Nitrogen-doped black titania for high performance supercapacitors

Chongyin Yang¹, Xin Wang⁴, Wujie Dong¹, I-Wei Chen², Zhou Wang¹, Jijian Xu¹, Tianquan Lin¹, Hui Gu¹ and Fuqiang Huang^{1,3*}

ABSTRACT For energy storage system, it is still a huge challenge to achieve high energy density and high power density simultaneously. One potential solution is to fabricate electrochemical capacitors (ECs), which store electric energy through surface ion adsorption or redox reactions. Here we report a new electrode material, heavy nitrogen-doped (9.29 at.%) black titania ($\text{TiO}_{2-x}\text{N}_x$). This unique hybrid material, consisting of conductive amorphous shells supported on nanocrystalline cores, has rapid N-mediated redox reaction ($\text{TiO}_{2-x}\text{N}_y + z\text{H}^+ + ze^- \leftrightarrow \text{TiO}_{2-x}\text{N}_y\text{H}_z$), especially in acidic solutions, providing a specific capacitance of 750 F g^{-1} at 2 mV s^{-1} (707 F g^{-1} at 1 A g^{-1}), great rate capability (503 F g^{-1} at 20 A g^{-1}), and maintain stable after initial fading. Being a new developed supercapacitor material, nitrogen-doped black titania may revive the oxide-based supercapacitors.

Keywords: black titania, supercapacitor, nitrogen-dopant, N-mediated redox reactions

INTRODUCTION

Transition metal oxides have been extensively studied as potential electrode materials. In supercapacitors, they accept ion adsorption as in electrochemical double-layer capacitors; in addition, they store energy *via* cation redox, like batteries but just on surface [1]. However, such electrodes except for RuO_2 cannot serve as both cathode and anode. Moreover, their power and energy densities as well as endurance still fall short of the requirements for practical electrochemical capacitor (EC) applications [2]. Recently, we demonstrated nitrogen doping can activate unexpectedly large, fast redox activities in few-layer car-

bon [3], which otherwise is electrochemically inert and exhibits only electrical double-layer capacitance (EDLC). Like graphene, many partially reduced transition metal oxides feature excellent conductivity. Therefore, we hypothesized that a similar approach could also convert transition metal oxides into promising EC materials. Specifically, we suspect that an anionic network with N^{3-} substituting O^{2-} may allow enhanced redox capacity; meanwhile, facile polarized charge transfer in the cationic network may enable rapid kinetics. This two-prong approach could endow additional high-rate capacitance to a transition metal oxide.

Commercial rechargeable Li-ion batteries have excellent energy densities ($E_s \sim 100\text{--}250 \text{ W h kg}^{-1}$) but inadequate power densities ($P_s < 0.5 \text{ kW kg}^{-1}$) and lifetimes (< 2000 cycles) [4,5]. In comparison, an EC that combines the high power density of EDLC and the high redox energy density of pseudocapacitor would be very promising. This prospect has driven recent advances in aqueous ECs by engineering either electrode nanostructures or electrode redox reactions [6–13]. The first approach seeks to increase electrochemical activities and decrease internal electric loss by using, e.g., carbon electrodes with sub-nanometer pores or nano-fibers [14,15]. The second approach seeks to employ transition metal oxides traditionally reserved for aqueous batteries (e.g., MnO_2 , NiO and RuO_2) to enable pseudocapacitor mechanisms [16]. However, neither approach has succeeded in reaching the target with Li-ion batteries' energy density and supercapacitors' power density.

