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Hollow $SnO_2@Co_3O_4$ core–shell spheres encapsulated in three-dimensional graphene foams for high performance supercapacitors and lithium-ion batteries

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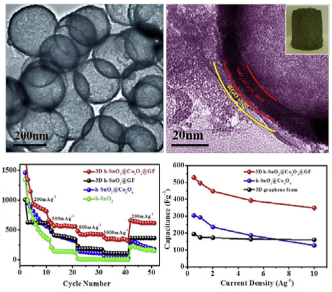
HIGHLIGHTS

- 3D graphene foams encapsulated hollow $SnO_2@Co_3O_4$ spheres was synthesized.
- Core-shell hollow $SnO_2@Co_3O_4$ spheres with mesoporous shells and high surface area.
- 3D graphene foams provided highly conductive networks and flexible buffering matrix.
- The 3D architecture showed excellent performance for supercapacitors and LIBs.

GRAPHICAL ABSTRACT



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ABSTRACT

Hollow $SnO_2@Co_3O_4$ spheres are fabricated using 300 nm spherical SiO_2 particles as template. Then three-dimensional graphene foams encapsulated hollow $SnO_2@Co_3O_4$ spheres are successfully obtained through self-assembly in hydrothermal process from graphene oxide nanosheets and metal oxide hollow spheres. The three-dimensional graphene foams encapsulated architectures could greatly improve the capacity, cycling stability and rate capability of hollow $SnO_2@Co_3O_4$ spheres electrodes due to the highly conductive networks and flexible buffering matrix. The three-dimensional graphene foams encapsulated hollow $SnO_2@Co_3O_4$ spheres are promising electrode materials for supercapacitors and lithium-ion batteries.

1. Introduction

Electrochemical energy storage devices, such as lithium-ion batteries (LIBs) and supercapacitors, are the most popular power

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supplies in portable electronic devices and have been intensively developed for renewable energy due to their high energy storage density and conversion efficiency [1–8]. Carbon materials are widely used not only directly for electrode active materials of LIBs and supercapacitors but also as conductive network materials for electrodes [9–13]. However, the low storage capability of traditional carbon materials limits their further wide applications as electrode active materials.

In recent years, transition metal oxides have been widely explored as alternative electrode materials for supercapacitors and LIBs owing to their high theoretical specific capacities compared with the commercially used graphite and active carbon [14–18]. Especially, complex oxides of transition metals [19], such as $ZnMn_2O_4$ [20], $NiCo_2O_4$ [21], $ZnCo_2O_4$ [22], Fe_2O_3–Co_3O_4 [23], SnO_2–Co_3O_4 [24], Co_3O_4@MnO_2 [25], have attracted much attention for their synergistic effect in enhancement of reversible capacity, structural stability, and electrical conductivity. However, most transition metal oxides and complex oxides show poor rate capability and cycling performances because of their low conductivity and large volume expansion/contraction during the long-term charge/discharge cycling.

Various strategies have been developed to solve these problems. Such as fabrication of hollow metal oxide nanostructures which could provide short electron-transporting paths and a high surface-to-volume ratio [26–28]. Modification of metal oxide nanomaterials with carbon (especially graphene in recent years) conductive materials is another very promising method to improve electronic conductivity and accommodate volume change of metal oxide active materials during cycling [29–34].

Herein, we report hybrid structure of hollow SnO_2@Co_3O_4 core–shell spheres (h-SnO_2@Co_3O_4) encapsulated in three-dimensional (3D) graphene foams as electrode materials for high performance supercapacitors and LIBs. The 3D graphene foams encapsulated h-SnO_2@Co_3O_4 architectures (3D h-SnO_2@Co_3O_4@GF) illustrates much higher capacity, cycling stability and rate capability relative to the single or two components. The 3D graphene foams could enhance the electrical conductivity of the overall electrode and protect against the volume changes during electrochemical processes. The hollow core–shell structure also could shorten the electron/ion diffusion path and avoid volume change.

2. Experimental section

2.1. Synthesis of hollow SnO_2@Co_3O_4 spheres

Hollow SnO_2 spheres were prepared by using spherical SiO_2 particles as template. Firstly, 1.8 g $CO(NH_2)_2$ and 0.266 g $Na_2SnO_3\cdot 3H_2O$ was dissolved in 34 mL DI water, then 18 mL ethanol was added in the solution under mildly stir for about 30 min, 4 mL colloidal SiO_2 solution (60 mg mL^{-1}) prepared according to the literature [35] was added into the above solution. The mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave at 170 °C for 36 h. After the autoclave cool down, the products were centrifuged and washed with DI water several times. The SiO_2 cores can be etched in 2 M NaOH at 45 °C for 4 h. The hollow spheres were centrifuged and dried at 110 °C.

