



General self-template synthesis of transition-metal oxide microspheres and their excellent charge storage properties

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ABSTRACT

Transition metal oxides are promising electrode materials for electrochemical energy storage and conversion to replace the precious metal-based electrode materials. Herein, we demonstrate a universal method for making flower-like transition metal oxides (NiO, Co₃O₄, NiCo₂O₄) microspheres as excellent electrode materials for electrochemical capacitors. These as-obtained flower-like microspheres organized from a large number of ultrathin nanosheets, which can provide high surface area and abundant mesoporous structures. Furthermore, the as-fabricated NiO, Co₃O₄ and NiCo₂O₄ microspheres exhibit high specific capacities of 1210.6, 802.5 and 842.5 F g⁻¹ at a current density of 0.5 A g⁻¹. Those microspheres also show good cyclability with capacities retention of 94.7%, 87% and 88.6% after 3000 cycles. The general self-template method holds great potential for the fabrication of high-performance charge storage devices.

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1. Introduction

Many efforts have been devoted to studying the energy storage devices due to the increasing future energy use and consequent environmental impacts. Supercapacitors, one of the energy storage devices, have attracted worldwide attention because of their unique characteristics of high power density, fast charge/discharge process, long cycle life and excellent reversibility [1,2], as well as their potential applications in many fields such as mobile electronics, power resources, transportation and aerospace systems [3,4]. To achieve the high-performance charge storage properties, considerable interests have been taken in electrode materials for electrochemical capacitors using transition metal oxides including NiO, Co₃O₄ and NiCo₂O₄ [5–7]. These metal oxides can be considered as the most promising electrode materials for charge storage and power delivery owing to their low cost, environmental friendly and high theoretical capacitance [1,8]. However, the preparation of high specific and good stability electrode materials is still a challenge. To solve these problems, many research have been committed to design the nanostructure and morphology of the

materials, such as nanoparticles (Co/CNTs) [9], nanotubes (NiCo₂O₄) [10], nanofibers (carbon-doped Co₃O₄) [11] and nanosheets (CoS_{1.097}/N-doped C, CoO_x) [12,13].

Nanosheets materials are considered as the new popular materials with admirable electronic properties for their high specific surface area and energy storage [14], which plays great important on electrochemical performance by facilitating the high transport rates for both electrons and electrolyte ions. For example, Du et al. suggested that the NiO nanosheet in microspheres show high specific capacitance (762 F g⁻¹ at 1 A g⁻¹) due to their high surface area and porosity [15]. Liu et al. have synthesized NiCo₂O₄@NiCo₂O₄ core/shell nanoflake arrays, which exhibit high areal specific capacitances of 1.55 F cm⁻² (787 F g⁻¹) at 2 mA cm⁻² (1 A g⁻¹), mainly attributed to their unique core/shell and nanosheet structure [16]. The porosities can also shorten ion/electron diffusion distance and accelerate the kinetic process [17–19]. Liao et al. have prepared hierarchical Co₃O₄ microspheres, which display a specific capacitance of 483.8 F g⁻¹ at 1 A g⁻¹ and good cycling stability (10.5% lose after 2000 cycles) because of their large surface area and unique hierarchical porous structures [20]. Therefore, it is necessary to develop ultrathin high specific and good stability ultrathin metal oxide electrode materials for the purpose of satisfying the advanced energy storage devices.

In the past few years, extensive research has focused on hollow and porous nanostructures for charge storage, such as porous NiO nanoflake arrays [21], starfish-shaped porous Co₃O₄/ZnFe₂O₄

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hollow nanocomposite [22] and hollow NiCo_2O_4 submicrospheres [23]. Unfortunately, a large number of the preparation processes are complex and poisonous. Most of the research only consider the method for individual metal oxide which is not suitable for others. Therefore, universality of preparation becomes increasingly vital to the basic research and application of materials. For example, the research of combination of cellulose nanocrystal aerogels for supercapacitor with enhanced performance is made by Yang et al. [24]. Moreover, Wang et al. demonstrates general synthesis of transition metal oxide (NiO , Co_3O_4 , NiCo_2O_4) nanotubes with enhanced oxygen evolution reaction (OER) performances [25]. Thus, it is necessary yet very challenging to seek efficient, clean and sustainable preparation methods for fabricating a variety of materials with enhanced energy storage properties using a universal method.

Herein, we report a universal and general self-template method to synthesize transition metal oxides (NiO , Co_3O_4 and NiCo_2O_4) microspheres organized from a large number of ultrathin nano-sheets via a facile and universal hydrothermal method. This kind of microspheres exhibit excellent charge storage performances. The universality of the approach is a great promotion to the development of advanced electrode materials for high-power battery-type devices [26,27].

