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Monodisperse nickel/cobalt oxide composite hollow spheres with mesoporous shell for hybrid supercapacitor: A facile fabrication and excellent electrochemical performance

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ABSTRACT

A flow atomization method that is suitable for commercial preparation was employed to fabricate the monodisperse nickel/cobalt oxide composite (NCOC) hollow spheres by means of silica as the template. The prepared hollow spheres present a spinel NCOC and mesoporous shell structure with a specific surface area of 343 m^2 g^{-1} and a mean pore size of 2.5 nm. The monodisperse NCOC hollow-sphere electrode exhibits a maximum specific capacity of 175 mAh g^{-1} at 1 A g^{-1} and delivers a 92.5% capacity retention after 50,000 cycles, suggesting superior long cycle stability. A hybrid supercapacitor with a total mass of 5 mg cm^{-2} has been assembled using monodisperse NCOC hollow spheres as positive electrode and nitrogen-doped mesoporous carbon derived from the pyrolysis of polypyrrole as negative electrode material. This device can be operated in a potential region of 0–1.5 V, displays a high energy density of 38.5 Wh kg^{-1} at a power density of 750.8 W kg^{-1}, and remains at 22.9 Wh kg^{-1} at 21.4 kW kg^{-1}. The long-term cyclic life up to 20,000 cycles with 9.5% capacitance loss also meets the growing demand for mass-produced energy-related devices.

1. Introduction

Over the past decade, nanostructured materials with mesoporous structures have attracted the attention of numerous researchers in the energy field because these materials keep their chemical compositions away from thermodynamic equilibrium state and possess unique physical and chemical properties [1–4]. In particular, high-performance supercapacitors depend on the microstructures of the electrode materials [5] and mesoporous structures with enormous specific surface area, and suitable pore pathways meet the requirements of high capacity (capacitance) because abundant electrolytes can be adsorbed on the electrode materials or Faraday reactions can occur on the interface between electrode and electrolyte solution at a high rate [6–9].

Nickel and cobalt oxides have been demonstrated to be the important electrochemical materials that are applied in supercapacitor devices because of their excellent characteristics such as high capacity, stable structure, environmental friendliness, and low cost [10–12]. However, the electronic conductivities of these materials are too low to satisfy the demands of electron transfer that occurs in electrochemical reactions [13]. Nickel and cobalt oxides have to be composited with relatively expensive materials, such as rGO [14], CNTs [15], CNFs [16], and conducting polymers [17], which have high electronic conductivities. Bimetallic nickel/cobalt oxide with a mole ration of NiO:CoO = 1:2 (known as $NiCo_2O_4$), which is characterized as a spinel structure with Ni^{2+} located at the octahedral site and Co^{2+}/Co^{3+} occupying both octahedral and tetrahedral sites [18], has been demonstrated to possess excellent electronic conductivity and high electrochemical capacity compared with single nickel oxide and cobalt oxide [19,20].

Numerous nanostructured NCOC samples have been synthesized in previous references for application as electrode materials in supercapacitors. Typically, Zhang et al. [21] employed a solution approach to deposit mesoporous NCOC nanosheets on different substrates, and the prepared nanosheet on nickel foam presents a maximal areal capacitance of 3.51 F cm^{-2}. Zhu et al. [22] proposed a solid-state reaction route to prepare NCOC nanorods with specific capacitance that can reach 565 F g^{-1} and exhibit a long cycle life. Wang et al. [23] synthetized nanostructured $NiCo_2O_4$ with a 5–10 nm spinel phase through a co-precipitation process, and the sample delivers a high specific capacitance of 671 F g^{-1} at 1 A g^{-1}.

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As a type of nanostructured material, hollow spheres have been constructed using various techniques and displayed outstanding performances in different fields [24–28]. In the present study, a facile preparation of monodisperse NCOC hollow spheres with mesoporous shells was proposed by means of high-speed N_2 gas flow atomization method incorporated with silica template. The structure characters of the synthetized samples were evaluated by XRD, FESEM, HRTEM, and N_2 absorption–desorption. The results of electrochemical analysis indicated that monodisperse NCOC hollow spheres possess excellent electrochemical performance and potential for application in energy conversion devices.

2. Experimental

2.1. Material synthesis

In a typical preparation, 6.0 g cobalt nitrate hexahydrate and 3.0 g nickel nitrate hexahydrate were dissolved in 50 mL ethanol to form a clear solution. A silica sol catalyzed by nitric acid was added to the aforementioned solution to prepare the precursor solution for atomization.

An 8 mL volume of precursor solution was added to an atomizing chamber (with diameter and height of 3 cm and 10 cm) equipped with a plastic fan. The high-speed gas flow (N_2:O_2 = 9:1) with a flow rate of 20 L min^{-1} was introduced from the bottom of the atomizing chamber, and the formed fog drops along with the gas flow were passed through a quartz tube preheated to 500 °C. The particles were collected in a 0.22 μm millipore polyvinylidene fluoride (PVDF) membrane supported on a Buchner funnel connected to a circulating water vacuum pump. The collected particles were immersed in a sodium hydroxide solution (20 wt%) at 50 °C for 48 h. The particles were washed thoroughly by water and ethanol, centrifuged at a rotation speed of 8000 rpm, and then dried at 100 °C for 10 h to finish the synthesis of the monodisperse NCOC hollow spheres.

