Hollow porous silicon oxide nanobelts for high-performance lithium storage

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HIGHLIGHTS

- Facile template-directed route for the formation of hollow porous SiO₂ nanobelts.
- Unique microstructural features of hollow nanobelts with porous walls.
- Markedly enhanced Li-storage capability in terms of capacity retention and so forth.

GRAPHICAL ABSTRACT
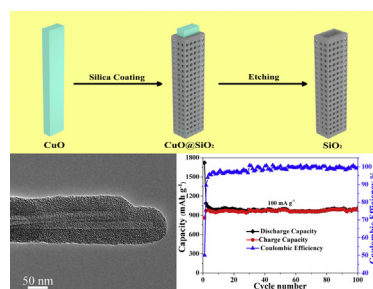
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ABSTRACT

A simple, green, and scalable methodology has been developed for the formation of hollow porous SiO₂ nanobelts, which demonstrates high reversible capacities, excellent capacity retention, and high rate capability as an anode for lithium-ion batteries (LIBs). The facile synthetic approach and superior Li-storage capabilities of hollow porous SiO₂ nanobelts make it an ideal anodic candidate for advanced LIBs with high energy density, long cycle life, and high power density.

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1. Introduction

Silicon-based materials including silicon, silicon-based alloys, and silicon oxides possess high safety and specific capacities, and thus have been considered to be promising anodic candidates to replace commercial graphitic anodes for advanced lithium-ion batteries (LIBs) [1–20]. Among them, silicon oxide (SiO₂) is emerging as an important anodic category owing to its natural abundance, environmentally benign, low cost, and ease of preparation [15–24]. However, bulk crystalline SiO₂ is generally considered to be electrochemically inactive for lithium storage due to its strong Si–O bond and poor electrical conductivity [16,24]. Up to now, considerable research efforts have been devoted to realize the reversible lithium-storage behavior of SiO₂ anodes through their morphology and crystallinity control. For example, various SiO₂-based samples including SiO₂ thin film [15], milled SiO₂ product

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[16], hollow porous SiO_2 nanocubes [17], SiO_2 nanospheres [18], and SiO_2–C nanohybrids [20–24] have been carefully designed and further exhibit enhanced lithium-storage capabilities. However, the state-of-the-art anodic performances especially cycling stability of SiO_2 anodes are not satisfactory, and the feasibility of SiO_2 as an advanced anode for LIBs in electric vehicles and smart grids remains to be further explored.

Herein, we demonstrate a simple, green, and scalable methodology for the formation of hollow porous SiO_2 nanobelts using CuO nanobelts as templates. When examined as a potential anode for LIBs, the hollow porous SiO_2 nanobelts exhibits remarkable lithium-storage capabilities in terms of high specific capacities, excellent cycling performance, and high rate capability.

2. Experimental

2.1. Synthesis of hollow porous SiO₂ nanobelts

The CuO nanobelts was prepared *via* a simple wet chemical method using $CuCl_2 \cdot H_2O$ and NaOH as reactants [25]. Subsequently, porous SiO_2 layer was coated on the surface of CuO templates through facile hydrolysis–condensation reactions of tetraethyl orthosilicate (TEOS) in the presence of cetyltrimethylammonium bromide (CTAB). Briefly, 0.1 g CuO nanobelts and 0.16 g CTAB were dispersed into a mixed solution containing 30 mL distilled water, 120 mL ethanol, and 1.5 mL ammonia (28 wt %), and then 1 mL TEOS was added dropwise and the mixture was further stirred for 6 h at room temperature (25 °C). The resulting product was centrifuged, washed with distilled water and ethanol, yielding the $CuO@SiO_2$ nanobelts. Finally, the hollow porous SiO_2 nanobelts can be obtained by dissolving the CuO templates with a 1 M HCl solution under stirring for 2 h.

2.2. Characterization

The morphology, composition, and structure of the products were characterized by transmission electron microscopy (TEM, Hitachi H-7650, 120 kV), scanning electron microscopy (SEM, JEOL JSM-7600F) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F, 200 kV) equipped with an energy-dispersive X-ray spectrometer (EDS, Thermo Fisher Scientific, NORAN System 7). X-ray powder diffraction (XRD) measurements were conducted on a Rigaku D/max-RC diffractometer using Cu-Kα radiation ($\lambda = 0.15406$ nm) and operating at 45 kV and 100 mA. Fourier transform infrared (FT-IR) spectra were carried out on a Bruker Tensor 27 spectrometer. Nitrogen adsorption/desorption measurements were carried out by a Micromeritics TriStar II 3020 V1.03 analyzer at 77 K. The surface area, pore volume and diameter of the sample were calculated using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively.

