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Short Communication

Hierarchical-structure anatase TiO_2 with conductive network for high-rate and high-loading lithium-ion battery

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Titanium dioxides have been extensively investigated as promising anodes for Lithium ion batteries (LIBs) because of the high–rate capacity and cyclability, as well as the improved safety over graphite anode [1,2]. However, as a typical insertion–type anode, anatase TiO_2 exhibits low conductivity (10^{-12} S cm^{-1} for electron conductivity [3] and 10^{-17}–10^{-10} cm^2 s^{-1} for Li^+ ion diffusion coefficient [4]) and poor specific capacity (only accommodate <0.5 Li per bulk TiO_2 unit [5]), severely limiting its practical applications.

The electrochemical performances of TiO_2 can be effectively improved using various approaches [6], for example by designing various nanostructures [7], element doping [8], and compositing with graphene [9,10] or metal oxides [11]. However, there are few reports considering about both the super high-rate (>4,000 mAh g^{-1}) and high mass loading (>2 mg cm^{-2}) of TiO_2 electrodes. Under such conditions, the sluggish ionic and electronic transport of the activate materials, insufficient electronic conductive network (including thick electrodes crack and delaminate from the current collector), and poor electrolyte infiltration will become fatal for the electrochemical performances [12]. In this work, we successfully prepare high-loading electrodes with a conductive network based on hierarchical micro–nano TiO_2 (microclews) intertwined by multiwalled carbon nanotubes (CNTs), which demonstrates excellent high-rate capacity and cyclability. After 2,000 fast cycles at 10,000 mA g^{-1}, the as-synthesized electrodes (denoted as TiO_2 MCs @ CNTs hereafter) deliver a specific capacity of 105 mAh g^{-1}. At a high mass loading of 6.4 mg cm^{-2}, the electrodes possess a specific capacity of 220 mAh g^{-1}, and retain 164 mAh g^{-1} after 250 cycles at 100 mA g^{-1}. The $LiFePO_4$ vs. TiO_2 MCs@CNTs full battery exhibits specific capacity of 126 mAh g^{-1} at a current density of 1,000 mA g^{-1} and reserves 97.6 mAh g^{-1} after 3,000 cycles.

Fig. S1 (online) schematically illustrates the synthesis route of TiO_2 MCs and TiO_2 MCs@CNTs electrodes, and thermogravimetry analysis of TiO_2 MCs precursor in Fig. S2 (online) demonstrates continuous weight loses until 400 °C. The tetragonal anatase TiO_2 MCs (Fig. S3 online) with diameter of around 4–8 μm, hold the 3D hierarchical structure composed of 1D nanobelts after annealing (Fig. 1a and Fig. S4 online) [13]. The specific surface area (218 m^2 g^{-1}, Fig. S5 online) is less than that of 1D counterpart [14], which could reduce the side reaction and enhance the tap density of the electrode. CNTs well entwined around the TiO_2 MCs could enhance the flexibility of the electrode and favor in achieving high loading (6.0 mg cm^{-2}) (Fig. 1b and Figs. S6, S7 online). The lattice distances (Fig. 1b) and the Raman spectrum (Fig. S8 online) confirm the co-existence of TiO_2 and carbon nanotubes, and the transmission electron microscopes energy-dispersive X-ray spectroscopy (TEM-EDS) elemental mapping (Fig. S9 online) demonstrates that CNTs are uniformly distributed around TiO_2 MCs, resulting in a 3D conductive network.

