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Tuning the Carbon Content on TiO$_2$ Nanosheets for
Optimized Sodium Storage

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Abstract

Titanium dioxide (TiO$_2$) has been considered as a promising anode candidate for sodium ion batteries (NIBs). In this work, we report the synthesis of anatase TiO$_2$ nanosheets coated by nitrogen doped carbon derived from dopamine precursor (TiO$_2$@C) as high performance anode materials for NIBs applications. The carbon contents can be controlled from 2.6 wt% to 10.4 wt% by varying the polymerization time of dopamine. X-ray diffraction patterns confirm there is no phase change after carbon coating. When employed as an anode for NIBs, the TiO$_2$@C composites exhibit improved electrochemical performances in terms of higher specific capacity and better cycling stability compared to pure TiO$_2$ nanosheets. Notably, with a carbon content of 4.8 wt%, the TiO$_2$@C nanosheets delivers a reversible capacity of 180 mA h g$^{-1}$ and shows stable cycling performance with no discharge capacity decay from 2$^{nd}$ cycle onward over 50 cycles. Even at high current density of 10 C, the capacity still remains 82 mA h g$^{-1}$. The excellent cycling stability and rate performances can be
ascribed to the protective effects of carbon coating layer which reserves the structure stability and enhances electrical conductivity during cycling.

*Key words:* TiO₂ nanosheets, carbon coating, anode, sodium storage

1. Introduction

There are increasing demands of rechargeable batteries in large-scale applications such as stationary electrical storage and electric-powered transportation vehicles [1, 2]. Lithium-ion batteries (LIBs) are considered as promising candidates because of their advantages such as long cycle life and high energy density [2, 3]. However, limited global lithium reserve can be depleted if large-scale production of LIBs is realized in the near future. Therefore, sodium ion batteries (NIBs) have attracted increasing attention from researchers as alternatives to LIBs due to the low cost and natural abundance of sodium sources [4]. However, the interactions between Na ions and the storage hosts vary greatly from those between lithium ions and lithium analogues because of the larger ionic radius and higher redox potential of Na than Li [5, 6]. Large interstitial space within the crystallographic structure of electrode materials is required for adequate electrochemical capacity and cyclability when considering large sodium ions.

Recently, significant progress has been made on the exploration of cathode materials by several research groups. Most of the researches are focused on lithium analogues, such as transition metal oxides and polyanionic materials which are now considered as high-performance electrode materials in LIBs [7-12]. In the case of anode part, graphite, the most utilized anode for commercial LIBs, was proved to have limited
sodium intercalation capability [13]. In the last few years, hard carbon and partially graphitic carbonaceous nanostructured materials were explored and exhibited reversible sodium insertion/extraction capability due to the large interlayer distance; however the rate capabilities are limited due to their physical properties [14, 15]. Other materials, including carbon, Sn, P, Sb and metal alloys, have also been demonstrated as promising sodium anode materials with high charge storage, while their applications were hindered by the large volume changes [16-19]. Meanwhile, another class of titanium based materials remains relatively unexplored in NIBs system. Amongst them, anatase TiO$_2$ which was previously investigated as a lithium-ion host material in LIBs due to its low price, high safety, non-toxicity, abundance in the earth’s crust, and negligible volume change(<4%) during Li$^+$ insertion/extraction [20-26], has attracted great attention. Yet the reports on TiO$_2$ as Na anode material are quite limited up to date [23, 27-29]. Nevertheless the theoretical study by Hagfeldt et al. demonstrated the activation barrier for sodium insertion into the TiO$_2$ anatase crystal lattice was supposed to be close to that for lithium which indicates promising candidate role of TiO$_2$ in NIBs considering the large sodium ionic radius [27].

