Cite this: *Chem. Commun.*, 2015, 51, 7614

Received 26th January 2015,
Accepted 16th March 2015

DOI: 10.1039/c5cc00728c

www.rsc.org/chemcomm

Carbon clad TiO₂ nanotubes: fabrication and use in 3D-RuO₂ based supercapacitors†

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In this work we introduce a facile procedure that allows a highly conformal coating of self-organized TiO₂ nanotubes (NTs) with a graphite-like thin carbon layer. This provides a platform to enhance the functionality of TiO₂ nanotubes for a wide range of applications. Here we show that such modified nanotubes can serve as a 3D scaffold for an ideal decoration with RuO₂ nanoparticles. Used as 3D pseudocapacitor electrode, capacitance values of up to 80 times higher than plain TiO₂ NTs, and a very high yield of utilization of RuO₂ (872 F g⁻¹) and excellent long-term cycling stability can be reached.

Supercapacitors have attracted wide attention due to the strongly increasing demand in technology for high power density energy storage devices.¹ According to the charge storage mechanism, two categories of supercapacitors can be distinguished: (i) electrical double layer capacitors (EDLCs that rely on non-faradaic electrode charge storage processes),² and (ii) electrochemical capacitors that to a large extent rely on faradaic processes, that is, the switching of redox states of the material while charging/discharging the electrode.³ Redox switching in this case is accompanied with ion-intercalation into the pseudo capacitive material to maintain overall charge neutrality. For many years already the gold standard for supercapacitor materials is RuO₂, as it provides intrinsically fast, high and reversible intercalation properties, and a comparably high electron conductivity.^{4,5a} For example, hydrous ruthenium oxide (HRO) has been reported to show a high mass specific capacitance of 600 to 750 F g⁻¹. Nevertheless, the theoretical specific capacitance of 1400 to 2200 F g⁻¹ is even higher.^{5b} This difference between the experimental data and

theoretical value is due to a non-ideal efficiency of utilization of HRO for charge storage.⁶ With a view to more efficiently exploit the expensive HRO, it should be ideally dispersed as nanoparticles of only a few nanometers in diameter (comparable to the diffusion length of the intercalating species) on a suitable electron-conductive scaffold.

In order to provide an ideal scaffold, the most desirable electrode geometry is one that provides an optimized ion diffusion path through the electrolyte and into the solid. To address these requirements, recently self-ordered nanotubular arrays of various materials (TiO₂,⁷ TiO₂-V₂O₅,⁸ Co₂O₃)⁹ have been explored directly for their supercapacitive performance. Nevertheless, most straightforward are electrodes based on self-organized TiO₂ nanotube layers. The fabrication of such well-defined TiO₂ nanotube layers can be achieved by a simple self-organizing anodization of Ti in a suitable electrolyte.¹⁰ The resulting vertically aligned TiO₂ nanotube layers provide an adjustable geometry (diameter, length), crystallinity, and are directly back-contacted by the Ti metal sheet where they are grown from; *i.e.* they provide an ideal electrode configuration. As a result, such TiO₂ nanotube arrays have, except for uses as photoelectrochemical, biomedical or other electrode applications, also been explored for supercapacitor electrodes. Previous findings, however, show only a limited success, due to the comparably sluggish redox switching properties of TiO₂ (in all crystal polymorphs), and even more problematic is the limited electrical conductivity of the TiO₂ nanotubes.¹¹ As a result, various modification techniques have been investigated that decorate or dope the TiO₂ nanotubes with various materials, either to increase the tube's conductivity and/or to improve their redox switching properties.¹²

An ideal route to combine the advantages of the nanotube features with an optimized use of RuO₂ would be a uniform anchoring of a thin RuO₂ nanoparticle layer with a sufficiently high surface density to provide an interconnected electron conduction pathway. However, this is not easy to achieve with plain TiO₂ NTs. A main problem is that a suitable anchoring/decoration chemistry is not established up to now, and generally does not lead to sufficiently conducting systems (as we will show below).¹³

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† Electronic supplementary information (ESI) available: Experimental section, calculations of capacitance, SEM, electrochemical test are included. See DOI: 10.1039/c5cc00728c

To overcome these issues, in the present work we first apply a highly defined, conductive and conformal graphitic carbon cladding to TiO_2 nanotubes. This coating then can be further modified using established carbon chemistry to anchor an active RuO_2 nanoparticle layer on the tube walls. The process leads to RuO_2 decorated C/ TiO_2 nanotube arrays that show significantly enhanced and stable pseudocapacitor properties.