Hollow SnO_2@Co_3O_4 spheres were prepared by deposition method [36]. Typically, 0.1 g SnO_2 hollow spheres, 0.18 g $Co(NO_3)_2\cdot 6H_2O$, 1 g PVP and 2.4 g $CO(NH_2)_2$ were dispersed in 100 mL DI water. The solution was then heated at 80 °C for 10 h with mild stirring. The obtained powers were washed by DI water, dried and annealed at 500 °C for 1 h in air to obtain hollow SnO_2@Co_3O_4 spheres.

2.2. Synthesis of 3D graphene foams encapsulated hollow SnO_2@Co_3O_4 spheres

Graphene oxide (GO) nanosheets were synthesized by modified Hummers method [37]. h-SnO_2@Co_3O_4@GO was fabricated by coating GO nanosheets on h-SnO_2@Co_3O_4 in solution. Briefly, 200 mL APS-modified h-SnO_2@Co_3O_4 dispersion (0.5 mg mL^{-1}) was added into a 250 mL GO suspension (0.2 mg mL^{-1}) under mild mechanical stirring to render the spheres surface positively [38]. h-SnO_2@Fe_2O_3@GO was then obtained after centrifugation and washing with DI water. 3D h-SnO_2@Co_3O_4@GF was prepared by hydrothermal method based on the assembling of h-SnO_2@Co_3O_4@GO and GO nanosheets, combining with cryodesiccation. In a typical process, h-SnO_2@Co_3O_4@GO was homogeneously dispersed in 60 mL GO suspension (2 mg mL^{-1}), sealed in a 100 mL Teflon-lined stainless steel autoclave and keep at 180 °C for 12 h. After the autoclave was naturally cooled to room temperature, the obtained 3D architecture was taken out and cryodesiccated at -50 °C and 23 Pa for 48 h.

To make comparison, 3D graphene foams wrapped hollow SnO_2 spheres (3D h-SnO_2@GF) were synthesized using the above same method only without Co_3O_4.

2.3. Characterization

Morphologies of samples were characterized by a FEI Nova NanoSEM 450 field emission scanning electron microscopy (SEM). Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) mappings investigations were performed using a JEOL JEM 2100F instrument operated at 200 kV. The chemical compositions of the samples were determined by EDS. The crystalline structure was investigated by X-ray power diffraction (XRD) on a D/max-2500 V diffractometer with Cu Ka radiation at $\lambda = 1.5418$ Å. Raman spectra were collected using a confocal Lab RAM HR800 spectrometer (Horiba JobinYvon, FR.) and an excitation wavelength of 514 nm from an argon ion laser. Brunauer–Emmett–Teller (BET) surface area of samples was measured using a Micromeritics ASAP 2020 (Micromeritics, USA).

2.4. Electrochemical measurements

Working electrode for supercapacitors was prepared by mixing an active material (80 wt%) with carbon black (10 wt%) and PTFE (10 wt%) in isopropanol. The slurry of the mixture was rolled to a thickness of ~100 μm and left to dry in an oven at 80 °C for 24 h. Then, the film was cut into a suitable shape and pressed on nickel foam under 10 MPa, which was used as the current collector. The typical mass loading on one electrode was between 2 and 4 mg. Electrochemical measurement was carried out using two-electrode configuration, with 6 M KOH as electrolyte. The symmetrical super capacitors consisted of two symmetric working electrodes, which were assembled together with one piece of cellulose paper separator sandwiched in between electrodes. Nickel foam was used as the current collector and the entire configuration was sealed by PET membrane. All the electrochemical measurements, including voltammetry (CV) measurements, galvanostatic charge/discharge tests and EIS tests with a frequency loop from 10^5 Hz to 10 mHz at the amplitude of the sinusoidal voltage of 10 mV, were carried on an electrochemical workstation (Zennium Zahner, Germany).

LIBs electrochemical experiments were carried out in CR2032 coin type cells. The working electrodes were prepared by mixing the samples (h-SnO_2, h-SnO_2@Co_3O_4, 3D h-SnO_2@GF and 3D h-SnO_2@Co_3O_4@GF), acetylene carbon black, and polyvinylidene fluoride (PVDF) at a weight ratio of 80:10:10 and pasted on pure copper foil. Lithium foil was used as the counter electrode and the