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

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**Publication Details**

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Keywords
ion, batteries, C, nanosheet, anode, crystalline, enhanced, TiO2, rate, capability, lithium

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Crystalline TiO$_2$@C nanosheet anode with enhanced rate capability for lithium-ion batteries†

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TiO$_2$@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 TiO$_2$@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 TiO$_2$. Among them, anatase TiO$_2$ is widely considered to be the most electroactive host for lithium-ion insertion.$^9$ TiO$_2$ is structurally stable with small volume changes ($\approx$4%) during Li ion insertion/extraction processes and intrinsically safe because it does not support electrochemical deposition of Li.$^{10}$ Moreover, its high working voltage (more than 1.5 V vs. Li, carbon-based anode at $\approx$0.1 V vs. Li) enables extremely high rate operation by preventing lithium plating on the electrode.$^{11-13}$ Nevertheless, one obvious disadvantage of TiO$_2$ 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 TiO$_2$ anode.$^{19,20}$ There are numerous studies on reducing the lithium diffusion length by synthesizing TiO$_2$ nanomaterials, such as TiO$_2$–B nanowires,$^{21-25}$ mesoporous rutile,$^{26}$ and nanosized anatase TiO$_2$.$^{26}$

Recently, following the first demonstration by Yang et al.$^{27}$ the synthesis and application of unique anatase TiO$_2$ nanocrystals (NCs) with exposed $\{001\}$ high-energy facets have been

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‡ These authors have equal contribution to this paper.

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Fig. 1 (a) XRD patterns of TiO$_2$ and TiO$_2$@C nanosheets; (b) TGA curve of TiO$_2$@C.
reported by some groups.\textsuperscript{3,28,29} Theoretical and experimental studies found that the \{001\} facets of anatase TiO\textsubscript{2} are especially reactive.\textsuperscript{30–35} In order to solve the problems of TiO\textsubscript{2} with poor lithium ionic and electrical conductivities, we have synthesized TiO\textsubscript{2}@C nanosheets with a high percentage of \{001\} facets using our novel coating method.\textsuperscript{36–39} The as-synthesized TiO\textsubscript{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.\textsuperscript{37–39} After carbonization, the surfaces of the TiO\textsubscript{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\textsubscript{2} and TiO\textsubscript{2}@C could be indexed to the anatase structure of TiO\textsubscript{2} (PDF #21-1272). It should be noted that the degree of crystallinity for TiO\textsubscript{2}@C was improved when the materials were annealed at 600 °C. The carbon content of the TiO\textsubscript{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\textsubscript{2} gas.

The morphology of the as-synthesized TiO\textsubscript{2} and TiO\textsubscript{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\textsubscript{2} and TiO\textsubscript{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\textsubscript{2} was not

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

Fig. 3 Cyclic voltammograms (CVs) for the first 3 cycles of (a) TiO\textsubscript{2} nanosheet and (b) TiO\textsubscript{2}@C nanosheet electrode at a scan rate of 0.2 mV s\textsuperscript{-1}.
changed after carbon coating. The nanosheets have a diameter of about 50 nm, similar to those reported in the literature. Compared to the HRTEM image of the TiO2 (Fig. 2f), a carbon layer can be found on the surfaces of the TiO2@C nanosheets, with a thickness of the carbon layer of about 1 nm. Moreover, it was also found that the TiO2@C nanosheets are highly crystalline, which is consistent with the XRD results. The TiO2@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 TiO2 nanosheets.

To study the electrochemical performance of the TiO2 and TiO2@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 TiO2 lattice. The cathodic/anodic peaks correspond to the discharge/charge profiles. The redox peaks of both the TiO2 and the TiO2@C electrodes, centred at the positions of 1.65 V and 2.0 V, are consistent with the results of previous studies. The discharge/charge capacities in the 1st cycle are 185.7/183.6 mA h g⁻¹ for the TiO2@C, and 159/151.5 mA h g⁻¹ for the TiO2, respectively. After 50 cycles, the discharge/charge capacities of the TiO2@C nanosheet electrode still remain at 145.8/145 mA h g⁻¹, respectively, indicating better electrochemical performance than the pure TiO2 nanosheet sample. The enhancement of the capacity can be attributed to the amorphous carbon on the surfaces of the TiO2 nanosheets.

The discharge capabilities of the TiO2 and TiO2@C nanosheet electrodes at different current densities between 1C and 10C are shown in Fig. 4d. The TiO2@C nanosheet electrode clearly shows higher specific capacity than the TiO2 nanosheet electrode. In particular, the discharge capacity of the TiO2@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 TiO2@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 TiO2 nanosheet electrode, however, is only 126, 82, 57, and 47 mA h g⁻¹ at 1C, 2C, 5C, and 10C, respectively.

![Fig. 4](a) Discharge–charge profiles of TiO2 at the 1C rate; (b) discharge–charge profiles of TiO2@C at the 1C rate; (c) cycling performances and coulombic efficiency of the TiO2 and TiO2@C at the charge–discharge rate of 1C; (d) discharge rate capability of TiO2 and TiO2@C at different C rates.
returns back to 5C after 20 cycles at 10C, the discharge capacity of the TiO$_2@$C nanosheet electrode recovers to 75 mA h g$^{-1}$, which is higher than that of the TiO$_2$ nanosheet electrode. These results described here indicate that the TiO$_2@$C nanosheet electrode has better cycling performance and rate performance than the TiO$_2$ nanosheet electrode. As stated above, the enhanced electrochemical performance of the TiO$_2@$C nanosheet electrode can be attributed to the high crystallinity, high proportion of exposed {001} facets, and carbon coating of the TiO$_2$ nanosheets.

In summary, TiO$_2@$C nanosheets have been synthesized by a facile solvothermal/annealing method. The as-synthesized TiO$_2@$C nanosheets show better performance than the bare TiO$_2$ 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 TiO$_2$ nanosheets. This method might be extended to the synthesis of other carbon-coated composite materials for energy storage.

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Notes and references