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Abstract

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Keywords

ion, batteries, c, nanosheet, anode, crystalline, enhanced, tio₂, rate, capability, lithium

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Yang, F., Zhu, Y., Li, X., Lai, C., Guo, W. & Ma, J. (2015). Crystalline TiO₂@C nanosheet anode with enhanced rate capability for lithium-ion batteries. *RSC Advances: an international journal to further the chemical sciences*, 5 (119), 98717-98720.

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Cite this: *RSC Adv.*, 2015, 5, 98717

Received 9th September 2015
Accepted 10th October 2015

DOI: 10.1039/c5ra18410j

www.rsc.org/advances

Crystalline TiO₂@C nanosheet anode with enhanced rate capability for lithium-ion batteries†

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TiO₂@C nanosheets have been obtained by a facile solvothermal method using titanate butoxide and hydrofluoric acid as precursors, followed by our novel carbon coating technique using oleic acid as the carbon source. The TiO₂@C nanosheet anode shows a high discharge capacity of 145.8 mA h g⁻¹ after 50 cycles and excellent rate capability.

Lithium-ion batteries (LIBs) have attracted enormous interest from the scientific community and industry for decades, due to their long cycle life, high energy storage density, very small memory effect, and environmental benignity.^{1–5} To enhance the performance of LIBs, a variety of materials have been studied as alternative electrode materials.⁶ Among the various anode materials, titanium dioxide has received wide attention because of its low cost, long cycle life, and minimal environmental impact.^{7,8} There are four polymorphs of TiO₂. Among them, anatase TiO₂ is widely considered to be the most electroactive host for lithium-ion insertion.⁹ TiO₂ is structurally stable with small volume changes (<4%) during Li ion insertion/extraction processes and intrinsically safe because it does not support electrochemical deposition of Li.^{6,10} Moreover, its high working voltage (more than 1.5 V vs. Li, carbon-based anode at ~0.1 V vs. Li) enables extremely high rate operation by preventing lithium plating on the electrode.^{11–13} Nevertheless, one obvious disadvantage of TiO₂ is that it has poor lithium ionic and electrical conductivities,^{14–16} and this limits the charge/discharge rate.^{17,18} It has been widely

reported that the cycling stability and intercalation activity depend on the morphology of the TiO₂ anode.^{19,20} There are numerous studies on reducing the lithium diffusion length by synthesizing TiO₂ nanomaterials, such as TiO₂-B nanowires,^{21–25} mesoporous rutile,¹⁸ and nanosized anatase TiO₂.²⁶

Recently, following the first demonstration by Yang *et al.*,²⁷ the synthesis and application of unique anatase TiO₂ nanocrystals (NCs) with exposed {001} high-energy facets have been

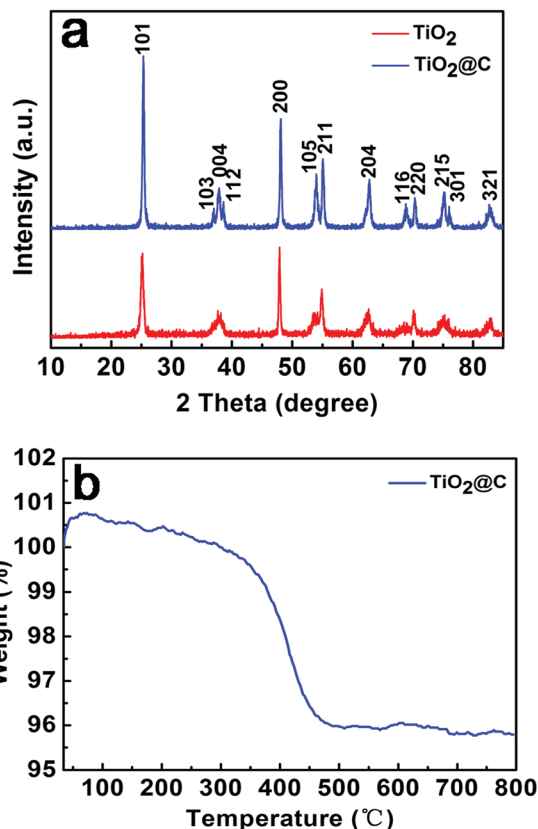


Fig. 1 (a) XRD patterns of TiO₂ and TiO₂@C nanosheets; (b) TGA curve of TiO₂@C.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ra18410j

‡ These authors have equal contribution to this paper.

