Electronic Supplementary Information

Carbon Cladded TiO_2 Nanotubes: Fabrication and Use in 3D- RuO_2 Based Supercapacitors

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Experiments

Preparation of carbon cladded TiO_2 nanotubes(C/TiNTs)

The TiO_2 nanotube layers (TiNTs) were prepared by anodization of Ti foils (99.6% purity, Advent, England) in an electrolyte consisting of ethylene glycol containing 0.135 M NH_4F and 1M H_2O at 50 V for 2 h, 4 h, 6 h, 8 h and 12 h at room temperature. These tubes were prepared by two-step anodization and corresponding SEM images are shown in Fig. S1. Two electrode configurations were used with Ti foils as the working electrode, and a platinum gauze serving as the counter electrode. After the anodization, the samples were washed by deionized (DI) water stream (drop by drop) to remove the organic electrolyte on the sample surface. To obtain a crystallized sample, the layers were annealed in Argon at 450 °C for 1 h. To prepare the reference sample TiNTs (without graphite coating), the freshly prepared samples after anodization were dipped into ethanol for 24 h, and then annealed in air at 450 °C for 3h.

Preparation of hydroxylated C/TiNTs

Hydroxylated C/TiNTs were prepared by immersing above samples (50V, 4h) in a sealed beaker containing 30% H_2O_2 aqueous solution [S1] at 30°C, 45°C, 60 °C in a drying oven.
PAS treatments were completed by immersing above samples (50V, 4h) in to 0.05% PAS solution (water/ethanol =4vol. /1 vol.) for 12h. After 12h reaction, the samples were taken out, rinsed with DI water and dried at 80°C in a drying oven.
Cyclic voltammetry was performed to characterize samples at a scan rate of 5 mV/s (as shown in Fig. S2). Treatments at 45°C and 60°C in H_2O_2 result in a similar capacitance response, and both conditions lead to much better results than the H_2O_2 treatment at 30°C. Since the sample layer treated at 60°C is easy to peel off from Ti substrate, 45°C was selected as an optimized temperature for the H_2O_2 treatment considering all the factors.

Preparation of RuO_2 decorated C/TiNTs (RuO_2-C/TiNTs)

The uniform decoration of RuO_2 NPs was obtained by precipitation of Ru^{3+} precursor in alkaline solution. C/TiNTs samples were immersed into 10 mM $RuCl_3$ (water/ethanol =80w.%/20 w.%) for 12 h at 60°C, following with soaking in 0.1mM NaOH solution for 12h at same conditions. Samples were washed with deionized water droplet, dried in a N_2 stream, and then annealed at 150 °C for 2h in furnace under Ar atmosphere.

An optimized $RuCl_3$ treatment was explored for the factors: i) concentration (Fig. S3), ii) temperature (Fig.S4), and iii) ultrasonic duration time during the $RuCl_3$ treatment process (Fig. S5). The results show that C/TiNTs treated in 10mM $RuCl_3$ at 60°C with ultrasonic treatment for 10 min yield the best capacitance response.

Characterization

The morphologies of the nanostructures were characterized using a field-emission scanning electron microscopy (Hitachi FE-SEM S4800, Japan) and transmission electron microscopy (TEM, JEOL 2000). The crystallinity and phase of prepared samples were characterized by RAMAN (LabRAM XoloRA， HORIBA JOBIN YVON S.A.S) and XRD (Philips, USA). X-ray photoelectron spectra (XPS) were recorded on a Perkin–Elmer Physical Electronics 5600 spectrometer using Al Kα radiation at 13 kV as excitation source. The takeoff angle of the emitted photoelectrons was 45^o. The mass of Ru on the samples was determined by ICP-MS instrument (Agilent 7500). For this, the samples were dissolved in concentrated 1 mL HNO_3 and 2 mL H_2O_2 in a microwave digester at 200 ^oC for 10 min. The reported results of the samples are the average of three replicates.

Four point probe measurement (RTS-9, China) were performed at room temperature under ambient pressure with a standard of Si (R_0=62.7 Ω/□). The resistance obtained reflects the property of the whole layer.

