Semimetallic core-shell TiO₂ nanotubes as a high conductivity scaffold and use in efficient 3D-RuO₂ supercapacitors

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Abstract

In the present work we report on TiO₂ nanotube arrays (TNTAs) that were converted to a conductive scaffold established via an optimized reduction treatment in Ar/H₂. These conductive TNTAs are then employed for RuO₂ nanoparticle decoration. The effect of the Ar/H₂ treatment is evaluated by electron energy loss spectroscopy (EELS) and electron paramagnetic resonance (EPR). The results show that, under ideal conditions, buried Ti³⁺ states are formed, with a higher concentration in the inner shell of the nanotube. Together with the capacitive and conductive performance, investigated by solid-state conductivity and electrochemical measurements, we find that 20 μm long TNTAs, annealed at 550°C in Ar/H₂, yield an optimized and stable structure that provides a remarkably low resistivity of 13.5 KΩ/tube (vs. 70.2 MΩ for non-treated nanotubes). In cycling experiment, with a loading of only 0.048 mg.cm⁻² RuO₂ a specific capacitance of 1297 F.g⁻¹ can be reached. The reason for this highly efficient use of RuO₂ is that the conducting core-shell scaffold provides a unique, well dispersed RuO₂ nanoparticle structure (~2.8 nm), which is responsible for the high specific capacitance, and moreover yields an excellent long-term cycling stability.

Keywords: TiO₂ nanotube; semimetallic TiO₂; cyclic voltammetry; supercapacitor

1.Introduction

Over the past decades, as a result of the increasing energy demands, energy conversion and storage technologies have been the focus of intense research. Very promising candidates for electrochemical storage are supercapacitors, due to their high power density and long cycle life, that can be combined with a fast charge-discharge rate [1–4]. Based on the charge storage mechanism, supercapacitors are usually classified in two categories, that is, electrical double layer capacitors (EDLCs) and pseudocapacitors [5]. EDLCs consist of non-faradaic charge separation at the electrode/electrolyte interface, whereas pseudocapacitors mainly

are governed by a faradaic process at the electrode. This grants pseudocapacitors a potentially higher specific capacitance and energy density through the charging/discharging of the electrode's internal contribution of redox-state switching [1,5,6].

For many years the gold standard for supercapacitor materials is hydrous ruthenium oxide that provides fast and reversible intercalation properties as well as an intrinsic high electron conductivity [5,7,8]. However, the high cost of RuO₂ prevents its wide commercial use in bulk forms. In nanostructured forms, on the other hand, it tends to easily agglomerate during cycling; this leads to a decrease in the active area and the specific capacitance [5,7,8]. While the theoretical mass specific capacitance is 1400 to 2200 F.g⁻¹, the reported experimental values are significantly lower [9] - this difference is mostly due to an inefficient use of RuO₂ (i.e. due to the use of nanoparticle structures that only partially can be intercalated during a charging cycle). In this respect, small-sized RuO₂ nanoparticles (of only a few nm in diameter, i.e. comparable in size to the intercalation depth of the intercalating species), well dispersed on a suitable electron-conductive 1D scaffold with a high specific surface area would represent an ideal platform for an efficient use of the precious RuO₂ [8].

An ideal scaffold provides an electrode geometry with an optimized ion diffusion path through the electrolyte and into the solid – such as a 1D conducting nanotubular or nanowire array. An example of a highly controllable 1D array is given by self-ordered anodic TiO₂ nanotubes (TNTAs). Usually, such TNTAs are obtained by self-organizing electrochemical anodization of Ti and offer a well-controlled morphology, vertically aligned on the substrate. These structures have been previously explored for supercapacitor applications [10], however due to generally insufficient conductivity, earlier works [9] reported a maximum capacity of 872 F.g⁻¹. Additional efforts towards increasing the conductivity and for achieving higher capacitance of TiO₂ nanostructures have been investigated, e.g. doping [11-13], surface

engineering (decoration) [9,14], and particularly self-doping by reduction, forming Ti^{3+} donor species¹⁵ including reduction in H_2 [16]. However, Ti^{3+} species formed on the surface of the nanostructure are highly unstable (reoxidation by O_2 , air, or water) [15]. Therefore, long term stability is a crucial issue if self-doped TNTAs are used as a conductive electrode in cycling applications.

