Aerosol synthesis of trivalent titanium doped titania/ carbon composite microspheres with superior sodium storage performance

Doudou Guan¹, Qiang Yu¹, Chang Xu¹, Chunjuan Tang^{1,2}, Liang Zhou¹ (\bowtie), Dongyuan Zhao¹, and Liqiang Mai^{1,3} (\bowtie)

¹ State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, International School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China

² Department of Mathematics and Physics, Luoyang Institute of Science and Technology, Luoyang 471023, China

³ Department of Chemistry, University of California, Berkeley, California 94720, United States

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ABSTRACT

Trivalent titanium doped titania/carbon (TiO_{2-x}/C) composite microspheres have been prepared by a facile aerosol method (ultrasonic spray pyrolysis) using titanium (IV) bis(ammonium lactato)dihydroxide (TiBALDH) as the sole precursor. The obtained TiO_{2-x}/C microspheres have particle sizes in the range of 400–1,000 nm. When evaluated as anode material for sodium-ion batteries (SIBs), they provide a high reversible capacity of 286 mA·h·g⁻¹ with good cycling performance. A capacity of 249 mA·h·g⁻¹ can be achieved after 180 cycles at 50 mA·g⁻¹, which is more than three times higher than that of white TiO₂ microspheres (77 mA·h·g⁻¹). The superior sodium storage performance of these TiO_{2-x}/C composite microspheres can be attributed to the simultaneous introduction of Ti³⁺ and oxygen vacancies, ultrafine grain size, as well as the conductive carbon matrix. This study provides a facile and effective approach for the production of TiO_{2-x}/C nanocomposites with superior sodium storage performance.

1 Introduction

In recent years, extensive efforts have been dedicated to the development of sodium-ion batteries (SIBs) because of their low cost, abundant sources, and great potential to overcome the drawbacks of lithium-ion batteries (LIBs) in large-scale energy storage [1–4]. However, the large radius of the sodium ion (0.102 nm) makes it difficult to find perfect host materials for rapid and reversible Na⁺ insertion/extraction [5]. Fortunately, significant progresses have been made in the development of anode materials, such as hard carbon [6–9] and Sb-based materials [10–14]. However, for practical applications, the present achievements

Address correspondence to Liang Zhou, liangzhou@whut.edu.cn; Liqiang Mai, mlq518@whut.edu.cn

at the laboratory scale are still unsatisfactory. Hard carbon materials, based on an intercalation mechanism, can be produced at a reasonable cost; however, their capacity and cycling stability still need to be improved. For Sb-based materials, they are based on alloying or the combination of alloying and conversion mechanisms. This feature endows them with high capacity; however, this is accompanied by a huge volume expansion during Na⁺ intercalation, which is detrimental to the cycling performance.

Titanium dioxide (TiO₂), which is nontoxic, low-cost, abundant, and environmentally benign, has been extensively studied in photocatalysis [15], photovoltaics [16], LIBs [17–20] and SIBs [21]. TiO₂ has several polymorphs, including amorphous TiO₂ [22, 23], rutile [24, 25], anatase [26–32], brookite [33], and TiO₂ (B) [34, 35]. Theoretically, TiO₂ can deliver a sodium storage capacity of 335 mA·h·g⁻¹ at a relatively low but safe potential (~0.8 V vs. Na⁺/Na) [21]. However, some concerns still remain about the intrinsic poor conductivity of TiO₂.

One effective way to solve this issue consists in compositing TiO₂ with conductive carbon. Kim et al. [27] reported carbon-coated anatase TiO₂ nanorods, which can deliver an initial capacity of 193 mA·h·g⁻¹ at a current density of 10 mA·g⁻¹. Huang et al. [36] synthesized a graphene-coupled TiO₂ composite with high rate capability and long cycle life. Besides, the authors further demonstrated the charge storage mechanism of intercalation pseudocapacitance in graphene-TiO₂, which fulfilled the excellent rate and cycling performance requirements. The second approach to improve the sodium storage performance of TiO₂ is to introduce Ti³⁺ and oxygen vacancies through a reduction reaction. Ji et al. [37] synthesized black TiO₂ nanoparticles with a diameter of 30 nm through simple hydrolysis and reduction processes. The black TiO₂ nanoparticles delivered specific capacities of 207.6 and 91.2 mA·h·g⁻¹ at 0.2 and 20 C, respectively. This demonstrates that the introduction of Ti³⁺ and oxygen vacancies in TiO₂ may not only enhance the intrinsic electronic conductivity but also improve the kinetics of Na⁺ uptake/release. The third approach to enhance the electrochemical performance of TiO₂ is downsizing. Passerini et al. [31] synthesized 11 nm-TiO₂ nanoparticles with carbon coating. The composites showed a high capacity of 242 mA· $h\cdot g^{-1}$, which was much higher than that of 40 nm-TiO₂/C (189 mA· $h\cdot g^{-1}$). Thus, it is worthwhile to integrate the above-mentioned three methods to further boost the sodium storage performance of TiO₂.