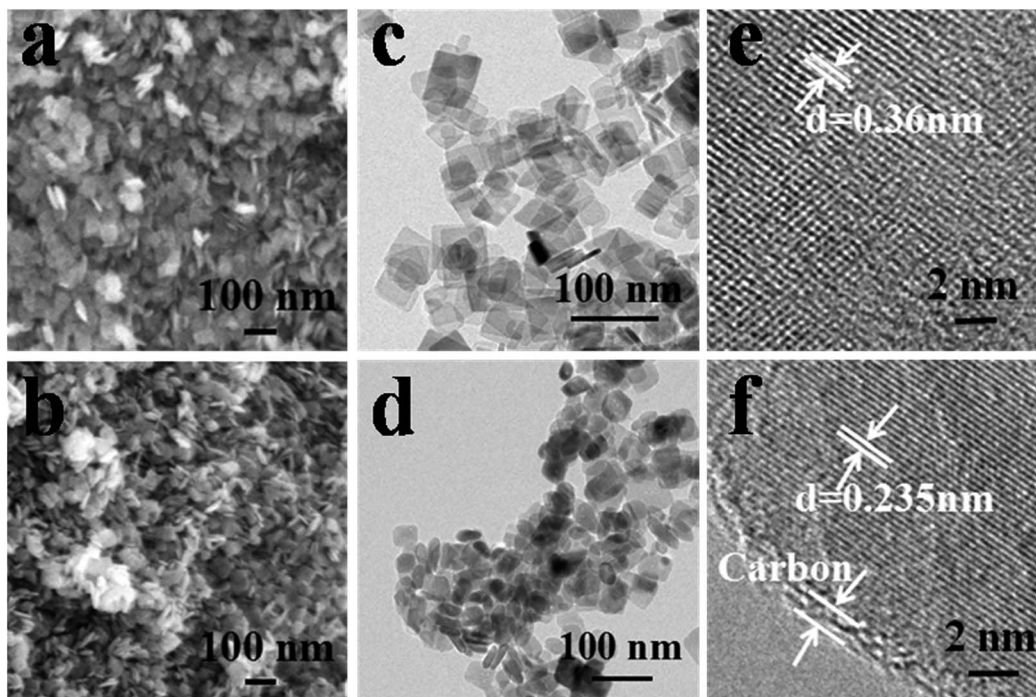


Fig. 2 (a, c and e) SEM, TEM, and HRTEM images of TiO_2 nanosheets; (b, d and f) SEM, TEM, and HRTEM images of $\text{TiO}_2@C$ nanosheets.

