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Oriented synthesis of Co_3O_4 core-shell microspheres for high-performance asymmetric supercapacitor

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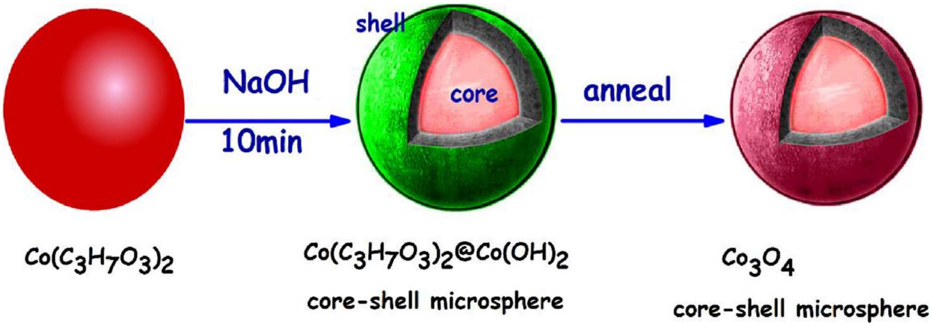
GRAPHICAL ABSTRACT

Illustration of the formation process of Co_3O_4 core-shell microspheres.



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ABSTRACT

Herein, Co_3O_4 core-shell microspheres are successfully designed and synthesized via a new rapid and energy-efficient room temperature interfacial-reaction and applied to supercapacitors for the first time. Morphological characterizations of the Co_3O_4 core-shell microspheres are carried out by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), showing their microsphere shape with diameter approximately 1 μm. The unique structure not only provides abundant active sites but facilitates ions and electrons transitive process. As a consequence, the intriguing structural advantages endow Co_3O_4 core-shell microspheres with outstanding electrochemical performances: 261.1 F/g at a current density of 0.5 A/g; excellent cycle stability of 90.2% capacity retention over continuous 2000 cycles. When being paired with active carbon (AC), the resulting asymmetrical supercapacitor manifests a high energy density of 16.6 Wh/kg at a power density of 883 W/kg. Overall, this oriented approach provides a new and facile idea to fabricate core-shell or hollow-out structure as high-performance electrode for supercapacitors.

1. Introduction

There is an ever urgent need to develop alternative energy storage devices, as a key part of the entire clean energy chain, for both energy storage and energy harvesting, to address the rapid depletion of fossil energy and ever-worsening environmental pollution [1]. As one of the

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most promising energy storage devices, supercapacitors have taken a large and increasing share of the energy market by virtue of combining high power output of dielectric capacitors together with high specific capacity of batteries. Meanwhile, supercapacitors exhibit some dazzling advantages such as fast charging property, great reliability and outstanding cycle behavior. According to the energy storage mechanisms, there are two types of supercapacitors: electrical double-layer capacitors (EDLCs) and pseudocapacitors [2]. The core of supercapacitors is the electrode material, which directly dominates the performance of energy storage [3]. Representative electrode materials for supercapacitors are carbon materials [4,5], transition metal oxides/hydroxides [6], conductive polymers [7] and their composites [8,9]. Carbon represents an attractive electrode material due to its different allotropes, various structures and abilities for existence under different dimensionalities [10]. However, it is restricted by relatively low specific capacity which can be easily eliminated by the employment of transition metal oxides [11].

Recently, transition metal oxides are considered to be potential candidates for their outstanding specific capacity compared with carbon-based materials. Because they have a wide variety of oxidation states to enable efficient redox charge transfer [12–14], such as RuO_2, NiO and MnO_2 [15]. Among them, Co_3O_4, an environmentally friendly candidate, is considered as one of the most attractive options due to its low cost, favorable theory capacitance, long-term performance and good corrosion stability [16–18]. However, Co_3O_4 systems are limited by several adverse factors such as poor electrical conductivity and volume changes during cycle process, poor reversibility and degradation of capacity at higher current densities [19]. For this, the electrochemical performances of Co_3O_4-based materials, especially their capacitive behaviors, have been widely investigated. For example, Wang et al. designed the porous Co_3O_4 nanowires, which delivered an improved supercapacitive properties [20]; Du et al. reported the hollow Co_3O_4 boxes as electrode materials for supercapacitors with high capacitance and excellent cycling performance [21]; Meher et al. designed high porosity, ultralayered Co_3O_4 with outstanding electrochemical stability [22].

