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Enhanced supercapacitance in anodic TiO₂ nanotube films by hydrogen plasma treatment

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Abstract

One-dimensional anodic titanium oxide (ATO) nanotube arrays hold great potential as electrode materials for high-performance electrochemical supercapacitors. However, their poor electronic conductivity limits their practical applications. Here, we develop a hydrogen (H₂) plasma treatment method to greatly improve the electrochemical performance of ATO electrodes. Compared with pristine ATO, the nanotubes treated by H₂ plasma illumination (ATO-H) present a rough and amorphous layer at the surface of the nanotubes with simultaneously incorporated Ti³⁺ and –OH groups. At a current density of 0.05 mA cm⁻² in charge–discharge measurements, the specific capacitance of the ATO-H electrode has substantially increased ~7.4 times, with a value as high as 7.22 mF cm⁻². Moreover, the novel ATO-H electrode has also exhibited excellent rate capability (6.37 mF cm⁻² at a current density of 2 mA cm⁻²) and cycling performance with no degradation after 10 000 cycles.

S Online supplementary data available from stacks.iop.org/Nano/24/455401/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Nowadays, significant research effort continues in the investigation of one-dimensional (1D) anodic titanium dioxide (ATO) nanotube arrays due to their remarkable functionalities in light harvesting [1–3], electrochromic switching [4], environmental sensing [5], energy storage devices [6], etc. The 1D feature of ATO nanotube arrays provides a large specific surface area as well as a direct pathway for charge transport, thus holding promising capabilities in supercapacitors [7, 8]. However, the specific capacitances based on pristine (without intentional doping) ATO are generally limited to less than 1 mF cm⁻², mainly due to the poor electrical conductivity [9]. Hence,

improvement in the conductivity of ATO nanotubes turns out to be an important issue for enhanced capacitance. Aiming at enhancing conductivity and electrochemical performance, bandgap engineering has been conducted by introducing metal [10] or nonmetal impurities [11] that generate donor or acceptor states in the bandgap. However, overcoming the problems such as charge recombination and thermal/electrochemical instability arising from the dopant incorporation is still a great challenge [12].

Alternatively, self-doping that produces donor states by introducing oxygen vacancies (Ti^{3+} sites) in TiO_2 lattices provides another approach for band structure engineering [13], and delivers significantly improved visible to infrared response [13, 14], electrical conductivity and electrochemical activity [15]. For instance, Salari et al [16] demonstrated an improved specific capacitance by optimizing thermal treatment under an argon atmosphere. The annealing process in an oxygen-poor environment leads to the evolution of oxygen vacancies, which is responsible for the performance boost. Although a specific capacitance (i.e. capacitance per unit planar area) of 2.6 mF cm⁻² obtained at a scan rate of 1 mV s^{-1} was fairly high in comparison with the previous reports, it dropped to about 0.6 mF cm⁻² at higher scan rate of 100 mV s^{-1} , indicating the poor rate capability. More recently, a substantial improvement in the capacitive performance was realized in high-temperature hydrogenated ATO nanotubes [15]. A specific capacitance of 3.24 mF cm^{-2} was achieved at a scan rate of 100 mV s⁻¹, which can be ascribed to the enhanced electrode conductivity associated with the effective hydrogen induced Ti^{3+} sites.

So far the most effective self-doping methods are conducted at high temperature [15, 17] or by a long duration process [13]. In addition, it is known that titanium is susceptible to hydrogen embrittlement [18]. This will hinder the application of the H_2 annealing process in the modification of ATO nanotubes, generally grown on a titanium substrate. It is worth noting that the plasma technique is well known as a powerful and versatile method for surface modification (e.g. cleaning, etching, doping) and film deposition by taking advantage of the higher reactivity of excited elements compared with their corresponding analogs of gas phase [19]. In this work, hydrogenated ATO nanotube films are demonstrated by low-temperature plasma treatment. The subsequent characterizations indicate effective doping as well as excellent electrochemical performance.

