

Double-shelled CeO₂@C hollow nanospheres as enhanced anode materials for lithium-ion batteries

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1 Experiment

1.1 Materials

Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9%), acetylene black, N-methyl-2-pyrrolidinone (NMP), and polyvinylidene fluoride (PVDF) were purchased from Sigma-Aldrich Co.. Polyvinyl pyrrolidone (PVP, K30), resorcinol, formaldehyde (37 wt.%), ethanol, hydrochloric acid (HCl, 37 wt.%), ethylene glycol, ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28 wt.%) were purchased from Sinopharm Chemical Reagent Co., Ltd. and directly used without further purification. Ultrapure water (18.2 M Ω cm) was used throughout all experiments.

1.2 Synthesis of CeO_2 hollow nanospheres

0.5 g of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.2 g of polyvinyl pyrrolidone (PVP) were dissolved in 15 mL of ethylene glycol. Then, the solution was added with 1 mL of 1 mol L⁻¹ HCl. Then, kept stirring for 30 min, the clear solution was obtained, and then transferred that to a Teflon-lined autoclave of 20 mL and heated at 160 °C for 3 h. After the Teflon-lined autoclaves were cooled to room temperature, the dark grey products were gathered by centrifugation and washed thrice with ultrapure water and absolute alcohol in sequence. Finally, the produced CeO_2 hollow spheres were dried at 80 °C overnight and collected. For comparison, CeO_2 solid spheres were fabricated using 1 mL of water instead of 1 mL of HCl.

1.3 Characterization

The morphology and microstructure of the samples were investigated by field emission scanning electron microscopy (FESEM), transmission electron microscopy

(TEM) and high-resolution TEM (HRTEM). The chemical constitutions were characterized by energy dispersive X-ray spectroscopy (EDS) integrated into a TEM system. The X-ray diffraction (XRD) patterns were recorded using a Bruker D8-ADVANCE (40 kV, 40 mA) powder X-ray diffractometer with Cu K α ($\lambda = 0.15406$ nm) radiation. Thermogravimetric analysis (TGA) was performed using a TGA 1500 DSP-SP analyzer heated from room temperature to 600 °C at a ramp rate of 10 °C min⁻¹ in air. A N₂ adsorption–desorption apparatus (Micromeritics, TriStar 3020) was used to determine the surface area, the pore volume, and the pore size distribution. The surface areas were calculated by Brunauer–Emmett–Teller (BET) method. The pore diameters were estimated from the desorption branches of the isotherms obtained by the Barrett–Joyner–Halenda (BJH) model. Raman measurements were recorded using a Renishaw in Via9 Raman microscope with a 50 \times objective and a 532 nm laser irradiation to focus the laser beam into a spot with a diameter of approximately 1 μ m. The sample composition was determined through X-ray photoelectron spectroscopy (XPS) by using a PerkinElmer PHI 5300 spectrometer with a monochromatic Mg K α X-ray source operated at 12.5 kV and 250 W. The survey spectra were obtained between 0 and 1200 eV, and C 1s with a binding energy of 284.6 eV was used as the reference.

1.4 Electrochemical measurements

The electrochemical measurements were examined by using 2032 two-electrode coin cells assembled in an Ar-filled glove-box (Universal (2440/750), Mikrouna, China). The working electrode was composed of active material, carbon black, and

polyvinylidene fluoride at a weight ratio of 7:2:1 in N-methyl 2-pyrrolidone solvent. The obtained slurry was coated on a Cu foil by using a scraper machine and dried in a vacuum oven at 90 °C for 24 h to remove the remaining solvent. Then, the electrode film was pressed and cut into circular discs with a diameter of 12 mm. The mass loading of the sample was approximately 1.3 mg cm⁻². The test cells were assembled in an Ar-filled glove box with metallic lithium foil as counter electrodes. 1.0 mol L⁻¹ LiPF₆ in a mixture of ethylene carbonate, dimethylcarbonate, and ethylmethyl carbonate at a volume ratio of 1:1:1 was added as the electrolyte, and a porous polypropylene film (Celgard 2400) served as the separator. A PARSTAT 4000 electrochemical workstation was used for cyclic voltammetry (CV) from 3.0 V to 0.01 V (versus Li⁺/Li) at a scan rate of 0.5 mV s⁻¹ and for electrochemical impedance spectroscopy (EIS) from 100 kHz to 0.01 Hz with a perturbation of 5 mV. Galvanostatic charge/discharge cycles were implemented on a battery measurement system (LAND-CT2001A) at various current densities in the range of 100–1000 mA g⁻¹ in the cut-off voltage range of 3.00–0.01 V versus Li⁺/Li at room temperature.