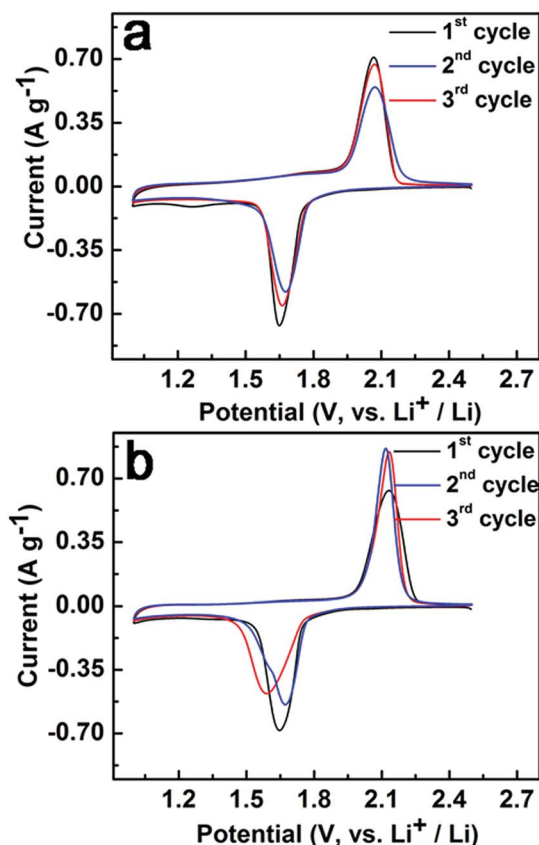


Fig. 3 Cyclic voltammograms (CVs) for the first 3 cycles of (a) TiO_2 nanosheet and (b) $\text{TiO}_2@C$ nanosheet electrode at a scan rate of 0.2 mV s^{-1} .

reported by some groups.^{2,28,29} Theoretical and experimental studies found that the {001} facets of anatase TiO_2 are especially reactive.^{30–35} In order to solve the problems of TiO_2 with poor lithium ionic and electrical conductivities, we have synthesized $\text{TiO}_2@C$ nanosheets with a high percentage of {001} facets using our novel coating method.^{36–39} The as-synthesized $\text{TiO}_2@C$ nanosheets show high reversible capacity and improved rate capability, indicating that they are promising as anode for materials for LIBs.

In this work, we used a carbon coating technique devised by our group that uses oleic acid as the carbon source, since the oleic acid molecules have carboxyl groups, which can be firmly attached to the surface of the titanium dioxide.^{37–39} After carbonization, the surfaces of the TiO_2 nanosheets are tightly coated with carbon layers. To confirm the structures and components of the as-synthesized three samples, X-ray diffraction (XRD) characterization was performed. As shown in Fig. 1a, all the diffraction peaks of TiO_2 and $\text{TiO}_2@C$ could be indexed to the anatase structure of TiO_2 (PDF #21-1272). It should be noted that the degree of crystallinity for $\text{TiO}_2@C$ was improved when the materials were annealed at 600°C . The carbon content of the $\text{TiO}_2@C$ nanosheets was further confirmed by thermogravimetric analysis (TGA). Fig. 1b indicates that the composite materials had a weight loss of about 4.98% above 350°C , which is due to the oxidation of carbon to CO_2 gas.

The morphology of the as-synthesized TiO_2 and $\text{TiO}_2@C$ samples was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM). Fig. 2a and b presents SEM images of the TiO_2 and $\text{TiO}_2@C$ samples, which are in the form of nanosheets and a nanosheet composite, respectively. As shown in the TEM images (Fig. 2c and d), the shape of the TiO_2 was not

