

Short communication

## Novel TiO<sub>2</sub>/C nanocomposites for anode materials of lithium ion batteries

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### Abstract

Here we reported an effective method to prepare TiO<sub>2</sub>/C core–shell nanocomposites as active anode materials for lithium ion batteries with markedly ameliorated electrochemical performance. At first, a precursor, polyacrylonitrile coated nano-TiO<sub>2</sub> particles, was formed by emulsion polymerization. Then the precursor was heat-treated under argon atmosphere to achieve the nanocomposites. The conductive carbon shell enveloped TiO<sub>2</sub> nanoparticles and suppressed the aggregation of nanoparticles during cycling. Meanwhile, it combined closely with the nanocores, significantly enhanced kinetics of lithium intercalation and de-intercalation and diffusion coefficient of lithium ion. This provides a good way to improve the cycling and kinetics of nanoanode materials.

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*Keywords:* Lithium ion battery; Anode; Core–shell; Nanocomposite; Electrochemical performance

### 1. Introduction

Since the commercialization of lithium secondary batteries in the early 1990s, their development has been rapid. Nowadays, improving the preparation technology and electrochemical performance of their electrode materials is a major focus. Recently, nanomaterials for anode of lithium ion batteries stimulated great interest since all of them showed a higher reversible capacity than that of the respective micrometer materials [1–5]. However, there are still some distances for their practical application. The most critical problem is the aggregation of nanoparticles, giving rise to poor cycle performance [6]. Homogeneous dispersion of nanoparticles in a matrix and synthesis of metal-encapsulated spherical hollow carbon were tried to improve cycling behavior. However, neither of the above methods achieved marked progress [7–9].

Titanium dioxide, an insertion host material exhibiting relatively high lithium diffusion, has long been investigated as a positive electrode, later attracted high attention as a negative electrode constructed in combination with a high-voltage cathode like LiCoO<sub>2</sub>. The application of TiO<sub>2</sub> has been limited by the structure instability to lithium intercalation de-intercalation reaction, giving rise to rapid capacity fading [10,11].

In this work, we used an effective method to synthesize carbon coated titanium oxide nanocomposites as anode materials for lithium ion batteries to enhance their capacity retention. More interestingly, the kinetics of lithium intercalation and de-intercalation was also improved.

### 2. Experimental

The preparation process is shown as following, different from the reported methods to synthesize core–shell nanocomposites [12]. First, a core–shell shaped TiO<sub>2</sub>/polyacrylonitrile (PAN) precursor was synthesized via emulsion polymerization. Then, the precursor was heat-treated to turn into core–shell TiO<sub>2</sub>/C nanocomposites. The detail for one experiment is given. OP<sub>9</sub> (1.2 g as surfactant) was dispersed in deionized water (200 ml) to form micelles. Then titanium oxide nanoparticles (2.5 g, Haitai Company, China) were added and sonicated for 30 min to achieve uniform dispersion. The mixture of 2,2'-azobis(isobutyronitrile) (AIBN, 0.015 g as initiator) and acrylonitrile (3.0 g, as monomer) was added for the emulsion polymerization. Degassing was carried out for 1 h under gentle stirring, then the temperature was increased to 60 °C and the mixture was polymerized for 12 h under argon atmosphere to form a core–shell shaped TiO<sub>2</sub>/polyacrylonitrile precursor. After drying, the TiO<sub>2</sub>/PAN precursor was heat-treated at 800 °C to turn the PAN shell into a carbon one, thus TiO<sub>2</sub>/C nanocomposites were synthesized.

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Core–shell nanocomposites were identified using a powder X-ray diffractometer with monochromatized Cu K $\alpha$  radiation. Morphological observation was done by TEM (JEOL JEM 2011).