2. Characterization data

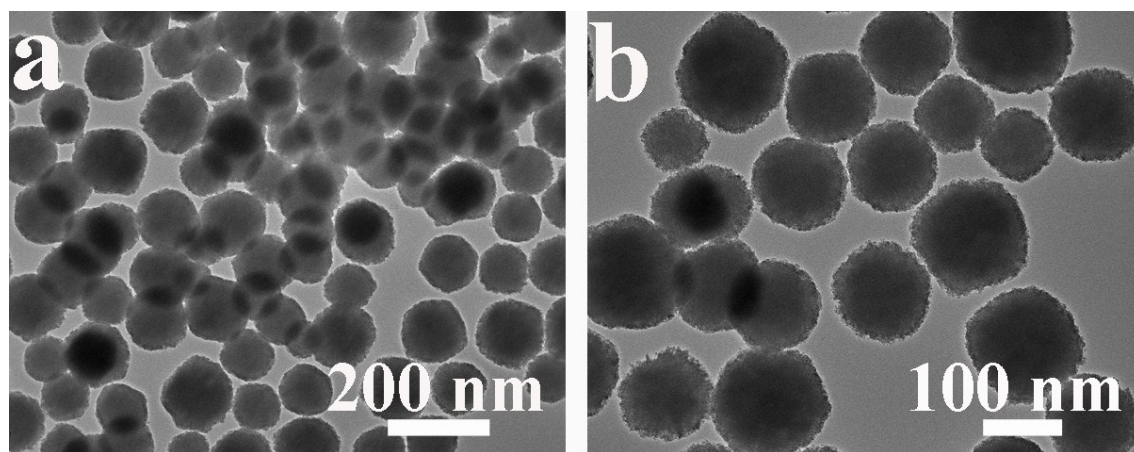


Fig. S1 TEM images of the CeO₂ solid spheres.

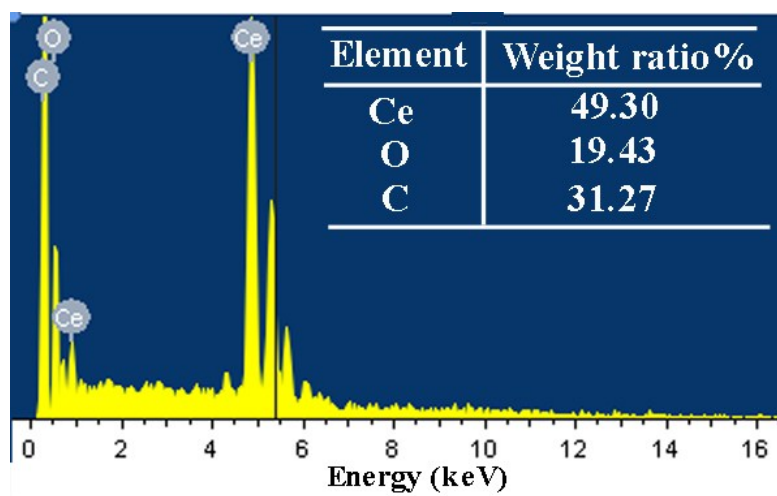
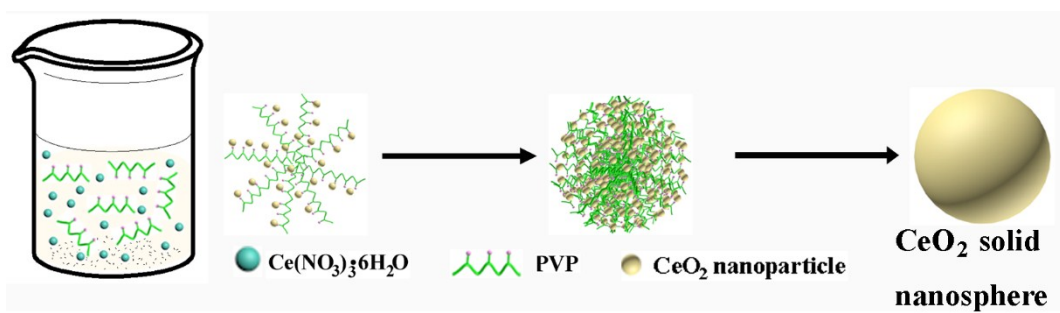


Fig. S2 EDS pattern of CeO₂@C.