The electrochemical properties of the as-prepared samples were explored with cyclic voltammetry (CV) and galvanostatic charge-discharge test measurements in a CHI660 work station (CH Instruments, Inc, Shanghai). The nanotube arrays were used as the working electrodes (10 mm in electrode diameter). A Pt foil and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The stabilities of the electrodes were tested by galvanostatic charge-discharge tests during 1000 cycles at a current density of 0.5 mA/cm^2. All the measurements were performed in 1M H_2SO_4 aqueous solution at room temperature, except results presented in Fig. S9 that was carried out in 0.1 M KCl containing 2 mM $Fe\ (CN)_6^{3-/4-}$.

Calculation of the specific capacitance from CV curves

The specific capacitance is calculated from voltammetric response according to the equation [S2]:

$$C_{sp} = \frac{1}{m\nu(V_f - V_i)}\int_{V_i}^{V_f} I(V)dV \qquad (1)$$

where C_{sp}, m, ν is 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 TiO_2 nanotube layer is 0.25 mg according to the difference of weight before and after scratching 10 pieces of TiO_2 nanotube layers. The carbon layer is calculated to be 0.16 mg/piece by averaging the difference of 10 samples with and without carbon layer (samples annealed at 450 ° C for 3h).

Calculation of the specific capacitance from charge-discharge test

The discharge specific capacitance is calculated from the discharge curves using the following equation [S3]:

$$C = \frac{I\Delta t}{m\Delta V} \qquad (2)$$

where I (A), Δ t (s), m (g), and Δ V (V) are the discharge current, discharge time consumed in the potential range of Δ V, mass of the active materials (or mass of the total electrode materials), and the potential windows, respectively.

Calculation of specific capacitance based on RuO_2

The specific capacitance of RuO_2 is calculated after subtracting the charge of C/TiNTs or TiNTs substrate according to the following equation:

$$C(RuO_2) = \frac{Q(RuO_2 - C/TiNTs) - Q(C/TiNTs)}{\Delta V \times m(RuO_2)} \qquad (3)$$

$$C(RuO_2) = \frac{Q(RuO_2/TiNTs) - Q(TiNTs)}{\Delta V \times m(RuO_2)} \qquad (4)$$

where Δ V is the applied potential window, and m (RuO_2) is the mass of RuO_2 on each sample.

References

[S1].R. Vellacheri, V. K. Pillai, S. Kurungot, *Nanoscale.*, **2012**, *4*, 890–896.

[S2].X. Liu, P.G. Pickup, *J. Solid State Electrochem*., **2010**, *14*, 231–240.

[S3].D M. MacArthur, *J. Electrochem. Soc.,* **1970**, *117*, 422-426.