In the present work, we present a simple and effective strategy to provide conductivity by buried Ti^{3+} centers, and use the material as scaffold for RuO_2 decoration. In this, we combine the advantages of the reduced TNTAs including high surface area, charge directionality, and stable Ti^{3+} states with a small amount of RuO_2 decoration to form a 3D supercapacitive platform. In a first step, a TiO_2 nanotube array is grown on a Ti metal substrate by self-organizing anodization. Then the tubes are self-doped through an optimized annealing in an Ar/H_2 reductive environment. Under these optimized conditions, a stable Ti^{3+} core structure is created within the tube wall. Then, the reduced scaffold is decorated with a thin layer of separated RuO_2 nanoparticles – this provides an ideal synergy between the highly conductive TNTAs and the RuO_2 nanoparticles.

2. Material and methods

2.1. Preparation of TNTAs and Ar/H_2 - TNTAs

TNTAs layers were prepared by anodization of Ti foils (99.6% purity, Advent, England) in an electrolyte consisting of 1.5 M lactic acid (LA, DL-lactic acid, 90%, Fluka), 0.1 M ammonium fluoride (NH_4F), and 5 wt% deionized H_2O in ethylene glycol (99 vol %) held at a temperature of 60°C for 6 to 18 min (20-60 μm).

To establish a uniform nanotube geometry, we used a two-step anodization treatment [10]. Here the anodic TNTAs layers from a first anodization were removed by ultra-sonication. The resulting dimpled surface was used for a second anodization under the same experimental

conditions, and tubes were grown to 20-60 μm length. A two electrode configuration was used with Ti foils as the working electrode, and a platinum plate serving as the counter electrode. After the anodization, the samples were dipped into ethanol for 6 h. Anatase TNTAs were obtained by annealing the amorphous sample in a rapid Thermal Annealer (Jipelec JetFirst 100) at 450°C for 1 hour in air with a heating/cooling rate of 30°C min⁻¹. Then the nanotube layers were reduced by annealing in Ar/H₂ 10% under different temperatures.

2.2. RuO₂ Decoration

A uniform decoration with RuO₂ nanoparticles was obtained by precipitation of a Ru³⁺ precursor in alkaline solution. For this, TNTAs samples were immersed into 10 mM RuCl₃ for 14 h at 60°C, followed by soaking in 0.1mM NaOH solution for 14h under the same conditions.

2.3. Materials characterization

The morphology of the samples was investigated using a scanning electron microscope (SEM) Hitachi FE-SEM 4800. A high resolution transmission electron microscope (HRTEM, FEI TITAN G2 60-300) was used to characterize the nanoscopic morphology of the samples as well as to characterize the local structural and compositional aspects of the nanotubes and the RuO₂ decoration. The composition and the chemical states were further characterized using X-ray photoelectron spectroscopy (XPS, PHI 5600, US), and peak positions were calibrated with the Ti2p peak at 458.0 eV. Solid-state conductivity measurements were carried out in an adapted scanning electron microscope (SEM, TESCAN LYRA3 XMU) by 2-point measurements using a semiconductor characterization system (Keithley 4200-SCS). Tungsten tips were used as electrical contacts between tube tops and the substrate. Resistivity values were then obtained from the I-V curves (5 mV/s sweep rate). EPR spectra were recorded using a JEOL JES-X-320 operating at X-band frequency (~9.1 GHz), equipped with a variable temperature control ES 13060DVT5 apparatus, and were performed on powdered samples at 123 K. The cavity Q

quality factor was kept above 7000 in all measurements, highly-pure quartz tubes were employed (Suprasil, Wilmad, < 0.5 OD). The filling factors were optimized and kept constant in all experiments. Other experimental conditions used within the acquisition procedures were as follows: modulation frequency of 100 KHz, modulation amplitude of 0.5 mT, time constant of 30 ms, applied microwave power of 0.2 mW, sweep time of 240 s, and phase of 0 deg. The accuracy on the g-values reported were obtained using MnO EPR standard (JEOL internal standard).

2.4. Electrochemical characterization

Electrochemical properties and capacitance measurements were carried out in a classical three electrode set-up in 0.5 M Na₂SO₄. For this, the TNTAs on the metal substrates were used as working electrode, a platinum plate was used as a counter electrode, and an Ag/AgCl (3 M KCl) electrode served as a reference electrode. The electrochemical properties and capacitance measurements of the samples were studied by cyclic voltammetry (CV) and galvanostatic charge/discharge (chronopotentiometry) using an Autolab PGSTAT 30 Potentiostat/Galvanostat.