The nanoscale TiO_2 shortens ion transport pathway, the micro-scale framework decreases the unnecessary side reactions as well as the volume expansion of electrode during cycling, and the porous texture structure favors the infiltration of electrolyte. As a result, the pure TiO_2 MCs electrodes illustrate an outstanding high–rate performance and good reversibility at low mass loading (1.0 mg cm^{-2}) (Figs. S10, S11 online). The specific capacity could achieve 255 and 121.6 mAh g^{-1} at 100 and 4,000 mA g^{-1}, respectively. Even at 16,000 mA g^{-1}, the electrodes still have a specific capacity of 49 mAh g^{-1}. Besides, after long cycling at 2,000 mA g^{-1} for 5,000 cycles and at 4,000 mA g^{-1} for about 4,000 cycles, the TiO_2 MCs electrodes could still maintain 81.9 and 42 mAh g^{-1},

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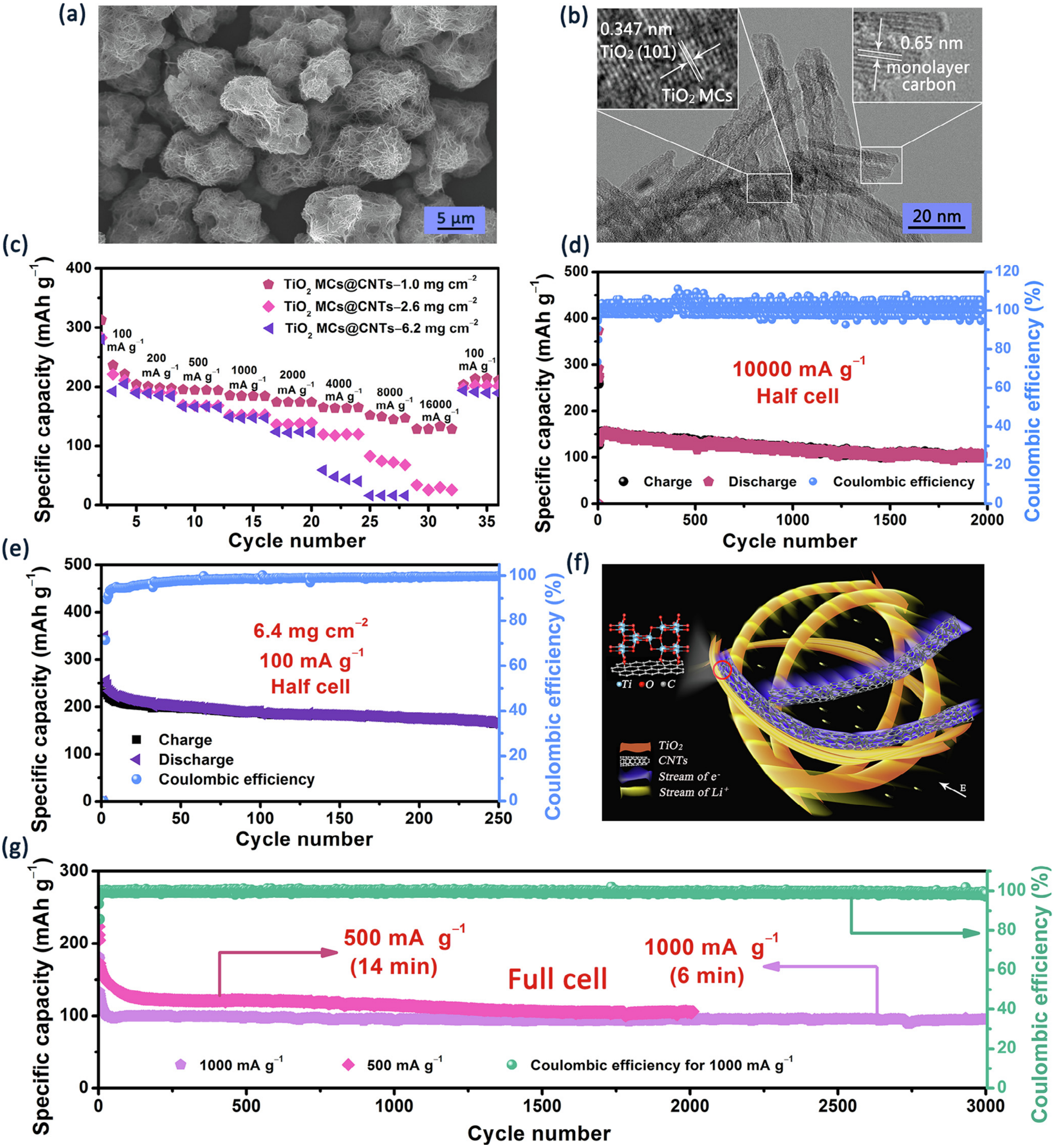