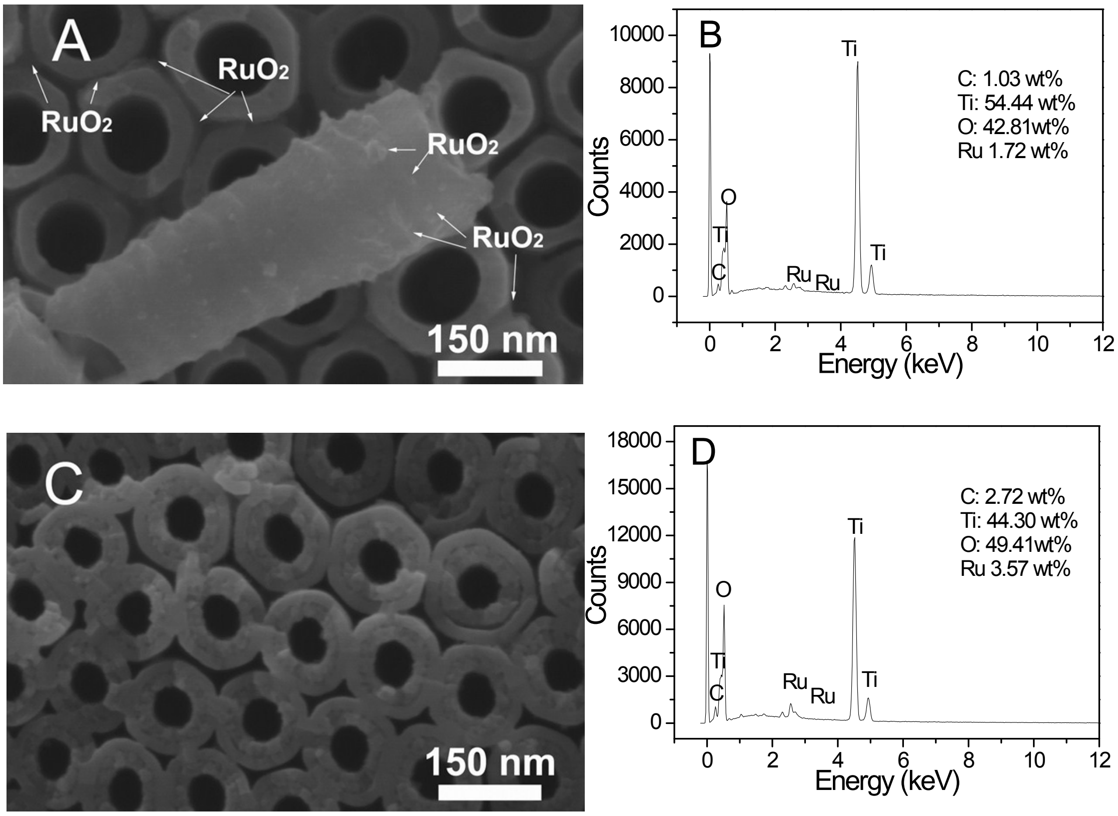

Figure S1. SEM image and EDS analysis of RuO_2/TiNTs (A and B) and RuO_2-C/TiNTs (C and D).

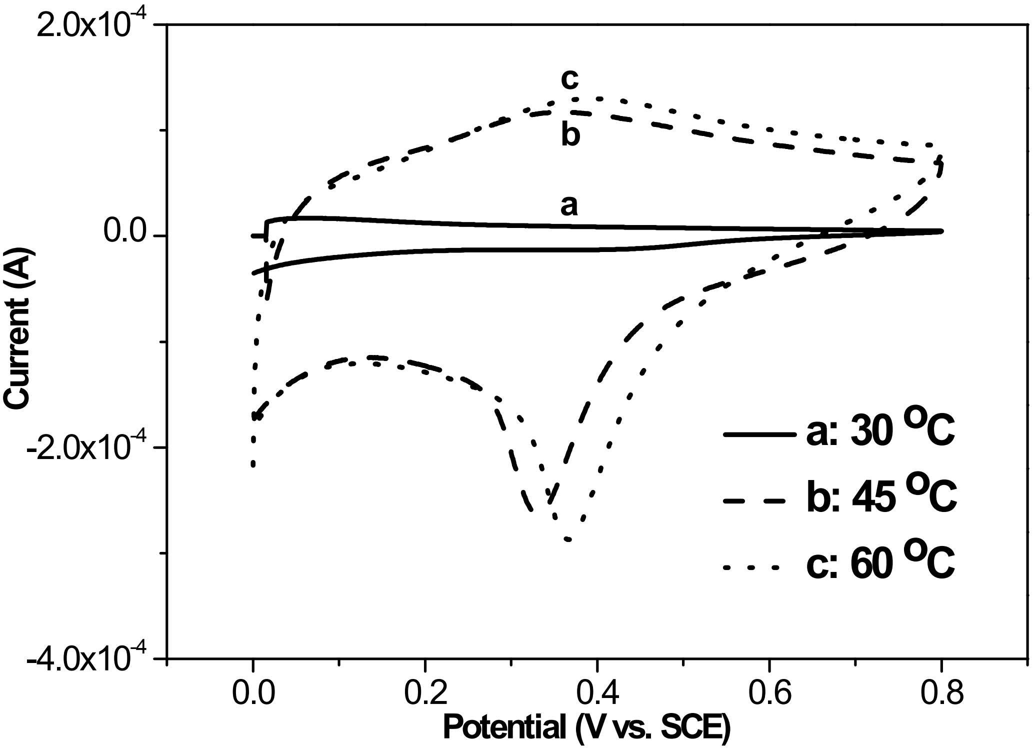

Figure S2. Cyclic voltammetry for RuO_2-C/TiNTs treated under different temperatures in H_2O_2. Measurements were performed in 1 M H_2SO_4 at a scan rate of 5 mV/s.