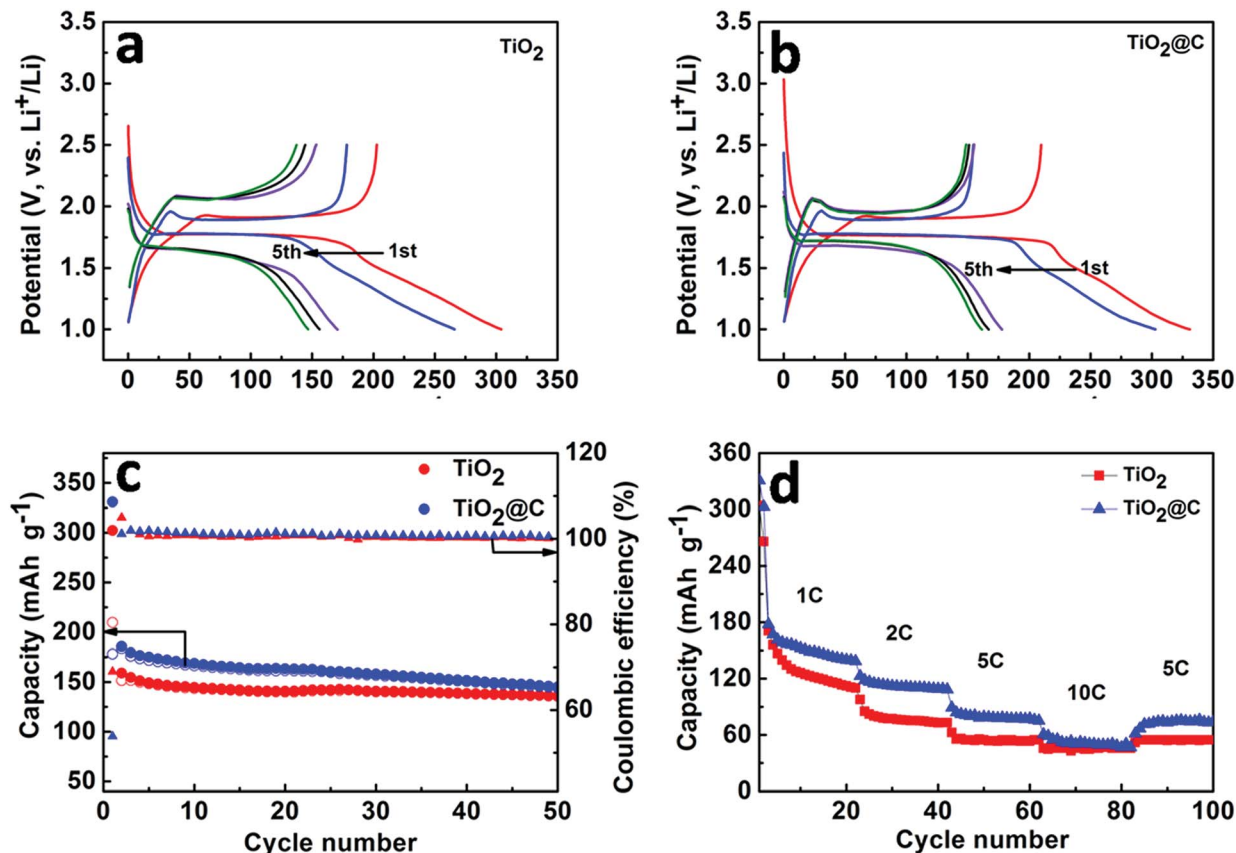


Fig. 4 (a) Discharge-charge profiles of TiO_2 at the 1C rate; (b) discharge-charge profiles of $\text{TiO}_2@\text{C}$ at the 1C rate; (c) cycling performances and coulombic efficiency of the TiO_2 and $\text{TiO}_2@\text{C}$ at the charge-discharge rate of 1C; (d) discharge rate capability of TiO_2 and $\text{TiO}_2@\text{C}$ at different C rates.

changed after carbon coating. The nanosheets have a diameter of about 50 nm, similar to those reported in the literature.³² Compared to the HRTEM image of the TiO_2 (Fig. 2f), a carbon layer can be found on the surfaces of the $\text{TiO}_2@\text{C}$ nanosheets, with a thickness of the carbon layer of about 1 nm. Moreover, it was also found that the $\text{TiO}_2@\text{C}$ nanosheets are highly crystalline, which is consistent with the XRD results. The $\text{TiO}_2@\text{C}$ nanosheets are expected to be a promising anode material owing to their high crystallinity, high proportion of exposed {001} facets (the lattice distance is 0.235 nm), and carbon coating of the TiO_2 nanosheets.