Titania has been extensively studied as a photocatalyst

¹ State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

² Department of Materials Science and Engineering, University of Pennsylvania, Pennsylvania, PA 19104-6272, USA

³ State Key Laboratory of Rare Earth Materials Chemistry and Applications and National Laboratory, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

⁴ College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, China

* Corresponding author (email: huangfq@mail.sic.ac.cn)

and anode in dye-sensitized solar cells [17,18]. The recent discovery of highly conductive reduced TiO_2 —also an excellent photocatalyst [19,20] with remarkable microwave absorption [21–24], and supercapacitor-like Li storage [25], naturally portends its use in ECs. Indeed, conducting TiO_2 whiskers grown on conducting carbon mats have been used to support a MnO_2 redox electrode and a nanostructured carbon electrode in an asymmetrically-structured EC [6]. But as an active material with surface redox reactions, nanostructured TiO_2 itself only features a modest capacitance [26]. We nevertheless chose titania to study because of its low density and structure; we also viewed the corner-connected TiO_6 octahedral network favorable for high conductivity since it should remain stable and connected even after substantial O^{2-} removal and N^{3-} substitution.

Herein, a N-doped black titania ($\text{TiO}_{2-x}\text{:N}$) in a H_2SO_4 electrolyte can indeed provide high specific capacitance via rapid N-mediated redox reactions ($\text{TiO}_{2-x}\text{N}_y + z\text{H}^+ + ze^- \leftrightarrow \text{TiO}_{2-x}\text{N}_y\text{H}_z$), especially in acidic solutions, providing a specific capacitance of 750 F g^{-1} at 2 mV s^{-1} (707 F g^{-1} at 1 A g^{-1}), fast charging/discharging (503 F g^{-1} at 20 A g^{-1}), and maintain stable after initial fading (75% after 2000 cycles).

EXPERIMENTAL SECTION

Materials

Preparation of black titania electrodes is schematically illustrated in Fig. S1. Preparation of TiO_{2-x} and $\text{TiO}_{2-x}\text{:N}$ was described elsewhere [19,27]. Briefly, titania powders were precipitated from a TiCl_4 (Alpha Aesar) solution by adjusting pH to reach 7, followed by freeze-drying and grinding. The powders were reduced at 550°C by molten Al, in vacuum ($5 \times 10^{-4} \text{ Pa}$), then partially nitridized at 500°C for 4 h in NH_3 (300 sccm) to obtain $\text{TiO}_{2-x}\text{:N}$. Graphene foam was grown by chemical vapor deposition on a fugitive nickel foam—later removed by 0.5 mol L^{-1} HCl etching, as free-standing three-dimensional (3D)-graphene foam [28].

Material characterizations

Transmission electron microscopy (TEM), scanning TEM (STEM), and selected area electron diffraction (SAED) were conducted using a Tecnai-F20 microscope (FEI Co., USA) at 200 kV. Scanning electron microscopy (SEM) was conducted using a Supra 55 microscope (Carl Zeiss, Germany) at 1 kV. X-ray diffraction (XRD) patterns were obtained using a Bruker diffractometer (D8 FOCUS) at 40 kV and 40 mA with Cu K α radiation ($\lambda = 0.15418 \text{ nm}$).

X-ray photoelectron spectroscopy (XPS) was performed in an RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K α radiation ($h\nu = 1253.6 \text{ eV}$). Electron paramagnetic resonance (EPR) spectra were collected using a Bruker EMX-8 spectrometer at 9.44 GHz at 300 K. Magnetization versus magnetic field (M - H) was measured in a Physical Property Measurement System (Quantum Design).

Electrochemical characterization

Electrochemical measurements were conducted using an electrochemical workstation (CHI 760E). Properties of the active material (titania) were measured using three-electrode aqueous cells with a titania working electrode (embedded in a 3D-graphene current collector), a Pt counter electrode ($45 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$) and an Ag/AgCl reference electrode (Fig. S1 in Supplementary information).

Calculation of electrochemical properties

When the electrode contained a non-titania current collector (e.g., 3D-graphene), its weight was measured with and without titania loading. The weight of the active material (M_{TiO_2}) of the electrode was calculated using Equation (1),

$$M_{\text{TiO}_2} = M_{\text{electrode}} - M_{\text{collector}}, \quad (1)$$

where $M_{\text{electrode}}/M_{\text{collector}}$ are the weights of the loaded electrode and unloaded current collector, respectively.