The two electrode coin-type half-cells were assembled for electrochemical performance evaluation. 85 wt% TiO<sub>2</sub> nanoparticles or TiO<sub>2</sub>/C nanocomposites were mixed with 10 wt% acetylene black (AB) as a conductive additive and 5 wt% poly(vinylidene fluoride) as a binder. The mixture slurry was coated on copper foil. After drying, it was cut into small pieces and assembled into coin-type model cells under argon atmosphere in a glove box. These pieces were used as working electrodes, Li metal as the counter electrode, Celgard 2400 as the separator, and 1 mol l<sup>-1</sup> LiPF<sub>6</sub> DEC/EC/DMC (w/w/w = 1/1/1) as the electrolyte. Cycling tests of the coin-type half-cells were performed in the voltage range of 1.4–2.5 V with a constant current 0.1 mA (0.25 C). Cyclic voltammetry (CV) of TiO<sub>2</sub> and TiO<sub>2</sub>/C electrodes were also measured at the range of 1.4–2.5 V at scanning rates of 0.1, 0.2, 0.3, 0.4, and 0.5 mV s<sup>-1</sup>, respectively.

### 3. Results and discussion

#### 3.1. Characterization of the nanocomposites

Fig. 1a is the TEM micrograph of the precursor TiO<sub>2</sub>/PAN. It shows that titanium oxide nanoparticles were coated with PAN shell. The TEM micrograph of the TiO<sub>2</sub>/C core–shell nanocomposite is shown in Fig. 1b, which presents a clear core–shell structure in which the core combines more closely with the carbon shell in comparison with that synthesized by another way [9].

The X-ray diffraction of TiO<sub>2</sub>/C nanocomposites confirms that the titania cores of the nanocomposite are in the form of rutile. By changing the ratio of TiO<sub>2</sub> and the monomer and the experimental conditions such as the amount of surfactant and the initiator, the thickness of carbon shell and the number of nanoparticles of TiO<sub>2</sub> in the shell could be adjusted.

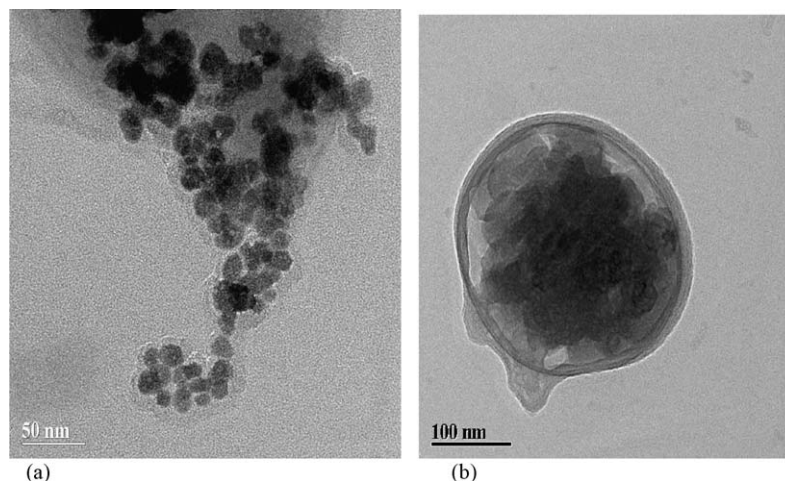


Fig. 1. TEM micrographs of TiO<sub>2</sub>/polyacrylonitrile (a) and TiO<sub>2</sub>/C (b) core–shell nanoparticles.