To study the electrochemical performance of the TiO_2 and $\text{TiO}_2@\text{C}$ electrodes, cyclic voltammetry (CV) measurements were carried out at a scan rate of 0.2 mV s^{-1} . As shown in Fig. 3a and b, we chose the potential window of 1–2.5 V, which is appropriate for Li-ion insertion/extraction into/out of the anatase TiO_2 lattice. The cathodic/anodic peaks correspond to the discharge/charge profiles. The redox peaks of both the TiO_2 and the $\text{TiO}_2@\text{C}$ electrodes, centred at the positions of 1.65 V and 2.0 V, are consistent with the results of previous studies.^{21,35,40}

In order to compare the electrochemical properties of both the $\text{TiO}_2@\text{C}$ and the TiO_2 nanosheets, the cycling stability of the electrodes was examined by constant current charge-discharge testing. Fig. 4a and b shows the charge-discharge voltage profiles of the TiO_2 and $\text{TiO}_2@\text{C}$ electrodes at the 1C ($1\text{C} = 336 \text{ mA g}^{-1}$) current rate. The profiles are similar to the typical profiles of

anatase TiO_2 . The cycling performance and coulombic efficiency of the TiO_2 and $\text{TiO}_2@\text{C}$ nanosheet electrodes are shown in Fig. 4c. Clearly, the $\text{TiO}_2@\text{C}$ electrode shows a high storage capacity in comparison with the TiO_2 nanosheet electrode. The discharge/charge capacities in the 1st cycle are $185.7/183.6 \text{ mA h g}^{-1}$ for the $\text{TiO}_2@\text{C}$, and $159/151.5 \text{ mA h g}^{-1}$ for the TiO_2 , respectively. After 50 cycles, the discharge/charge capacities of $\text{TiO}_2@\text{C}$ nanosheet electrode still remain at $145.8/145 \text{ mA h g}^{-1}$, respectively, indicating better electrochemical performance than the pure TiO_2 nanosheet sample. The enhancement of the capacity can be attributed to the amorphous carbon on the surfaces of the TiO_2 nanosheets.³⁵ The coulombic efficiencies of both the TiO_2 and the $\text{TiO}_2@\text{C}$ nanosheet electrodes are nearly 100%, except for the first cycle, as shown in Fig. 4c.

The discharge capabilities of the TiO_2 and $\text{TiO}_2@\text{C}$ nanosheet electrodes at different current densities between 1C and 10C are shown in Fig. 4d. The $\text{TiO}_2@\text{C}$ nanosheet electrode clearly shows higher specific capacity than the TiO_2 nanosheet electrode. In particular, the discharge capacity of the $\text{TiO}_2@\text{C}$ nanosheet electrode is about 141 mA h g^{-1} at 1C after 20 cycles. Moreover, the discharge capacity drops gradually as the current density increases. For the $\text{TiO}_2@\text{C}$ nanosheet electrode, the discharge specific capacities are 116, 88, and 55 mA h g^{-1} at 2C, 5C, and 10C, respectively. The discharge capacity of the TiO_2 nanosheet electrode, however, is only 126, 82, 57, and 47 mA h g^{-1} at 1C, 2C, 5C, and 10C, respectively. When the discharge rate

returns back to 5C after 20 cycles at 10C, the discharge capacity of the TiO₂@C nanosheet electrode recovers to 75 mA h g⁻¹, which is higher than that of the TiO₂ nanosheet electrode. These results described here indicate that the TiO₂@C nanosheet electrode has better cycling performance and rate performance than the TiO₂ nanosheet electrode. As stated above, the enhanced electrochemical performance of the TiO₂@C nanosheet electrode can be attributed to the high crystallinity, high proportion of exposed {001} facets, and carbon coating of the TiO₂ nanosheets.

In summary, TiO₂@C nanosheets have been synthesized by a facile solvothermal/annealing method. The as-synthesized TiO₂@C nanosheets show better performance than the bare TiO₂ nanosheets as anode material for the lithium-ion battery, with a specific capacity of 185.7 mA h g⁻¹ in the initial cycle and 145.8 mA h g⁻¹ after 50 cycles, as well as better rate capability, higher than for the pure TiO₂ nanosheets. This method might be extended to the synthesis of other carbon-coated composite materials for energy storage.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant no. 51302079). We also thank Dr Tania Silver from the Institute for Superconducting and Electronic Materials (University of Wollongong) for revising our manuscript.

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