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Spray-Pyrolysis-Assisted Synthesis of Yolk@Shell Anatase with Rich Oxygen Vacancies for Efficient Sodium Storage

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Herein, yolk@shell structured anatase TiO₂ microspheres are produced by a facile spray-pyrolysis-assisted method. Through introducing oxygen vacancies by hydrogen treatment, yolk@shell structured TiO₂ microspheres are also obtained. The as-synthesized yolk@shell TiO₂ demonstrates a high reversible capacity (230.7 mAh g⁻¹ after 200 cycles at 0.05 A g⁻¹) and remarkable long-cycling stability (capacity retention of 91.7% after 1000 cycles at 1 A g⁻¹). DFT calculations reveal that introducing oxygen vacancies in TiO₂ enhances the electrical conductivity, lowers the sodiation energy barrier, and facilitates Na⁺ diffusion kinetics. This work sheds light on the rational design of high-performance electrode materials through integrating the yolk@shell structure and oxygen vacancies.

Introduction

Titanium dioxide (TiO₂) has attracted extensive research attention due to its wide applications in photocatalysis, solar cells, energy storage, and other realms. ¹⁻⁴ As a well-known semiconductor, TiO₂ has plenty of advantages: abundance, low cost, structural stability, safety, and pollution free, etc. ⁵ For the specific application in sodium-ion batteries (SIBs), TiO₂ possesses high theoretical capacity (335 mAh g⁻¹), suitable Na⁺ accommodation sites, and good structural stability. However, the low intrinsic electrical conductivity and ion diffusivity limit the sodium storage performance of TiO₂.⁶⁻⁸ To tackle these challenges, carbon coating, foreign element doping, and defect engineering have been applied to TiO₂.⁹⁻¹⁴ Among these strategies, defect engineering is especially promising. As demonstrated by Ji et al. recently, the introduction of oxygen vacancies in TiO₂ could not only improve the electrical conductivity but also promote the Na⁺ intercalation.¹⁵

Yolk@shell structure is a unique design composed of nanoparticulate core, thin shell, and cavity in between.¹⁶ When applied in secondary batteries, the yolk@shell design is especially effective in accommodating the volume change, alleviating the mechanical stress, and shortening the ion diffusion lengths.¹⁷⁻²¹ It is expected that integrating the yolk@shell design and defect engineering in TiO₂ would further boost its sodium storage performances. However, to the knowledge of our best, there is no report on yolk@shell structured TiO₂ with rich oxygen vacancies for sodium storage.

In this work, yolk@shell structured anatase TiO₂ microspheres with rich oxygen vacancies (denoted as yolk@shell TiO₂) are produced through a facile spray pyrolysis process followed by hydrogen treatment. Benefiting from the integration of yolk@shell design and oxygen vacancies, the resultant yolk@shell TiO₂ demonstrates significantly enhanced specific capacity and rate capability when compared to pristine yolk@shell TiO₂. Density functional theory (DFT) calculations articulate that the introduction of oxygen vacancies in anatase TiO₂ promotes the electrical conductivity, lowers the sodiation energy barrier, and facilitates the Na⁺ diffusion kinetic.

Experimental

Synthesis of yolk@shell TiO₂ and TiO₂: A facile spray pyrolysis method was used to prepare the yolk@shell TiO₂. First, 5 mL of titanium (IV) bis (ammonium lactato)dihydroxide (TIBALDH) (50 wt.% in H₂O) and 8.7 g of sucrose was dissolved in 95 mL of water. Afterwards, the solution was pumped into an ultrasonic atomizer (USP 20, Siansonic Technology Co., Ltd). The produced vapour was blown into a quartz tube by flowing air, and the quartz tube was preheated to 900 °C. A black intermediate product was collected. The yolk@shell TiO₂ was obtained after annealing the black intermediate at 600 °C for 5h in air. To...
prepare yolk@shell TiO$_2$$_x$, the yolk@shell TiO$_2$ was annealed in flowing H$_2$/Ar (5%/95%) at 600 °C for 5 h.