Fig. 1. (Color online) Characterization and electrochemical performances of TiO_2 MCs@CNTs. (a) Field emission scanning electron microscope (FESEM) image of TiO_2 MCs. (b) High-resolution transmission electron microscope (HRTEM) images of TiO_2 MCs@CNTs. (c) Rate performance of TiO_2 MCs@CNTs electrodes with various mass loadings at different current densities of 100–16,000 mA g^{-1}. (d) Cyclability at a current density of 10,000 mA g^{-1} of TiO_2 MCs@CNTs electrodes (1.0 mg cm^{-1}). (e) Cycling stability and coulombic efficiency of TiO_2 MCs@CNTs electrode (6.4 mg cm^{-2}) at 100 mA g^{-1} for 250 cycles. (f) Schematic diagram for rapid Li^+ and e^- transport in 3D conductive network of TiO_2 MCs@CNTs electrode. (g) Discharge specific capacity and coulombic efficiency of $LiFePO_4/TiO_2$ MCs@CNTs full cell in long cycling at current densities of 1,000 and 500 mA g^{-1}.

respectively. But the pure TiO_2 MC electrodes with mass loading of 2.3 and 4.3 mg cm^{-2} cannot sustain such high-rate capacity because of the poor electron conductivity.

The 3D flexible CNTs network could solve the problem above by enhancing the conductive network and structural stability, as shown in Fig. 1c. For mass loading of 1.0 mg cm^{-2}, the TiO_2 MCs@CNTs electrodes illustrate a specific capacity of 243 and 149.1 mAh g^{-1} at a current density of 100 and 8,000 mA g^{-1}, respectively. More crucially, the electrodes exhibit unexceptionable discharge specific capacity of 128.3 mAh g^{-1} at 16,000 mA g^{-1}, remaining 65% of the specific capacity at 200 mA g^{-1}, much higher than that of the pure TiO_2 MCs electrodes (Fig. S12 online). Moreover, the voltage platform is still obvious even at 4,000 mA g^{-1}, implying a stable bulk lithium insertion process and extraordinary ionic conductivity (Fig. S13 online). Furthermore, the TiO_2 MCs@CNTs electrodes exhibit long cycling performances at 2,000 and 4,000 mA g^{-1}, retaining 108.5 and 102.2 mAh g^{-1} after 5,000 cycles (33% and 143% improvement than the pure TiO_2 MCs electrodes) (Fig. S14 online). Under ultrahigh current density of 10,000 mA g^{-1}, the TiO_2 MCs@CNTs electrodes exhibit an excellent cyclability, retaining 70% specific capacity after 2,000 cycles with almost 100% coulombic efficiency (Fig. 1d and Fig. S15 online). All above results confirm that the conductive CNTs network stimulates the potential performance of TiO_2 MCs in high-rate capacity and long-cycling capability.

The charge transfer and the structural stability at the electrode-scale could be the limiting factor at high mass loading. The rate performance in Fig. 1c shows that TiO_2 MCs@CNTs (2.6 mg cm^{-2}) can deliver capacity of 193 mAh g^{-1} at the current density of 100 mA g^{-1} (Fig. S16 online), and reveal a perfect reversibility even after charge/discharge at ultrahigh current density of 16,000 mA g^{-1}, compared favorably with the pure TiO_2 MCs electrodes (Fig. S17 online). Impressively, at a high loading of 6.2 mg cm^{-2}, TiO_2 MCs@CNTs achieves an extraordinary specific capacity of 225 mAh g^{-1} at a current density of 100 mA g^{-1} and maintains 164 mAh g^{-1} after 250 cycles (Fig. 1e). The TiO_2 MCs@CNTs with mass loading of 3.0 mg cm^{-2} under 500 mA g^{-1} exhibits 122 mAh g^{-1} after 1,000 cycles with almost 100% coulombic efficiency (Fig. S18 online). To sum up, owing to the synergistic effects of TiO_2 MCs and CNTs micro–nano architectures, TiO_2 MCs@CNTs electrodes demonstrate excellent high-rate and high-loading performances, surpassing the reported counterparts (Table S1 online).

