



In-situ TEM on the coalescence of birnessite manganese dioxides nanosheets during lithiation process



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ABSTRACT

Nanostructure is believed to produce great benefits for anode materials in lithium ion batteries (LIBs) by enhancing lithium ion transfer, accommodating large volume change and increasing surface area. Whether the nanostructure (especially the porous nanostructure) could be well held during charging/discharging process is one of the most commonly concerned issues in LIBs research. The dynamic evolution of birnessite manganese dioxides nanosheets during lithiation process is investigated by *in-situ* transmission electron microscopy (TEM) for the first time. The TiO₂@MnO₂ core-shell nanowires are used as the anode and Li metal as the counter electrode inside the TEM. Interestingly, the lithiation process is confirmed as MnO₂ and Li converting to Li₂O and Mn. The original porous structure of the nanosheets is hard to preserve during lithiation process due to lithiation-induced contact flattening.

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1. Introduction

Manganese dioxide has received substantial attention as anode materials in lithium ion batteries (LIBs) due to its high theoretical specific capacities, environmental benignity and natural abundance [1,2]. However, there are still two major obstacles for its practical application. The first and most important one is the large volumetric expansion during the charging/discharging processes, resulting in severe particle agglomeration and unsatisfactory cycling performance; the other one is the virtually ubiquitous large coulombic inefficiency observed in the first cycle. Nanostructure is believed to produce great benefits for the anode materials. The nanostructured materials could greatly increase the surface area and also accommodate large change in volume. This strategy is especially suitable for nanostructured MnO₂, such as nanorods/nanowires, nanotubes and nanosheets with or without porous structures [3–5]. The vacant space provided by the porous nanostructures can accommodate the structural strain and facilitate fast Li⁺ insertion/extraction kinetics, leading to improved rate and cycling performance.

Pure nanostructured MnO₂ still endures the disadvantages of low conductivity and particle agglomeration. Therefore, carbon was introduced into MnO₂ nanomaterials to form homogenous

C@MnO₂ composites. An excellent example is the coaxial C@MnO₂ nanotube array electrodes with good cyclic stability and capacity [6]. Various coaxial X@MnO₂ nanorods/nanowires were also explored to enhance the conductivity of MnO₂ and stabilize the nanostructure [1–3,7,8].

In our previous studies, TiO₂@MnO₂ core-shell nanowires were successfully prepared for high performance supercapacitors [9]. The TiO₂@MnO₂ core-shell nanowires showed a high capacitance of 120 F g⁻¹ (0.1 A g⁻¹) and excellent cycling stability (93% capacitance retention after 3000 cycles). The structure of the MnO₂ nanosheets should keep unchanged during the charge/discharge processes as suggested by the excellent cycling stability. However, considering the notable difference between electrons in supercapacitors and Li⁺ ions in LIBs, it is still an open question that whether the MnO₂ nanosheets can retain the morphology during Li⁺ insertion/extraction processes, which is one of the most commonly concerned issues in LIBs research as well.

In-situ transmission electron microscopy (TEM) is a powerful technique to reveal the dynamic microstructure evolution of electrode materials. Thanks to J.Y. Huang's group's pioneer works of the *in-situ* lithiation and delithiation in TEM, plenty of fresh results about the dislocation associated lithiation, layer-by-layer lithiation and even cracking were obtained continuously [10–12].

In this study, we adopted *in-situ* TEM to reveal the real time change of the MnO₂ porous nanostructure during Li⁺ insertion processes. It is found that the origin MnO₂ porous nanostructure could not be retained during Li⁺ insertion processes, which may be

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the main reason of the large coulombic inefficiency observed in the first cycle.

2. Experimental section

2.1. Synthesis of $\text{TiO}_2@ \text{MnO}_2$ core-shell nanowires

Commercial anatase TiO_2 powders (0.4 g) were put into aqueous solution of 10 M NaOH (35 mL) in a Teflon-lined stainless steel autoclave (50 mL). The autoclave was kept at 180 °C for 48 h. After hydrothermal treatment, the resulting precipitates were acidwashed (0.1 M HCl solution) to realize the full-ion exchange from Na^+ to H^+ . The final white products were then dried in vacuum at 80 °C for 8 h, and then calcined at 400 °C for 3 h in air to obtain the anatase TiO_2 nanowires. Then 25 mg TiO_2 were dispersed in KMnO_4 solution (40 mL, 0.01 M) by ultrasonication for 10 min. The mixed solution was then transferred into the Teflon-lined stainless steel autoclave. The autoclave was directly put in an electric oven at 140 °C for 24 h and then cooled to room temperature. The black resultants were collected by centrifugation and dried at 60 °C for 12 h in a vacuum oven.

