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Design of a three-dimensional-network $Li_2ZnTi_3O_8$ co-modified with graphene nanosheets and carbon nanotubes as a high performance anode material for lithium-ion batteries

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3D $Li_2ZnTi_3O_8$ conductive network co-modified with graphene nanosheets and carbon nanotubes is successfully synthesized by a two-step reaction. The conductive structure is largely advantageous to its electrochemical performance for $Li_2ZnTi_3O_8$. When cycled for 550 cycles, 81.3% and 84.2% of the capacities for the 2nd cycle is kept at 1 and 2 A g^{-1}, respectively. After 300 cycles, 175.5, 153.3 and 144.9 mAh g^{-1} are obtained at 3, 4 and 5 A g^{-1}, respectively. The excellent cyclic performance and the large specific capacities at high rate are due to the good conductive network of the $Li_2ZnTi_3O_8$ active particles, large pore volume, small particle size, and good kinetics behavior.

1. Introduction

The rapid development of hybrid electric vehicles (HEVs) and electric vehicles (EVs) needs high power sources. Lithium-ion batteries (LIBs) become promising energy storage devices of HEVs and EVs owing to the high energy density, reliable cycle life and environmental friendliness. In commercial LIBs, graphite is the usual anode material. However, its safety and rate capability are poor, which restricts the application of graphite in power LIBs. To meet the demand for high power and good safety, many new anode materials have been researched [1–8].

Recently, the cubic spinel $Li_2ZnTi_3O_8$ (LZTO) has attracted great interests because of its wide Li^+ diffusion channels, good safety, abundant as well as environment-friendly raw materials, and simple synthetic process [9–17]. Compared with $Li_4Ti_5O_{12}$, $Li_2ZnTi_3O_8$ has larger theoretical capacity of 227 mAh g^{-1}, and lower working potential of 0.5–0.8 V (vs. Li/Li^+). In spite of the advantages above, the electronic conductivity is low and the rate capability needs to be further improved for LZTO. Various measures have been taken, such as coating with conductive materials, doping with alien ions and reducing particle size [18–23], to improve the whole electrochemical performance of LZTO. Among the strategies mentioned above, carbon coating is an effective and economic technique, which can improve the electronic conductivity of LZTO and inhibit the growth of LZTO particles in heat treatment. Therefore, various carbon sources have been used to enhance the electrochemical performance of LZTO, such as lithium citrate, asphalt, titanium isopropoxide, β-cyclodextrin, chitin, acetyl glucosamine, sucrose, oxalic acid, citric acid, alginic acid, ZIF-8, EDTA, gelatin and Tween 80 [9,10,18,19,24–30]. Uniform and thin carbon layer can improve the electronic conductivity and benefit the diffusion of Li^+ ions. Thus, effective carbon coating with LZTO is a crucial factor for the high rate capability and good cyclic performance.

Graphene nanosheets (GNS) are considered as ideal carbon source to modify cathode and anode materials for LIBs [31–35] owing to its high electronic conductivity. However, the conductivity is low in the vertical direction for GNS. In addition, GNS easily form irreversible agglomerates due to the existence of van der Waals force. So constructing the overall conductivity of GNS networks is urgently necessary.

In the paper, we firstly report the fabrication of 3D conductive

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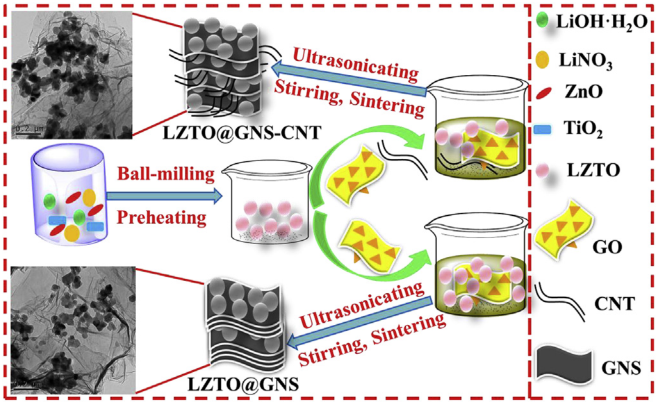

Fig. 1. Schematic illustration for the synthesis process of the LZTO@GNS and LZTO@GNS-CNT anode materials.

network consisting of 1D carbon nanotubes (CNT) and 2D graphene nanosheets (GNS) to modify LZTO, as demonstrated in Fig. 1. The conductivity of GNS in vertical direction can be enhanced via bridging GNS with CNT vertically and the aggregations of GNS can be inhibited due to the existence of CNT in the G planes. The 3D conductive network can provide smooth transport pathways for electrons, and open channels for Li$^+$ ions diffusion. The LZTO nanoparticles enwrapped into the 3D conductive network exhibit high rate capability and cyclic performance.

2. Experimental

2.1. Synthesis of graphene oxide (GO) sheets

GO sheets were fabricated via a modified Hummers method [36,37] and based on our previous work [38]. The synthesis process was shown in Supplementary Materials.