The mass specific capacitance and areal capacitance is calculated from the CV curves using the following equations:

$$C_{ar} = \frac{1}{Av(V_f - V_i)} \int_{V_i}^{V_f} I(V) dV \quad (1)$$

$$C_{sp} = \frac{1}{mv(V_f - V_i)} \int_{V_i}^{V_f} I(V) dV \quad (2)$$

where A , C_{sp} , m , v is electrode surface area, specific capacitance (F/g), mass of the active electrode material, and scan rate, respectively. V_f and V_i are the integration potential limits of the voltammetric curve, and $I(V)$ is the voltammetric current. The weight of one TiO₂ nanotube layer is 1.6 mg according to the difference of weight before and after scratching 10 pieces of

TiO₂ nanotube layers. The RuO₂ weight is calculated to be 0.048 mg/cm⁻² by averaging the difference of 10 samples with and without RuO₂ nanoparticles.

The specific capacitance of RuO₂ is calculated after subtracting the charge of Ar/H₂-TNTAs or TNTAs substrate according to the following equations:

$$C_{RuO_2}^{Ar/H_2} = \frac{Q(Ar / H_2 - RuO_2) - Q(Ar / H_2)}{\Delta V \times m_{RuO_2}} \quad (3)$$

$$C_{RuO_2} = \frac{Q(RuO_2) - Q(Anatase)}{\Delta V \times m_{RuO_2}} \quad (4)$$

where ΔV is the applied potential window, and m (RuO₂) is the mass of RuO₂ on each sample. For long term stability measurement, the CV and charge/discharge measurements were repeated for 1000 cycles and data extracted every 50 cycle.

3.Results and Discussion

Figure 1 shows SEM and TEM characterization of the anodic TNTAs used in this work. These tubes were grown as described in the experimental section, on a Ti foil in an ethylene glycol (EG) based electrolyte and then converted to anatase by air annealing. The nanotubes shown in Figure 1a-c have an outer diameter of ≈ 150 nm and length of 20 μ m (the layer thickness can be easily adjusted between 20-60 μ m by the anodization time - see Figure A1). Figure 1a-i represents the nanotubes at various stages, i.e. after air annealing to anatase, after reduction at 550°C Ar/H₂ (Ar/H₂-TNTAs) and after RuO₂ decoration (the treatment conditions represent optimized conditions as discussed later). Important to note is that nanotubes grown in organic electrolytes consist of a two layer wall-structure, with an inner carbon-rich shell and an outer shell (clearly apparent in Figure 1e) [17]. For the Ar/H₂-TNTAs, thermally induced microcracks are observed (Figure A2c,d) and the porosity of the inner layer is increased due to the “burn-off” of carbon species during annealing (Figure 1g). Moreover, C, Ti and O HRTEM

maps confirm the depletion of carbon contamination from the inner layer and the increase in porosity with the Ar/H₂ treatment (see Figure A3a-c).

Using a RuO₂ nanoparticle deposition treatment, as described in the experimental section, the TNTAs become uniformly decorated from the top and throughout the entire tube length (Figure 1h,i, and A3d). The average RuO₂ particle size is ≈ 2.8 nm (see Figure A4a,b), and the RuO₂ loading is 3% (0.048 mg.cm⁻²) - see Figure A4c. XPS confirms the presence of RuO₂; Figure 1j shows high resolution spectra of the RuO₂ decorated Ar/H₂-TNTAs, compared with the bare Ar/H₂-TNTAs. Despite the fact that the Ru3d peak has a strong overlap with C1s, the presence of RuO₂ is clearly evident with Ru3d peaks of the oxide at 281.1 eV and at 285.3 eV as shown in Figure 1j. Additionally, one can see a broadening of *i*) the Ti2p_{1/2} peak at lower binding energies (≈ 462 eV), which is due to the presence of the Ru3p_{3/2} peak (≈ 463 eV [18]; and of *ii*) the O1s peak, due to the presence of ruthenium oxide and OH bonds (Figure A5a).

In order to optimize the reduction treatment conditions of the nanotubular structures regarding conductivity and to create stable buried Ti³⁺ species, we evaluated different annealing temperatures for the Ar/H₂ treatments, i.e., from 450 °C to 600 °C.