The capacitance according to the enclosed area of CV curves at 30°C is lower than others. There is only slight increase compared with the capacitance obtained at room temperature (not shown). At 45°C, the capacitance increases strongly, and the morphology was not damaged after immersion. At 60°C, the tube arrays are peeled off easily and no obvious enhancement of capacitance can be seen compared to treatment at 45°C. Considering all the factors, 45°C was selected to perform the H_2O_2 treatment. Fig. 2c shows clearly that H_2O_2 treatment on TiNTs leads to a better electrochemical response than PAS treated or untreated C/TiNTs, which results from the increase in the number of negative charges on C/TiNTs surface.

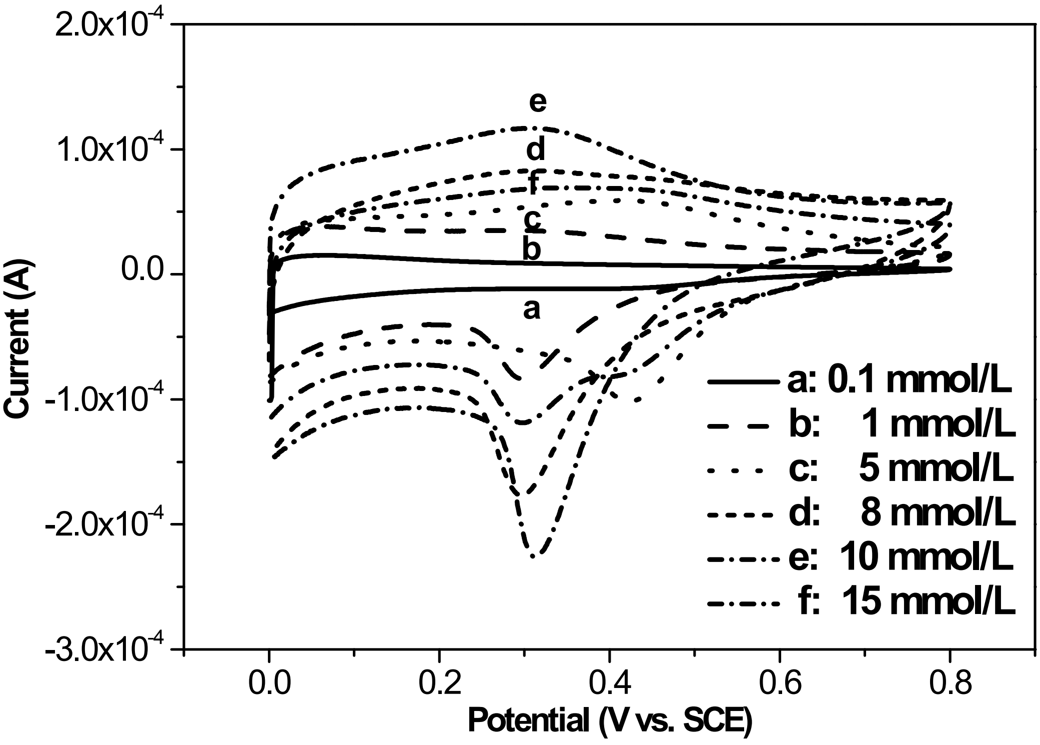

Figure S3.Cyclic voltammetry for RuO_2-C/TiNTs treated by different $RuCl_3$ incubation concentrations. Measurements were performed in 1 M H_2SO_4 at a scan rate of 5 mV/s at room temperature.

Fig. S3 shows that the electrochemical response increases with increasing $RuCl_3$ concentration from 0.1mM to 10mM, but decreases for the concentration of 15mM. Possibly, at the higher concentration, the nanotubes are blocked by the Ru deposits, which hamper efficient charge exchange.

