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Design and synthesis of $CoFe_2O_4$ quantum dots for high-performance supercapacitors

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ABSTRACT

A series of novel $CoFe_2O_4$ quantum dots have been synthesized via solvothermal method with different solvents including ethylene glycol, 1,2-propanediol and 1,3-propanediol followed by heat-up route. And the typical monodisperse $CoFe_2O_4$ quantum dots possess narrow size distribution. The results indicate that the quantum confinement effects on the electrochemical performance are obvious including the largest initial specific capacitance of 1269.0 F g^{-1} at 12 A g^{-1}, the highest specific capacitance retention of ~91.1% after 10000 cycles at 20 A g^{-1}, and the maximum specific energy value of 25.2 W h kg^{-1} at the corresponding specific power value of 4247 W kg^{-1}. In addition, after a long charge/discharge process at a high current density, it is shown that it's hard to keep the phase stability for $CoFe_2O_4$, and it is certain to transform the element chemical states (especially cobalt) on $CoFe_2O_4$ quantum dots' surface.

1. Introduction

In the past decade, the rapid stride of industrialization has resulted in increased demand for energy [1–3]. However, due to the nonrenewable petroleum resources, alternate energy sources are needed urgently [4–7]. Because of the fast charge/discharge rate, long cycle life, low cost and high power density, supercapacitors (SCs), as efficient energy storage devices, have attracted considerable attention and have been intensively investigated [8–10]. Generally, the transition metal oxides (*e. g.* NiO, Co_3O_4, Fe_2O_3, MnO_2) are used as electrode materials for one of the typical SCs (pseudocapacitors, PCs) [11]. And due to the large theoretical specific capacitance (*e. g.* 2583 F g^{-1} for NiO, 3560 F g^{-1} for Co_3O_4, 1379 F g^{-1} for MnO_2), the wide potential window (0–0.40/0.55 V) and the environmental compatibility, they have been researched extensively recently [12,13]. However, their common poor electrical conductivity greatly limits their practical applications [14,15]. In order to improve the electrochemical activity, and the ion diffusion and electron transport efficiency, various binary metal oxides (*e. g.* $MnCo_2O_4$, $FeCo_2O_4$, $ZnCo_2O_4$) have been reported as advanced PCs due to the synergistic effect of the metal component with strong chemical activity (*e. g.* Mn, Fe, Zn) [16–19]. Porous yolk-shell $MnCo_2O_4$ microspheres deliver a specific capacitance of 761.3 F g^{-1} at 5 A g^{-1} [20]. Flower-like $FeCo_2O_4$ and $CoFe_2O_4$ show discharge specific capacitances over 900.0 F g^{-1} at 12 A g^{-1} and remain ~80.0% after 6000 cycles [21]. Self-assembled peony-like $ZnCo_2O_4$ exhibits 440.0 F g^{-1} at 1 A g^{-1} [22]. $NiCo_2O_4$ hollow microspheres with tunable numbers and thickness of shell obtain 400.0–700.0 F g^{-1} at 5 A g^{-1} and maintain ~77% after 1700 cycles [23]. Despite of the obtained progress, it is still highly essential to design and synthesize novel binary metal oxides to further enhance the electrochemical performance (*e. g.* the cycling performance, the rate capability, the specific energy value) for SCs.

In the most cases, the energy storage capacity of electrode materials depends on the corresponding morphology and micro/nano-structure. Till now, kinds of diversified morphologies (*e. g.* nanotubes, nanospheres, nanorods, nanosheets, nanoflowers,

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nanowires, nanocages) have been designed for PCs [24–28]. Among them, quantum dots (QDs) have attracted significant interest due to the high surface area, a number of active sites, the short diffusion length for ions and the quantum confinement effects [29,30]. SnO_2 QDs (~25 nm) show only 9% loss when the scan rate increasing from 20 mV s^{-1} to 500 mV s^{-1} [31]. $MnCO_3$ QDs (~1.2 nm) exhibit a high specific capacitance of over 1400.0 F g^{-1} at 15 A g^{-1} and remain ~91.3% after 10000 cycles [32]. ZnO QDs (~2.3 nm) demonstrate a reversible specific capacity of 890.0 mAh·g^{-1} over 1000 cycles at 2 A g^{-1} [33]. $ZnCo_2O_4$ QDs (3.0–5.0 nm) exhibit a discharge capacity of ~670 mAh·g^{-1} over 2000 cycles at 2 A g^{-1} [34]. Therefore, the QDs' size effects on the above binary metal oxides may enhance the electrochemical performance (*e. g.* the specific capacitance, the specific capacitance retention) in the PCs field.

Herein, in the present work, $CoFe_2O_4$ as a representative binary transition metal oxide has been produced. The $CoFe_2O_4$ QDs have been prepared via solvothermal method with different solvents including ethylene glycol, 1,2-propanediol and 1,3-propanediol followed by heat-up route. The structure, chemical state, morphology and size were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscope (TEM). Furthermore, the electrochemical performance of the $CoFe_2O_4$ QDs was investigated including the specific capacitance, the power density and the cycle life.