The capacitance (C , in F g^{-1}) from cyclic voltammetry (CV) curves at different sweep rates was calculated using Equation (2)

$$C = A / 2mvV, \quad (2)$$

where A is the integrated area of the CV loop (in W), m is the mass of active materials, v is the sweep rate (in V s^{-1}), and V (in V) is the width of the potential window.

The capacitances from the galvanostatic (CC) curves at different current densities were calculated using Equation (3)

$$C = it / mV, \quad (3)$$

where i is the current applied (in A), t is the discharge time (in s), and V is the width of the potential window. The blank electrode without active materials was also tested under the same condition, which was deducted for calculating the specific capacitance of the active materials.

RESULTS AND DISCUSSION

N-doped black titania, $\text{TiO}_{2-x}\text{:N}$, by annealing/doping (in flowing NH_3) a black titania (referred to as TiO_{2-x}) pre-

pared from a low-cost, scalable aluminum-reduction process [19]. The as-obtained $\text{TiO}_{2-x}\text{:N}$ has a high surface-area, $263 \text{ m}^2 \text{ g}^{-1}$, and can be easily incorporated into electrodes and ECs as shown in Fig. S1. Nominally nanocrystalline anatase according to XRD (Fig. 1a), both $\text{TiO}_{2-x}\text{:N}$ and TiO_{2-x} crystallites actually have an amorphous shell (Fig. 1b) [20]. In TiO_{2-x} , the amorphous shell presumably formed when the anatase lattice collapsed to relieve the strain from O^{2-} depletion and $\text{Ti}^{4+}/\text{Ti}^{3+}$ conversion. While amorphous structure does not necessarily enhance electrochemical activity, we found it makes N^{3-} substitution easier in forming $\text{TiO}_{2-x}\text{:N}$. High resolution transmission electron microscopy (HRTEM) images revealed $\text{TiO}_{2-x}\text{:N}$ powders as agglomerates of $\sim 10\text{--}20 \text{ nm}$ near-spherical nanoparticles with an amorphous shell of $\sim 2 \text{ nm}$ thick, which would constitute 50%–80% of the particle volume. To discern the nanostructure, the same-region imaging was performed using high angle annular dark-field STEM (HAADF-STEM), as shown in Fig. 1c and e, and dark-field TEM (DF-TEM), as shown in

Fig. 1d and f. The HAADF-STEM images show scattered low-density regions (porous pockets) of various sizes most likely 3D distribution (Fig. 1c, e). The corresponding DF-TEM images suppress the contrast in the crystalline cores and highlight the amorphous surface layer (Fig. 1d, f). In DF-TEM, by selecting a specific diffraction axis in the SAED, the core being a single crystal shows a dark contrast while the amorphous shell with random short-range order reveals random bright points (see Fig. 1d). Lastly, by selecting all the diffraction axes in the SAED (Fig. 1g), the DF-TEM image shows a fuzzy amorphous shell surrounding a (colored according to crystalline orientation) crystalline core with some sharp edges (Fig. 1f). Thus, the overall impression is porously packed, crystalline-core/amorphous-shell, nanoparticles.

The concentration of N in $\text{TiO}_{2-x}\text{:N}$ determined by XPS (Fig. 2a) was 9.29 at.%. According to O 1s XPS, the surface of $\text{TiO}_{2-x}\text{:N}$ has a lower level of oxidation and/or O/OH adsorption than TiO_{2-x} (Fig. 2b). On the other hand, while Ti 2p XPS indicates increased Ti^{3+} (and

Figure 1 Structure and nanostructure. (a) XRD patterns of Al-reduced titania before (TiO_{2-x}) and after ($\text{TiO}_{2-x}\text{:N}$) nitrogen doping. (b) HRTEM image. (c) HAADF-STEM image of $\text{TiO}_{2-x}\text{:N}$. (d) High resolution DF-TEM image for the same region as (c). (e) HAADF-STEM image of $\text{TiO}_{2-x}\text{:N}$ at a lower magnification. (f) DF-TEM image for the same region as (e), with different crystallite orientations indicated by different colors according to the SAED pattern in (g).