2.3. Electrochemical measurements of hollow porous SiO₂ nanobelts

Electrochemical measurements were performed by 2025 type coin cells that were assembled in an Ar-filled glovebox (IL-2GB, Innovative Technology). The anodes were constructed as follows: 70 wt% hollow porous SiO_2 nanobelts, 15 wt% Super P carbon black, and 15 wt% poly(vinylidene fluoride) (PVDF) in N-methyl-2-pyrrolidene (NMP) were mixed, and the slurry was coated on the surface of copper foam at room temperature and dried under vacuum at 120 °C for 12 h. The loading density of the hollow porous SiO_2 nanobelts on copper current collectors was *ca.* 1.5 mg/cm^2. The counter electrode was lithium foil, and the electrolyte solution was 1 M LiPF$_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC)
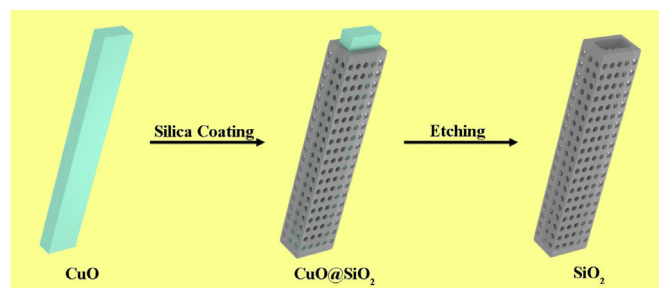

Fig. 1. Schematic illustration for the synthesis of the hollow porous SiO_2 nanobelts.

(1:1 v/v). Last, the cells were aged for 12 h before further measurements. A galvanostatic cycling test of the assembled cells was carried out on a Land CT2001A system in the potential range of 0.01–3.0 V. Cyclic voltammetry (CV) measurements were recorded on a CHI 660C electrochemical workstation in the potential range of 0.0–3.0 V at a scan rate of 0.1 mV s^{-1}, and electrochemical impedance spectroscopy (EIS) tests were performed on a CHI 760D electrochemical workstation with the frequency ranging from 100 kHz to 0.01 Hz and an ac signal of 5 mV in amplitude. The voltages mentioned herein were referred to Li$^+$/Li redox couple. All the electrochemical measurements were conducted at 20 °C.

3. Results and discussion

Fig. 1 illustrates the schematic diagram for the formation of the hollow porous SiO_2 nanobelts. As depicted, the CuO nanobelts was prepared *via* a simple wet chemical method, and serves as a template in this synthetic route. Specifically, CuO nanobelts has been transformed into $CuO@SiO_2$ intermediates and SiO_2 products after subsequent silica coating and etching processes. Fig. 2 shows the XRD patterns of the samples in different stages of evolution. As observed, the crystalline phase of the samples changes from monoclinic CuO (JCPDS No. 05-0661) in the template to amorphous SiO_2 in the final product, indicating the successful removal of CuO template.

The morphological and structural features of the corresponding samples were examined by SEM and TEM. Fig. 3 show the SEM and TEM images of the CuO templates (a,b), $CuO@SiO_2$ intermediates (c,d), SiO_2 products (e,f). As can be seen, the CuO template manifests a typical belt-like morphology with a smooth surface (Fig. 3a
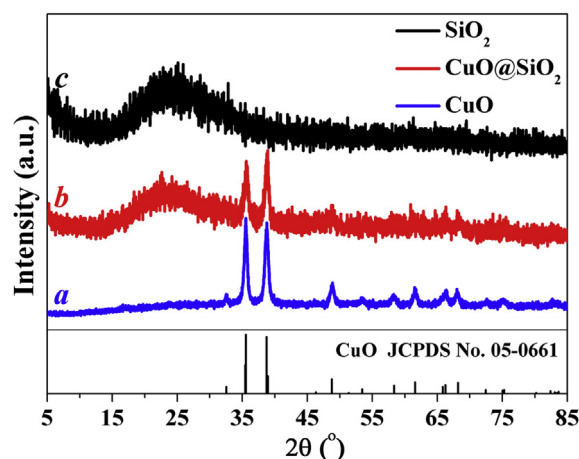

Fig. 2. XRD patterns of the CuO nanobelts (curve *a*), $CuO@SiO_2$ nanobelts (curve *b*), and hollow porous SiO_2 nanobelts (curve *c*).