It is well known that reductive treatments of TiO₂ promote formation of Ti³⁺ sites. However, XPS cannot confirm unambiguously the formation of Ti³⁺ centers, due to reoxidation of the surface exposed Ti³⁺ to Ti⁴⁺ in ambient air that occurs relatively easily, as shown in Figure 1j and A5b, leaving only minute amounts of reduced Ti³⁺ sites within the detection range of XPS – this is also well in line with literature [11]. To detect Ti³⁺ species, electron paramagnetic resonance spectroscopy (EPR) can be used to detect the presence of traces of spin active (d^1 , $S=1/2$) Ti³⁺ species. The EPR spectra of the Ar/H₂ treated TNTAs, recorded at 123 K (Figure 2a-b), validate the formation of spin active centers in these materials. In particular, upon increasing the temperature of the reduction process, from 450 °C to 600 °C, oxygen vacancies are formed that leave behind two unpaired electrons, hence promoting the formation of the Ti³⁺ centers. A sharp resonance signal characterized by small peak-to-peak field-width

($\Delta B_{pp} = 6.9$ Gauss) and centered at $g = 1.997$ (perpendicular component) is observed in all samples; the signal increased in intensity from 450 °C to 550 °C and then decreased at 600 °C. The resonance line at $g = 1.997$ is associated to Ti^{3+} cations located in regular positions in the lattice (due to removal of oxygen from the lattice). Other resonances are detected at both lower and higher magnetic fields. Broad signals appeared in the low field region in all annealed samples, with g value falling around 2.07. The signature is associated with the formation of an oxygen-based radical, such as a superoxide/oxide radical anion, providing an electron-hole site (O_2^-/O^- , h^+) [19-20]. Other broad components, in the form of dispersion signals, emerge in the high field region (340-360 mT) with g -resonances at ~ 1.92 -1.86 (Figure 2b). The resonance around $g = 1.86$ can be attributed to the parallel component of Ti^{3+} centers located in regular lattice positions while the resonance at 1.92 indicates the presence of Ti^{3+} centers dislocated from the regular position (interstitial Ti^{3+}) [21-23]. The broad nature suggests the existence of dipolar interactions active among this type of interstitial Ti^{3+} centers that render the parallel component of regular Ti^{3+} difficult to detect. The interstitial Ti^{3+} sites appear to cluster closer to each other (in space) compared to those Ti^{3+} sites that are located in the regular lattice positions. The EPR spectrum observed for the 600 °C Ar/ H_2 sample, in particular, stands apart from those obtained at lower annealing temperatures. For similar systems heated above 600 °C. Here we suggest that in the 600 °C Ar/ H_2 sample the Ti^{3+} centers belonging to the regular lattice positions are not lost, but rather migrate towards interstitial sites (see Fig. 2b). We can anticipate here that the presence of both regular and interstitial Ti^{3+} centers, the presence of electron-hole pairs (O_2^-/O^- , h^+) and their subtle balance represent key factors affecting the capacitance performance – as will be discussed below, in the context of solid-state conductivity measurements. The bulk reduction mainly rises the nature of non-stoichiometric TiO_2 within the increase of point, linear and planar bulk defects. One of the point defect which increases by reduction is the oxygen vacancy. Formation of oxygen vacancy causes a Ti^{3+} center as neighbor of a Ti^{4+} site. This is the reason why it can be seen by EPR. By increasing temperature higher

than 550, Ti^{3+} can move to the interstitial place in lattice due to a higher thermodynamic stability in interstitial position at that temperature [24].

Considering the identification and distribution of Ti^{3+} in inner and outer layer of the nanotubes, we acquired electron energy loss spectra (EELS) for 550°C Ar/ H_2 -TNTAs and for the reference, of anatase TNTAs (Figure 2c,d). The Ti $L_{2,3}$ -edge reflects the Ti3d unoccupied states that split into the t_{2g} and e_g sub-bands (due to the octahedral coordination of Ti atoms with O atoms) [25]. In fact, $t_{2g}-e_g$ states are extremely sensitive to the presence of point defects.²⁵ With the increase of d electrons, coinciding with the decrease of the formal charge of the Ti ions (i.e., the formation of Ti^{3+}), the occupation number of the antibonding orbital increases and the $t_{2g}-e_g$ splitting becomes smaller. By comparing the outer layer of air annealed and of Ar/ H_2 -TNTAs, the $t_{2g}-e_g$ splitting is 1.88 eV vs. 1.84 eV in L_3 and 1.81 eV vs. 1.70 eV in L_2 ; thus, there is only a 2% decrease observed for Ar/ H_2 -TNTs L_3 peak splitting and 6% for L_2 . However, in the inner shell there is a significant decrease, of 23.58%: $t_{2g}-e_g$ splitting of 1.95 eV vs. 1.49 eV for the L_2 peak splitting and of 1.95 eV vs. 1.7 eV in L_3 , this can be related to the presence of Ti^{3+} in its lattice. Namely, EELS measurements establish the presence of higher density of Ti^{3+} states in the inner layer of the nanotubes as compared to the outer layer. This indicates the formation of a core-shell structure, where the core is rich in Ti^{3+} . This may be ascribed to reoxidation of the Ti^{3+} states in the shell whereas the Ti^{3+} species in the core remain protected, i.e. providing a higher stability of these Ti^{3+} states against reoxidation and thus enabling a long-term conductivity.

