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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 TiO_2 microspheres are produced by a facile spray-pyrolysis-assisted method. Through introducing oxygen vacancies by hydrogen treatment, yolk@shell structured $TiO_{2.x}$ microspheres are also obtained. The assynthesized yolk@shell $TiO_{2.x}$ 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 TiO_2 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

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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 mA h 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 TiO_2 .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.¹⁷⁻²³ 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.

Herein, yolk@shell structured anatase TiO₂ microspheres with rich oxygen vacancies (denoted as yolk@shell TiO_{2-x}) 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 TiO_{2-x} 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 TiO_{2-x}: 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

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Electronic Supplementary Information (ESI) available: XPS spectrum of yolk@shell TiO₂ and TiO_{2.x}; TG curves of yolk@shell TiO_{2.x}; SEM, TEM, HRTEM images and SAED pattern of yolk@shell TiO₂; EDS elemental mappings of yolk@shell TiO₂ and TiO_{2.x}; N₂ sorption results of yolk@shell TiO₂ and TiO_{2.x}; CV and GCD curves of yolk@shell TiO₂; SEM images of yolk@shell TiO_{2.x} before and after cycling; XRD patterns of yolk@shell TiO_{2.x} before and after cycling. See DOI: 10.1039/x00x0000x

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Fig. 1 Schematic diagrams showing (a) the ultrasonic spray pyrolysis process and (b) formation mechanism of yolk@shell structured TiO_{2-x}

prepare yolk@shell TiO_{2-x}, the yolk@shell TiO₂ was annealed in flowing H₂/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 spinresonance spectroscopy (ESR) results were collected at room temperature using a A300 Bruker ESR spectrometer. The XRD patterns were obtained by a Bruker D8 Advance X-ray diffractometer using Cu-Ka 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 JEOL JEM-2100F. Raman spectra were obtained 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: То evaluate the electrochemical performance of yolk@shell TiO_{2-x} and TiO₂, 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 NaClO₄ 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, TiO₂/C composites are prepared by spray pyrolysis from TiBALDH and sucrose (Fig. 1a). Afterwards, the TiO₂/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 TiO₂ are annealed in H₂, yielding yolk@shell TiO₂. 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 TiO₂ is white, while it turns gray after annealing in H₂ (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. 2a). However, the signal for oxygen vacancy is barely invisible for the pristine TiO₂. 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

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Fig. 2 (a) ESR spectra, (b) XRD patterns, (c) Raman spectra, (d) Ti 2p XPS spectrum, (e) O 1s XPS spectrum, and (f) Mott-Schottky plots of yolk@shell TiO₂ and TiO_{2-x}.

peaks, and both samples can be indexed to pure-phase anatase (JCPDS NO. 21-1272). When compared to TiO₂, the (101) diffraction of yolk@shell TiO_{2-x} shows a mild left shift, suggesting a subtle expansion in lattice parameters with the introduction of oxygen vacancies.²⁷ In addition, the yolk@shell TiO_{2-x} manifests broadened diffraction peaks. Both TiO_{2-x} and TiO₂ 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 for TiO₂ 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 TiO₂ possess characteristic Ti and O peaks. The highresolution Ti 2p spectrum of yolk@shell TiO₂ (Fig. 2d) show two peaks at 458.8 and 464.5 eV, corresponding to the $2p_{3/2}$ and $2p_{1/2}$ 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 TiO₂, 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-x} shows an obviously smaller slope than TiO₂, suggesting its higher carrier density. The specific carrier densities of TiO₂ and TiO_{2-x} are determined to be 5.7×10^{22} cm⁻³, 1.4×10^{23} cm⁻³,

respectively. The increase in carrier density is mainly ascribed to the introduction of oxygen vacancies. $^{\rm 32}$

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. Highresolution TEM (HRTEM) images of TiO_{2-x} (Fig. 3e) reveals the typical lattice fringes of anatase TiO₂. 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. S2 and S3). N₂ 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 m² 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 Ti⁴⁺ to

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Fig. 3 Morphology characterizations of yolk@shell TiO_{2.x}. (a, b) SEM images, (c, d) TEM images, (e) HRTEM image and (f) SAED pattern.