2. Experimental details

2.1. Fabrication of ATO nanotube arrays

Ti foils (0.2 mm thickness, Nano Ark Inc.) are firstly cleaned in acetone, ethanol and deionized water successively by ultrasonication after an annealing process (450 °C for 2 h). Self-organized ATO nanotube films (2 cm \times 2 cm) are prepared by two-step anodization of the Ti foils in an ethylene glycol electrolyte containing 0.5 wt% NH₄F and 2 vol% H_2O as described in our previous literature [2, 3]. In brief, the first-step anodization is performed at 60 V for 2 h in a conventional two-electrode configuration with a carbon rod as cathode electrode. The as-obtained nanotube films are removed from the Ti foil with adhesive tape. The second-step anodization is performed under the same conditions as the first process. Finally, the as-prepared ATO nanotubes are annealed at 150 °C for 2 h, then up to 450 °C for 3 h. The crystallized ATO nanotube films, denoted as pristine ATO, are used for the subsequent plasma treatments.

2.2. Hydrogen plasma treatment

The ATO nanotube films are loaded into the processing chamber of the plasma-enhanced chemical vapor deposition (PECVD) system and preheated in a vacuum at 320 °C for 30 min before plasma illumination. Hydrogen plasma is then induced with a radio-frequency power source (13.56 MHz, 40 W) along with hydrogen gas flow at 100 sccm under 50 Pa. The hydrogenation treatment is set as 1.5 h followed by 1 h cooling down before taking the sample out.

2.3. Material and device characterization

The morphology and crystal structure of as-obtained samples are characterized by field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM) and x-ray diffractometer (XRD). X-ray photoelectron spectroscopy (XPS, Shimadzu-Kratos AXIS Ultra DLD) and Raman spectroscopy (DXR Raman microscope with 532-nm excitation laser) are employed for composition and chemical state analysis. Electrochemical performance of the nanotube films is evaluated, using an Autolab PGSTAT302N/FRA2, in 2 M Li2SO4 aqueous solution in a three-electrode configuration, where a Ag/AgCl (3 M KCl) electrode is used as reference electrode and a Pt foil as counter electrode. Cyclic voltammetry (CV) and galvanostatic charge-discharge tests are performed over the potential range from -0.3 to 0.6 V with an active area of 1.2 cm^2 . The calculation methods for areal capacitance, power and energy density from galvanostatic charge-discharge curves can be found in the supplementary data (available at stacks.iop.org/Nano/24/455401/mmedia). Electrochemical impedance spectroscopy (EIS) measurements are carried out in the frequency range from 100 kHz to 0.01 Hz with AC signal amplitude of 10 mV at 0 V DC bias potential.

3. Results and discussion

3.1. Morphology and structural characterization

Figures 1(a) and (b) display the FESEM images of pristine ATO and ATO with H₂ plasma post-treatment (denoted as ATO-H). 2-h anodization yields an ATO film with a thickness of about 14.5 μ m. Highly oriented nanotube arrays can still be observed in ATO-H films with slightly reduced tube wall thickness and outer diameter. Additionally, the side-wall of the nanotubes presents a highly rough surface after hydrogen plasma illumination. This unique structure is attributed to the hydrogen plasma etching effect [20] that increases specific surface area. XRD patterns of the nanotube films with and without H_2 plasma treatment are shown in figure 1(c). All peaks can be indexed to anatase TiO₂ (JCPDF No. 21-1272) excluding the peaks at 40.05°, 52.87° and 70.05° originated from Ti metal. Although the plasma induced hydrogen species have shown superior reductive abilities to transform TiO₂ to Ti_2O_3 at elevated temperatures [21], the XRD patterns do not represent phase change in our present moderate processing condition. The average crystallite sizes (D) of ATO and ATO-H are about 32.0 and 25.6 nm, estimated from (101) and (200) peaks by using Scherrer's equation [22]. The reduction of particle size is believed to be caused by the etching effect of H₂ plasma that can also be deduced from the morphology evolution (figure 1(b)). Interestingly, while



Figure 1. FESEM images of highly oriented (a) ATO and (b) ATO-H nanotubes. The inset of (a) shows a lower magnification view of ATO film with a thickness of 14.5 μ m. (c) XRD patterns of ATO and ATO-H films, respectively. (d) Photographs of the ATO and ATO-H nano-powder showing different colors.

scraping the ATO nanotube powders off Ti foil substrates with a razor blade, a distinct color evolution is observed: ATO is white whereas ATO-H appears dark gray (figure 1(d)). The evolution of optical properties and much enhanced electrochemical performance (discussed below) could be ascribed to the increased defect density [13] and electrical conductivity [15] as revealed by the following structure and electrochemical analysis.