Figure 2 XPS, magnetic hysteresis and EPR spectra of TiO_2 , TiO_{2-x} and $\text{TiO}_{2-x}\text{:N}$. (a) N 1s and (b) O 1s core-level XPS of titania powder before (TiO_2) and after Al-reduction (TiO_{2-x}), and after further nitrogen doping ($\text{TiO}_{2-x}\text{:N}$). Main peak in O 1s XPS around 529.9 eV is assigned to Ti–O bonds, and shoulder at around 532 eV is due to adsorbed hydroxyl groups. (c) Ti 2p XPS of TiO_2 , TiO_{2-x} , and $\text{TiO}_{2-x}\text{:N}$, and their de-convolutions. Same spectra of TiO_{2-x} and TiO_2 suggest surface oxidation of Ti^{3+} (and possibly some Ti^{2+}) due to exposure to atmospheric O_2 and H_2O . (d) M - H and (e) EPR spectra of TiO_2 , TiO_{2-x} , and $\text{TiO}_{2-x}\text{:N}$ showing $\text{TiO}_{2-x}\text{:N}$ being intermediate between TiO_2 and TiO_{2-x} .

possibly some Ti^{2+}) concentration on $\text{TiO}_{2-x}\text{:N}$ compared with TiO_2 (Fig. 2c), TiO_{2-x} has the same surface concentration of Ti^{3+} (possibly including some Ti^{2+}) as TiO_2 . This suggests that surface oxidation may have occurred when the samples were exposed to the ambient air; as a result, the difference between different forms of titania is obliterated. A more definitive bulk-representing measure of Ti^{3+} comes from its magnetic signature. Relative to TiO_2 and TiO_{2-x} , $\text{TiO}_{2-x}\text{:N}$ has an intermediate magnetization (Fig. 2d) and EPR spectrum (Fig. 2e, the data is normalized by the weights of samples), both due to paramagnetic Ti^{3+} . The data of bulk transport measurement shown in Table S1 further indicates that $\text{TiO}_{2-x}\text{:N}$ has a lower carrier concentration than TiO_{2-x} , but a higher conductivity because of the higher carrier mobility (TiO_2 was too resistive to measure at room temperature). Since (a) NH_3 atmosphere having a partial pressure of hydrogen can cause reduction, while N^{3-} substitution of O^{2-} can be charge-compensated by either (b) Ti^{3+} to Ti^{4+} conversion (oxidation) or (c) oxygen vacancy creation, and both higher oxygen vacancies and higher carrier concentrations will lower the mobility, our $\text{TiO}_{2-x}\text{:N}$ re-

sults of net $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$ conversion and higher mobility suggest (b) overwhelms (a), and (c) is insignificant.

Electrochemical properties of $\text{TiO}_{2-x}\text{:N}$, TiO_{2-x} , and TiO_2 were measured in a three-electrode cell with a Pt counter electrode and an Ag/AgCl reference electrode (Fig. S1). A small amount of carbon black was used to improve the inter-particle contact of $\text{TiO}_{2-x}\text{:N}$ and to reduce the electrode resistance, and a 3D-graphene foam was used as the current collector [28] (Unless otherwise noted, containing 0.5 mg $\text{TiO}_{2-x}\text{:N}$ in each electrode. See EXPERIMENTAL SECTION for sample details, symbol definitions and data calculations). To avoid H_2 (at $<0 \text{ V}_{\text{RHE}}$ = reversible hydrogen electrode voltage) and O_2 evolutions (at $>1.23 \text{ V}_{\text{RHE}}$) from water, we selected the following voltage windows: $\sim 0.2\text{--}0.9 \text{ V}_{\text{RHE}}$ at pH 0 ($0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution), corresponding to $0\text{--}0.7 \text{ V}_{\text{Ag/AgCl}}$. The dramatic improvement of $\text{TiO}_{2-x}\text{:N}$ over TiO_2 is evident from the CV plots (Fig. 3a) at pH 0 at 2 mV s^{-1} : a specific capacitance C_s of 750 F g^{-1} for $\text{TiO}_{2-x}\text{:N}$, vs. 15 F g^{-1} for TiO_2 and 240 F g^{-1} for TiO_{2-x} . At other scan rates ($5\text{--}100 \text{ mV s}^{-1}$), the $\text{TiO}_{2-x}\text{:N}$ electrode also performed well (Fig. 3b and d upper), giving 665 F g^{-1} at