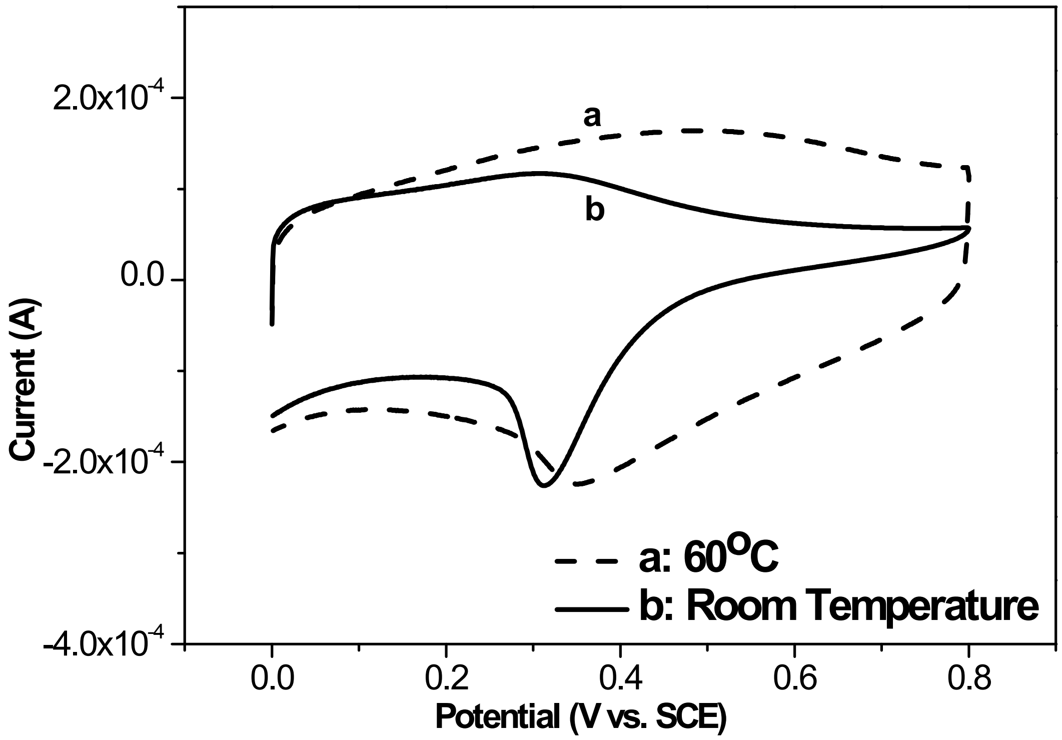

Figure S4. Cyclic voltammetry for RuO_2-C/TiNTs treated at different $RuCl_3$ (10mM) incubation temperatures. Measurements were performed in 1 M H_2SO_4 at a scan rate of 5 mV/s.

Figure S4 shows that an increase of the reaction temperature in the $RuCl_3$ and NaOH solution can significantly enhance the capacitance.

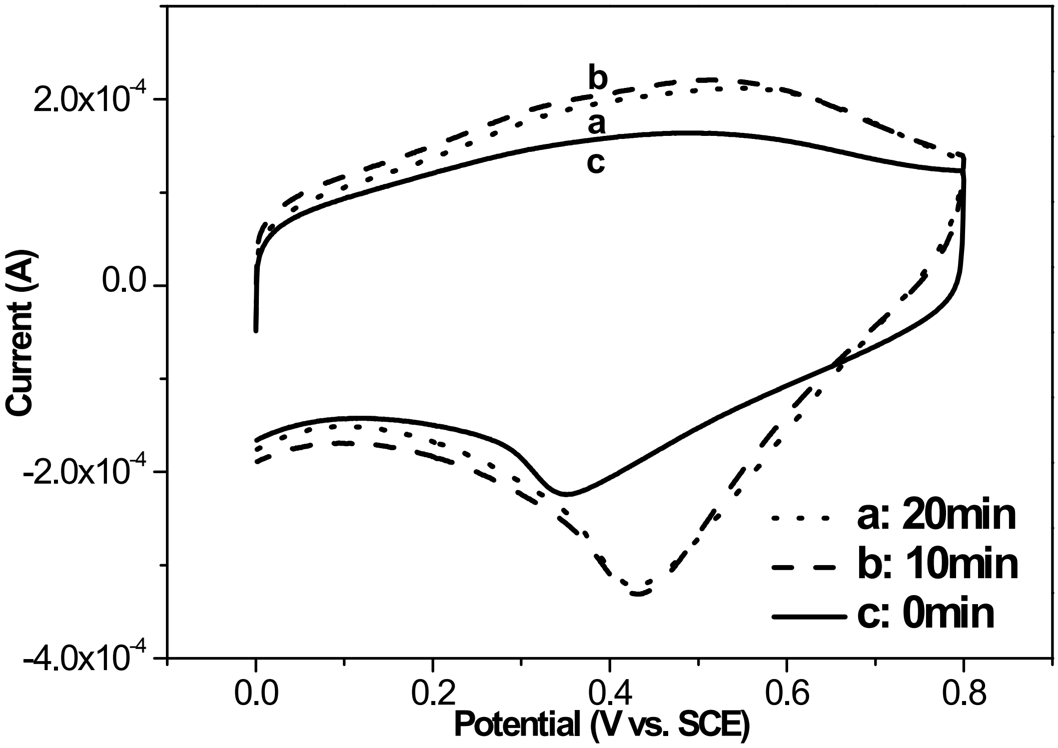

Figure S5. Cyclic voltammetry for RuO_2-C/TiNTs treated by different $RuCl_3$ (10mM, 60 °C) incubation durations by sonication. Measurements were performed in 1 M H_2SO_4 at a scan rate of 5 mV/s.

