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Highly-crystalline ultrathin gadolinium doped and carbon-coated $Li_4Ti_5O_{12}$ nanosheets for enhanced lithium storage

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HIGHLIGHTS

- Ultrathin Gd^{3+} doped and carbon-coated $Li_4Ti_5O_{12}$ nanosheets are prepared.
- The nanosheets have single-crystal nature with a thickness of about 10 nm.
- The nanosheets have high electrical conductivity and large Li^+ diffusion coefficient.
- The benefits stem from synergistic effects by ultrathin structure, doping and carbon coating.
- The nanosheets demonstrate superior lithium storage performance.

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ABSTRACT

Highly-crystalline gadolinium doped and carbon-coated ultrathin $Li_4Ti_5O_{12}$ (LTO) nanosheets (denoted as LTO-Gd-C) as an anode material for Li-ion batteries (LIBs) are synthesized on large scale by controlling the amount of carbon precursor in the topotactic transformation of layered ultrathin $Li_{1.81}H_{0.19}Ti_2O_5 \cdot xH_2O$ (H-LTO) nanosheets at 700 °C. The characterizations of structure and morphology reveal that the gadolinium doped and carbon-coated ultrathin LTO nanosheets have high crystallinity with a thickness of about 10 nm. Gadolinium doping allows the spinel LTO products to be stabilized, thereby preserving the precursor's sheet morphology and single crystal structure. Carbon encapsulation serves dual functions by restraining crystal growth of the LTO primary nanoparticles in the LTO-Gd-C nanosheets and decreasing the external electron transport resistance. Owing to the synergistic effects rendered by ultrathin nanosheets with high crystallinity, gadolinium doping and carbon coating, the developed ultrathin LTO nanosheets possess excellent specific capacity, cycling performance, and rate capability compared with reference materials, when evaluated as an anode material for lithium ion batteries (LIBs). The simple and effective strategy encompassing nanoscale morphological engineering, surface modification, and doping improves the performance of LTO-based anode materials for high energy density and high power LIBs applied in large scale energy storage.

1. Introduction

The increasing demand for consumer electronics and green transportation spurs the development of intercalated compounds especially for high-performance lithium-ion batteries (LIBs) that can store and deliver energy efficiently [1–4]. Spinel $Li_4Ti_5O_{12}$ (LTO) has been demonstrated to be promising anode materials in high-performance LIBs because of its flat charging/discharging plateau at a high potential of 1.55 V vs. Li/Li^+, zero-strain feature towards lithium insertion/extraction, and excellent environmental benignity [5–10]. Unfortunately, practical application of spinel LTO in hybrid electric vehicles and large-scale energy storage has been hampered because of the unsatisfactory rate capability which cannot meet the demand for a high power density due to kinetic problems associated with the poor electrical conductivity (ca.10^{-13} S cm^{-1}) and small lithium diffusion coefficient (ca. 10^{-9} to 10^{-13} cm^2 s^{-1}) [8,11–13]. To overcome these hurdles, many

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strategies have been made to ameliorate the rate capability of LTO, for instance, developing various nano/microstructured materials, elemental doping, and surface modification with highly conductive additives. Lou et al. have synthesized mesoporous LTO hollow spheres and observed relatively high rate performance of 104 mA h g^{-1} at 20 C [14]. Isovalent and aliovalent doping (e.g., Br^{6+}, Zr^{4+},V^{5+}, Zn^{2+}, Al^{3+} and Sc^{3+}) have been observed to increase the electronic conductivity of LTO [8,15–22]. Various carbon-modified spinel LTO composites have attained more than 90% of the theoretical capacity and superior rate capability [11,13,14,23–39]. In particular, by using flexible current collectors such as carbon nanotubes and fibers, flexible LTO composite electrodes have been obtained [11,40]. In addition, combining LTO with conducting metallic nanoparticles can also improve the rate performance of LTO electrodes [41–44]. These improvements are noteworthy, but still insufficient for power and flexibility-oriented applications. It is thus highly desirable to further address the conductivity deficiency of pristine LTO via new composition modulations and nanoengineering combination strategies [30].