**Materials Characterization:** X-ray diffraction (XRD) was applied to characterize the crystal phase of the samples. Electron spin-resonance spectroscopy (ESR) results were collected at room temperature using an A300 Bruker ESR spectrometer. XRD patterns were obtained by a Bruker D8 Advance X-ray diffractometer using Cu-Kα radiation. Field-emission scanning electron microscopy (FESEM, JEOL-7100F) was conducted to study the morphology of the samples. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were carried out on a Renishaw INVIA micro-Raman spectroscopy system. Brunauer–Emmett–Teller (BET) surface areas were calculated from nitrogen sorption isotherms measured by Tristar II-3020 at 77 K. X-ray photoelectron spectroscopy (XPS) spectra were accomplished by a VG Multilab 2000 instrument.

**Electrochemical measurements:** To evaluate the electrochemical performance of yolk@shell TiO$_2$$_x$ and TiO$_2$, 2016 type coin cells were assembled in glove box filled with Ar. The slurry containing 60 wt.% of active materials, 30 wt.% of acetylene black, and 10 wt.% of carboxymethyl cellulose binder in deionized water was coated onto a copper foil and dried at 70 °C for 6 h. The mass loading of active material was 1 – 1.5 mg cm$^{-2}$. The electrolyte was composed of 1 M NaClO$_4$ in a mixture of ethylene carbonate/dimethyl carbonate (1:1 by volume) with 5 wt.% of fluoroethylene carbonate. Galvanostatic charge/discharge test was conducted in the potential window of 0.01 – 3.0 V on a battery testing system (LAND CT 2001A). Both cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out on multichannel Potentiostats.

**Results and discussion**

The yolk@shell structured anatase TiO$_2$$_x$ microspheres are produced by a simple and convenient spray-pyrolysis-assisted process followed by hydrogen treatment. As depicted in Fig. 1, there are three primary procedures to prepare the yolk@shell TiO$_2$$_x$. First, TiO$_2$/C composites are prepared by spray pyrolysis from TiBALDH and sucrose (Fig. 1a). Afterwards, the TiO$_2$/C microspheres are calcined in air, during which the external surface and inner core are not homogeneously heated. Instead, a temperature gradient exists from the surface to the core (the so-called non-equilibrium heat treatment). Under this circumstance, heterogeneous contraction happens and yolk@shell TiO$_2$ microspheres are obtained (Fig. 1b). Finally, the yolk@shell TiO$_2$ are annealed in H$_2$, yielding yolk@shell TiO$_2$$_x$ with rich oxygen vacancies.

The presence of oxygen vacancies in yolk@shell TiO$_2$$_x$ can be generally told from the color of the samples; the yolk@shell TiO$_2$ is white, while it turns gray after annealing in H$_2$ (Fig. 1b). ESR is also employed to further validate the presence of oxygen vacancy in TiO$_2$$_x$. A strong signal with a g value of 2.003 arising from oxygen vacancy is detected for the yolk@shell TiO$_2$$_x$ (Fig. 1b). However, the signal for oxygen vacancy is barely invisible for the pristine TiO$_2$. The ESR results unambiguously demonstrate the presence of oxygen vacancies in TiO$_2$$_x$.11, 14

XRD patterns are collected and shown in Fig. 2b. The yolk@shell structured TiO$_2$ and TiO$_2$$_x$ show identical diffraction
blue shift for the most intensive Raman peak from 145.8 cm$^{-1}$ to 148.2 cm$^{-1}$, indicating the introduction of oxygen vacancies.27 In addition, the yolk@shell TiO$_{2-x}$ manifests broadened diffraction peaks. Both TiO$_{2-x}$ and TiO$_2$ show characteristic Raman bands of anatase (Fig. 2c),27 and the TiO$_{2-x}$ displays obviously broadened bands. Meanwhile, the introduction of oxygen vacancy is accompanied by a distinct blue shift for the most intensive Raman peak from 145.8 cm$^{-1}$ to 148.2 cm$^{-1}$ for TiO$_{2-x}$,15 According to previous studies,28,29 the blue shift is caused by the oxygen vacancies.