Fig. 1 gives an overview of the process steps used in this work (Fig. 1a), as well as the morphology of the tube layers in scanning electron microscopy (SEM) (Fig. 1b) and transmission electron microscopy (TEM) (Fig. 1c), relevant XRD patterns after

different modification steps (Fig. 1d), and the resulting effect of the treatment steps on the current voltage cycling behaviour (Fig. 1e).

In a first step we grow anodic TiO_2 nanotube layers on Ti in an ethylene glycol/ NH_4F / H_2O electrolyte – this results in nanotubes with an outer diameter of 150–200 nm and a tube length of 3.1–6.4 μm for anodization times from 2 h to 12 h (see ESI†). Nanotubes grown in EG based electrolytes usually consist of a two-shell structure,¹⁴ with an inner carbon rich shell that results from organic fragments of decomposed electrolyte as well as adsorbed ethylene glycol on the tube walls (as indicated in Fig. 1 and in the ESI† Experimental section). In this work we exploit the presence of this inner layer to convert it to a uniform carbon (graphitic) cladding on the inside of the TiO_2 nanotubes. For this we avoid any cleaning post treatment of the tubes (see ESI†) and anneal the carbon-contaminated tubes directly under argon conditions at 450 °C. Reference TiNTs were prepared by soaking the fresh samples in ethanol for 24 h, and then annealing in air at 450 °C (Fig. 1b(D)), this latter procedure dissolves and burns off carbonaceous remnants to a large extent.

From the transmission electron microscopy (TEM) images in Fig. 1c top it is apparent that as-prepared TiO_2 NTs contain a carbon-rich organic layer. After annealing in argon, the TiO_2 NTs indeed consist of a two-shell structure (SEM in Fig. 1b). In this case the inner cladding shell is approx. 10 nm thick (Fig. 1b and c), while reference TiO_2 NTs (Fig. 1b, D) are clearly thinner and clean tube walls are formed (ESI† gives differences in EDS analysis).

For the carbon cladded tubes, XRD patterns (Fig. 1d) indicate the formation of anatase TiO_2 nanotubes, and XPS and Raman measurements confirm the presence and nature of the carbon layer after annealing. It is evident from XPS ($\text{C}1\text{s}$ peak at 283.8 eV) and from Raman measurements (Fig. 2a and b) that graphitic carbon is formed. In Raman, two bands corresponding to carbon can be observed at 1346 cm^{-1} and 1586 cm^{-1} (inset), which are

Fig. 1 (a) An overview of the process steps to prepare RuO_2 -C/TiNTs from TiNTs. (b) SEM images of carbon loaded samples, C/TiNTs (A, B and C), and bare TiNTs (D). (c) TEM images of the bare TiNTs before annealing (upper row) and RuO_2 -C/TiNTs samples (lower row). (d) XRD patterns of RuO_2 -C/TiNTs. (e) Cyclic voltammetry for TiNTs, C/TiNTs, RuO_2 -TiNTs and RuO_2 -C/TiNTs measured in 1 M H_2SO_4 at a scan rate of 5 mV s^{-1} .

Fig. 2 (a) XPS high resolution $\text{C}1\text{s}$ peak of C/TiNTs before (left) and (right) H_2O_2 treatment. (b) Raman spectra of TiNTs, C/TiNTs and RuO_2 -C/TiNTs (inset: enlarged from 1200–1700 cm^{-1} of C/TiNTs). (c) Cyclic voltammetry of RuO_2 -C/TiNTs with different surface treatments of C/TiNTs by H_2O_2 or polyacrylic acid sodium salt. Experiments were performed in 1 M H_2SO_4 at a scan rate of 5 mV s^{-1} .

attributed to the carbon defect-induced Raman band (the D band), and the ordered graphitic structure (the G band), correspondingly. The appearance of a G band indicates the presence of graphitized carbon in the nanotubes.¹⁵

This graphitic layer is uniformly present on the entire inside of the tubes and provides an excellent stage for further modification of the tube wall. In order to exploit two common strategies towards RuO₂ attachment on graphitic carbon we investigated an H₂O₂ and alternatively a PAS (polyacrylic acid sodium salt) route (Fig. 2c).¹⁶ The hydroxylated C/TiNTs were then decorated with Ru-oxide using RuCl₃ that can react with the –OH groups on the tube walls *via* condensation reaction. For PAS treated C/TiNTs, Ru³⁺ can be adsorbed and react with the negatively charged walls. The results show that the H₂O₂ treatment yields a better electrochemical performance. The hydroxylation efficiency by H₂O₂ is related to the incubation temperature (shown in Fig. S2, ESI†). The RuCl₃ exposure procedure was optimized in view of concentration (Fig. S3, ESI†), temperature (Fig. S4, ESI†), use and exposure to ultrasonication (Fig. S5, ESI†), as well as tube length (Fig. S6, ESI†), as outlined in the ESI†. The best electrochemical response was obtained for C/TiNTs prepared by anodization in F[–] containing electrolyte for 4 h, followed by a treatment in 30% H₂O₂ at 45 °C, and exposure to 10 mM RuCl₃ at 60 °C for 10 min under ultrasonication.

