



Research paper

Porous carbon-wrapped cerium oxide hollow spheres synthesized via microwave hydrothermal for long-cycle and high-rate lithium-ion batteries



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ABSTRACT

Porous hollow structures have attracted tremendous interests due to their geometrical beauty, unique structural features and fascinating physicochemical properties. In the present work, we developed a general procedure for the synthesis of hollow nanostructured carbon-wrapped cerium oxide (CeO₂/C) via a microwave hydrothermal process without any surfactants or hard templates. The electrochemical performances of CeO₂/C specimen were tested as anode materials in lithium ion batteries. The results showed that CeO₂/C hollow spheres exhibited an exceptional cyclic stability with a high reversible capacity of 313 mA h g⁻¹ after 500 cycles at a high current density of 1000 mA g⁻¹ without signs of further degradation and also presented an excellent rate performance from 1000 to 10000 mA g⁻¹. The improved performances were attributed to the homogeneous carbon with 3D network structure in hollow spheres and the Ce³⁺ in the oxygen-deficient fluorite-like CeO_{2-x} on the surface of ceria nanoparticles, which enhanced the conductivity of CeO₂ hollow spheres, suppressed the aggregation of active particles and reduced the apparent activation energy to facilitate the kinetics of Li⁺ insertion-extraction. The unique hollow structure of CeO₂ wrapped by conductive carbon have made CeO₂ a promising candidate for future applications in various metal oxide electrodes to mitigate the mechanical degradation and capacity fading, critical for developing advanced electrochemical energy storage systems with long-cycle life and high-rate performance.

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1. Introduction

Lithium ion batteries (LIBs) have been widely used in portable electronics, electric tools and electric vehicles [1–3] due to their superior properties such as high energy density, long cycle life and good environmental compatibility [4,5]. In order to satisfy the ever-growing demands on high-capacity and high-power LIBs, great efforts have been made on transition metal oxides [6,7], which possess much higher capacity compared with widely-used graphite in commercial LIBs. However, the main challenges in the implementation of metal oxide electrodes are their large volume variation and poor electronic conductivity during the charge/discharge process [8]. As a kind of important transition metal oxides, CeO₂ shows fluorite structure [9,10], and the oxidation state

of cerium can mutate quickly between Ce(III) and Ce(IV) [8,11], leading to its wide applications in solid-state fuel cells [12], oxygen storage materials [13] and catalytic supporters [14]. The CeO₂ nanoparticles displayed imperceptible volumetric and morphological changes during the lithiation/delithiation process [8], which made it a possible candidate as an anode material for LIBs in the future in case that its electronic conductivity can be improved greatly.

It is well known that carbon materials have high electronic conductivity that can effectively improve the conductance of active materials and always act as buffering matrix to suppress the aggregation of active particles in the electrode [11]. So numerous efforts have been made to synthesize carbon material/metal oxides complexes for LIBs, such as SnO₂@carbon composite [15], grapheme-encapsulated Fe₃O₄ [16] and Co₃O₄-graphene nanoflowers [17]. During the passed couple of years, a variety of CeO₂ and carbon composites with different morphologies and microstructures, including nanocomposite [18], nanospheres [11,19] and

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nanorods [20] have been synthesized to enhance its electronic conductivity as anode materials in LIBs. Specially, CeO_2 -graphene nanocomposite prepared by hydrothermal method exhibited improved specific capacity of 605 mA h g^{-1} at 50 mA g^{-1} after 100 cycles [18]. Core-shell $\text{CeO}_2@\text{C}$ nanospheres synthesized by hydrothermal carbonization showed an initial discharge specific capacity of 863 mA h g^{-1} in the potential range of 3.0–0.0V [11]. Graphene/ CeO_2 /CMK-3 composites with a hierarchical structure prepared by a template method maintained the specific capacity of about 550 mA h g^{-1} at 100 mA g^{-1} after 100 cycles [20]. All these CeO_2 materials achieved good electrochemical performances at the expense of the complex preparation process and long synthesizing time [21–23]. Moreover, electrochemical performances of CeO_2 have not been investigated at large current densities for lithium ion battery in previous reports.

Herein, we report a simple microwave hydrothermal method by using gas templates to synthesize hollow spheres composed by carbon-wrapped CeO_2 nanoparticles (noted as CeO_2/C). The structure, shape and formation process of CeO_2/C were investigated by SEM, TEM, XRD, Raman and BET. And we further demonstrated their promising properties as anode materials for lithium-ion batteries. The results showed that CeO_2/C hollow spheres exhibited improved discharge capacity and remarkable long-cycle stability (313 mA h g^{-1} at 1000 mA g^{-1} with 100% retention after 500 cycles), and excellent high-rate capacity (even at the large current density of $10000 \text{ mA h g}^{-1}$).

2. Experimental

2.1. Materials

All chemicals were of analytical grade and used as received without further purification. Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), polyvinylidene fluoride (PVDF) and N-methyl-2-pyrrolidone (NMP) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. And deionized (DI) water was produced by Milli-Q-Reference water system (Millipore Co., USA).