XPS survey spectra (Fig. S1) show that both yolk@shell TiO$_{2-x}$ and TiO$_2$ possess characteristic Ti and O peaks. The high-resolution Ti 2p spectrum of yolk@shell TiO$_2$ (Fig. 2d) shows two peaks at 458.8 and 464.5 eV, corresponding to the 2p$_{1/2}$ and 2p$_{3/2}$ peaks of Ti(IV), respectively. Two additional peaks at 457.4 and 462.3 eV can be observed for yolk@shell TiO$_{2-x}$, which can be assigned to the 2p$_{3/2}$ and 2p$_{1/2}$ peaks of Ti(III).30 To keep electroneutrality, the presence of Ti(III) is accompanied by the appearance of oxygen vacancy. As for the O 1s spectra (Fig. 2e), both samples contain two components centered at 530.1 and 532.1 eV. The first component is originated from Ti–O–Ti, while the second component is related to either surface Ti–OH or oxygen vacancy.15,31 The obvious intensity increase for the second peak indicates the successful introduction of oxygen vacancy in yolk@shell TiO$_{2-x}$.

To characterize the electrical properties of yolk@shell TiO$_{2-x}$ and TiO$_2$, Mott–Schottky plots are measured through electrochemical impedance tests. Both samples display a positive slope (Fig. 2f), indicating their n-type semiconductor character. According to the Mott–Schottky equation, the carrier density is inversely proportional to the slope value, and the TiO$_2$ shows an obviously smaller slope than TiO$_{2-x}$, suggesting its higher carrier density. The specific carrier densities of TiO$_2$ and TiO$_{2-x}$ are determined to be $5.7 \times 10^{22}$ cm$^{-3}$, $1.4 \times 10^{23}$ cm$^{-3}$, respectively. The increase in carrier density is mainly ascribed to the introduction of oxygen vacancies.32

FESEM and TEM are employed to observe the detailed structure of the as-prepared products (Fig. 3 and Fig. S2). FESEM images (Fig. 3a, b) show that the TiO$_{2-x}$ is generally composed of yolk@shell spheres with smooth surface and sizes varying from 400 to 1000 nm. TEM images (Fig. 3c, d) further confirms the yolk@shell structure of TiO$_{2-x}$, which consists of a solid spherical core surrounded by a relatively thin shell. The size of inner core is approximately 300 – 500 nm, while the thickness of shell is around 50 nm. Meanwhile, the whole yolk@shell sphere is built up with a large number of primary nanoparticles. High-resolution TEM (HRTEM) images of TiO$_{2-x}$ (Fig. 3e) reveals the typical lattice fringes of anatase TiO$_2$. The measured interplanar distances of 0.35, 0.24, and 0.19 nm correspond to the (101), (004), and (200) lattice planes, respectively. The (101), (004), (200), and (211) diffraction rings can be clearly observed in the SEAD pattern of TiO$_{2-x}$, testifying its polycrystalline feature.15,27 The control sample shows a similar yolk@shell structure with little difference in morphology and size (Fig. 52 and S3). N$_2$ sorption results demonstrate the mesoporous structure of both TiO$_2$ and TiO$_{2-x}$, which are caused by the random packing of primary nanoparticles (Fig. S4). The specific surface area of the pristine TiO$_2$ and oxygen vacancy-rich TiO$_{2-x}$ are 20.39 and 18.01 m$^2$ g$^{-1}$, respectively. Thermogravimetric analysis (TGA) were conducted to obtain the x value in TiO$_{2-x}$ (Fig. S5). The value of x was calculated to be approximately 0.015.