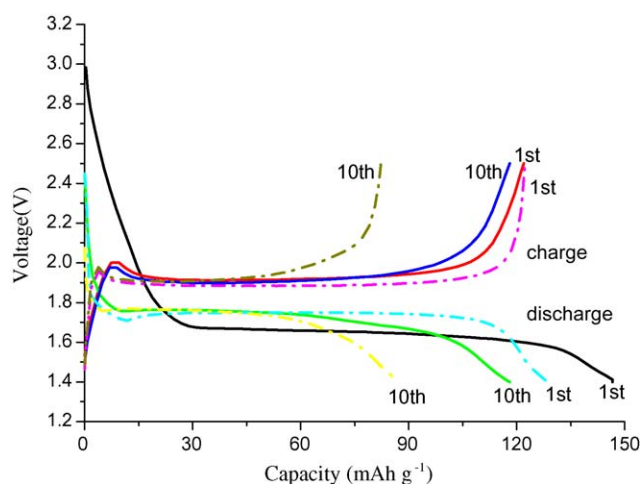


Fig. 2. Discharge and charge profiles of TiO<sub>2</sub> nanoparticles and TiO<sub>2</sub>/C core–shell nanocomposite at a constant current density of 0.25 C between 1.4 and 2.5 V (solid line: TiO<sub>2</sub>/C; dashed line: TiO<sub>2</sub>).

#### 3.2. Discharge and charge performance

The discharge and charge curves of TiO<sub>2</sub> and TiO<sub>2</sub>/C (87/13, w/w) electrodes in 1 mol l<sup>-1</sup> LiPF<sub>6</sub> DEC/EC/DMC (w/w/w = 1/1/1) are illustrated in Fig. 2. The charge and discharge capacity of carbon shell in TiO<sub>2</sub>/C nanoparticles could be ignored since the intercalation voltage of lithium ion into the prepared amorphous carbon material is below 0.8 V [13,14]. The anode of TiO<sub>2</sub> nanoparticles showed a rapid capacity fading and retained only 67.5% of the original capacity after 10 cycles. It is well known that nanoparticles have a very high surface energy and can easily agglomerate. Even at room temperature, the dispersion of nanoparticles needs quite some time for ultrasonication. In the case of cycling, lithium intercalation and de-intercalation will enhance the aggregation tendency of nanoparticles and worse and worse cycling behavior was achieved [3].

In the case of TiO<sub>2</sub>/C nanocomposite, after 10 cycles, the charge capacity still remained 96.7% (i.e., 118 mAh g<sup>-1</sup> titania) of its original capacity (i.e., 122 mAh g<sup>-1</sup> titania), which

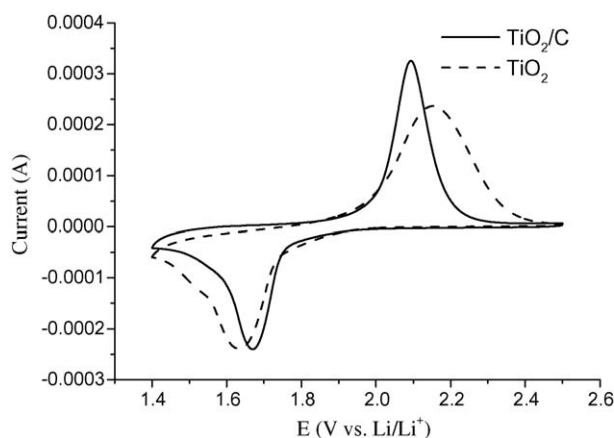


Fig. 3. Cyclic voltammograms of  $\text{TiO}_2$  and  $\text{TiO}_2/\text{C}$  electrodes measured at the range of 1.4–2.5 V at the scanning of  $0.1 \text{ mV s}^{-1}$ .

is much higher than that of  $\text{TiO}_2$ . It shows that the  $\text{TiO}_2/\text{C}$  core-shell nanocomposite has a better capacity retention capability. The main reason is that the coated carbon shell can suppress the aggregation of  $\text{TiO}_2$  nanoparticles and thus increase their structure stability during cycling. Of course, the particles of the nanocomposites will also aggregate. However, the existence of nanocarbon shell prevented the direct aggregation of the nanoparticles of  $\text{TiO}_2$ , and the nanoproperties of the core particles were always retained.

As to the passing of lithium ions through this kind of nanocarbon shell of the nanocomposites, it is very clear to understand. At first, carbons from heat-treatment of PAN at a temperature  $< 1000^\circ\text{C}$  are amorphous and consist of a lot of micropores, which can definitely be passages for lithium ions [14–16]. In addition, it has been shown that lithium ions can pass through nanooxides layers such as  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SnO}_2$  and  $\text{ZrO}_2$  and without any problem and the coating layers can provide better rate capability [17]. Furthermore, lithium ions can pass through copper foils very easily though they do not intercalate into or form alloys with copper [18].