Figure S5 shows that the electrochemical response is higher with sonication treatments but it is not further enhanced after 10min sonication. Hence, 10 min was selected to perform the sonication treatment.

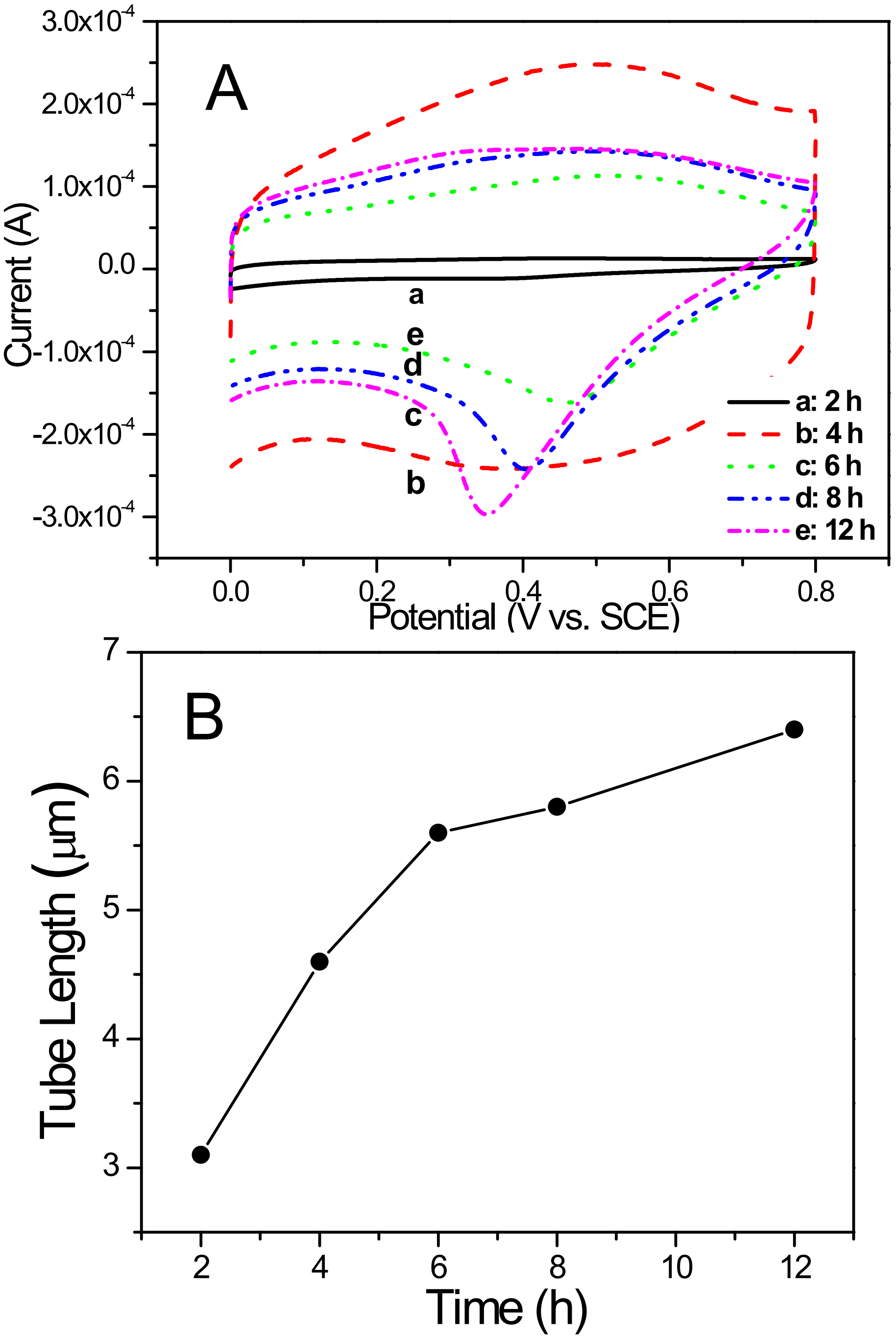

Figure S6. (A) Cyclic voltammetry for RuO_2-C/TiNTs prepared from different anodization time. Measurements were performed in 1 M H_2SO_4 at a scan rate of 5 mV/s. (B) The tube length of the TiNTs prepared by different anodization