In this work, trivalent titanium doped titania/carbon (TiO_{2-x}/C) composite microspheres were fabricated by a facile aerosol method (ultrasonic spray pyrolysis) [38, 39]. The constructed TiO_{2-x}/C integrates the three above-mentioned design principles: (1) TiO_{2-x}/C contains a considerable amount of Ti³⁺ and oxygen vacancies, (2) TiO_{2-x} has an ultrafine grain size (< 10 nm), and (3) TiO_{2-x} is homogeneously distributed within an amorphous carbon matrix. Benefiting from this rational design, the obtained TiO_{2-x}/C composite microspheres provided a high specific capacity (286 mA·h·g⁻¹ at 50 mA·g⁻¹) and excellent cycling stability (retaining 249 mA·h·g⁻¹ after 180 cycles at 50 mA·g⁻¹) in sodium storage applications.

2 Experimental

2.1 Preparation of TiO_{2-x}/C composites

In a typical synthesis, 5 mL of titanium(IV) bis(ammonium lactato)dihydroxide (TiBALDH) (50 wt.% in H₂O) was dissolved in 45 mL of deionized water and stirred for 30 min. After that, the aqueous solution was pumped into an ultrasonic atomizer and atomized at an ultrasonic power of 8.0 W (USP 10, Siansonic Technology Co., Ltd). The resulting mist was then blown into a quartz tube by flowing air at a speed of 5 L·min⁻¹; the quartz tube was preheated to 600 °C. A brown intermediate was collected by an electrostatic collector. TiO_{2-x}/C composite microspheres were obtained by annealing the brown intermediate under H_2/Ar (5%/95%) atmosphere at 600 °C for 5 h with a temperature ramping rate of 5 °C·min⁻¹. White TiO₂ (W-TiO₂) microspheres were obtained by calcining the same intermediate in air at 600 °C for 5 h.

2.2 Materials characterization

X-ray diffraction (XRD) patterns were collected using a Bruker D8 Discover X-ray diffractometer equipped with a Cu K α radiation (λ = 1.5418 Å). Scanning electron microscope (SEM) images were obtained on a JEOL-7100F SEM at 20 kV. Transmission electron microscope (TEM) images were obtained on a JEM-2100F TEM with an accelerating voltage of 200 kV. Energy dispersive X-ray spectra (EDS) were measured on an Oxford IE250 system. Brunauer–Emmett–Teller (BET) surface areas were calculated from nitrogen sorption isotherms measured at 77 K using a Tristar-3020 instrument. X-ray photoelectron spectra (XPS) were recorded on a VG Multilab 2000 X-ray photoelectron spectrometer. Raman spectra were obtained using a Renishaw inVia micro-Raman spectroscopy system. Thermogravimetric differential scanning calorimetry (TG–DSC) was performed using a STA 449F3 instrument. Carbon content analysis was also determined by Vario EL cube CHNSO elemental analyzer.

2.3 Electrochemical characterization

In order to evaluate the electrochemical behavior, 2016 type coin cells were assembled in a glove box filled with argon. The working electrodes were composed of 70 wt.% of active material, 20 wt.% of acetylene black, and 10 wt.% of carboxymethyl cellulose (CMC) binder; the mass loading of the active material was ~1.5 mg·cm⁻². Metallic sodium foil was used as the anode. The electrolyte was composed of 1 M NaClO₄ dissolved in a mixture of ethylene carbonate/ dimethyl carbonate (EC/DMC, 1:1 by volume) with 5 wt.% of fluoroethylene carbonate (FEC) as additive. Galvanostatic charge/discharge (0.01-2.5 V) measurements were performed on multichannel battery testers (LAND, CT2001A). Cyclic voltammetry (CV, 0.1–2.5 V) was performed on a CHI1000C electrochemical workstation. Electrochemical impedance spectroscopy (EIS) experiments were recorded on Autolab potentiostat/galvanostat (PGSTAT302N).