To reveal the ionic transport kinetics in the TiO_2 MCs@CNTs electrodes, we conducted the Electrochemical impedance spectroscopy (EIS) measurement (Fig. S19 online) and calculated the Li-ion diffusion coefficient (D_{Li}) (Table S2 online). The results demonstrate that more efficient ions and electrons transports are provided in TiO_2 MCs @CNTs than in the pure TiO_2 MCs. It is remarkable that the D_{Li} of TiO_2 MCs is much higher than the previously reported titanium oxides-based anode materials (Table S3 online). From the CV curves at different scan rates (Figs. S20, S21 online), the charge storage was found to be both surface-controlled and diffusion-controlled in TiO_2 MCs@CNTs, but only diffusion–controlled in pure TiO_2 MCs. This phenomenon is probably ascribed to the coupled interface between TiO_2 and CNTs (confirmed by Fourier transform infrared (FT-IR) spectra in Fig. S22 (online) [15]), indicating abundant phase boundaries between TiO_2 and CNTs, which is in favor of high rate capacity and cyclability [16]. The superiority of hierarchical–structure TiO_2 with conductive network can be schematically shown in Fig. 1f. The hierarchical-structure TiO_2 MCs supply rapid ions transport channels, and CNTs grant high-speed electron conductivity as well as keep robustness of the thick electrode during cycling, while the chemical coupled interface provides more specific capacity.

To prove the potential application of TiO_2 MCs@CNTs, full cells were fabricated using TiO_2 MCs@CNTs as the anode and commercial $LiFePO_4$ as the cathode. The full battery demonstrates excellent reversible rate capability when currents range from 50 to 1,000 mA g^{-1} (Fig. S23 online). Remarkedly, it can deliver an energy density of 85.5 and 48.5 Wh kg^{-1} at a power density of 19 and 485 W kg^{-1}, respectively, and could be charged up to 70% within 6 min (Fig. S24 online). The full cell also illustrates excellent cyclability, yielding a super high discharge specific capacity of 105 mAh g^{-1} after 2,000 cycles at 500 mA g^{-1}. Even when the current density reaches 1,000 mA g^{-1}, it can still deliver an extraordinary capacity of 97.6 mAh g^{-1} after 3,000 cycles with almost 100% coulombic efficiency and 92.9% of the capacity retention (after 20 cycles' activation) (Fig. 1g and Fig. S25 online), implying a promising potential in real-life applications like fast-charging and long-life batteries.

In summary, we have successfully designed a 3D hierarchical electrode with high mass loading by interface–coupling between CNTs and TiO_2 MCs. Owing to the superiorities of hierarchical micro–nano TiO_2 structures and the improvement of electron conductivity and mechanical robustness by flexible CNTs networks, as well as the interface Li^+ storage by chemical coupled interface between CNTs and TiO_2 MCs, the as-obtained electrode demonstrates extraordinary electrochemical performances. The anode exhibits 105 mAh g^{-1} after 2,000 cycles at 10,000 mA g^{-1}. Under the high-loading (6.4 mg cm^{-2}), the electrode delivers a large capacity of 220 mAh g^{-1} at a gentle current and still reserves 164 mAh g^{-1} after 250 cycles. The full battery exhibits 97.6 mAh g^{-1} after 3,000 cycles at 1,000 mA g^{-1}. The design protocol could have more inspiration and guidance in achieving high-loading electrodes with enhanced high-rate capacity and cyclability for the application in energy storage devices.

Conflict of interest

The authors declare that they have no conflict of interest.

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Author contributions

Xinghua Liu performed the experiments. Lijiang Zhao, Shitong Wang, Meng Chao, Yutong Li, and Jin Leng participated in the discussion on experimental results. Junying Zhang and Zilong Tang directed this project.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scib.2019.06.022.

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