Figure 2(a) shows the TEM image of two adjacent nanotubes with crystalline nanoparticles (D = 25-50 nm) arranged along the nanotubes. It is worth noting that oxygen bubbles have been proposed to be generated (TiO₂ \rightarrow Ti⁴⁺ + O₂ + 4e⁻) during the vigorous anodic growth [23, 24]. Consequently, bubble growth and coalescence are responsible for the formation of oxygen filled cavities at tube boundaries [24]. A close view of the nanotubes displays strong evidence of gas bubbles generated in the anodizing process. Nano-sized voids embedded in tube walls, not confined only at the tube boundaries, with the sizes of 1–5 nm can be frequently observed. The featured characteristics become more significant after plasma treatment due to the pronounced etching effect at defect sites (inset of figure 2(a)).

High resolution TEM imaging of the ATO and ATO-H is further conducted to analyze the crystal structure evolution. Figure 2(b) presents the image of the ATO observed through the $[11\overline{1}]$ zone axis and the corresponding FFT pattern, showing the (101) and (011) facets with an interfacial angle of 82.4° [25]. After hydrogen plasma irradiation, the ATO-H nanocrystal presents a core–shell structure with an amorphous surface layer of 1–2-nm thickness (figure 2(c)). Similar transformation has been recently reported on H₂ annealed TiO_2 nanoparticles, where a hydrogen induced disordered structure and simultaneous self-doping at the surface layer renders a narrowed bandgap with much improved visible light response [26]. Because of the high reactivity of the plasma excited hydrogen element compared with the gas phase, the disordered shell layer can be formed in 1.5 h plasma illumination at a moderate temperature. It is also believed that hydrogen dopant is dominantly located in the shell layer to passivate the active dangling bonds.

The structural properties are further characterized by Raman spectroscopy. The six Raman-active modes of anatase phase can be found at 144.7 cm⁻¹ (E_g), 195.8 cm⁻¹ (E_g), 394.4 cm⁻¹ (B_{1g}), 515.0 cm⁻¹ (A_{1g}), 636.5 cm⁻¹ (E_g) and 519 cm⁻¹ (B_{1g}, superimposed with the 515.0 cm⁻¹ band), in the ATO samples, which is in accord with the XRD results (figure 2(d)) [27]. A slight blue-shift and broadening of the strongest Eg peak can be observed in the ATO-H film, which is ascribed to the phonon confinement effects (inset of figure 2(d)) [28]. It is known that finite grain size (<10 nm) or short correlation length due to the presence of defects is responsible for the phonon confinement. In the present case, the relatively large crystal size (D > 20 nm)even after H₂ plasma treatment) obtained from XRD results rules out the possibility of size confinement effects. In other words, the H₂ plasma induced localized defect sites (oxygen vacancies) contribute the blue-shift and peak broadening in anatase crystal [13, 26]. After the electrochemical charge-discharge cycling test, further increased defect density can be recognized from the broadened black peak.

In addition, due to the high value of average surface free energies (0.90 J m^{-2} > {100} 0.53 J m^{-2} >



Figure 2. (a) TEM images of ATO nanotubes. The inset of (a) shows the voids embedded in ATO-H nanotubes. HRTEM images of (b) ATO and (c) ATO-H nanotubes. The inset of (b) presents the corresponding fast Fourier transform (FFT) pattern. (d) Raman spectra in the range of $80-800 \text{ cm}^{-1}$ for the ATO, ATO-H and ATO-H after running the electrochemical charge–discharge cycling test.



Figure 3. (a) Ti 2p and (b) O 1s XPS spectra of ATO and ATO-H.

{101} 0.44 J m⁻²), the {001} facet of anatase TiO₂ holds superior adsorption, electronic, and photocatalytic properties, and accordingly has attracted extensive interest. A quantitative value of the percentage of exposed anatase TiO₂ facets is estimated by calculating the Raman peak intensity ratio of the E_g (144.7 cm⁻¹) and A_{1g} (515.0 cm⁻¹) peaks [29]. The value of ~7% is similar to that of conventional anatase nanoparticles. Thus, higher catalytic or transport performance is expected to be achieved by engineering the facets during anodization or post-processing.

