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Abstract

Structural design and modification are effective approaches to regulate the physicochemical properties of TiO₂, which play an important role in achieving advanced materials. Herein, a plasma-assisted method is reported to synthesize a surface-defect-rich and deep-cation-site-rich S doped rutile TiO₂ (R-TiO_{2-x}-S) as an advanced anode for the Na ion battery. An amorphous shell (≈ 3 nm) is induced by the Ar/H₂ plasma, which brings about the subsequent high S doping concentration (≈ 4.68 at%) and deep doping depth. Experimental results and density functional theory calculations demonstrate greatly facilitated ion diffusion, improved electronic conductivity, and an increased mobility rate of holes for R-TiO_{2-x}-S, which result in superior rate capability (264.8 and 128.5 mAh g⁻¹ at 50 and 10 000 mA g⁻¹, respectively) and excellent cycling stability (almost 100% retention over 6500 cycles). Such improvements signify that plasma treatment offers an innovative and general approach toward designing advanced battery materials.

Keywords

sodium, extraordinary, tio₂, endow, doping, storage, cation-site, performance, deep, shell, amorphous, plasma-induced

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Plasma-induced amorphous shell and deep cation-site S doping endow TiO₂ with extraordinary sodium storage performance

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Keywords: sodium ion battery; titanium dioxide; deep cation-site S doping; amorphous shell; rate performanc

Structural design and modification are effective approaches to regulate the physicochemical properties of TiO_2 , which play an important role in achieving advanced materials. Herein, we report a plasma-assisted method to synthesize a surface-defect-rich and deep-cation-site-rich S doped rutile TiO_2 (R- $\text{TiO}_{2-x}\text{-S}$) as an advanced anode for the Na ion battery. An amorphous shell (~ 3 nm) is induced by the Ar/ H_2 plasma, which brings about the subsequent high S doping concentration (~ 4.68 at. %) and deep doping depth. Experimental results and density functional theory calculations demonstrate greatly facilitated ion diffusion, improved electronic conductivity, and an increased mobility rate of holes for R- $\text{TiO}_{2-x}\text{-S}$, which result in superior rate capability (264.8 mAh g^{-1} and 128.5 mAh g^{-1} at 50 mA g^{-1} and 10000 mA g^{-1} , respectively) and excellent cycling stability (almost 100% retention over 6500 cycles). Such improvements signify that plasma treatment offers an innovative and general approach toward designing advanced battery materials.

Sodium ion batteries (SIBs) have attracted great research enthusiasm for scalable stationary energy storage systems due to the low cost and natural abundance of sodium resources, and its similar intercalation mechanism to lithium ion batteries (LIBs).^[1] Nevertheless, the much larger ionic radius of sodium (1.02 Å) than that of lithium (0.76 Å) makes it more difficult to find suitable electrode materials for effective and durable accommodation of sodium ions. Titanium dioxide (TiO₂) has received enormous attention as a sodium ion battery anode due to its high theoretical capacity (335 mAh g⁻¹), suitable sodiation pathways and low volume expansion upon sodiation.^[2, 3] The low sodium ion mobility within pristine TiO₂ crystal, however, together with its poor intrinsic conductivity, originating from its large band gap (3.0 eV), leads to the preferential location of the available active sites for high-rate sodium intercalation in the surface layer, resulting in inferior sodium storage performance.^[4-6]

Very recently, many experimental results have revealed that doping TiO₂ with heteroatoms could introduce sufficient defects and oxygen vacancies, which would result in significantly facilitated intrinsic electronic conductivity.^[7, 8] Consequently, various forms of heteroatom-doped TiO₂ (such as with N,^[8, 9] B,^[7] Nb,^[10] Sn,^[11] and S^[12]) have been synthesized, and enhanced sodium storage performance has been demonstrated. Theoretical calculations suggested, however, that only when the concentration of dopant is sufficiently high to continuously induce a vacancy band of electronic states in the band gap of TiO₂, can any significant improvement of the electronic conductivity be achieved.^[13] Otherwise, a low dopant level can only introduce localized oxygen vacancy states, which would destroy the electronic mobility and dramatically impair the efficiency of doping.^[14] Moreover, it has been shown computationally that deep cation-site doping could narrow the band gap of TiO₂ to a large extent, resulting in higher intrinsic electronic conductivity.^[14, 15] The doping depth is always confined to near the surface, however, and the doping concentration is relatively low due to the limited solubility of substitutional dopants in bulk

TiO₂. In addition, relevant work with respect to the effects of deep cation-site doping on the sodium storage performance of TiO₂ is currently lacking. Therefore, it is desirable to achieve high doping concentrations together with deep doping in bulk TiO₂.