### 3.3. Cyclic voltammetry

Fig. 3 shows the cyclic voltammograms (CVs) of  $\text{TiO}_2$  and  $\text{TiO}_2/\text{C}$  electrodes measured between 1.4 and 2.5 V at the scanning rate of  $0.1 \text{ mV}$ . It shows that the separation between reduction and oxidation peaks ( $\Delta V$ ) of  $\text{TiO}_2/\text{C}$  nanocomposites decreased compared with that of the original  $\text{TiO}_2$  nanoparticles, demonstrative of a better reversibility of nanoparticles after coating by carbon shell [19]. The results from CV data at different scan rates present much more interesting phenomena. We found the oxidation peak current at different scan rates was in proportion to root of the scan rate,  $v^{1/2}$ , indicating that the reaction kinetics was controlled by the diffusion step. Moreover, based on the CV data at different scan rates and the following equation:

$$I_p = 2.69 \times 10^5 A n^{3/2} C_0 D^{1/2} v^{1/2}$$

where  $n$  is the number of electrons per molecule during the intercalation,  $A$  the surface area of the anode,  $C_0$  the concentration

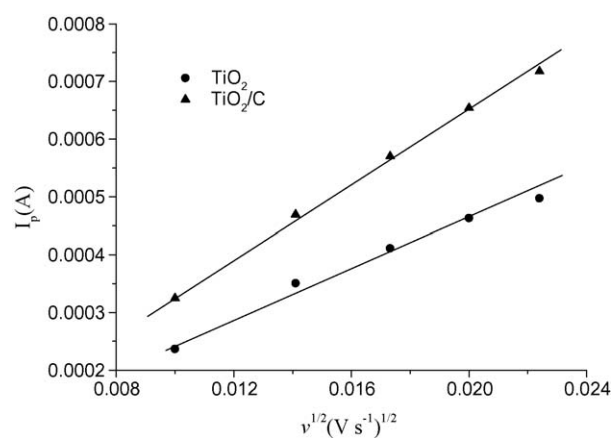


Fig. 4. Relationship between  $I_p$  and  $v^{1/2}$  of  $\text{TiO}_2$  nanoparticles and the core-shell  $\text{TiO}_2/\text{C}$  nanocomposite.

of lithium ions,  $D$  the diffusion coefficient of lithium ion and  $v$  is the scan rate. A linear relationship between  $I_p$  and  $v^{1/2}$  was obtained as shown in Fig. 4, and the diffusion coefficient of lithium ions in both  $\text{TiO}_2/\text{C}$  nanocomposite and  $\text{TiO}_2$  nanoparticles were calculated according to the slopes. It was found that the diffusion coefficient of lithium ion in  $\text{TiO}_2/\text{C}$  nanocomposite ( $1.07 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ) was about one order of magnitude higher than that in  $\text{TiO}_2$  nanoparticles ( $1.97 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ ), indicating that the carbon shell at the surface of  $\text{TiO}_2$  nanoparticles was beneficial for the diffusion of lithium ions since it is conductive. This effect is similar to that of carbon coating in the cathode materials, which also favors lithium intercalation and de-intercalation [20]. Of course, different thickness of the coated carbon shell will present different effects.

## 4. Conclusion

Our prepared  $\text{TiO}_2/\text{C}$  core-shell nanocomposites as anode materials for lithium ion batteries present a better cycle performance and a higher diffusion coefficient of lithium ions compared with the virginal  $\text{TiO}_2$  nanoparticles. The main reason is ascribed to the existence of conductive carbon shells and their close combination with the cores. The carbon shell suppressed the aggregation of  $\text{TiO}_2$  nanoparticles and thus increased their structure stability during cycling. This provides an effective way to improve the cycling and kinetics of nanoanode materials.

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