Figure 3 Electrochemical performance. (a) CV curves of TiO_{2-x}N and TiO_{2-x} scanned at 2 mV s^{-1} in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ aqueous electrolyte. TiO_2 shows no activity. (b) Rate capability spanning over 2 to 100 mV s^{-1} . (c) Galvanostatic charge/discharge (CC) curves of TiO_{2-x}N electrode measured at 1–20 mA (1–20 A g^{-1}). (d) Rate capability spanning over 1 to 20 A g^{-1} and 2–100 mV s^{-1} . (e) Cole-Cole plot of complex impedance of TiO_{2-x}N electrode, with frequency marked at two locations. Inset: phase angle versus frequency. (f) Retained capacitances of TiO_{2-x}N in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ after 2000 CV cycles at a scan rate of 100 mV s^{-1} .

10 mV s^{-1} and 455 F g^{-1} at 100 mV s^{-1} . The specific capacitance was further determined from the galvanostatic charge/discharge (CC) plot (Fig. 3c), giving 707 F g^{-1} at 1 A g^{-1} . At a very high current density of 20 A g^{-1} (Fig. 3c and d below), the CC curve at a charge/discharge time of $\sim 17 \text{ s}$ (typically achievable only in high-rate double-layer capacitors) still features a capacitance of 503 F g^{-1} . Furthermore, from the CC curve's voltage discontinuity of 1.1 mV (an enlarged view in Fig. S2) at 1 A g^{-1} (actual current is 0.5 mA), we obtained an equivalent series resistance (ESR) of $\sim 2.2 \Omega$. Thus, the high-rate capacitance of TiO_{2-x}N electrodes is outstanding, especially in acidic environments.

Dynamic EIS further confirms fast electrochemical kinetics of TiO_{2-x}N electrodes. Unlike TiO_2 and TiO_{2-x} electrodes of a higher DC resistance and lower capacitance (Fig. S3), the TiO_{2-x}N electrode displays a purely capacitive behavior in the Cole-Cole plot (Fig. 3e) with a small complex impedance above $\sim 10 \text{ Hz}$. The plateau phase angle of -75° at 0.01 Hz indicates a close-to-ideal capacitor (inset in Fig. 3e), and the characteristic frequency $f_0 = 0.12 \text{ Hz}$ at -45° when resistive impedance equals capacitive impedances gives a time constant $\tau_0 = 1/f_0$ of 8.3 s . (Activated-carbon ECs have $\tau_0 \sim 10 \text{ s}$ [29], and N-doped few-layer graphene has $\tau_0 \sim 2.1 \text{ s}$ [3]. At the high-

frequency limit (e.g., 10 kHz), the real-part impedance of 2Ω matches the ESR estimated from the CC curve (2.2Ω). Cycling performance was also evaluated: at 100 mV s^{-1} , the CV curves in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ electrolyte suffer a fast initial fading but remain stable after then, retaining 75% of the initial capacitances after 2000 cycles. The fast fading at the beginning may be due to the N loss, as explained later. Table 1 compares the performance of the TiO_2 -based supercapacitors. Obviously, although most of the TiO_2 -based supercapacitors prepared by *in-situ* oxidation of Ti foil/mesh show high surface capacitances, the workability is also limited. Differently, TiO_{2-x}N powder can be used easily and exhibits excellent performance.