time. Anodization was made in Ethylene glycol containing electrolyte (0.135 M NH_4F and 1M H_2O) at 50 V for 2h, 4 h, 6h, 8h and 12h respectively.

Figure S6 shows that nanotubes anodized for 4h (4.6µm length) yield the best capacitance data.

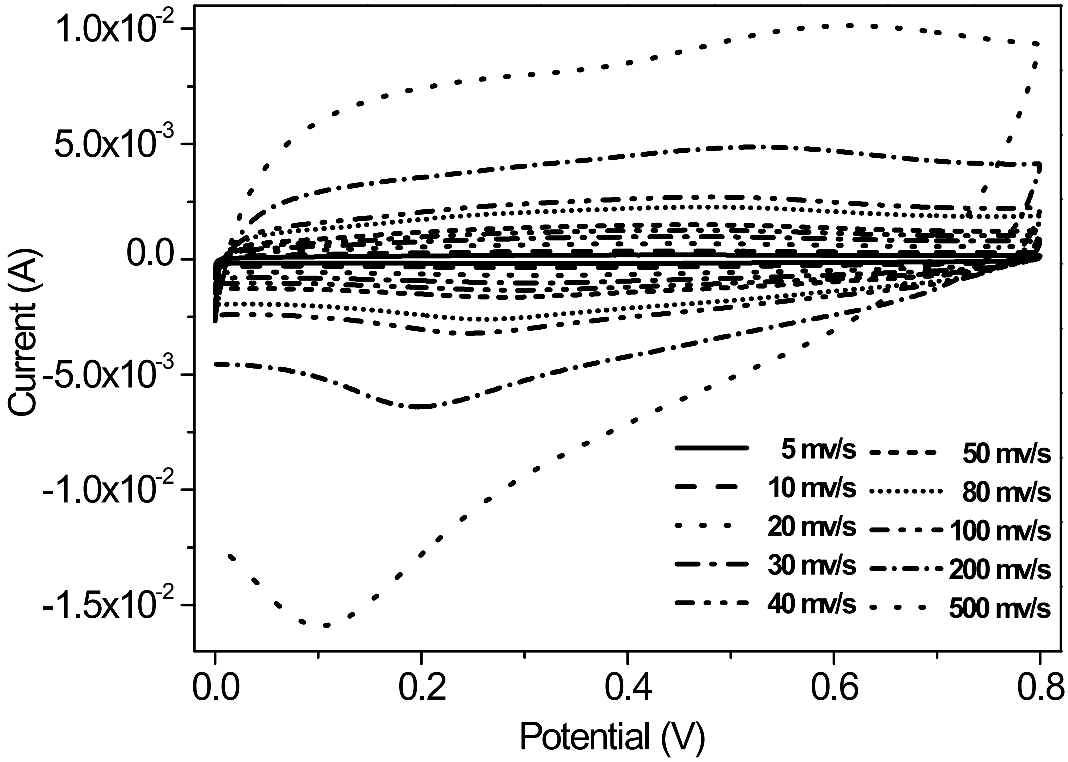

Figure S7. Cyclic voltammetry of RuO_2-C/TiNTs at different scan rates of TiNTs, C/TiNTs, RuO_2-TiNTs and RuO_2-C/TiNTs at the scan rate of 5, 10, 20, 30, 40, 50, 80, 100, 200, 500 mV/s.