Recently, Xiong et al. reported that amorphous TiO$_2$ nanotubes exhibited increasing capacities from 60 to 150 mA h g$^{-1}$ in 15 cycles at 0.05 A g$^{-1}$ [23]. Xu et al. reported nanocrystalline anatase TiO$_2$ as Na-ion hosts for the first time and a capacity of 150 mA h g$^{-1}$ can be retained after 100 cycles [24]. Kim et al. reported TiO$_2$@C nanorods were able to exhibit higher reversible capacities, better cycling stability and superior rate capabilities than pristine TiO$_2$ nanorods [28]. The promising electrochemical performances of TiO$_2$ have encouraged further investigation as anode materials for NIBs. Carbon-coated TiO$_2$ microsphere electrodes delivered a high capacity (155 mA h g$^{-1}$) with excellent capacity retention over 50 cycles [30]. The working mechanism of
sodium insertion in TiO$_2$ was investigated by Wu et al. which revealed that irreversible formation of metallic titanium, sodium superoxide, and oxygen during the process [31]. A number of works on TiO$_2$ nanostructured materials have been reported recently, such as carbon coated TiO$_2$ hollow spheres and TiO$_2$ nanocubes [32-34]. Although the practical application of TiO$_2$ in NIBs is still far away, these encouraging results suggest that the fabrication of nanostructured TiO$_2$ and conductive carbon coating layer may benefit the sodium ion and electron diffusion, leading to superior electrochemical properties.

Herein, anatase TiO$_2$ nanosheets synthesized from a hydrothermal method are examined as an anode material for NIBs application. A nitrogen-doped carbon layer derived from dopamine is employed to increase the conductivity and further stabilize Na$^+$ insertion behaviors. The TiO$_2$@C composite with a carbon content of 4.8 % exhibit the best cycling stability and rate performance. Our study reveals it is important to tailor the carbon contents of TiO$_2$@C composites to achieve optimized sodium storage. The idea of tailoring the carbon contents can also be used to guide the synthesis of other metal/metal oxide-carbon composites for optimized electrochemical performance as NIBs anode materials.

2. Experimental Section

2.1. Synthesis of TiO$_2$ Nanosheets

The TiO$_2$ nanosheets were synthesized according to previous work [35]. In a typical synthetic process, 10 mL of Ti(OBu)$_4$ and 1.2 mL of 50 wt% hydrofluoric acid solution were mixed in a Teflon-lined autoclave with a volume of 35 mL. It should be noted that the whole process should be performed in a fume hood with well personal protection
and extreme caution. Then the autoclave was kept at 200 °C for 24 h. After cooling down to room temperature, the white precipitates were collected by centrifugation and washed with ethanol and distilled water for several times. Finally the products were dried in an oven at 50 °C overnight and then annealed at 400 °C in air for 2 hours.

For the carbon coating, the annealed TiO₂ (50 mg) were dispersed in 10 mM Tris-buffer (pH: ~8.5) by ultrasonication for one hour to form a uniform suspension. Dopamine (25 mg) was then added to the suspension under stirring. To obtain different amount of carbon coating in the final products, the polymerization process was kept for three different periods of time (1, 1.75 and 2.5 h). Finally, the three obtained TiO₂/polydopamine samples were carbonized at 750 °C for 5 h in Ar atmosphere to produce TiO₂@C nanocomposites which are hereafter named as TiO₂@C-1 for 1 h, TiO₂@C-2 for 1.75 h and TiO₂@C-3 for 2.5 h, respectively.

2.2. Materials Characterization

The morphologies of the prepared samples were observed through scanning electron microscopy (SEM, JEOL 7001F) operated at 15 kV and transmission electron microscopy (TEM, JEOL 2010, equipped with energy-dispersive X-ray spectroscopy for compositional analysis) at 200 kV. The crystalline structures of the materials were obtained on a Bruker Advanced X-Ray Diffractometer with Cu Kα radiation (λ=0.15406 nm) at a scanning rate of 1°/min. X-ray photoelectron spectra (XPS) were acquired on a Kratos Axis ULTRA X-ray Photoelectron Spectrometer using a monochromatic Al KR (1486.6 eV) X-ray source and a 165 mm hemispherical electron energy analyzer. The thermogravimetry analysis (TGA) were conducted on a TGA/DSC1 STAR® System in flowed air environment (50-700 °C, 5 °C min⁻¹).
2.3. Electrochemical Measurement