2.2. Synthesis of LZTO@GNS-CNT and LZTO@GNS

All chemicals were analytical reagent (A.R.). The LZTO@GNS-CNT anode was synthesized via a molten-salt method similar to our previous work [19]. TiO$_2$ (anatase), LiOH·H$_2$O, LiNO$_3$ and ZnO were ball-milled for 5 h with Li/Zn/Ti = 2.4:1:3. The molar ratio of LiOH·H$_2$O to LiNO$_3$ was 0.38:0.62. The mixture was dried at 80 °C for 12 h in air, pre-heated at 250 °C for 3 h and then 600 °C for 4 h in air, mixed with GO sheets and CNT by ultrasonically treating for 2 h, stirring for 24 h in ethanol, dried at 80 °C in air and finally sintered at 700 °C for 3 h in N$_2$/H$_2$ (V: V = 93: 7). The mass ratio of GO sheets to CNT was 7:1. The obtained material was denoted as LZTO@GNS-CNT. The LZTO@GNS was prepared via the same processes without CNT.

2.3. Physical characterization and electrochemical measurements

The related physical and electrochemical performance measurements were shown in Supplementary Materials in detail.

3. Results and discussion

The diffraction peaks of LZTO@GNS and LZTO@GNS-CNT can be well attributed to the spinel LZTO (JCPDS#44-1037) (Fig. 2a). In addition, the diffraction peak of G is observed, indicating that the GO was reduced to G at 700 °C in a reductive atmosphere, which was further confirmed by the XPS and Raman results (Fig. S1 and Fig. S2). The G content in LZTO@GNS and LZTO@GNS-CNT is 6.24 wt% (Fig. S3). The lattice parameters (Table S1) obtained from the XRD data, are similar to the previous reports [20,39–43].

The SEM images (Fig. 2b–c) show that the two samples are

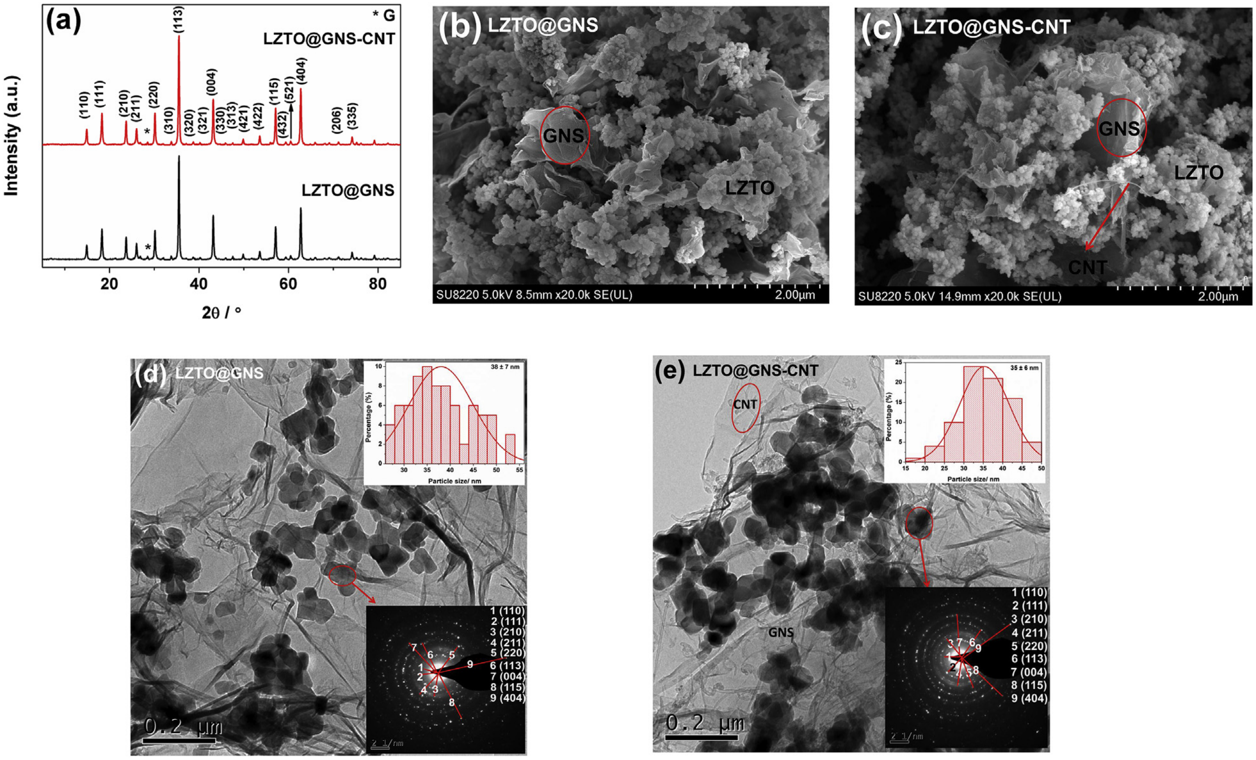

Fig. 2. (a) X-ray diffraction patterns of the LZTO@GNS and LZTO@GNS-CNT; SEM images of (b) LZTO@GNS and (c) LZTO@GNS-CNT; TEM images, histograms of particle size distribution (inset, top) and selected area electron diffraction (SAED) pattern (inset, bottom) of (d) LZTO@GNS and (e) LZTO@GNS-CNT.