Interestingly, several recent pioneering works have shown that designing materials with amorphous features could accelerate ionic and electronic diffusion.^[16] Siegel et al. demonstrated that amorphous Li₂O₂ features ionic conductivity that is larger by 12 orders of magnitude compared to its crystalline counterpart.^[17] Surface amorphous (SA)-TiO₂@graphene composite exhibited vastly improved lithium storage performance compared to crystalline TiO₂.^[18] Typically, defects and oxygen vacancies would be induced during the introduction of amorphous phase.^[18, 19] The defect-rich amorphous phase would improve the solubility of dopant atoms, consequently achieving not only a higher doping level, but also enhanced ion and electron diffusion.^[19, 20] Inspired by the above considerations, it is believed that combining a high concentration of deep cation-site dopants with surface amorphization would be a promising strategy to improve the anodic performance of TiO₂ for sodium ion batteries.

Herein, a unique surface-defect-rich and deep S-cation doped TiO₂ (R-TiO_{2-x}-S) was synthesized through a simple hydrolysis method followed by a plasma-assisted S doping strategy. An ultrathin amorphous shell generated by Ar/H₂ plasma treatment, followed by a high-concentration (~4.68 at. %) of S and deep S doping, gave rise to greatly improved intrinsic electronic conductivity and enhanced sodium ion diffusion in R-TiO_{2-x}-S. DFT calculation has shown that cation doping is more advantageous for reducing the band gap and accelerating the mobility rate of holes at the same doping concentration than anion doping. The advantages of the designed structure result in high reversible capacity, and outstanding long-term cycling stability and rate capability of R-TiO_{2-x}-S in SIBs.

We first synthesized TiO₂ precursor through a simple hydrolysis method. Then, the TiO₂ precursor was treated with Ar/H₂ plasma to form a thin amorphous TiO_{2-x} shell. This

amorphous shell possesses a large amount of defects (stable Ti^{3+} and oxygen vacancies), becoming more accessible to dopant atoms.^[19] S vapour, which is produced by the sublimation of S powder on the upstream side of the furnace (Figure S1, Supporting Information), subsequently doped into the defect-rich and surface loosely packed TiO_{2-x} , ensuring a high S doping concentration (~ 4.68 at. %) and deep S doping depth, thus forming the yellowish-brown R- TiO_{2-x} -S (**Figure 1**). For comparison, light-yellow R- TiO_2 -S (doping content of ~ 0.87 at. %) and light-gray defect-rich R- TiO_{2-x} were also prepared in similar way but without plasma treatment (R- TiO_2 -S) or without S doping (R- TiO_{2-x}) (Figure 1). (The details are included in the Experimental section in Supporting Information.)

The morphology of all the samples was characterized by scanning electron microscopy (SEM). The pristine R- TiO_2 shows a flower-like morphology with an average particle size of about 500 nm, and the crystal size and morphology are well maintained after Ar/ H_2 plasma treatment and S doping (Figure S2a-2d, Supporting Information). The transmission electron microscope (TEM) images show that the size of each petal is about 250 nm in length and 50 nm in width (Figure S2e-2h, Supporting Information). From the magnified TEM images, we can see that the flower is heavily populated with nanopores about 10-12 nm in size (Figure S3a and 3b, Supporting Information), which is further supported by the pore size distribution results (Figure S3a and S3b, Supporting Information). The BET surface areas for R- TiO_2 and R- TiO_{2-x} -S are 46.33 and 53.15 $\text{m}^2 \text{g}^{-1}$, respectively. Interestingly, the specific surface area of R- TiO_{2-x} -S increased after plasma treatment, which is in good agreement with Xu's work.^[21] They proved that the plasma treatment could effectively engrave NiO nanosheets with more exposed surface area per unit mass. Thus, the increased surface area of R- TiO_{2-x} -S in our work may be caused by the surface amorphization with the assistant of plasma. The porous flower-like morphology and higher surface area of R- TiO_{2-x} -S could effectively prevent aggregation and improve the electrode/electrolyte contact, leading to better electrochemical properties.^[4, 22]