3 Results and discussion

The synthesis of the TiO_{2-x}/C and W-TiO₂ composite microspheres includes two steps (Fig. 1): (1) ultrasonic spray pyrolysis and (2) subsequent annealing in either H₂/Ar (5%/95%) or air. TiBALDH, a water soluble molecule, was used as the sole precursor. In contrast with conventional Ti precursors, such as titanium tetrachloride (TiCl₄) and titanium alkoxide (Ti(OM)₄), TiBALDH does not undergo quick hydrolysis and condensation upon contact with water. The excellent water stability of TiBALDH originates from its saturated octahedral coordination as well as the stable chelating structure. In step 1, the TiBALDH aqueous solution is atomized into micrometer-sized droplets; carried by the flowing air, the droplets fly into the heating zone. Here, the TiBALDH is concentrated and partially decomposed, forming a brown intermediate. During annealing in H₂/Ar in step 2, the organic moiety of TiBALDH is converted into amorphous carbon, while Ti⁴⁺ is partially reduced to Ti³⁺, leading to the formation of TiO_{2-x}/C composites. If the intermediate is annealed in air, W-TiO₂ microspheres can be obtained.

Figure 2(a) illustrates the XRD patterns of the TiO_{2-x}/C and W-TiO₂ microspheres. The W-TiO₂ microspheres could be identified as a mixture of anatase (96.4%) (JCPDS NO. 21-1272) and rutile (3.6%) (JCPDS NO. 21-1276) phases. In the case of the TiO_{2-x}/C composite microspheres, all the diffractions could be indexed to the anatase phase. No diffractions from carbon could be detected, implying an amorphous feature of carbon. The absence of a rutile phase indicates that the in situ generated carbon suppresses its formation in TiO_{2-x}/C , which is in good agreement with a previous study [31]. On the basis of the Rietveld refinement, the unit cell parameters *a*, *b*, and *c* of the anatase phase were acquired (Table S1 in the Electronic Supplementary Material (ESM)). For the TiO_{2-x}/C composite microspheres, the lattice parameters were determined to be a = b = 3.8110 Å and c = 9.5189 Å, while for the W-TiO₂ microspheres, the lattice parameters of the anatase phase were a = b = 3.7857 Å and c = 9.5175 Å. Compared with the W-TiO₂ microspheres, the lattice parameters a, b, and c of the TiO_{2-x}/C composite microspheres are obviously expanded, as reflected by the slight left-shift of the (101) diffraction. The expanded lattice parameters of the TiO_{2-x} grains originate from the larger ionic radius of Ti³⁺ (0.56 Å) compared to Ti⁴⁺ (0.48 Å) [40]. Another obvious difference is that the diffraction peaks of the TiO_{2-x}/C composite microspheres are universally much wider than those of W-TiO₂, suggesting a much smaller average grain size. By applying the Scherrer equation to the (101) diffraction, the average crystallite sizes of the TiO_{2-x}/C and W-TiO₂ microspheres were determined to be 7.6 and 16.8 nm, respectively. Two reasons are



Figure 1 Schematic synthesis of the TiO_{2-x}/C and W-TiO₂ microspheres. Step 1: ultrasonic spray pyrolysis. Step 2: annealing in H₂/Ar (5%/95%) or air.



Figure 2 (a) XRD patterns and (b) Raman spectra of the TiO_{2-x}/C and W- TiO_2 microspheres.

responsible for the smaller crystallite size of TiO_{2-x}/C : (1) the *in situ* generated carbon from the decomposition of TiBALDH inhibits the overgrowth of TiO_2 [41]; (2) the Ti^{3+} ions and accompanying oxygen vacancies break the lattice periodicity and octahedral symmetry of [TiO_6] to a certain degree, resulting in a disorder-induced lattice strain and grain size reduction [42].

Figure 2(b) depicts the Raman spectra of TiO_{2-x}/C and W-TiO₂. Five bands located at 155.7, 204.3, 398.6, 515.3, and 637.2 cm⁻¹ can be observed for the W-TiO₂ microspheres, in agreement with Ref. [43]. On the other hand, the Raman spectra of the TiO_{2-x}/C composite microspheres showed an obvious blue shift, peak broadening, and intensity weakening. According to previous Refs. [37, 43-45], such differences in the Raman spectra can be caused by the grain size reduction (< 10 nm) and the existence of oxygen vacancies induced by Ti^{3+} .