In our previous study of N-doped few-layer carbon, N is covalently bonded to the C network and thus permanently attached to the latter. To investigate the stability of N in TiO_{2-x}N , we held it at the maximum potential of the electrochemical test (see below) for various times, then checked its XPS signal (Fig. 4a–c). Indeed, after the first 24 h during which some N was lost (Fig. 4a), while subsequent XPS and EPR spectra all showed little change after many days (Fig. 4a–c, d). Therefore, the nitridized product is stable in the electrochemical environment of active ECs. Moreover, after holding the electrode at 0.7 V ,

Table 1 Performance comparison of the TiO₂-based supercapacitors

Electrode materials	Specific capacitance	Electrolyte	Ref.
TiO _{2-x} :N	750 F g ⁻¹ @2 mV s ⁻¹ 707 F g ⁻¹ @1 A g ⁻¹	0.5 mol L ⁻¹ H ₂ SO ₄	This work
TiO ₂ nanotube array	3.113 mF cm ⁻² @10 μA cm ⁻²	1.0 mol L ⁻¹ H ₂ SO ₄	[30]
TiO ₂ nanoribbon-nanotube	1.394 mF cm ⁻² @10 μA cm ⁻²		
TiO ₂ nanowire-nanotube	0.539 mF cm ⁻² @10 μA cm ⁻²		
TiO ₂ nanotube	911 μF cm ⁻² @1 mV s ⁻¹	1 mol L ⁻¹ KCl	[31]
TiO ₂ powder	181 μF cm ⁻² @1 mV s ⁻¹		
TiO _{2-x} nanotube	900 μF cm ⁻² @1 mV s ⁻¹	1 mol L ⁻¹ KCl	[32]
Hydrogenated TiO ₂ nanotube	14.95 mF cm ⁻² @10 mV s ⁻¹	0.5 mol L ⁻¹ Na ₂ SO ₄	[26]
	3.24 mF cm ⁻² @100 mV s ⁻¹		
H-TiO ₂ @C	253.4 F g ⁻¹ @10 mV s ⁻¹	5 mol L ⁻¹ LiCl	[5]
TiO ₂ @C	197.1 F g ⁻¹ @10 mV s ⁻¹		
Nitrided TiO ₂ nanoparticle	85.7 mF cm ⁻² @10 mV s ⁻¹	0.5 mol L ⁻¹ Na ₂ SO ₄	[33]
TiO ₂ nanotube	158 μF cm ⁻² @1 mV s ⁻¹	1.0 mol L ⁻¹ H ₂ SO ₄	[35]
TiO ₂ /Nb ₂ O ₅ nanotube	1536 μF cm ⁻² @1 mV s ⁻¹		
Nitrided TiO ₂ /Nb ₂ O ₅ nanotube	37 mF cm ⁻² @1 mV s ⁻¹		
TiO ₂ nanocrystals	146 F g ⁻¹ @0.2 A g ⁻¹	1 mol L ⁻¹ KOH	[35]
Ti-rich TiO ₂	3.8 mF cm ⁻² @25 μA cm ⁻²	0.5 mol L ⁻¹ Na ₂ SO ₄	[36]
TiO _{2-x} /Ti	81.75 mF cm ⁻² @2 mV s ⁻¹	1.0 mol L ⁻¹ H ₂ SO ₄	[37]

Figure 4 Mechanism investigation. (a–c) The corresponding N 1s, O 1s and Ti 2p XPS spectra of electrochemically treated TiO_{2-x}:N electrodes. Electrodes were held at 0.7 V (vs. Ag/AgCl, oxidation potential) for 48 and 96 h. (d) EPR spectra of pristine TiO_{2-x} and TiO_{2-x}:N electrodes. The latter was also electrochemically treated for up to 96 h. Electrodes were held at 0.7 V (vs. Ag/AgCl, oxidation potential) for 48 h and then 0 V for 48 h.