High resolution TEM (HRTEM) images of all the samples are shown in **Figure 2a-d**. R-TiO₂ displays a highly crystalline structure with a lattice *d*-spacing of 0.16 nm, corresponding to the (220) lattice planes of rutile phase (Figure 2a). After S doping, a very thin amorphous shell less than 1 nm in thickness appears on the R-TiO₂-S particles (Figure 2b). Notably, the Ar/H₂ plasma treatment results in much more obvious amorphous shells (~3 nm) for R-TiO_{2-x} (Figure 2c), and the shell thickness is well retained after the S incorporation (Figure 2d). The element mapping images show homogeneous distributions of Ti, O, and S elements in the R-TiO₂-S and R-TiO_{2-x}-S (Figure 2e-f₃). The energy dispersive X-ray spectroscopy (EDX) results demonstrate a much higher doping concentration in R-TiO_{2-x}-S (4.79 at. %) than in R-TiO₂-S (0.76 at. %), suggesting that the loosely packed defect rich amorphous shell is beneficial for the S diffusion into TiO₂ crystal, consequently resulting in a higher doping concentration in R-TiO_{2-x}-S (Figure S5a and S5b, Supporting Information).

The X-ray diffraction (XRD) patterns of all the samples (Figure S6a, Supporting Information) show mixed phases with the main diffraction peaks in accordance with the rutile phase (JCPDS#21-1276, P42/mnm (136)), and a few peaks labelled with stars correspond to the anatase phase (JCPDS#21-1272, I41/amd (141)). The effects of S doping on the phase and crystal structure of the TiO₂ were further investigated by Rietveld refinement, and the lattice parameters are summarized in Table S1, Supporting Information. Interestingly, compared to the pristine R-TiO₂ ($a = b = 4.5966 \text{ \AA}$ and $c = 2.9597 \text{ \AA}$) (Figure S6b, Supporting Information), the lattice parameters of R-TiO₂-S are increased ($a = b = 4.5982 \text{ \AA}$ and $c = 2.9602 \text{ \AA}$), while those for R-TiO_{2-x}-S are decreased ($a = b = 4.5939 \text{ \AA}$ and $c = 2.9576 \text{ \AA}$) after the different S doping processes (Figure 2g and Figure 2h). When S occupies O sites and forms Ti-S bonds, the lattice parameters would increase. Deeper substitution on Ti sites, however, would form S-O bonds, leading to decreased lattice parameters. Therefore, we can deduce that the S atoms mainly occupy the O sites in R-TiO₂-S, while they tend to replace Ti on the deeper Ti sites in R-TiO_{2-x}-S after the Ar/H₂ plasma treatment. Raman spectra of all the

samples show typical Raman modes of TiO_2 (Figure S6c, Supporting Information).^[4] The obvious shifting and broadening of the Raman peaks of R-TiO_{2-x} and $\text{R-TiO}_{2-x}\text{-S}$ indicate that the original symmetry of the TiO_2 lattice is reduced, which may be due to the introduction of defects and the surface amorphization after the Ar/H_2 plasma treatment.^[23]