To explore the specific influences of oxygen defects on sodium storage, electrochemical characterizations are performed in sodium-ion half cells. Fig. 4a shows the initial three CV curves of yolk@shell TiO$_{2-x}$. Different from the succeeding cycles, the first cathodic process reveals a broad reduction peak at approximately 1.05 V, which is correlated to the formation of solid electrolyte interface (SEI) layer. Another peak at about 0.5 V can be assigned to the reduction of Ti$^{4+}$ to...
The corresponding oxidation of Ti$^{3+}$ to Ti$^{4+}$ is observed at 0.78 V in the following anodic sweep. For the second and third scans, the reduction peak moves a little toward right to a potential of 0.63 V and the oxidation peak moves to 0.85 V. Besides, the second and third circles overlap well on the whole, implying the good reversibility of the corresponding redox reactions. As a contrast, the CV data of yolk@shell TiO$_2$ are provided in Fig. S6a.

Representative galvanostatic charge/discharge profiles of TiO$_{2-x}$ at 0.05 A g$^{-1}$ are shown in Fig. 4b. The sodiation/desodiation mainly occurs at 0.01 – 1.5 V. The first discharge capacity reaches 327.4 mAh g$^{-1}$, while the first charge capacity is 192.6 mAh g$^{-1}$. The irreversible capacity loss is ascribed to the formation of SEI on electrode surface and the trapping of sodium ions in the anatase lattice. The initial coulombic efficiency (ICE) is calculated as 58.8% for TiO$_{2-x}$ (Fig. S7 and S8). For comparison, the ex-situ SEM images of yolk@shell TiO$_2$ were also collected (Fig. S7). Not only the anatase crystal structure but also the yolk@shell morphology can be maintained well after 100 cycles at 0.05 A g$^{-1}$, verifying the excellent structural stability of yolk@shell structured TiO$_{2-x}$.

Fig. 4e depicts the rate performances of the two anatase samples. As expected, the TiO$_{2-x}$ demonstrates higher capacity than the TiO$_2$ at any current density. For TiO$_{2-x}$, the capacity decreases mildly from 221.6 to 200.5, 181.1, 147.1, 121.5, 95.8, and 68.6 mAh g$^{-1}$, when the current density increases from 0.05 to 0.1, 0.2, 0.5, 1, 2, and 5 A g$^{-1}$, respectively. A relatively high capacity of 201.2 mAh g$^{-1}$ can be recovered when the current density comes back to 0.05 A g$^{-1}$. While for TiO$_2$, the capacity decreases below 50 mAh g$^{-1}$, when the current density reaches 1 A g$^{-1}$.

EIS is used to further elucidate the influences of oxygen defects on the enhanced overall sodium storage performance of TiO$_{2-x}$. From the Nyquist plots (Fig. 4f), the charge-transfer resistance of TiO$_{2-x}$ ($R_{ct} = 158.8$ Ω) is much lower than that of TiO$_2$ ($R_{ct} = 320.6$ Ω), confirming a smoother charge-transfer process on the electrode-electrolyte. Fig. 4g presents the frequency ($\omega$) and $Z'$ values at low frequency region, the slope of which is correlated to solid state ion diffusivity. The ion diffusivity values at room temperature are calculated to be $1.68 \times 10^{-8}$ and $6.74 \times 10^{-9}$ cm$^2$ s$^{-1}$ for TiO$_{2-x}$ and TiO$_2$, respectively. Obviously, the introduction of oxygen vacancies in TiO$_2$ leads to a boost in Na$^+$ diffusivity, which is in good agreement with previous studies. The Bode plots (Fig. 4h) are also used to
prove the promoted Na\textsuperscript{+} diffusion kinetics in TiO\textsubscript{2-x}. According to the literatures\textsuperscript{35, 36}, the low-frequency contribution of the Bode plots is associated with the Na\textsuperscript{+} diffusion within the electrode. To be specific, the smaller the phase angle, the faster the Na\textsuperscript{+} diffusion.\textsuperscript{37} The TiO\textsubscript{2-x} exhibits an obviously smaller phase angle at the low-frequency region (below 10 Hz), demonstrating its faster Na\textsuperscript{+} diffusion kinetics.