Fig. 1 shows a schematic for the synthesis of monodisperse NCOC hollow spheres. Principally, a liquid droplet from the atomizing chamber underwent heating and solvent evaporation on the surface of droplet and formed a desiccated shell. The solvent within the sphere was subsequently volatilized though the pore passageway of the desiccated shell, and the concentrated solution was attached to inner surface on the basis of the wetting mechanism until the liquid was completely evaporated to structure a solid micro-sphere. After removing the silica template, the monodisperse NCOC hollow spheres was synthesized through the facile route.

2.2. Material characterization

The synthesized samples were carried out in an X-ray photoelectron spectroscopy (XPS) to study the existing elements and their valence, in an X–ray diffractometer (XRD) to investigate the crystalline structure, and in a field emission scanning electron microscopy (FESEM) and high resolution transmission electron microscope (HRTEM) to observe micromorphologies. N_2 adsorption/desorption experiment was employed to analyze the specific surface and pore size distribution. The detailed operations were supplied in Supplementary Materials.

2.3. Electrochemical measurements

Standard three- and two-electrode systems were employed to measure the electrochemical properties of the monodisperse NCOC hollow spheres electrode and hybrid supercapacitor, respectively. The detailed preparation procedure for working electrode and assembly method for hybrid supercapacitor, along with the electrochemical measurements, were also described in Supplementary Materials.

3. Results and discussion

3.1. Structural characteristics of monodisperse NCOC hollow spheres

X-ray photoelectron (XPS) measurement was further employed to investigate the oxidation state and the detailed elemental composition, and the result was shown in Fig. 2. The presence of Ni, Co, O and C elements was clearly observed from the survey spectrum (Fig. 2a) and no silicon element existed in this sample. The C 1s peak at 284.5 eV was used to correct all the binding energies, and the Ni 2p, Co 2p and O 1s emission spectra were fitted by means of a Gaussian fitting method. In the Co 2p spectra, the binding energies at 781.1 and 798.5 eV, and 780.1 and 796.2 eV, are indexed to Co^{2+} and Co^{3+}, respectively [29]. The peaks located at 855.6 and 872.4 eV are ascribed to Ni^{2+}, while the fitting peaks at 856.9 and 874.5 eV can be attributed to Ni^{3+} [30]. From the high resolution spectrum of O 1s, there are three peaks at 531.1, 532.1, and 532.6 eV, corresponding to the signatures of three oxygen species, which are due to the metal–oxygen bond, oxygen in hydroxyl groups and oxygen ions in low coordination at the surface [31,32].

The crystalline structure of the as-obtained sample, as determined by XRD, is shown in Fig. 3a. We found that the diffraction peaks located at 18.9°, 31.1°, 36.8°, 38.4°, 44.7°, 55.4°, 59.0°, 65.3°, 77.1°, 82.0°, 90.3°, and 93.7° were well-defined and belonged to the (111), (220), (311), (222), (400), (422), (511), (440), (533), (444), (642), and (731) lattice planes of spinel $NiCo_2O_4$ (PCPDF No. 73-1702) without the formation of a secondary phase. However, the relatively low intensities imply inferior crystallinity, which may be mainly attributed to the steric effect of silica to hamper the growth of NCOC crystals in the heat treatment process [33].

A typical FESEM image of the as-prepared NCOC hollow spheres

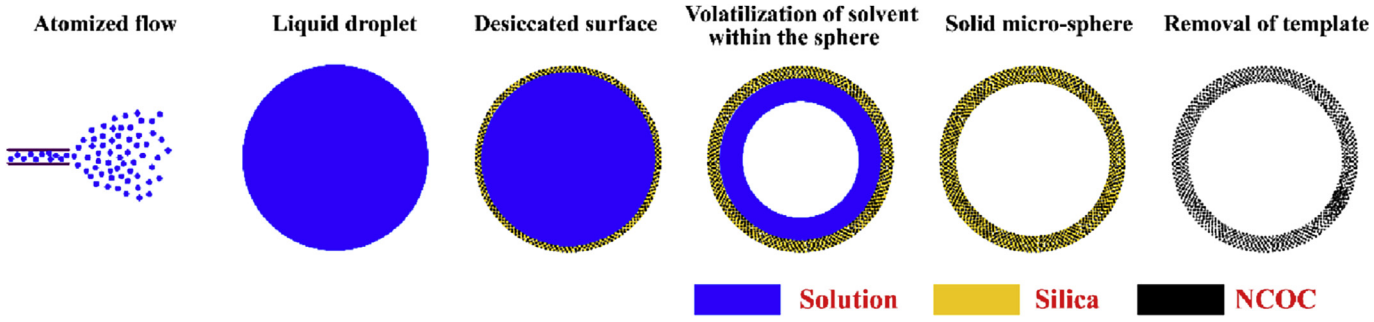

Fig. 1. Schematic for the synthesis of monodisperse nickel/cobalt oxide composite hollow spheres.