The surface chemical states of all the samples were further investigated by X-ray photoelectron spectroscopy (XPS) measurements. The survey XPS spectra (Figure S6d, Supporting Information) indicate the successful doping of S into $\text{R-TiO}_{2-x}\text{-S}$ and $\text{R-TiO}_2\text{-S}$. $\text{Ti}^{3+} 2p_{3/2}$ (456.6 eV) and $\text{Ti}^{3+} 2p_{1/2}$ (461.9 eV) peaks appear in the Ti 2p spectrum for R-TiO_{2-x} , verifying the introduction of Ti^{3+} by plasma treatment (Figure S6e, Supporting Information).^[24] The Ti 2p and O 1s peaks are shifted to lower energy states, suggesting the introduction of defects as a result of S doping and Ar/H_2 plasma treatment (Figure S6e and S6f, Supporting Information).^[4] It is seen that both S^{2-} and S^{4+} species are observed in the S 2p spectra of $\text{R-TiO}_{2-x}\text{-S}$ and $\text{R-TiO}_2\text{-S}$ (Figure 2i).^[12] In the case of $\text{R-TiO}_2\text{-S}$, the dominant S state is the S^{2-} species (161.7 and 164.0 eV), corresponding to the replacement of O^{2-} by S^{2-} in the surface, while most of the S states change into S^{4+} ions (168.8 eV) in the $\text{R-TiO}_{2-x}\text{-S}$ after plasma treatment.^[25] As is well known, the S^{4+} in the samples may originate from possible surface absorbed SO_3^{2-} or S substitution on Ti^{4+} sites in the crystal. To distinguish the S state, according to the method in reference,^[26] we thoroughly rinsed the $\text{R-TiO}_{2-x}\text{-S}$ sample with diluted HCl and retested the XPS spectrum of S 2p. After rinsing, the dominant state of S is still S^{4+} , although the peak intensity was slightly decreased, demonstrating that the S mainly replaced the Ti^{4+} in $\text{R-TiO}_{2-x}\text{-S}$, further confirming that the change in the XRD results is caused by the different doping sites in these two samples (Figure S7, Supporting Information).^[12] The quantitative analysis results demonstrate that the S contents in $\text{R-TiO}_{2-x}\text{-S}$ and $\text{R-TiO}_2\text{-S}$ are 4.68 at. % and 0.87 at. %, respectively. It has been proved that S substitution for Ti^{4+} ions in the TiO_2 crystal is more difficult than the substitution for O^{2-}

ions.^[15, 20] In our case, the concentration of S greatly increases, and the S doping is deeper, revealing much easier doping of S into TiO₂ after Ar/H₂ plasma treatment.

Time-of-flight–secondary ion mass spectrometry (TOF-SIMS) measurements were applied to detect the presence and the distribution of S element in all the samples. As shown in **Figure 3a**, R-TiO₂ and R-TiO_{2-x} show no signal of S element, indicating the absence of S in those two samples. For R-TiO₂-S, the signal intensity of S is definitely present, although it remains steady as the sputtering depth increases, verifying that the S species are almost entirely confined to the surface.^[27] In the case of R-TiO_{2-x}-S, the signal intensity of S is significantly increased, suggesting a higher concentration of S. Moreover, the intensity rises as the sputtering depth increases, indicating the deeper doping depth of S in R-TiO_{2-x}-S.^[27] All these measurements confirm that a higher concentration and deeper doping of S are achieved in R-TiO_{2-x}-S compared to R-TiO₂-S sample.

The presence of defects (Ti³⁺ or oxygen vacancies) was further investigated by electron paramagnetic resonance (EPR) measurements (Figure 3b and c). A signal at about g-factor, $g = 2.003$, is observed for R-TiO₂-S, R-TiO_{2-x}, and R-TiO_{2-x}-S, which originates from the unpaired electrons trapped by oxygen vacancies.^[28] As shown, another signal at $g = 1.996$, corresponding to Ti³⁺ species, appears in R-TiO_{2-x}, which can be ascribed to the partial reduction of TiO₂ by Ar/H₂ plasma (Figure 3c).^[24] Previous work has demonstrated that incorporating foreign atoms into metal oxides would modify their defect features.^[20, 29] As expected, the content of oxygen vacancies in R-TiO_{2-x} decreases significantly after S doping, and the signal for Ti³⁺ almost disappears, which may be caused by the incorporation of S atoms. We collected ultraviolet–visible (UV-vis) absorption spectra for all the samples, which are shown in Figure 3d. The absorption sharp edge shows an obvious red shift with a reduced band gap after plasma treatment and S doping, indicating enhanced electronic conductivity (Table S2, Supporting Information).