The working electrode was prepared by mixing active materials, acetylene black and polyvinylidene fluoride (PVDF) in a weight ratio of 8 : 1 : 1. N-Methyl-2-pyrrolidone (NMP) was later added to form homogenous slurry which was then casted on a copper foil. The resultant electrode film was subsequently dried in a vacuum oven at 120 °C overnight. Electrodes punched from the copper film were then assembled into 2032 coin cells in a glove box (MBraun, Germany) with oxygen and water less than 0.1 ppm. A piece of sodium foil and a solvent of 1 M NaClO4 in propylene carbonate (PC) were employed as counter electrodes and electrolyte, respectively, which were separated by a glass fiber membrane (GF/B, Whatman). The cyclic voltammetry (CV) curves were obtained on an electrochemistry workstation (CHI660E) in the voltage range of 0.01-2.5 V at a scan rate of 0.1 mV s⁻¹. Electrochemical Impedance Spectra (EIS) was collected on the CHI660E electrochemical workstation at room temperature. The galvanostatic charge/discharge tests were performed on a Land Battery Tester (LAND, 5V10mA) at 33 mA h g⁻¹ (0.1 C). The specific capacities were calculated based on the mass of whole active materials in the electrodes.

3. Results and Discussion

The crystalline structures of pristine TiO2 nanosheets and TiO2@C samples are investigated by X-ray diffraction (XRD) (Fig.1a). All the identified XRD peaks are well corresponded to the anatase phase with the tetragonal space group of I41/amd(141). No peaks of other phases can be detected, suggesting good reservation of the pristine crystalline structure even after calcination at high temperature in an inert atmosphere. To determine the carbon contents of TiO2@C nanosheets composites, TGA analysis were carried out in air from 50 °C to 700 °C with a heating rate of 5 °C min⁻¹. It is
obvious that the carbon contents increases proportionally with the polymerization time (Fig. 1b). The slight weight loss below 200 °C can be ascribed to the evaporation of the residual moisture, whereas the major weight loss between 200 °C and 500 °C is attributed to the combustion of carbon in air. The carbon contents are determined to be approximately 2.6 wt% for TiO$_2$@C-1, 4.8 wt% for TiO$_2$@C-2 and 10.4 wt% for TiO$_2$@C-3.

The pristine TiO$_2$ nanosheets and TiO$_2$@C-2 were characterized by XPS analysis to study their surface chemical compositions. Compared with pristine TiO$_2$ nanosheets, TiO$_2$@C-2 with carbon coating has a decreased intensity in Ti2p and O1s peaks, whereas an increased intensity in C1s peak. In addition to the presence of Ti, O and C elements in the pristine TiO$_2$ nanosheets, the overall XPS spectrum of TiO$_2$@C-2 also verifies the existence of N element on the particle surface as shown in Fig. 2a, which originates from the nitrogen containing carbon precursor. The high resolution scan of N1s peak in Fig. 2b can be fit into tree peaks assigned to primary and secondary and tertiary amine of polydopamine, respectively[36, 37]. It has been demonstrated nitrogen-doping can enhance the electrical conductivity and ion permeability, which is beneficial for the improvement of electrochemical properties [38, 39].

The structure and morphology of the obtained pristine TiO$_2$ nanosheets and TiO$_2$@C composites were further investigated by the SEM and TEM analysis. The SEM images in Fig. 3a clearly demonstrate an overview of the uniform bare TiO$_2$ nanosheets with diameters of 50-100 nm. After carbon coating, TiO$_2$@C nanocomposites show distinguishable platelet shape similar with the pristine TiO$_2$, indicating well preservation of original structure without severe aggregation after polydopamine
coating and carbonization at high temperature (Fig. 3b-d). In line with the observation in SEM images, the low-magnification TEM images in Fig. 4a show the pristine TiO$_2$ nanosheets consist of rectangular platelets with well-defined square outline and flat surface in an average side length and thickness of 50-100 nm and 5 nm, respectively. After carbon coating, a thin carbon layer surrounding the TiO$_2$ nanosheets can be observed, while no significant change in the structure and morphology of TiO$_2$@C is found (Fig. 4b and c for sample TiO$_2$@C-2). The high-resolution TEM (HRTEM) image recorded from a single nanosheet of TiO$_2$@C-2 in Fig. 4d presents well-resolved lattice fringes with spacing of 3.56 Å, corresponding to the (101) interplane spacing of anatase TiO$_2$. The thickness of uniform carbon layer on TiO$_2$ nanosheets is measured to be approximately 2 nm. The energy-dispersive X-ray spectroscopy (EDS) analysis indicates that Ti, O, C, and N are homogeneously distributed throughout the TiO$_2$@C-2 composite (Fig. 5). Combining these results with the TEM images in Fig. 4, we can conclude that carbon layers should be successfully coated on the surface of TiO$_2$ nanosheets.