Besides the five bands from the anatase phase, two additional bands located at 1,343.5 and 1,594.4 cm⁻¹, corresponding to the D and G bands of carbon, could also be observed in the TiO_{2-x}/C composite microspheres [27]. The I_D/I_G ratio was 1.05, confirming the amorphous nature of carbon.

TG analysis was used to determine the carbon content of TiO_{2-x}/C (Fig. S1 in the ESM). The weight loss under 200 °C was caused by the evaporation of the adsorbed water, while the slight weight gain (1.0 wt.%) in the temperature region of 500–550 °C could be associated with the oxidation of Ti³⁺. Finally, the weight loss between 400 and 700 °C was assigned to the combustion of carbon. From the TG analysis, the carbon content of the TiO_{2-x}/C composite microspheres was estimated to be 16.5 wt.%. CHNSO elemental analysis was also employed to quantify the carbon content of TiO_{2-x}/C, which was found to be 19.7 wt.%.

The morphology and microstructure of the TiO_{2-x}/C composite microspheres are shown in Fig. 3. TiO_{2-x}/C is composed of microspheres with different sizes (400–1,000 nm) and a smooth surface (Figs. 3(a)–3(d)). The high resolution TEM (HRTEM) image shown in Fig. 3(e) displays clear lattice fringes of 0.35 nm, corresponding to the (101) lattice plane of anatase. The selected area electron diffraction (SAED) pattern shows a series of weak and concentric rings, corresponding to the (101), (004), (200), and (211) diffractions of anatase (Fig. 3(f)). The EDS element mapping results of TiO_{2-x}/C are shown in Fig. S2 in the ESM, from which the uniform distribution of Ti, O, and C in the sample can be discerned. The treatment of TiO_{2-x}/C with HF etched off the TiO₂ grains, leaving behind the carbon matrix. The carbon matrix showed a microspherical morphology similar to that of TiO_{2-x}/C , confirming the homogeneous distribution of TiO_{2-x} and C in the composites (Fig. S3 in the ESM). Similar to TiO_{2-x}/C , W-TiO₂ was also composed of polydisperse microspheres (Figs. 4(a)–4(d)).

The HRTEM image of W-TiO₂ clearly shows the (101) lattice fringes of anatase (Fig. 4(e)), while the SAED pattern displays a series of bright diffraction rings (Fig. 4(f)). The N₂ sorption results demonstrated that both TiO_{2-x}/C and W-TiO₂ possess low specific surface areas and total pore volumes (Fig. S4 in the ESM). Such a nonporous spherical structure is beneficial for achieving high tap density, and thus high volumetric energy density, when applied in batteries.

XPS was used to investigate the surface composition and valence states of the TiO_{2-x}/C and W-TiO₂ microspheres. The survey scan of TiO_{2-x}/C showed clear signals for C, Ti, and O (Fig. 5(a)). Figs. 5(b) and S5 in the ESM illustrate the Ti 2p spectra of TiO_{2-x}/C and W-TiO₂, respectively. Both TiO_{2-x}/C and W-TiO₂ exhibited two main peaks at 458.7 and 464.6 eV, corresponding to Ti⁴⁺ 2p_{3/2} and Ti⁴⁺ 2p_{1/2}, respectively [30]. For TiO_{2-x}/C , two additional peaks could be found at 456.5 and 462.2 eV. According to Ref. [46], these two peaks can be assigned to Ti³⁺ 2p_{3/2} and Ti³⁺ 2p_{1/2}, respectively. The XPS results unambiguously demonstrated the existence of Ti^{3+} in $TiO_{2-x}/C_{1/2}$ and the Ti³⁺/Ti⁴⁺ ratio was ~0.33. To further demonstrate the existence of oxygen vacancies, the O 1s spectrum of TiO_{2-x}/C was also provided (Fig. S6 in the ESM). The oxygen vacancy component could be clearly observed at 531.6 eV, which is consistent with the study reported by Yu and coworkers [32].



Figure 3 (a) and (b) SEM, (c) and (d) TEM, (e) HRTEM images, and (f) SAED pattern of the TiO_{2-x}/C composite microspheres.



Figure 4 (a) and (b) SEM, (c) and (d) TEM, (e) HRTEM images, and (f) SAED pattern of the W-TiO₂ microspheres.



Figure 5 (a) XPS survey spectrum of TiO_{2-x}/C . (b) High-resolution Ti 2p XPS spectra of TiO_{2-x}/C .