To evaluate the effects of the plasma-induced surface amorphous shell, high S doping

concentration, and deep doping depth towards improving the sodium storage performance of TiO_2 , the electrochemical properties of all the obtained samples were investigated. The first discharge and charge curves of all the samples at 50 mA g^{-1} in the voltage range of 0.01-3.0 V show a similar tendency, with an obvious plateau between 1.0 V and 1.2 V, which can be ascribed to the formation of solid-electrolyte interphase (SEI) films and electrolyte side reactions during the first sodiation process (**Figure 4a**).^[30] Clearly, all the samples exhibit excellent cycling stability (Figure 4b), and discharge capacities of 254.2, 192.7, 147.1, and 91.4 mAh g^{-1} are obtained after 100 cycles for R- $\text{TiO}_{2-x}\text{-S}$, R- $\text{TiO}_2\text{-S}$, R- TiO_{2-x} , and R- TiO_2 , respectively (Figure S8a, Supporting Information). As the current density increases to 200 mA g^{-1} , all the samples show a capacity increase in the initial few tens of cycles, and the capacity stays steady subsequently, which can be ascribed to the activation process.^[2, 4] Obviously, both surface-amorphization and S doping have positive effects towards improving the sodium storage performance of TiO_2 , leading to greatly enhanced discharge capacities (223.2 mAh g^{-1} for R- $\text{TiO}_{2-x}\text{-S}$, 195.4 mAh g^{-1} for R- $\text{TiO}_2\text{-S}$, and 174.1 mAh g^{-1} for R- TiO_{2-x} at 200 mA g^{-1}), while a discharge capacity of only 68.6 mAh g^{-1} is delivered for R- TiO_2 (Figure S8b, Supporting Information).

The impressive sodium storage performance of R- $\text{TiO}_{2-x}\text{-S}$ is further highlighted by its superior rate capability. As shown in Figure 4c, R- $\text{TiO}_{2-x}\text{-S}$ exhibits discharge capacities of 264.8, 243.7, 222.5, 183.8, 162.9, and 138.3 mAh g^{-1} at 50, 100, 200, 500, 1000, and 2000 mA g^{-1} , respectively. Even at 5000 and 10000 mA g^{-1} , discharge capacities of 111.3 and 101.9 mAh g^{-1} are obtained, respectively, and 257.5 mAh g^{-1} discharge capacity is attained when the current density recovers to 50 mA g^{-1} , indicating excellent reversibility. R- $\text{TiO}_{2-x}\text{-S}$ has 6.3 times higher discharge capacity than R- TiO_2 at 10000 mA g^{-1} , although R- $\text{TiO}_2\text{-S}$ and R- TiO_{2-x} only show 2.6 times and 3.2 times higher capacities, respectively. The charge-discharge curves of R- $\text{TiO}_{2-x}\text{-S}$ at different current densities show little shifting and only a small overpotential as the current density increases, further verifying its superior rate

performance (Figure 4d). Electrochemical impedance spectroscopy results (EIS) for all the samples (Figure S8c, Supporting Information) demonstrate much lower charge-transfer resistance and sodium ion diffusion resistance for R-TiO_{2-x}-S compared to the other samples, which may be ascribed to the increased electronic/sodium ion conductivities originating from the deep cation-site S doping and surface amorphization. Indeed, the electronic conductivities of R-TiO₂, R-TiO₂-S, R-TiO_{2-x}, and R-TiO_{2-x}-S were measured to be 2.78×10^{-8} , 4.91×10^{-7} , 2.93×10^{-7} , and 1.28×10^{-6} S cm⁻¹, respectively, according to the four-point probe measurement results. The rate capability of R-TiO_{2-x}-S here is superior to those of reported samples of pristine TiO₂, heteroatom doped TiO₂, and carbon coated TiO₂ with various morphologies (Figure S8d, Supporting Information).^[5, 10, 23, 31] Note that this present sample is without any carbon modification. The surface amorphization is likely to be one of the crucial factors behind the significantly enhanced rate capability of R-TiO_{2-x}-S, which would be more favorable for sodium ion diffusion and charge transfer at high rates.^[18] Moreover, the band gap of R-TiO_{2-x}-S decreased greatly after plasma assisted S doping, resulting in dramatically increased intrinsic electronic conductivity. The R-TiO_{2-x}-S electrode was sequentially cycled at 10000 mA g⁻¹ after the rate test to evaluate its long-term cycling stability at a high rate. Strikingly, it showed a discharge capacity of 128.5 mAh g⁻¹ with ~100% Coulombic efficiency over 6500 cycles, proving its excellent tolerance under ultra-fast insertion/extraction of sodium ions (Figure 4e). Compared with most reported TiO₂-based materials (Table S3, Supporting Information), the as-prepared R-TiO_{2-x}-S electrode shows extraordinary cycling stability. TEM images of R-TiO_{2-x}-S after 1000 cycles still show a well-maintained flower-like morphology, confirming the superiority of this robust three-dimensional structure (Figure S9, Supporting Information).