Solid-state conductivity measurements of the anatase and Ar/ H_2 -TNTAs are shown in Figure 3a,b. It is apparent that annealing in Ar/ H_2 significantly decreases the resistivity of the TNTAs (more than 1000 times) and moreover leads to a lower resistivity in comparison to pure argon or pure hydrogen treatments (see Figure A6a,b). The higher resistivity for pure hydrogen treatment could be due to the sintering of the TNTAs structure at the bottom in H_2 annealing,

which can act as a barrier against electron transfer (see Figure A6c,d). We can consider Ar as an inert gas in comparisons to H₂ in this range of temperature, so, Ar can dilute the H₂ atmosphere and decreasing the activity of H₂. Therefore, it does not lead to the same level of sintering or collapse of the tubular structure as it happens in pure H₂. Moreover, pure hydrogen treatments lead to severe hydrogen embrittlement of metallic Ti (Figure A6e,f) that severely affects the mechanical stability of the electrode and back contact's conductivity (i.e. of the Ti substrate) [26,27].

The electrochemical performance of the scaffolds was evaluated by cyclic voltammetry (CV) measurements for different temperatures of the reduction treatment (see Figure 3c). In line with solid state conductivity measurements, the cyclic voltammetry of Ar/H₂-TNTAs show a drastic increase in the CV current with an ideal rectangular curve shape, whereas the anatase TNTAs show a behavior far from ideal. In an ideal double-layer capacitor, the current flow is reversed immediately (with a very short time constant) upon reversing the potential, yielding a rectangular-shape of the voltammogram, with a current independent of the electrode potential for a given sweep rate [28-30]. The areal capacitance of the Ar/H₂-TNTAs is significantly higher than that of the anatase, for instance, for the 550°C Ar/H₂-TNTAs, one achieves an areal capacitance of 4.41 mF.cm⁻² at a scan rate of 100 mVs⁻¹, this is a 67-fold enhancement compared to the anatase TNTAs (0.065 mFcm⁻²). Additionally, the effect is also evident from the charging current density in charge/discharge conditions (Figure A7a,b). The areal capacitance shown in Figure 3d is related to the rate of ion diffusion in the electrode as well as to the electrode conductivity, and the improvement in the capacity of the reduced nanotubes can only be due to the enhanced electrical conductivity of the electrode (as for these experiments 20 μm TNTAs are used that ensure similar ion diffusion rates).

For optimal Ar/H₂ reduction conditions (550 °C), different TNTAs layer thicknesses (from 5 to 60 μm) were investigated by CV measurements. The results show that 20 μm is an optimal thickness for achieving maximum capacitance without a detachment (peeling-off) of

the TNTAs layer from the Ti substrate, as explained in supplementary information and shown in Figure A8a.

The results of this work thus show that anodic TiO_2 nanotubular layers subjected to a Ar/H_2 reductive treatment result in the formation of different (stable) Ti^{3+} states, as observed from EPR measurements (Ti^{3+} centers on regular lattice positions and interstitial Ti^{3+} centers). The distribution of such centers significantly influences the conductivity of the nanotubular layers; i.e. if both regular position Ti^{3+} and interstitial Ti^{3+} centers are present under optimized conditions (550°C Ar/H_2). For these tubes, the lowest resistivity of the tubes (by solid-state conductivity measurements) and the highest current density (in cyclic voltammetry) are measured.