Figure 6(a) shows the CV curves of the TiO_{2-x}/C composite microspheres in the potential window of 0.1–2.5 V (vs. Na⁺/Na) at a scan rate of 0.2 mV·s⁻¹. The irreversible broad peak located at 1.0 V of the initial cathode process was due to the formation of a solid electrolyte interface (SEI) film on the surface of the electrode [32]. The second and third cycles of TiO_{2-x}/C overlapped well, indicating a good reversibility.

The galvanostatic charge-discharge profiles and cycling performance of $\text{TiO}_{2-x}/\text{C}$ at the current density of 50 mA·g⁻¹ are shown in Figs. 6(b) and 6(c), respectively. In the first and second discharge processes, $\text{TiO}_{2-x}/\text{C}$ delivers high specific capacities of 458 and 286 mA·h·g⁻¹, respectively. The specific capacity was comparable to the state-of-the-art TiO₂ based anode materials in Refs. [47–49]. The initial capacity loss was relatively high (172 mA·h·g⁻¹), which may be caused

by the formation of an SEI film and the irreversible trapping of Na⁺ in TiO_{2-x}/C during the first cycle [49]. A capacity of 249 mA·h·g⁻¹ could be retained after 180 cycles, corresponding to a capacity retention of 87.2% (against the second cycle). The control sample, i.e., the W-TiO₂ microspheres, delivered a much lower capacity of 77 mA \cdot h·g⁻¹ (Fig. S7 in the ESM) under the same conditions. The longer cycling performance of the TiO_{2-x}/C microspheres at a higher current density of 100 mA·g⁻¹ is shown in Fig. S8 in the ESM. The TiO_{2-x}/C provided a capacity of 151 mA·h·g⁻¹ after 800 cycles. The rate performances of both samples are shown in Fig. 4(d). TiO_{2-x}/C exhibited specific capacities of 230, 204, 154, 104, and 63 mA·h·g⁻¹ at 50, 100, 200, 500, and 1,000 mA·g⁻¹, respectively. W-TiO₂ afforded a low capacity of 46 mA·h·g⁻¹ at 50 mA·g⁻¹, which further decreases with the increase of the current



Figure 6 (a) CV curves of $\text{TiO}_{2-x}/\text{C}$ at a scan rate of 0.2 mV·s⁻¹. (b) Selected galvanostatic charge–discharge profiles of $\text{TiO}_{2-x}/\text{C}$ at a current density of 50 mA·g⁻¹. (c) Cycling performances of $\text{TiO}_{2-x}/\text{C}$ and W-TiO₂. (d) Rate performances of $\text{TiO}_{2-x}/\text{C}$ and W-TiO₂.

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density. The enhanced rate performance of TiO_{2-x}/C can be ascribed to its improved electronic conductivity, which can be verified by the EIS results (Fig. S9 in the ESM).

To explore the sodium storage mechanism, the *ex situ* XRD patterns of TiO_{2-x}/C at different states (opencircuit, fully discharged, and fully charged states) were collected (Fig. S10 in the ESM).

In open-circuit state, TiO_{2-x}/C showed the typical diffractions of anatase. When it was discharged to 0.01 V, the characteristic peaks of the anatase disappeared. When it was recharged to 2.5 V, the main peak at 25.3° could be recovered to some extent. The *ex situ* XRD results indicate that the reversible specific capacity is likely delivered by the almost amorphous structure formed after sodiation. This deduction is in line with the study by Wu et al. [29].

The superior sodium storage performance of TiO_{2-x}/C can be ascribed to the following structural merits: (1) the simultaneous introduction of Ti^{3+} and oxygen vacancies boost the electrochemical activities of TiO_{2-x}/C [32, 37]; (2) the ultrafine grain size of TiO_{2-x}/C reduces the sodium ion/electron diffusion paths, which is beneficial to the rate capability; (3) the carbon matrix improves not only the electronic conductivity (Fig. S9 in the ESM) but also the structural stability of the sample, resulting in a good rate capability and excellent cyclability.

4 Conclusions

In summary, $\text{TiO}_{2-x}/\text{C}$ composite microspheres were synthesized by a facile aerosol method. Benefiting from their unique structural features, such as Ti^{3+} and oxygen vacancy co-doping, ultrafine TiO_{2-x} nanocrystals, and amorphous carbon matrix, the obtained $\text{TiO}_{2-x}/\text{C}$ microspheres offered a high sodium storage capacity of 286 mA·h·g⁻¹ at 50 mA·g⁻¹, retaining 249 mA·h·g⁻¹ after 180 cycles. This work provides a facile and effective approach for the production of TiO₂ based nanomaterials with superior sodium storage performance.

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