Despite that great progresses have been achieved on the aspect of the rate capability and cycling stability of those electrodes, there is still a big challenge in further improving the performance [24–31]. One of the effective strategies is the employment of hollow structures with different complex interiors as advanced electrodes, such as core-shell, yolk-shell, and multishell structures, because these special structures could inherit the advantages from both nanosized building blocks and hollow structures. Particularly, the core-shell structure materials have witnessed its triumph in lithium ion batteries and supercapacitors, these following key advantages must be considered: Firstly, the core-shell structure possesses larger reaction area and a close contact of electrolyte with the active materials, which further accelerate the redox reactions. Secondly, the hollow space between the core and shell can not only act as a barrier to prevent the encapsulated electroactive nanoparticles from aggregation, but also accommodate the large expansion that leads to failure and short cycle life of electrodes [32]. Moreover, the core structure in the complex hollow particles will improve the energy density of the electrodes by increasing the weight fraction of electrochemically active component [33]. Following this line of thought, an inspiration about the preparation of Co_3O_4 core-shell microspheres is emerged in our minds (Scheme 1). The design and preparation of electrochemical energy storage properties using Co_3O_4 core-shell microspheres have not been reported based on what we know.

As a proof of concept, the cobalt glycerolate microspheres are first synthesized and subsequently transform to $Co(C_3H_7O_3)_2@Co(OH)_2$ core-shell microsphere via interfacial reaction with NaOH, and then transform to Co_3O_4 core-shell microsphere after thermal decomposition, it is the first time to utilize Co_3O_4 core-shell microspheres via a facile and high-efficiency interfacial reaction as electrode materials. This approach is very versatile and can be applied to prepare binary or ternary metal oxides with tunable interior structure compared with previous works. Co_3O_4 plays the role as 'core' and 'shell' of the microspheres, which can increase the specific surface area obviously and provide valid exposure of active sites for redox reaction that is always taking place on the surface [34,35]. When measured in a three-electrode cell, the Co_3O_4 core-shell microspheres deliver a relatively high specific capacity of 261.1 F/g at a current density of 0.5 A/g. Besides, it also shows a satisfying cycle stability of 90.2% retention even after 2000 cycles. In addition, the assembled asymmetrical supercapacitor using Co_3O_4 core-shell microspheres possesses a relatively high energy density of 16.6 Wh/kg. The results clearly show that the well-governable Co_3O_4 core-shell microspheres are original and open a new area for electrode materials of supercapacitors and other energy storage devices.

2. Experimental

2.1. Substrate treatment

In a typical procedure, the Ni foam ($1 \times 4\ cm^2$) was carefully immersed into acetone with continuous ultrasound vibrations for 20 min in order to exclude the possible NiO. After that, it was rinsed with DI-water for several times. Then, the Ni foam was transferred outside then air-dry.

2.2. Synthesis of $Co(C_3H_7O_3)_2$

All the chemical reagents were directly used without any purification. Typically, 2 mM $Co(NO_3)_2{\cdot}6H_2O$ was directly put into 45 mL isopropanol and 8 mL glycerol under violent stirring for 1 h at room temperature to form a red homogeneous solution. After that, the liquid was transferred to a 50 mL Teflon-lined stainless-steel autoclave and maintained at 120 °C for 16 h and cooled to room temperature. After centrifugalization, the precipitate was rinsed with DI-water and ethanol, and dried at 60 °C for 12 h.

2.3. Synthesis of Co_3O_4

0.2 g the as-prepared $Co(C_3H_7O_3)_2$ were dispersed in 25 mL (0.25 M) NaOH solution for 10 min. After that, they were dried at 60 °C for 24 h. Then, the as-prepared samples were annealed at 350 °C for 2 h an increasing rate of 5 °C/min in air. The reaction process can be summarized as:

$$Co^{2+} + C_3H_8O_3 \rightarrow Co\ (C_3H_7O_3)_2 + 2\ H^+ \tag{1}$$

$$Co\ (C_3H_7O_3)_2 + 2OH^- \rightarrow Co\ (OH)_2 + 2\ C_3H_8O^{3-} \tag{2}$$

$$6Co\ (OH)_2 + 3O_2 \rightarrow 2\ Co_3O_4 + 6\ H_2O \tag{3}$$

2.4. Electrochemical measurements

The working electrode was prepared as following steps: 85 wt.% of Co_3O_4 core-shell microspheres were mixed with 10 wt.% of acetylene black and 5 wt.% of PTFE, then they were dispersed in 5 mL ethanol to form a slurry. Afterwards, the slurry was coated onto a piece of Ni foam ($1 \times 1\ cm^2$) as a current collector. The electrode was dried at 80 °C for 24 h before measurement. The electrochemical behaviors of Co_3O_4 Core-shell microspheres were performed on a CHI760E electrochemical workstation at room temperature in a three-electrode system. The three-electrode system consisted of platinum and saturated calomel electrodes as the counter and reference electrodes, respectively. Co_3O_4 core-shell microspheres on Ni foam were directly used as the working electrode in 3 M KOH as the electrolyte. The total specific capacity of the electrode was obtained on the basis of the following equation:

$$C = \frac{I \times t}{m \times \Delta V} \tag{4}$$