2.2. Preparation of CeO_2/C hollow spheres

CeO_2 precursor was synthesized through microwave hydrothermal process. Typically, 0.1 mol $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.05 mol $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ were dissolved in 1 L DI water at room temperature. After being stirred for 4 h, the obtained solution was transferred into quartz tube and then maintained at 150°C for 2 min under microwave condition with the wattage between 95 and 130 W (InitiatorTM Microwave System, Biotage Co., Sweden). Fig. S1 recorded the profiles of temperature (T), pressure (p) and power (P) during microwave hydrothermal process. After the system cooled totally, the solution became turbid. Then the obtained solution was filtrated, washed and dried to get the light-yellow precipitate of hollow sphere marked as CeOC. Finally, the CeOC

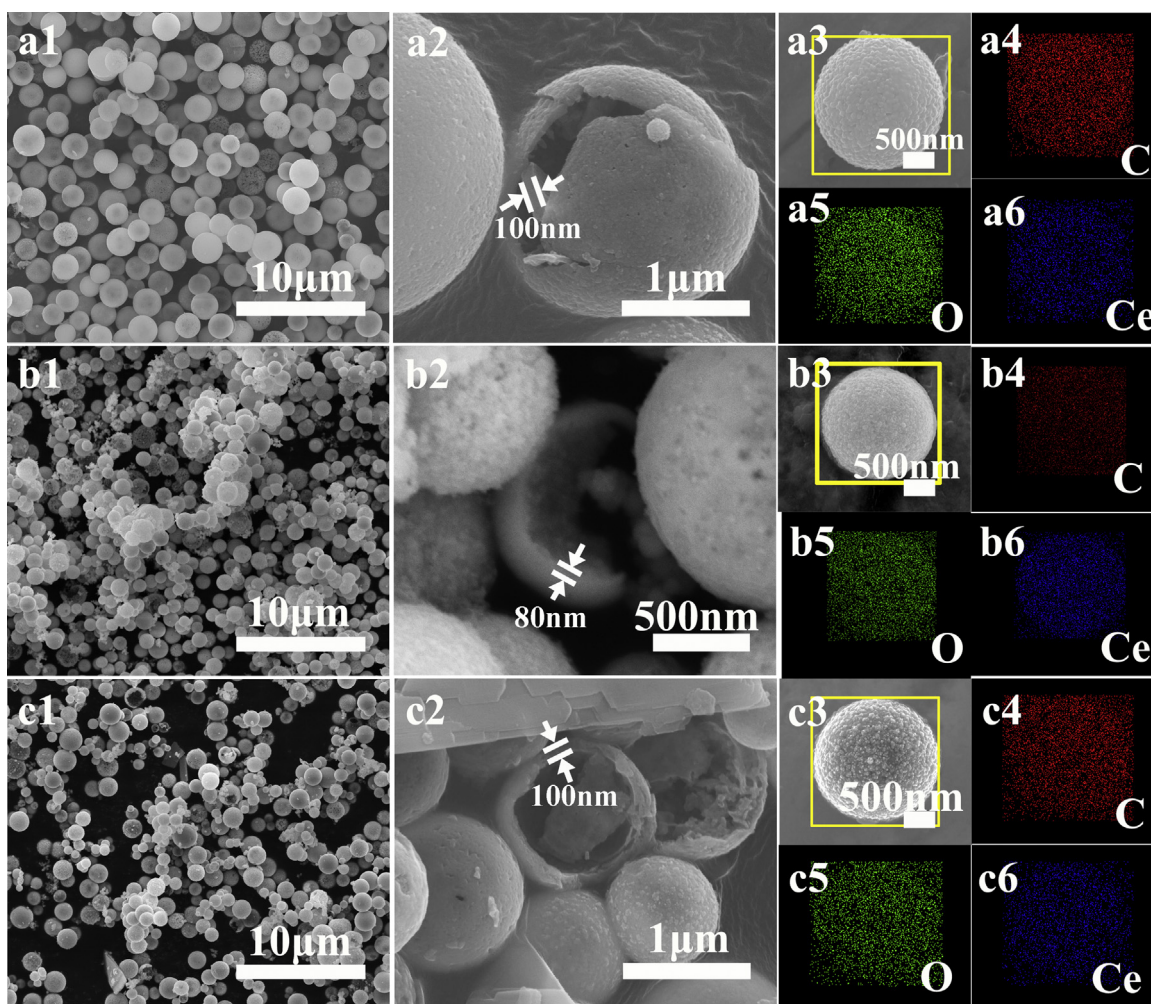


Fig. 1. SEM images of (a1–a3) CeOC, (b1–b3) CeO_2 and (c1–c3) CeO_2/C ; EDS element mapping images of (a4–a6) CeOC, (b4–b6) CeO_2 and (c4–c6) CeO_2/C .

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