Scheme S1 Schematic illustrations for the formation of the CeO₂ solid sphere.

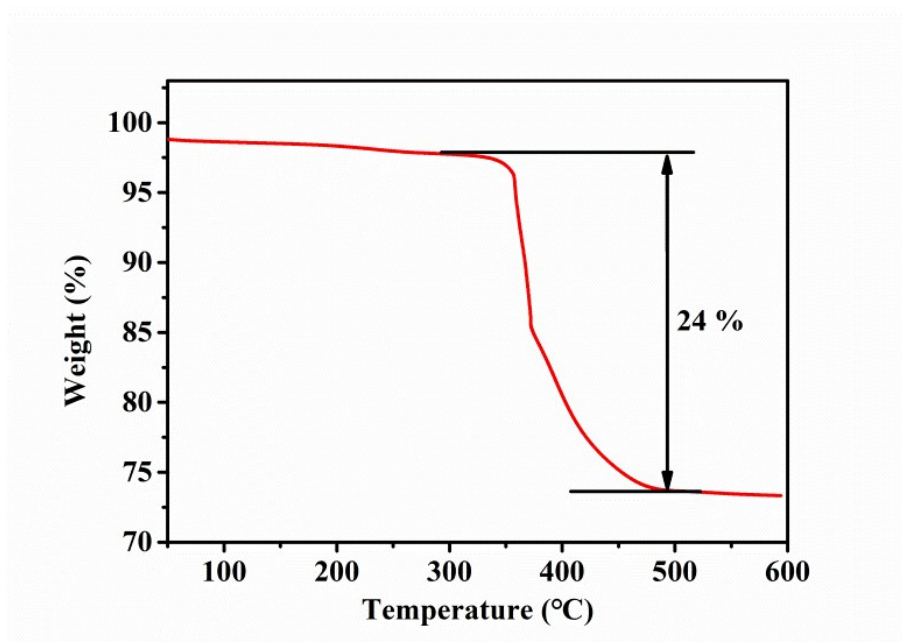


Fig. S3 TGA curve of CeO₂@C.

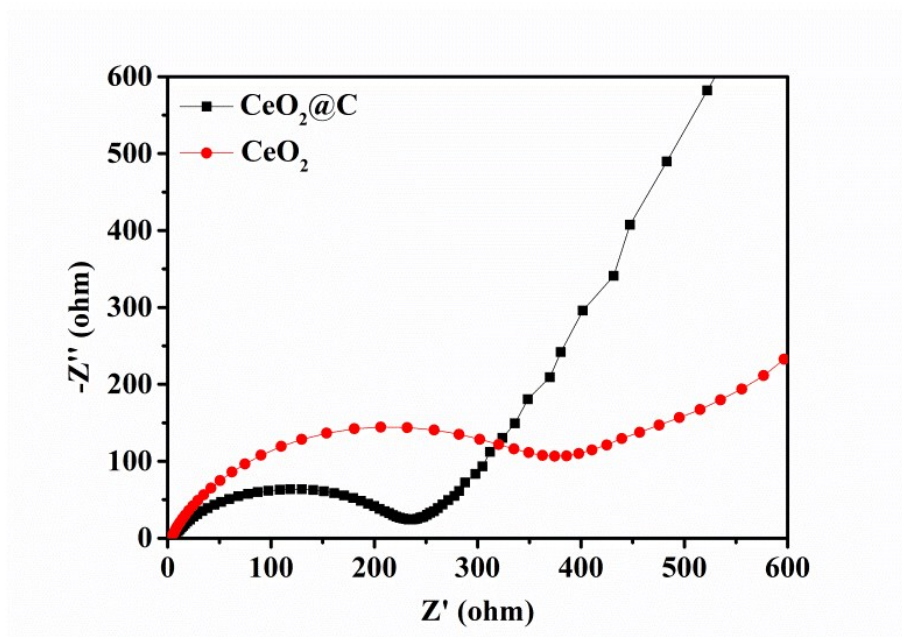


Fig. S4 Plots of CeO_2 and $\text{CeO}_2@C$ at the fresh cycle in the frequency range of 100 kHz to 0.01 Hz.