It has been proved that amorphous characteristics in active materials could accelerate their ionic and electronic diffusion.^[18, 32] To verify the effects of the amorphous shell on the sodium ion diffusion, we conducted cyclic voltammetry (CV) of R-TiO_{2-x} (Figure S10a,

Supporting Information) and R-TiO₂ (Figure S10b, Supporting Information). R-TiO_{2-x} shows the typical electrochemical characteristics of TiO₂-based anodes, with a pair of cathodic/anodic peaks at 0.76/0.84 V, while those for R-TiO₂ are at 0.67/0.86 V. Obviously, the voltage offset (ΔE_p) of R-TiO_{2-x} is much lower than that of R-TiO₂, indicating less polarization and faster electrochemical reaction kinetics after the introduction of the amorphous shell. The amorphous shell always possesses higher surface area compared to the crystalline structure, which would provide sodium ion access to the electrolyte/TiO₂ interface.^[33] Moreover, this amorphous shell is different from an ordinary amorphous structure. It has abundant defects, which could enhance electron transfer within the material.^[17]

To understand the difference of S doping concentration and doping site in modifying the electronic structure of TiO₂, we calculated the total density of states (TDOS) and the projected density of states (PDOS) of pristine, anion-site S doped (S@O) and cation-site S doped (S@Ti) rutile TiO₂ with different doping concentrations using 24-atom (4.17 at. %), and 162-atom (0.62 at. %) rutile supercells, respectively (Figure S11, Supporting Information). Clearly, the band gap decreases after both S@O and S@Ti (Table S4, Supporting Information). For S@O, the S 3p states are mixed with the valence band maximum (VBM) owing to the much higher atomic orbital energy level of the S 3p state than that of the O 2p state, thus resulting in an increased bandwidth of the valence band and a narrowed band gap (**Figure 5a and 5b**). S@Ti does not generate free carriers and the lone pair 3s state is present at the VBM, which also results in a decrease in the band gap (Figure 5a and 5b). The wave functions for the conduction band maximum (CBM) and VBM in 24-atom supercells of pure and S doped rutile TiO₂ show similar results (Figure 5c-f). As consequence, anion-site and cation-site S doping strategies have two different mechanisms of action on the band structure of rutile phase, between which, cation-site doping is more advantageous for reducing the band gap at the same doping concentration (Table S4, Supporting Information). Notably, with increasing

doping concentration, the band gap decreases gradually from 1.54 eV (0.61 at. % S doping concentration) to 0.98 eV (4.16 at. % S doping concentration) (Table S4, Supporting Information). Moreover, the calculated results for the carrier effective masses along different axes in 24-atom supercells of pure and S doped TiO₂ show a greatly decreased hole effective mass after S doping, which would increase the mobility of holes in the rutile and hence increase its intrinsic electronic conductivity (Table S5, Supporting Information). These calculation results indicate that cation-site S doping combined with a high doping concentration could effectively decrease the band gap and increase the mobility of holes in rutile to a greater extent, thus giving rise to better electronic conductivity.