2. Experimental section

Materials Preparation. All reagents are the analytical grade without further purification. According to the previous reports, the synthesis of $CoFe_2O_4$ QDs was carried out in two steps [35–37]. In the first step, 0.281 g of $CoSO_4·7H_2O$ (1 mmol), 0.556 g of $FeSO_4·7H_2O$ (2 mmol), 80 mL of ethylene glycol were added into a 150 mL beaker, and the above mixture was stirred magnetically at 40 °C for 15 min. Then, the resulting solution was transferred to a 100 mL Teflon-lined stainless steel autoclave, which was sealed and put in an oven at 160 °C for 10 h. After the above solvothermal synthesis, the autoclave was cooled down to room temperature naturally. And the precipitate as precursor in the autoclave was filtrated and washed 3 cycles by DI water. In the second step, the precursor was further annealed under air atmosphere at 900 °C for 12 h with a heating rate of 10 °C·min^{-1}, followed by a natural cool-down to the room temperature. The above product was marked as “Sample 1”. In addition, the other two products were prepared by using 1,2-propanediol and1,3-propanediol as solvent, respectively; when other parameters and operations were kept as the exact same as the above synthesis. And the corresponding products were named as “Sample 2” and “Sample 3”, respectively.

Materials Characterization and Electrochemical Measurements. The functional groups and thermogravimetric Analysis (TGA) of precursors were characterized by FT-IR (Perkinelmer, Lambda) and thermal analyzer (Netzsch, 409 PC). The phase purity and crystallinity were analyzed by XRD (Rigaku, D/Max-2000). The chemical states of samples were studied by XPS (ESCALAB, 250). The micro morphology was determined by TEM (FEI, Tecnai G2 F20). The electrical behavior of materials was studied by electrochemical workstation (Autolab, PGSTAT302 N). In addition, all electrochemical measurements including the composition of active electrode, the three-electrode system, and the test parameters of CV and EIS were the same as our previous works [37–39].

Calculations. The gravimetric specific capacitance (C_s, F·g^{-1}) was calculated according to the following equation [40]:

$$C_s = \frac{I\Delta t}{m\Delta V}$$

Where, *I* (A) is the discharge current, *m* (g) is the mass of active materials, Δt(s) is the discharge time, and ΔV (V) is the potential drop during discharge.

The other gravimetric specific capacitance (C_g, F·g^{-1}) was calculated form the CV curves according to the following equation:

$$C_g = \frac{\int Id_v}{mv\Delta V}$$

Where, *I* (A) is the voltammetric current, *m* (g) is the mass of active material, *v* (V·s^{-1}) is the scan rate, and ΔV (V) is the potential window of CV.

The specific energy (*E*, Wh·kg^{-1}) was calculated using the following equation:

$$E = \frac{0.5C_s(\Delta V)^2}{3.6}$$

Where, C_s (F·g^{-1}) is the gravimetric specific capacitance, and ΔV (V) is the potential drop during discharge.

The specific power (*P*, W·kg^{-1}) was calculated using the following equation:

$$P = \frac{3600E}{\Delta t}$$

Where, *E* (Wh·kg^{-1}) is the specific energy, and Δt(s) is the discharge time.

3. Results and discussion

Fig. 1 shows the FT-IR spectra of the as-prepared precursors with different solvents. According to the reaction mechanism in our previous reports [36,37], all of the precursors are similar stable metal-organic complexes; and Fig. S1 shows the possible schematic illustration for the fabrication of $CoFe_2O_4$ precursors. A broad peak centered at ~3443.4 cm^{-1} is assigned to the stretching vibrations of —OH, which may result from the OH^- absorbed by precursors. And a couple of obvious peaks at ~1644.3 cm^{-1} and ~1109.5 cm^{-1} correspond to the stretching vibration of $-CH_2-$ groups and the stretching vibration of the C—O bond in the metal-organic complexes. Moreover, a sensitive peak at 580.5–654.4 cm^{-1} reveals the Me—O (Me = Co and Fe) stretching vibration modes. Fig. 2 exhibits the TDA curves of precursors with different solvents under air

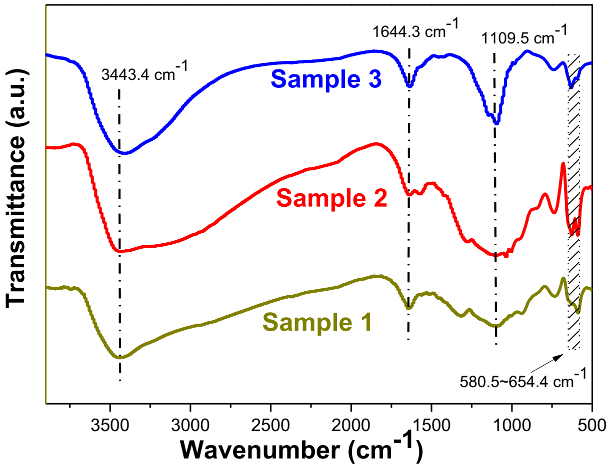

Fig. 1. FT-IR spectra of the precursors for Sample 1, Sample 2 and Sample 3.