The sodium insertion/extraction behaviors in TiO$_2$ nanosheets and TiO$_2$@C-2 were selected to investigate by CV measurement in the voltage range of 0.01-2.5 V (Fig. 6). Similar redox peaks can be identified from the CV curves of the pristine TiO$_2$ nanosheets electrode (Fig. 6a) and TiO$_2$@C-2 electrode (Fig. 6b), indicating identical electrochemical behaviors for TiO$_2$ nanosheets with or without carbon coating layer. In both of the CV curves, large irreversible peaks located at around 0.8 V in the first cathodic scanning are probably related to the irreversible decomposition of electrolyte and the formation of a solid electrolyte interphase (SEI) layer on the electrode surface which are common in most anode materials [39, 40]. A pair of redox peaks located at 0.6 V at cathodic scans and 0.8 V at anodic scans become pronounced during the
subsequent cycling, indicating stabilized Na\textsuperscript{+} intercalation/deintercalation processes. These peaks can be ascribed to the insertion/extraction of Na\textsuperscript{+} accompanied with the reversible Ti\textsuperscript{4+}/Ti\textsuperscript{3+} redox reaction [28].

The cycling performance of pristine TiO\textsubscript{2} nanosheets and TiO\textsubscript{2}@C electrodes were investigated in the voltage range from 0.01 V to 2.5 V at 0.1 C (33 mA g\textsuperscript{-1}). Figure 7a and 7b show the galvanostatic charge/discharge profiles of pristine TiO\textsubscript{2} nanosheets and TiO\textsubscript{2}@C-2. No well-defined voltage plateaus can be identified in these charge/discharge profiles except small plateaus in the voltage range of 1.0-0.3 V, which are different from the electrochemical behaviors of TiO\textsubscript{2} in LIBs [41]. An irreversible capacity larger than 350 mA h g\textsuperscript{-1} are observed in both electrodes in the 1\textsuperscript{st} cycle, resulting in relative low Coulombic efficiencies. The irreversible capacity loss is probably correlated with the formation of an SEI film as identified in the aforementioned CV test. Moreover, it is reported that the irreversible trapping of sodium ions in the TiO\textsubscript{2} lattice and structural rearrangement in TiO\textsubscript{2} lattice may also be responsible for the large capacity loss in the 1\textsuperscript{st} cycle[29, 33].

Figure 7c demonstrates the discharge capacities of pristine TiO\textsubscript{2} nanosheets and TiO\textsubscript{2}@C electrodes. The reversible discharge capacity of pristine TiO\textsubscript{2} nanosheets decreases from 210 mA h g\textsuperscript{-1} in the 2\textsuperscript{nd} cycle to only 65 mA h g\textsuperscript{-1} in the 50\textsuperscript{th} cycle, corresponding to a decrease of 2.95% per cycle. However, regardless of the carbon coating amount, all TiO\textsubscript{2}@C electrodes exhibit improved cycling stability. TiO\textsubscript{2}@C-2 with a carbon content of 4.8 wt\% shows the best capacity retention among the three electrodes. Even after 50 cycles, the discharge capacity is still as high as 180 mA h g\textsuperscript{-1}, which is almost 100 % of the discharge capacity in the 2\textsuperscript{nd} cycle. The Coulombic efficiency of TiO\textsubscript{2}@C-2 electrode also increases drastically to 95.2% after 5 cycles and
stabilizes over 98% from 10 cycles onward. Meanwhile, TiO$_2$@C-1 and TiO$_2$@C-3 electrodes also show much superior cycling stability compared with pristine TiO$_2$ nanosheets, but still inferior to TiO$_2$@C-2. Capacities of 142.2 mA h g$^{-1}$ and 153.8 mA h g$^{-1}$ are retained after 50 cycles for TiO$_2$@C-1 and TiO$_2$@C-3, respectively.