Among the various architectures, two-dimensional (2D) nanosheets with a thickness below 10 nm hold great promise in high-performance LIBs because of the short paths enabling fast lithium ion diffusion, large exposed surface, as well as abundant lithium insertion channels [12,28,45–51]. Ultrathin LTO nanosheets are also believed to exhibit a pseudocapacitive effect as the interaction takes place on the surface thus leading to the improved rate capability [48,51]. On the other hand, the construction of a stable separating thin carbon coating around LTO has been reported to be another effective strategy to improve the electrochemical performance of LTO electrodes due to enhancement in the charge transfer kinetics in the LTO electrodes and interfacial stability between the LTO and electrolyte [27,29,50]. Moreover, according to literature, doping lanthanide (Ln^{3+}) ions (such as La^{3+}, Y^{3+} and Gd^{3+}) with lower valence state yields oxygen ion vacancies in LTO, which could behave as ionic charge carriers to enhance intrinsic conductivity, thereby improving long-term cyclability and rate capabilities [15]. Despite recent research on LTO NSs, LTO with carbon encapsulation, and Ln^{3+} doped LTO, there have been few studies on highly-crystalline Ln^{3+} doped and carbon-coated ultrathin $Li_4Ti_5O_{12}$ (LTO) nanosheets. Compared to the conventional solid-state reaction, hydrothermal, or sol–gel method to prepare LTO nano/microstructures, large scale synthesis of highly-crystalline ultrathin LTO nanosheets with a thickness of 10 nm is quite challenging. In our previous reports, we found that using trivalent lanthanide (for example, Gd^{3+}) to substitute for quadrivalent titanium ions allows the final spinel LTO products to be stabilized, thereby preserving the precursor's sheet morphology via the topotactic transformation of ultrathin layered $Li_{1.81}H_{0.19}Ti_2O_5 \cdot xH_2O$ (H-LTO) at 700 °C [52]. In this paper, by controlling the amount of carbon precursor (D(t)-glucose monohydrate) in the topotactic transformation, large scale synthesis of ultrathin Gd^{3+} doped and carbon coated LTO nanosheets (denoted as LTO-Gd-C) with high crystallinity and a thickness below 10 nm is accomplished. Owing to the synergistic effects rendered by ultrathin nanosheets with high crystallinity, Gd^{3+} doping and carbon coating, the materials deliver superior electrochemical performance as anode materials in LIBs in terms of specific capacity, cycling performance, and rate capability.

2. Experimental details

2.1. Materials

The synthesis was carried out using commercially available reagents. The $GdCl_3$ $6H_2O$ was 99.99% pure and supplied by Sinopharm Chemical Reagent Company. All the other chemicals were analytical grade and used as received without further purification.

2.2. Synthesis of pure $Li_4Ti_5O_{12}$ (LTO)

The pure $Li_4Ti_5O_{12}$(LTO) was prepared using a hydrothermal method followed by calcination as reported by Wang et al. [12] In the typical synthesis procedures, 1.7 ml (5 mM) of tetrabutyl titanate (TBT) and 0.189 g of $LiOH \cdot H_2O$ were thoroughly mixed in 20 ml of ethanol at room temperature. The solution was mixed completely with a magnetic stirrer in a closed container for 24 h and 25 ml of deionized water were added to the container. After stirring for 0.5 h, the solution was transferred to a 50 ml Teflon-lined stainless autoclave and placed in an oven at 180 °C for 36 h to obtain $Li_{1.81}H_{0.19}Ti_2O_5 \cdot xH_2O$ (H-LTO). The white H-LTO powder on the bottom of the reactor was collected, washed with ethanol 3 times, and dried at 80 °C for 6 h. Finally, the white hydrothermal H-LTO product was heated to 700 °C for 6 h in a horizontal tube furnace in air to obtain the pure $Li_4Ti_5O_{12}$.

2.3. Synthesis of Gd^{3+} doped LTO (LTO-Gd) nanosheets

The experimental procedures described in Section 2.2 were used to prepare the H-LTO-Gd^{3+} precursor by doping with the appropriate amount of Gd^{3+} in the mixture consisting 1.7 ml (5 mM) of tetrabutyl titanate, 0.189 g of $LiOH \cdot H_2O$, and 20 ml of ethanol. The white hydrothermal H-LTO-Gd product was heated to 700 °C for 6 h in a horizontal tube furnace in air to obtain Gd^{3+} doped LTO nanosheets.

2.4. Synthesis of ultrathin Gd^{3+} doped and carbon coated LTO nanosheets

The ultrathin LTO-Gd-C nanosheets were prepared by controlling the amount of carbon precursor (D(t)-glucose monohydrate) used in the experimental procedures described in Section 2.3 for the LTO-Ln^{3+} doped LTO nanosheets. The H-LTO-Gd precursors were prepared using the experimental procedures described in Section 2.3. 200 mg of the H-LTO-Gd precursor were dispersed in 10 ml of ethanol under magnetic stirring to form Solution A. D(t)-glucose monohydrate in the amount corresponding to 2.5, 5, or 10 wt% of the H-LTO-Gd precursor was dissolved in 5 ml of ethanol to produce Solution B. Solution B was added dropwise to Solution A under stirring, followed by slow evaporation at 80 °C into a slurry. The slurry was heated under Ar/H_2(5%) at 700 °C for 6 h. The products with different nominal carbon contents were designated as LTO-Gd-C (2.5%), LTO-Gd-C (5%), and LTO-Gd-C (10%). For comparison, a composite corresponding to LTO-Gd-C (5%) without Gd^{3+} dopant was synthesized using H-LTO as the precursor and designated as LTO-C (5%).

2.5. Materials characterization

The crystal structure of the samples was determined by powder X-ray diffraction (XRD, Rigaku, D/MAX 2500) using a copper K_α radiation source ($\lambda = 0.154$ nm). X-ray photoelectron spectroscopy (XPS) measurements were performed using an Al K_α source (Kratos Analytical Ltd., UK) and the binding energy of 284.8 eV for C 1s was used as calibration. The morphology and microstructure of the samples were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi, S4800) equipped with energy-dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM, JEOL 2100F) equipped with selected-area electron diffraction (SAED). The Raman spectra were recorded on a Renishaw InVia system with the excitation laser (λ) of 532 nm. Thermal gravimetric and differential scanning calorimetry (TG-