Sample	**Resistance (kΩ/□)**
TiNTs	>1000
TiNTs (anatase)	570
C/TiNTs	475
RuO_2-C/TiNTs	6.6

Figure S8. Four point conductivity test for the RuO_2-C/TiNTs. (□ : sheet resistance)

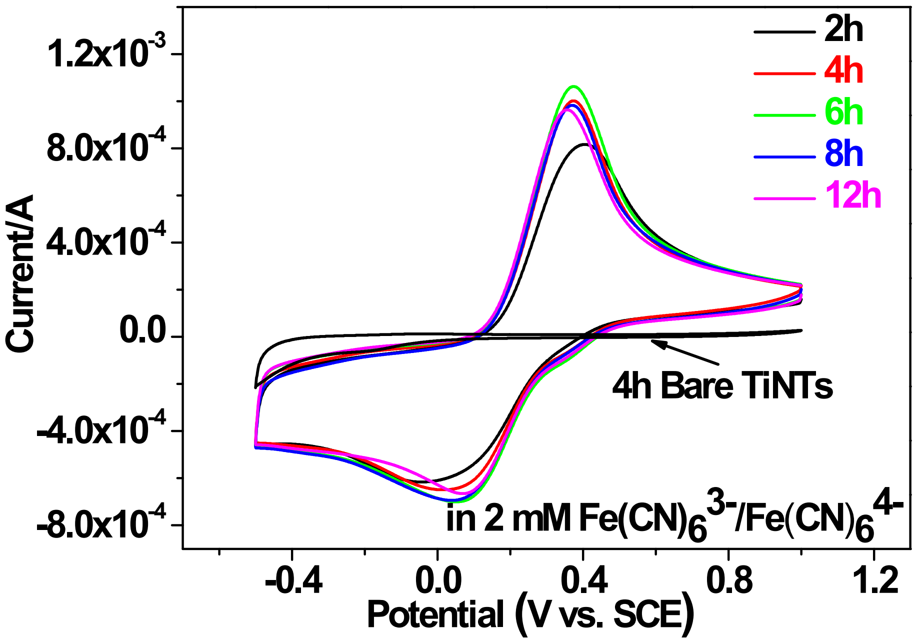

Fig. S9. Cyclic voltammetry of C/TiNTs prepared with different anodization times, i.e. different tube lengths. Experiments were performed in 0.1 M KCl with 2 mM Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ at a scan rate of 50 mV/s.

Fig. S9 shows the strongly increased conductivity for TiO$_2$ NTs by carbonization. Compared with bare TiNTs, the C/TiNTs electrodes clearly show a pair of oxidation and reduction peaks in a defined redox electrolyte.

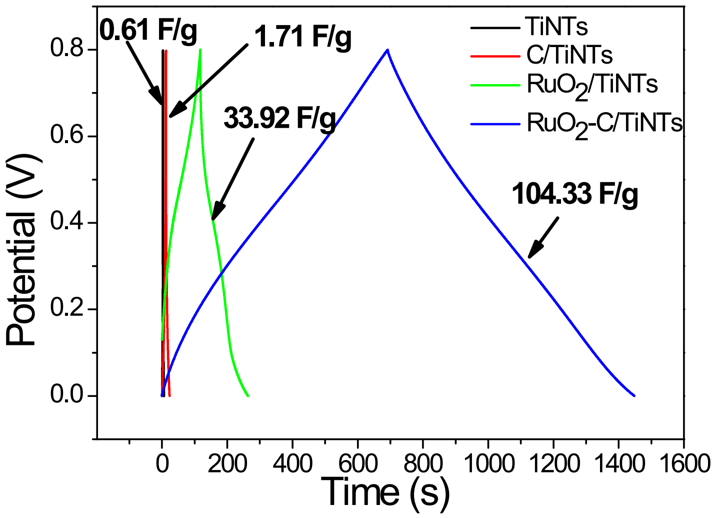

Figure S10. Charge-discharge test at 0.05 mA/cm^2 for the TiNTs, C/TiNTs, RuO_2-TiNTs and RuO_2-C/TiNTs.

Fig. S10 shows an obvious symmetric triangle shape of charge-discharge curves with ideal capacitive characteristics. It is apparent that the charge-discharge time of RuO_2-C/TiNTs (1447s) is longer than other samples, which reflects the enhancement of capacitance. According to Eq. (2), the capacitance calculated from charge-discharge curves is 0.61, 1.71, 33.92 and 104.33 F/g for TiNTs, C/TiNTs, RuO_2-TiNTs and RuO_2-C/TiNTs, respectively. These results are higher than that calculated from CV curves possible due to the lower current density that gives sufficient time for interaction of H^+ with RuO_2.