Figure 7d demonstrates the rate capability of pristine TiO$_2$ nanosheets and TiO$_2$@C at various current rates ranging from 0.1 C to 10 C. The advantages of carbon coating in rate performances become more significant especially at high current. The pristine TiO$_2$ electrode exhibits poor rate capabilities with almost no capacity delivered before the current density increase to 5 C, whereas higher rate capacities are achieved for the three TiO$_2$@C electrodes. It comes out that the best rate capability occurs in TiO$_2$@C-2, retaining 82 mA h g$^{-1}$ even at 10 C. The superior electrochemical performance indicates a more efficient and stabilized Na$^+$ insertion/extraction behavior in TiO$_2$@C. Moreover, tailoring the carbon contents of TiO$_2$@C is essential to achieve optimized electrochemical performances. The reason may be attributed to the growth of TiO$_2$ clusters is unable to be effectively suppressed during cycling when the carbon coating layer is too thin [42]; while too thick carbon layer will interrupt the efficiency of sodium insertion/extraction processes. Herein, the TiO$_2$@C-2 composite with moderate carbon content of 4.8 % is concluded to be the optimal composition which delivers the best electrochemical performances.

Nyquist plots obtained from EIS measurements of bare TiO$_2$ nanosheets and TiO$_2$@C electrodes after 10 cycles in full charged state are shown in Fig. 8. The spectra are constituted by a semicircle loop at high-to-medium frequencies and a straight line in the low frequency region. The corresponding diameter of the semicircle loop is related to the charge-transfer resistance at the electrode/electrolyte interface. It can be seen
that the diameters of the semicircle decreases after carbon coating, all the TiO$_2$@C electrodes exhibit lower resistance than the bare TiO$_2$ nanosheets. However, TiO$_2$@C-2 demonstrates the lowest interface charge transfer resistance among the three carbon coated electrodes which can further explain its superior cyclic and rate performances.

4. Conclusions

TiO$_2$ nanosheets have been investigated as an anode material for NIBs application. The carbon coating was revealed to be an effective strategy to reserve the structure integrity and improve the conductivity of electrodes. By tailoring the carbon contents of the TiO$_2$@C composites through controlling the polymerization time, excellent cycling stability and superior rate capabilities have been achieved. TiO$_2$@C-2 with a carbon content of 4.8 wt% delivers a high capacity of 180 mA h g$^{-1}$ even after 50 cycles with 100 % retention and outstanding rate capability (82 mA h g$^{-1}$ at 10 C). Our strategy can be extended to other electrode materials, such as Sn/SnO$_2$ and transition metal oxides, to achieve appropriate carbon content in the nanocomposites for optimized sodium storage.

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Fig. 1 (a) XRD patterns of the four types of TiO$_2$ materials; (b) TGA thermogram of the four types of composites.

Fig. 2 (a) XPS analysis of pristine TiO$_2$ nanosheets and TiO$_2$@C-2; (b) XPS spectra of the N1s peak for TiO$_2$@C-2.
**Fig. 3** SEM images of (a) bare TiO$_2$ nanosheets; (b) TiO$_2$@C-1; (c) TiO$_2$@C-2; (d) TiO$_2$@C-3.
Fig. 4 TEM images of (a) bare TiO$_2$ nanosheets and (b) TiO$_2$@C-2. (c, d) HRTEM images of TiO$_2$@C-2 nanoparticle.
Fig. 5 (a) low magnification TEM and (b) Scanning TEM (STEM) images, and EDS element maps of TiO$_2$@C-2 composite: (c) Ti, (d) O, (e) C, and (f) N.

Fig. 6 CV curves of (a) TiO$_2$ nanosheets and (b) TiO$_2$@C-2.
Fig. 7 Galvanostatic charge/discharge curves of (a) TiO$_2$ nanosheets and (b) TiO$_2$@C-2 at 0.1 C; (c) cycling performance at 0.1C and (d) the rate performances of four electrodes.

Fig. 8 Nyquist plots of four electrodes after cycling for 10 cycles.