As expected by decorating the Ar/H_2 -TNTAs with RuO_2 nanoparticles, a drastic effect on the electrode capacity is observed (Figure 3e, f), i.e. the capacitance is significantly enhanced and stable pseudo capacitor properties are achieved (due to the faradaic charge transfer, originating from a sequence of reversible redox reactions in RuO_2) [28]. This also reflects the excellent utilization of the individual RuO_2 nanoparticles, due to their small size (leading to a higher degree of intercalation into the particles), their dispersion over the tubes (electrolyte access to an individual particle) and their good connection to the electron collector [31]. As evident from Figure A4c, using the decoration approach described in the experimental section, indeed well-dispersed RuO_2 nanoparticles on TNTAs are obtained, with only 3 wt% RuO_2 loading. Moreover, we found that the Ar/H_2 treatment of the TNTAs leads to an increase in deposition sites for RuO_2 (i.e., a higher RuO_2 particle density). From Figure 3f it is evident that the advantageous use of reduced nanotubular scaffolds for RuO_2 decoration holds over a wide range of scan rates. By comparing the present data with the literature (as listed in Table A1), and taking into account the relative RuO_2 loading of such scaffolds, the results of this work show clearly higher capacitance values compared with similar supercapacitor structures. A most important feature for high-performance supercapacitors is a good cycling stability and, in this

respect, we tested the electrodes at a charge/discharge current density of $100 \mu\text{A}.\text{cm}^{-2}$ and the CV of electrodes at a scan rate of 100 mVs^{-1} for 1000 cycles. Ar/H₂-TNTAs exhibit a reduction of only 2.7% in their capacitance after 1000 cycles (Figure A8b) and no structural modification of the electrode after 1000 cycles (Figure A9a,b) is observed. After decoration with RuO₂, Ar/H₂-TNTAs show a similarly high stability (Figure A9c,d) with 91.2% initial capacity retention; the specific capacitance decreases from 1297 Fg^{-1} to 1194 Fg^{-1} .

4.Conclusions

In the present work we establish a stable, highly conductive TiO₂ nanotube based scaffold and exemplify its use as an electrode for RuO₂ decorated supercapacitors. Stable conductivity is created by reducing the TNTAs in an Ar/H₂ reductive atmosphere, forming buried (protected) Ti³⁺ states. These Ti³⁺ states are located in the core of tube (core-shell structure), thus providing a conductive core/outer shell structure. Additionally, a key factor to achieve an optimized conductivity is that Ti³⁺ is present in different lattice position (at regular lattice positions and as interstitials) – this configuration is found superior to single position Ti³⁺. Overall, these “buried” Ti³⁺ TNTAs represent an ideal conductive scaffold for electrochemical applications. In the present work we show a use as supercapacitor, where a low RuO₂ loading of only 3 wt% can reach a remarkable specific capacitance of 1297 F.g^{-1} .

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Figure Caption

Figure 1. (a-e) SEM and HRTEM images of anatase TiO_2 TNTAs, (f,g) 550°C Ar/ H_2 -TNTAs, (h-i) RuO_2 decorated 550°C Ar/ H_2 -TNTAs and (j) high resolution XPS spectra of the 550°C Ar/ H_2 -TNTAs bare and decorated with RuO_2 nanoparticles: Ti2p, C1s, Ru3d, and peak fitting of the Ru3d.

Figure 2. (a-b) X-band (9.154 GHz) EPR spectra recorded at 123 K of Ar/ H_2 -TNTAs annealed in the temperature range 450°C - 600°C , EELS spectra of the Ti-L_{2,3} edge for anatase TiO_2 TNTAs (black line) and 550°C Ar/ H_2 -TNTAs (red line), (c) inner layer and (d) outer layer.

Figure3. (a) the current–voltage characteristic of anatase TNTAs and Ar/ H_2 -TNTAs annealed in 450°C to 600°C (b) Resistivity of anatase TNTAs and Ar/ H_2 -TNTAs annealed in 450°C to 600°C . (c) CV curves of anatase TNTAs and Ar/ H_2 -TNTAs annealed in 450°C to 600°C , obtained at a scan rate of 100 mVs^{-1} . (d) Areal capacitance of TiO_2 samples measured as a function of scan rate. (e) CV curve of the RuO_2 decorated 550°C Ar/ H_2 -TNTAs compare to the reference samples. (f) Comparison of the specific capacitance of both RuO_2 decorated samples, i.e. 550°C Ar/ H_2 -TNTAs and reference anatase TNTAs, as a function of scan rates.

Figure 1

Figure 2

Figure 3