X-ray photoelectron spectroscopy (XPS) is used to distinguish the Ti 2p and O 1s valence environment of ATO films before and after H₂ plasma treatment. The Ti 2p peaks of both samples are fitted by asymmetric Gaussian curves as shown in figure 3(a). The binding energies of ATO located at 464.7 and 458.9 eV can be indexed to Ti^{4+} 2p_{1/2} and Ti^{4+} 2p_{3/2} peaks [15, 30]. After plasma treatment, the Ti^{3+} 2p_{1/2} peak at 457.8 eV becomes visible, indicating increased Ti^{3+} concentration [16]. Figure 3(b) shows the XPS

spectra of the O 1s core level of ATO and ATO-H. The peaks at 530.0 and 531.0 eV appearing in both samples correspond to the lattice oxygen of TiO₂ and oxygen vacancy-Ti³⁺ type surface states. The increased peak area of 531.0 eV in the ATO-H sample again suggests more oxygen vacancies are introduced. The shoulder peak located at 532.4 eV in the ATO-H curve is from Ti–OH on the surface [31]. The above Raman and XPS analyses represent similar results to those of high-temperature annealing in a H₂ atmosphere [15]. However, it was found that the annealing treatment of ATO nanotubes grown on Ti foils in a H₂ atmosphere at temperatures up to 450 °C causes a brittle Ti foil substrate, because titanium is susceptible to hydrogen embrittlement as mentioned above [18]. In contrast, H₂ plasma treatment at 320 °C can keep the toughness feature of Ti foils.

3.2. Electrochemical performance

Figure 4(a) presents *CV* curves of ATO and ATO-H electrodes in a three-electrode configuration at a scan rate of 100 mV s^{-1} .



Figure 4. (a) *CV* curves of ATO and ATO-H electrodes in a three-electrode electrochemical cell at a scan rate of 100 mV s⁻¹. (b) *CV* curves of ATO-H recorded at different scan rates from 0.1 to 1.2 V s^{-1} . (c) Dependence of the discharge current density (*J*) on the scan rate for the ATO-H electrode (linear relation is obtained up to 0.35 V s^{-1}). Galvanostatic charge–discharge curves of ATO-H obtained under (d) 0.05–0.5 mA cm⁻² and (e) 1–2 mA cm⁻². (f) Specific capacitance and Coulombic efficiency of ATO-H at different discharge current densities.

Compared with the poor performance of pristine ATO, the *CV* curve of the ATO-H electrode exhibits a quasi-rectangular shape. The integrated area of its *CV* curve is ~7.2 times larger than that of the ATO electrode, indicating the prominent enhancement after H₂ plasma treatment. Figure 4(b) shows the *CV* curves for the ATO-H electrode at different scan rates over the wide range from 0.1 to 1.2 V s⁻¹. Significantly, the curves can still keep quasi-rectangular shape as the scan rate is up to 1.2 V s⁻¹, manifesting the excellent capacitive behavior and high rate capability. In addition, the average discharge current density for the ATO-H electrode continues to increase linearly with the scan rate as high as 0.35 V s⁻¹ (figure 4(c)). The deviation of the linear dependence at higher scan rates is believed to result from the diffusion limit of electrolyte ions to the electrode materials [32].

The rate performances for the ATO and the ATO-H are also evaluated by galvanostatic charge-discharge test at different current densities. The results reveal distinct differences between ATO and ATO-H again. For the pristine ATO, the largest discharge current density appears to be limited to 0.05 mA cm^{-2} due to the big voltage drop of the discharge curve (figure S1 available at stacks.iop.org/Nano/ 24/455401/mmedia). A relatively low specific capacitance of 0.97 mF cm⁻² at 0.05 mA cm⁻² is obtained from the discharge curve in figure S1 (available at stacks.iop.org/Nano/ 24/455401/mmedia). In contrast, the H₂ plasma treatment delivers a much improved capacitance with excellent rate capability. The ATO-H electrode can be steadily operated over a wide range of applied current densities from 0.05 to 2 mA cm⁻² (figures 4(d) and (e)). The symmetric and linear curves indicate the high charge-discharge Coulombic efficiency of the ATO-H electrode at all operated current