To reveal the sodium storage mechanism and structure evolution of the TiO\textsubscript{2-x}, in-situ XRD analysis is performed. In general, the typical diffractions for anatase are maintained during the charge/discharge, suggesting the excellent structural stability of TiO\textsubscript{2-x} (Fig. 5a). In more detail, both the (101) and (200) diffractions shift leftward mildly and weaken in intensity during discharge (Fig. 5b). During charge, both diffractions shift rightward and strengthen in intensity. The in-situ XRD analysis suggests that the yolk@shell structured TiO\textsubscript{2-x} stores charge through Na\textsuperscript{+} insertion/extraction rather than conversion reaction. Based on the in-situ XRD results, the sodium storage processes of TiO\textsubscript{2-x} are proposed (Fig. 5c).

DFT calculations are performed to help us understand the role of oxygen vacancies to electronic properties, sodiation thermodynamics, and sodiation kinetics. The calculated density of states (DOS) and partial density of states (PDOS) of the pristine anatase TiO\textsubscript{2} and oxygen vacancy-rich anatase TiO\textsubscript{2} (TiO\textsubscript{2-x}) are shown in Fig. 6a, b. With the introduction of oxygen vacancy, the Fermi level of TiO\textsubscript{2} shifts toward the conduction band (CB) obviously, which implies an improved electron conductivity. The obtained sodiation energy barriers (i.e., the energies required for sodiation) for TiO\textsubscript{2} and TiO\textsubscript{2-x} are 1.076 and 0.782 eV, respectively. This indicates that the sodiation process becomes more energetically favorable with the presence of oxygen vacancy. Nudged elastic band (NEB) method calculations are conducted to evaluate the Na\textsuperscript{+} diffusion ability in TiO\textsubscript{2} and TiO\textsubscript{2-x}. The sodium diffusion pathways around the oxygen vacancy are shown in Fig. 6c, d and the corresponding diffusion energy barriers (Fig. 6e, f) are calculated to be 0.651 eV for the pristine TiO\textsubscript{2} and 0.394 eV for TiO\textsubscript{2-x}. The decrease in
The sodium storage performances of the as-designed yolk@shell anatase TiO$_2$ are compared with recently reported anatase TiO$_2$ (Fig. S9 and Table S1). The yolk@shell TiO$_2$ demonstrates overall competitive sodium storage performances, especially in terms of specific capacity and cycling stability. The superior sodium storage performance can be ascribed to the integration of oxygen defects and the yolk@shell design. The introduction of oxygen defects enhances the electrical conductivity, lowers the sodiation energy barrier, and facilitates the Na$^+$ diffusion. The yolk@shell design accommodates the volume fluctuations during charge/discharge, which boosts the Na$^+$ diffusion kinetics. The yolk@shell design accommodates the volume fluctuations during charge/discharge, which boosts the Na$^+$ diffusion significantly.

Conclusions

In summary, a facile spray-pyrolysis-assisted method was developed for the synthesis of yolk@shell anatase TiO$_2$ with rich oxygen vacancies. Benefited from the oxygen vacancies and the intricate yolk@shell design, the obtained yolk@shell TiO$_2$ demonstrates a specific capacity of 230.7 mAh g$^{-1}$ with excellent cycling stability. Moreover, theoretical computations demonstrate that introducing oxygen vacancies would enhance the electrical conductivity, lower the sodiation energy barrier, and facilitate the Na$^+$ diffusion of anatase TiO$_2$. This work sheds light on the rational design of high-performance electrode materials through integrating the yolk@shell architecture and oxygen vacancies.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

Yolk@shell structured TiO$_{2-x}$ with rich oxygen vacancies manifests high specific capacity and excellent cyclability in sodium storage.