Ti³⁺. The corresponding oxidation of Ti³⁺ to Ti⁴⁺ 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 TiO₂ 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. 4b, c), which is slightly higher than that of the pristine anatase TiO₂ (57.4%, Fig. S6b). When comparing the cycling behavior of TiO_{2-x} and TiO_2 , the TiO_{2-x} manifests much higher specific capacity and more durable performance owing to the presence of oxygen defects (Fig. 4c). Specifically, the TiO_{2-x} demonstrates a specific capacity of 230.7 mAh g⁻¹ after 200 cycles at 0.05 A g⁻¹ with no declining trend. In sharp contrast, the capacity of yolk@shell TiO₂ decreases continually with cycling, and a capacity of only 117.9 mAh g⁻¹ is retained after 200 cycles. When tested at 1 A g^{-1} (Fig. 4e), the TiO_{2-x} shows a capacity of 99.8 mAh g^{-1} after 1000 cycles, and the corresponding capacity retention is 91.7%. As for the TiO₂, the capacity after 1000 cycles is 60.4 mAh g⁻¹ and the capacity retention is only 75.5%. To elucidate the excellent cyclability of yolk@shell structured TiO2-x, ex-situ SEM

images and XRD patterns are collected (Fig. S7 and S8). For comparison, the *ex-situ* SEM images of yolk@shell TiO₂ 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 TiO₂ (R_{ct} = 320.6 Ω), confirming a smoother charge-transfer process on the electrode-electrolyte. Fig. 4g presents the frequency (ω) and Z' values at low frequency region, the slope of which is correlated to solid state ion diffusivity.³³ The ion diffusivity values at room temperature are calculated to be 1.68 × 10⁻⁸ and 6.74 × 10⁻⁹ cm² s⁻¹ for TiO_{2-x} and TiO₂, respectively. Obviously, the introduction of oxygen vacancies in TiO₂ leads to a boost in Na⁺ diffusivity, which is in good agreement with previous studies.³⁴ The Bode plots (Fig. 4h) are also used to

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Fig. 4 (a) CV curves of yolk@shell TiO_{2-x} in the potential window of 0.01–3.0 V (vs. Na⁺/Na) at the scan rate of 0.1 mV s⁻¹. (b) Galvanostatic charge/discharge profiles of TiO_{2-x} at a current density of 0.05 A g⁻¹. Cycling performances of TiO₂ and TiO_{2-x} at (c) 0.05 and d) 1 A g⁻¹. (e) Rate performances of TiO_{2-x} and TiO₂. (f) Nyquist plots, (g) Z' values as a function of $\omega^{-1/2}$ at low frequency region, and (h) Bode plots of TiO_{2-x}.

prove the promoted Na⁺ diffusion kinetics in TiO_{2-x}. According to the literatures,^{35, 36} the low-frequency contribution of the Bode plots is associated with the Na⁺ diffusion within the electrode. To be specific, the smaller the phase angle, the faster the Na⁺ diffusion.³⁷ The TiO_{2-x} exhibits an obviously smaller phase angle at the low-frequency region (below 10 Hz), demonstrating its faster Na⁺ diffusion kinetics.

To reveal the sodium storage mechanism and structure evolution of the TiO_{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_{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_{2-x} stores charge through Na⁺ insertion/extraction rather than conversion reaction. Based on the *in-situ* XRD results, the sodium storage processes of TiO_{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_2 and oxygen vacancy-rich anatase TiO_2 (TiO_{2-x}) are shown in Fig. 6a, b. With the introduction of oxygen vacancy, the Fermi level of TiO_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 TiO₂ and TiO_{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⁺ diffusion ability in TiO₂ and TiO_{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 TiO₂ and 0.394 eV for TiO_{2-x}. The decrease in



Fig.5 (a), (b) *In-situ* XRD patterns of $TiO_{2,x}$ during the first cycle. (c) The schematic diagram showing the sodium storage mechanism of $TiO_{2,x}$.

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Fig.6 Calculated DOS and PDOS of (a) pristine anatase TiO_2 and (b) $TiO_{2,x}$ with oxygen vacancies. The ball-stick structure models for Na⁺ diffusion pathway around the oxygen vacancy of (c) TiO_2 and (d) $TiO_{2,x}$. Na⁺ diffusion energy barriers of (e) TiO_2 , and (f) $TiO_{2,x}$.

diffusion energy barrier indicates that the introduction of oxygen vacancies can significantly facilitate the Na⁺ diffusion.

The sodium storage performances of the as-designed yolk@shell TiO_{2-x} are compared with recently reported anatase TiO₂ (Fig. S9 and Table S1). The yolk@shell TiO_{2-x} 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 facilitate the Na⁺ diffusion kinetics. The yolk@shell design accommodates the volume fluctuations during charge/discharge, which boosts the structural stability and thus cyclability significantly.

Conclusions

In summary, a facile spray-pyrolysis-assisted method was developed for the synthesis of yolk@shell anatase TiO_{2-x} with rich oxygen vacancies. Benefited from the oxygen vacancies and the intricate yolk@shell design, the obtained yolk@shell TiO_{2-x} 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.

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Conflicts of interest

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There are no conflicts to declare.

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