2.2. In-situ TEM setup

A nanosized half-cell LIB was constructed inside TEM for *in-situ* investigation and is schematically shown in Fig. 1 a. The *in-situ* TEM experiments were carried out in a JEM-2100 operating at 200 kV with the help of a Nanofactory TEM-STM holder. The $\text{TiO}_2@ \text{MnO}_2$ core-shell nanowires were attached onto the tip of a gold wire, serving as the anode. Some Li metal was stucked to a tip of tungsten wire, serving as the cathode. The unavoidable surface oxidation on the Li metal served as the solid electrolyte. A negative voltage (−2 V) was applied on the $\text{TiO}_2@ \text{MnO}_2$ core-shell nanowires with respect to the Li counter-electrode to initiate the lithiation process. The lithiation process started instantaneously, once the contact was established between $\text{TiO}_2@ \text{MnO}_2$ core-shell nanowires and the Li electrode.

3. Result and discussion

Fig. 1 b–f shows the microstructure of the $\text{TiO}_2@ \text{MnO}_2$ core-shell nanowires. The $\text{TiO}_2@ \text{MnO}_2$ nanowires are composed of quadrangular prism TiO_2 nanowires and MnO_2 nanosheets. The MnO_2

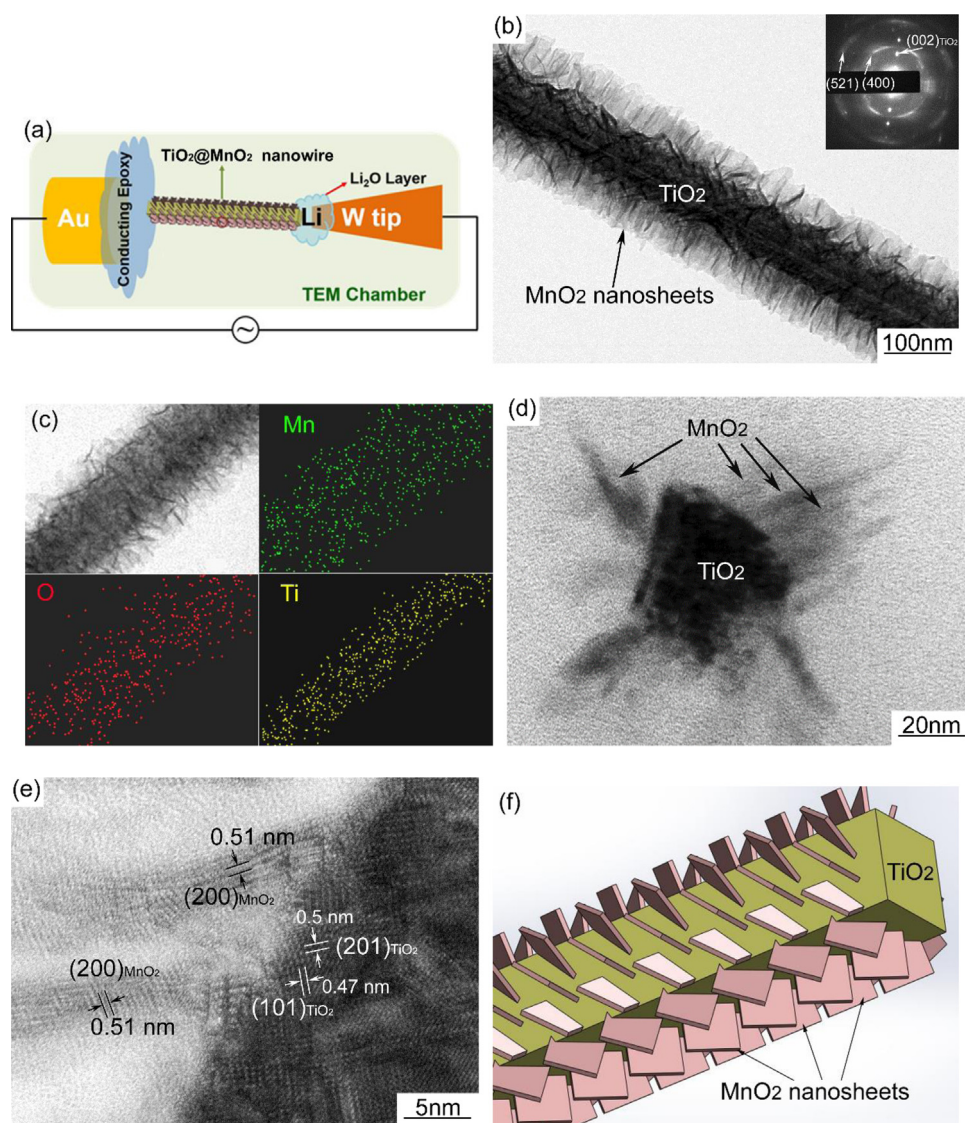


Fig. 1. TEM images of (a) schematical illustration of the *in-situ* experiment, (b) a single nanowire. Inset is a typical SAED pattern of the TiO_2 single crystal and MnO_2 nanosheets; (c) element mapping of a nanowire, (d) the cross-sectional TEM image, (e) high resolution TEM image of the interface of MnO_2 nanosheets and TiO_2 , (f) schematical illustration of the nanostructure of the $\text{TiO}_2@ \text{MnO}_2$ core-shell nanowires.

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