the binding energy of N, Ti, and O increased 4.1, 0.3 and 0 eV, respectively, meaning that the main energy storage site is N³⁻ in TiO_{2-x}:N, which accepted protons and

achieved a relatively high valence state. To be noted, the binding energy of N in AlN and NaN₃ is ~396 and 400.1 eV, respectively. So we can suspect that *z* is 2*y*–3*y* in

N-mediated redox reaction ($\text{TiO}_{2-x}\text{N}_y + z\text{H}^+ + ze^- \leftrightarrow \text{TiO}_{2-x}\text{N}_y\text{H}_z$). The calculated theoretical capacitance (molecular weight of $\text{TiO}_{2-x}\text{N}_y$ is $\sim 77.2 \text{ g mol}^{-1}$) of the above reaction is $664\text{--}997 \text{ F g}^{-1}$. Besides, some protons may form $-\text{OH}$ (Fig. 4b) and contribute some capacitance by a subordinate reaction of $\text{TiO}_{2-x} + y\text{H}^+ + ye^- \leftrightarrow \text{TiO}_{2-x-y}(\text{OH})_y$, which is the mechanism of the enhanced capacitance of black TiO_{2-x} when compared with white TiO_2 . Therefore, our measured capacitance of 750 F g^{-1} fall in between the estimated theoretical value.

CONCLUSIONS

The overall thermodynamic and kinetic results thus support our hypothesis: N can activate more copious and facile proton absorption/desorption reactions, and such reactions are facilitated by electron transport and $\text{Ti}^{4+}/\text{Ti}^{3+}$ conversion throughout TiO_{2-x}N . This simple approach has transformed titania into a promising new EC electrode material, a possibility hitherto unknown despite decades of research on closely related photon-enabled TiO_2 electrochemistry. Therefore, our approach that relies on N-doping may well find use in the future, aiding the transformation of other highly conductive matter into electrochemically materials for energy-storage applications.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

Chongyin Yang obtained his PhD under the supervision of Prof. Fuqiang Huang at Shanghai Institute of Ceramics of the Chinese Academy of Sciences (SICCAS). He is now an assistant research scientist at the Department of Chemistry and Biochemistry, University of Maryland. His research interests include the design, synthesis and application of supercapacitors and lithium-ion batteries.

Fuqiang Huang obtained his PhD in science from Beijing Normal University in 1996. Then he joined the State Key Lab of High Performance Ceramics & Superfine Microstructure at SICCAS, and became a full professor in 2003. His research interests focus on the new energy materials and devices. He put forward the concept of multiple physical quantities synergy in structure function region for energy conversion materials and the theoretical model of accumulation factor.

氮掺杂黑色二氧化钛用于高性能超级电容器

杨重寅¹, 王鑫⁴, 董武杰¹, 陈一苇², 汪宙¹, 徐吉健¹, 林天全¹, 顾辉¹, 黄富强^{1,3*}

摘要 对于储能系统, 同时实现高能量密度和高功率密度仍是一个巨大的挑战. 电化学超级电容器通过表面吸附或表面氧化还原反应实现储能, 是解决上述问题的潜在方法之一. 本论文报道了一种新型高氮掺杂(9.29 at.%)黑色二氧化钛(TiO_{2-x}N_x)超级电容器电极材料. 该材料具有独特的微观结构, 由高导电的非晶壳层和一个纳米晶核组成. 在酸性电解液中, 该材料可以通过氮参与的氧化还原反应(TiO_{2-x}N_y + zH⁺ + ze⁻ ↔ TiO_{2-x}N_yH_z)可逆地与质子结合实现能量的高效快速储存, 实现极高的比电容(2 mV s⁻¹扫速下容量高达750 F g⁻¹, 1 A g⁻¹电流密度下容量可达707 F g⁻¹)、高倍率特性(极高电流密度20 A g⁻¹时容量仍可达503 F g⁻¹)和长时间循环下的高稳定性. 作为一种新型超级电容器电极材料, 氮掺杂黑色二氧化钛或将引领金属氧化物型超级电容器的复兴.