2. Experimental section

2.1. Synthesis of NiO microspheres

Firstly, 0.3993 g L-aspartic was added into 15 mL deionized water. Next, 3 mL NaOH (2 M) aqueous solution was slowly added to the previous solution under stirring. Finally, 18 mL glycol (EG) and 0.872 g nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were mixed to the solution with vigorous stirring until the solution turn blue. Subsequently, the transparent blue solution was transferred to 50 mL Teflon-lined autoclave and maintained at 180°C for 16 h. The obtained precipitates were collected and washed several times with deionized water and anhydrous ethanol, then dried in vacuum at 40°C for 12 h. In order to obtain crystallized NiO , the as-prepared precursor NiO microspheres were heat-treated in air atmosphere at 350°C for 4 h with a heating rate of 1°C min^{-1} .

2.2. Synthesis of Co_3O_4 microspheres

The synthesis process of Co_3O_4 microspheres was same to the synthesis of NiO , except that the volumes of deionized water and EG were changed into 24 mL and 9 mL, respectively. 0.4365 g cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) took the place of 0.872 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. And the reaction time was shortened to 5 h.

2.3. Synthesis of NiCo_2O_4 microspheres

Meanwhile, NiCo_2O_4 microspheres were also fabricated as same as the preparation of NiO microspheres, only reducing the amount of L-aspartic and NaOH into half. 0.872 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was replaced by the mixture of 0.291 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.582 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The reaction time was also shortened to 5 h.

2.4. Materials characterization

The phase structure of samples was performed on X-ray diffraction (XRD) using a Rigaku D/max 2500PC X-ray diffractometer with $\text{Cu K}\alpha$ radiation. The microstructures and morphologies of samples were observed by scanning electron microscopy (SEM, JSM-7500F, JEOL) and transmission electron microscopy (TEM, JEM-2100F, JEOL). The element distribution (mapping test) was operated

on SEM. Nitrogen absorption and desorption isotherms and the Brunauer-Emmett-Teller (BET) surface areas of the samples were obtained using Quanta chrome surface and pore size analyzer.

2.5. Electrochemical measurements

The electrochemical performances of the products were carried out on electrochemical workstation (CHI660e, Shanghai) using a three electrode cell (Fig. S1), where Pt foil ($1\text{ cm} \times 1\text{ cm}$) served as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. KOH (6 M) aqueous solution was used as the electrolyte. The working electrode was prepared by mixing the as-prepared materials, acetylene black and Polytetrafluoroethylene (PTFE, Aldrich) binder with a weight ratio of 8:1:1. Afterwards, the hybrids were mixed with N-methyl-2-pyrrolidone (NMP) and then were pasted onto a nickel foam. Finally, the nickel foam was dried in vacuum at 60°C for 12 h and pressed under 10 MPa. The electrochemical properties of the supercapacitor electrodes were evaluated by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS). CV tests were carried on between 0 V and 0.5 V vs. SCE/V at the scan rates of 5, 10, 20, 50, 100 mV s^{-1} . GCD curves were measured in the potential range of 0–0.5 V vs. SCE/V at current densities of 0.5, 1, 2, 5 A g^{-1} . EIS measurements were operated in the frequency range from 0.01 Hz to 100 kHz under open circuit potential with an AC voltage of 5 mV. The specific capacitance could be calculated from the following equation:

$$C = I \times \Delta t / (m \times \Delta V) \quad (1)$$

where I (mA) represents the constant discharge, m (mg) symbolizes the weight of the active electrode, Δt (s) and ΔV (V) mean the total discharge time and potential drop during discharge, respectively.

3. Results and discussion

3.1. Synthetic process

The formation process of NiO , Co_3O_4 and NiCo_2O_4 microspheres is more similar to a self-template mechanism [25,28,29], as illustrated in Fig. 1. Take NiO as an example, Ni^{2+} ions will initially connect with the L-aspartic molecules ($\text{Ni}(\text{II})\text{-Asp}$) under the coordination characteristics of transition metal ions [30] to form $\text{Ni}(\text{II})\text{-Asp}$ complexes which will be fabricated as precursors

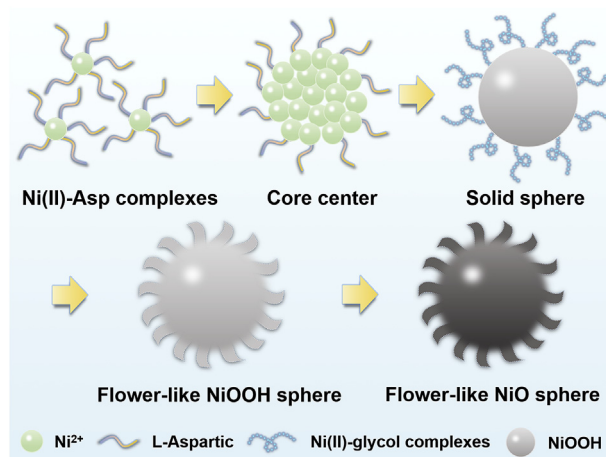


Fig. 1. Schematic illustration of the synthesis process of flower-like NiO , Co_3O_4 and NiCo_2O_4 microspheres.

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