In summary, an Ar/H₂ plasma-assisted S doping strategy was designed in this work to modify rutile TiO₂. By means of prior Ar/H₂ plasma treatment, an ultrathin surface amorphous shell (~3 nm) was induced, and a much higher S doping concentration and deep S doping (cation site doping) were achieved. When used as sodium ion battery anode, the as-prepared R-TiO_{2-x}-S exhibited significantly improved sodium storage performance compared with other control samples, with high discharge capacities of 264.8 mAh g⁻¹ and 128.5 mAh g⁻¹ at 50 mA g⁻¹ and 10000 mA g⁻¹, respectively, together with almost 100% capacity retention at 10000 mA g⁻¹ over 6500 cycles. This plasma-assisted S doped TiO₂ without any carbon coating showed ultrafast sodium insertion/extraction capability and extraordinary cycling stability, which outperformed most reported TiO₂ samples in the references. The experimental measurements and DFT calculations showed that the superior electrochemical performance of R-TiO_{2-x}-S can be attributed to its highly improved intrinsic electronic conductivity and accelerated sodium ion diffusion kinetics originating from the surface amorphization and deep S doping with high doping concentration. Such improvements signify that structural modification by plasma treatment is an effective strategy for improving the electrochemical performance of advanced battery materials.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. Synthesis process for $R\text{-TiO}_2\text{-S}$, $R\text{-TiO}_{2-x}$, and $R\text{-TiO}_{2-x}\text{-S}$.

Figure 2. HRTEM images of (a) R-TiO₂, (b) R-TiO₂-S, (c) R-TiO_{2-x}, and (d) R-TiO_{2-x}-S. Selected high-angle annular dark field (HAADF) images and the corresponding EDX mapping images for (e-e₃) R-TiO₂-S and (f-f₃) R-TiO_{2-x}-S. XRD patterns for the as-prepared (g) R-TiO₂-S and (h) R-TiO_{2-x}-S samples with Rietveld refinement. (i) S 2p XPS spectra of R-TiO₂-S and R-TiO_{2-x}-S. The insets in (b) and (d) are the respective line profiles along the red lines.

Figure 3. (a) TOF-SIMS depth profiles of S element for all the as-prepared TiO₂ samples. EPR images of (b) R-TiO₂ and R-TiO₂-S, and (c) R-TiO_{2-x} and R-TiO_{2-x}-S. (d) UV-vis absorption spectra of all the as-prepared TiO₂ samples.

Figure 4. (a) The initial charge/discharge curves of all the samples at 50 mA g⁻¹ in the voltage range of 0.01-3.0 V. (b) Cycling performances of all the samples at 50 mA g⁻¹. (c) Rate performances of R-TiO₂, R-TiO₂-S, R-TiO_{2-x}, and R-TiO_{2-x}-S. (d) Charge-discharge profiles of R-TiO_{2-x}-S at different rates. (e) Cycling performance and Coulombic efficiency of R-TiO_{2-x}-S at 10 A g⁻¹ over 6500 cycles.

Figure 5. Calculated total density of states (TDOS) and partial density of states (PDOS) of (a) pristine rutile TiO₂ and S doped 162 atom TiO₂ supercells with different doping sites, (b) pristine rutile TiO₂ and S doped 24 atom TiO₂ supercells with different doping sites. The average potentials of the host elements far away from the dopant are used to align the DOS. Square wavefunctions for the conduction band minimum (CBM) and valence band maximum (VBM) in 24-atom supercells of (c-d) pure TiO₂, (e-f) O-site S doped TiO₂ (S@O), and (g-h) Ti-site S doped TiO₂ (S@Ti) (electron density: $2 \times 10^{-5} \text{ e}/\text{\AA}^3$).

Surface amorphous TiO₂ with high content of cation site doped S is achieved with the assistant of plasma. Those features give rise to greatly improved intrinsic electronic conductivity and enhanced sodium ion diffusion of TiO₂, leading to superior sodium storage performance. This strategy opens a new avenue to design advanced materials for energy storage system.

Keyword

sodium ion battery; titanium dioxide; deep cation-site S doping; amorphous shell; rate performance

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Title

Plasma-induced amorphous shell and deep cation-site S doping endow TiO₂ with extraordinary sodium storage performance

TOC figure