added, followed by stirring for 1 h. After that, the above solution was transferred into a Teflon-lined autoclave (100 ml), sealed and put in an electric oven at 140 °C for 10 h, and then cooled down to ambient temperature naturally. Finally, the precipitation was filtered, washed with distilled water, vacuum dried and then calcined at 350 °C for 2 h in flowing argon at a ramping rate of 2 °C. To obtain the NCMONST, the as-prepared NCMO/CNT nanocomposite was calcinated at 450 °C for 2 h in air to remove the CNT templates. For a comparison, the nickel cobalt manganese oxide with nanosheet-like microsphere structure (NCMONSP) was also prepared in the absence of CNT.

2.2. Physicochemical properties characterization

The crystallographic analyses of samples were carried out by X-ray diffraction (XRD) (D/max-2550 Rigaku, Japan). The morphology and structure of samples were characterized by field-emission scanning electron microscopy (FESEM Nova NanoSEM 230) and transmission electron microscopy (TEM) (JEM-2100F, JEOL). The specific surface area and pore structure of the samples were determined by N_2 adsorption/desorption isotherm at 77 K (JW-BK 112) after degassing at 120 °C overnight.

2.3. Electrochemical measurements

The working electrodes were prepared by the mixed slurry containing active materials (80 wt.%), acetylene black (10 wt.%) and polyvinylidene fluoride (PVDF 10 wt.%) in N-methyl-2-pyrrolidone (NMP). The slurry was painted onto a nickel mesh with a area of 1 cm^2, then dried and pressed. Electrochemical measurements were performed on the electrochemical workstation (VersaSTAT3, Princeton Applied Research, USA) by using a three-electrode mode in an aqueous KOH (6.0 M) with nickel mesh and Hg/HgO as the counter and the reference electrode.

3. Results and discussions

3.1. Structural and morphological analysis

The fabrication process of NCMONST is schematically displayed in Fig. 1. Before the hydrothermal process, the CNT was dispersed well in the $KMnO_4$ solution at room temperature, and then the nanocrystalline will be formed on the surface of CNT due to the slow redox process according to Eq. (1) [24–26]. Subsequently, along with the occurrence of the redox reaction during the hydrothermal process, MnO_2 will continuously grow from the preformed nanocrystalline. Meanwhile, the metal ions (Ni^{2+}, Co^{2+}) can be oxidized, and their hydroxides will nucleate and grow accompanying with MnO_2 crystal growth. Finally, the novel architectures with hybrid nanosheet shells and a CNT core are formed via this simple hydrothermal method. After calcining in air, CNT is removed and a hole with a diameter of CNT is left in the nanosheet-like transition metal oxides, and thus the mesoporous NCMONST is successfully prepared.

$$4KMnO_4^- + 3C + H_2O \rightarrow 4MnO_2 + CO_3^{2-} + 2HCO_3^- \quad (1)$$

The morphology and hierarchical structure of the as-synthesized samples were shown by FESEM images in Fig. 2(a–d), respectively. As shown in Fig. 2a, NCMO grow uniformly on the surface of CNT template with an open and porous structure through this facile in situ growth method. The NCMO deposit densely on the surface of the CNT so that the CNT is not observed in Fig. 2a. However, it can be found from high-magnification FESEM image of NCMO/CNT in Fig. 2b that the nanosheet-like NCMO are well grown on the surface of CNT to form the nanocomposite, the diameter of the nanocomposites is about 0.5 μm. Clearly, the mesoporous NCMONST structure was generated after removing the CNT templates, as shown in Fig. 2c. Besides, it can be observed from the inset in Fig. 2c that the numerous micropores exist on the wall of the left nanotube-like hole, which is probably caused by CO_2 emission during the oxidation process of CNT. Evidently, both the open nanotube-like hole and the porous nanosheet-like NCMO wall can provide additional specific surface area. Therefore, the NCMONST has a higher specific surface area than the NCMO/CNT. In addition, NCMO nanosheets self-assembled to form microsphere in the absence of CNT as shown in Fig. 2d.

In order to analyze the structure of the as-synthesized NCMO, TEM and HTEM images of NCMO/CNT and NCMONST are shown in Fig. 3. It can be seen that the nanowire-like CNT core and NCMO nanosheet shell can be easily distinguished from the low-magnification TEM images in Fig. 3a. As illustrated in Fig. 3a, NCMO shell with a thickness of 0.2 μm is growth tightly and uniformly on the surface of the CNT with the diameter of 0.1 μm. Obviously, it is very clearly observed from Fig. 3b that the NCMONST maintains the former tubular and sheets-like structures after removed the CNT templates. The HTEM is used to investigate the lattice of the surface layer hybrid metal oxide. The lattice spacing of 0.48 nm and 0.256 nm are observed in Fig. 3c, which are in a good agreement with the theoretical interplanar spacing of $NiCo_2O_4$ (111) (JCPDS 20-0781) and MnO_2 (301) (JCPDS 44-0142) planes. Interestingly, the mesopore, which is marked with a red circle in Fig. 3c, can be viewed clearly from the magnified images, indicating the ultrathin NCMO nanosheets are also porous. The crystallographic structure of the NCMO/CNT-precursor and NCMONST were further examined by XRD as shown in Fig. 3d. The NCMO deposit so densely on the surface of the CNT that the diffraction peaks of CNT are not observed. All the diffraction peaks of the NCMO/CNT-precursor are either MnO_2 or hybrid oxides due to the birnessite-type MnO_2 (JCPDS 80-1098) or the (Co, Ni)$Mn_2O_4(OH)_2{\cdot}xH_2O$ (JCPDS 43-1459) phase without any impurity. The patterns of NCMONST reveal the nickel cobalt oxide ($NiCo_2O_4$) (JCPDS 20-0781) and the ramsdellite-type MnO_2 (JCPDS 44-0142) after the precursors are annealed at 450 °C for 2 h. Energy dispersive X-ray spectroscopy mapping shown in Fig. 3e provides more information about the element distribution within the NCMO/CNT nanocomposites. The Ni, Co, Mn and O signals are uniformly distributed over the backbone, whereas the C signals are dominant in the CNT region.

The surface area and pore-size distribution are two key factors for the electrode materials of supercapacitor. Therefore, the specific textural properties of the NCMO/CNT and NCMONST were further verified by the N_2 adsorption–desorption isotherm and BJH pore size distribution, and the results are shown in Fig. 4. The NCMO/CNT possesses the BET surface area of 120.2 $m^2\,g^{-1}$ with a