densities, as shown in figure 4(f). The novel ATO-H electrode delivers a specific capacitance of 7.22 mF cm⁻² at 0.05 mA cm^{-2} , with areal power density of 13.50 mW cm $^{-2}$ and energy density of 0.81 mWh cm^{-2} . Typically, an increase in discharge current densities will normally lead to the decrease of specific capacitance due to the ion diffusion limit [32]. Figure 4(f) shows the specific capacitance as a function of discharge current density for ATO-H. Only a small decrease occurs at the onset of current increase, followed by a transition to a quasi-steady-state value. Specifically, the areal specific capacitance, power density and energy density can reach 6.37 mF cm⁻², 18.40 mW cm⁻² and 0.72 mWh cm⁻² respectively at a current density of 2 mA cm⁻², in which an extra 36% of power density is obtained by sacrificing only 12% of specific capacitance. This outstanding rate performance reflects good capacitance retention for the ATO-H electrode. In addition, a rather low voltage drop (0.044 V) at a considerably high discharge current density of 2 mA cm^{-2} indicates the excellent conductivity of the ATO-H electrode (figure S2 available at stacks.iop.org/Nano/ 24/455401/mmedia). Taking account of the composition and chemical state of ATO-H, the improved electrical conductivity and the corresponding electrochemical performance are believed to be the results of increased charge carrier density due to the intentionally incorporated oxygen vacancies (or Ti³⁺ sites).

Electrochemical impedance spectroscopy (EIS) is an efficient tool to evaluate the electrochemical performance of supercapacitor electrodes. Figure 5 compares the Nyquist plots for ATO and ATO-H. As is apparent from the inset of figure 5, the ATO-H in the high frequency range shows an extremely small semicircle diameter, indicating low charge



Figure 5. Nyquist plots for (a) ATO and (b) ATO-H. The insets show the high frequency regions of the Nyquist plots.



Figure 6. Cycling performance of ATO-H at a current density of 0.1 mA cm^{-2} .

transfer resistance and ultrahigh conductivity of the electrode. Furthermore, the approximately vertical line in the low frequency part as shown in figure 5(b) demonstrates ideal capacitor characteristics for the ATO-H sample. The enhanced capacitive performance of ATO-H could be ascribed to two important factors: the improved conductivity of the electrode due to the increased carrier density, which leads to efficient charge carrier transport, and the highly rough surface induced by the plasma etching effect which offers larger specific surface areas for ion adsorption giving rise to an increase in capacitance.

The excellent long-term stability of the ATO-H electrode is also demonstrated by charge-discharge test up to 10000 cycles at a current density of 0.1 mA cm⁻² (figure 6). The ATO-H electrode presents unique capacitance retention with a ratio even exceeding 100% of initial capacitance after about 500 cycles. Thereafter, it is fairly constant. This behavior probably originates from a self-activation process of the electrode, i.e. the initial cycles allow sufficient absorption and intercalation/deintercalation of ions, which generates increased active sites and in turn the enhanced specific capacitance [33]. In addition, we studied the chemical structure of the electrode after 10000 cycles by Raman spectroscopy (figure 2(d), black line). The broadened E_g peak at low frequency indicates structural change, possibly because of the slightly increased defect density after the cycling test [34]. It is known that the incorporation of Ti^{3+} sites in

this self-doping process will generate abundant disordered states and lead to a negative effect on cycling stability. The surprising long-term stability could be ascribed to the passivation of dangling bonds by plasma induced hydrogen species [13].

4. Conclusions

In summary, we have demonstrated a plasma assisted hydrogenation method to enhance electrochemical properties of anatase ATO nanotube arrays for potential application in supercapacitors. The rough tubular surface with the introduction of Ti^{3+} and -OH groups is obtained through the $\rm H_2$ plasma treatment. This unique nanotube electrode can deliver capacitance of 7.22 mF cm^{-2} at 0.05 mA cm^{-2} and 6.37 mF cm⁻² at 2 mA cm⁻² with excellent rate capability and cycling stability. The substantially improved electrochemical performance by the plasma treatment can be attributed to increased specific surface area, outstanding conductivity and hydrogen passivation of disordered states. This approach offers a novel and effective technique to boost the specific capacitance, rate capability, and cycling stability of electrode materials for supercapacitors. Moreover, the well developed plasma technique in the semiconductor industry provides the feasibility of large scale treatment with the feature size down to micrometer scale, which possesses great potential in developing high-performance energy storage devices in integrated circuits.

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