The steps in the preparation process were monitored with XPS and TEM. XPS data in Fig. 2a show the XPS C1s peak of the graphitic C/TiO₂ (283.8 eV) – this, after H₂O₂ treatment, shows some specific features. Namely, an increase of the C–O peak (284.8 eV) due to the formation of OH groups on C/TiNTs after H₂O₂ treatment is apparent. After the RuCl₃ treatment, TEM (Fig. 1c, down) clearly shows the tube walls to be uniformly decorated with approx. 2 nm diameter particles, and corresponding XRD patterns show a peak at $2\theta \approx 35.1^\circ$ that is consistent with the presence of RuO₂.¹⁷ ICP-MS yields an overall Ru content of 7.28 wt%. However, for RuO₂ on bare TiO₂ nanotubes, the Ru loading is 5.38 wt%, and the particles tend to easily accumulate on the tube entrance and in the space between two nanotubes (ESI†); EDS data confirms that for these tubes less RuO₂ can be deposited (EDS in Fig. S1B and D, ESI†). If the tubes are modified with above RuO₂-C/TiNTs treatment, a strong effect on conductivity can be observed. This is evident from a semi-quantitative assessment using four point probe measurements (Fig. S8, ESI†) and cyclic voltammograms (Fig. S9, ESI†), where RuO₂-C/TiNTs have several decades' higher conductivity than as formed TiO₂ NTs.

More importantly, Fig. 1e and 3 show the drastic effect of the procedure in view of the electrochemical response of the electrodes. The cyclic *I*-*V* curves in Fig. 1e are taken in 1M H₂SO₄ at 5 mV s^{–1}. Bare TiO₂ nanotubes show virtually no pronounced hysteresis loop – if the capacitance is evaluated in terms of a specific capacitance one obtains 1.09 F g^{–1}. In contrast, the RuO₂ nanoparticle decorated C/TiNTs working electrodes exhibit the highest capacitance with a specific capacitance value of 88.05 F g^{–1} (eqn (1), ESI†). Particularly interesting is that for the RuO₂-TiNTs without carbon coating a much lower specific capacitance (28.49 F g^{–1}) is obtained.

If the specific capacitance is related to the amount of used (expensive) RuO₂ one obtains a remarkable value of 871.98 F g^{–1}. (Details of the calculation are given in the ESI†). This must be ascribed to the excellent utilization of the individual RuO₂ nanoparticles (higher degree of intercalation into the particles) and their good connection to an electron collector. In contrast, TiO₂ nanotubes that were directly decorated using RuCl₃ show a clearly inferior behaviour with a capacitance of only 369.21 F g^{–1} based on RuO₂ in Fig. 1e. The excellent capacitive behaviour of RuO₂-C/TiNTs is also reflected by the nearly anodic/cathodic mirroring and rectangular loop of CV curve. Moreover, with the increase of the scan rates up to 100 mV s^{–1} (Fig. S7, ESI†), the curves maintain their nearly rectangular shape, which shows a virtually ideal characteristic capacitive response.

Moreover, the advantage of carbon clad TiO₂ nanotubes combined with RuO₂ nanoparticles holds over a wide scan range (investigated from 5–500 mV s^{–1}). Fig. 3a shows that the RuO₂-C/TiNTs have a significantly higher specific capacitance than all other reference samples. Also from galvanostatic charge–discharge curves in Fig. S10 (ESI†), the charge–discharge time of RuO₂-C/TiNTs (1447 s) is longer than any other reference sample. According to eqn (2) (ESI†), the capacitance calculated from charge–discharge curves is 0.61, 1.71, 33.92 and 104.33 F g^{–1} for TiNTs, C/TiNTs, RuO₂-TiNTs and RuO₂-C/TiNTs, respectively. Additionally, the RuO₂-C/TiNTs provide a more linear and symmetric charge–discharge curve than the other reference systems, which is also evident from Fig. 3b. At these current densities (0.05 mA cm^{–2}, 0.25 mA cm^{–2} and 0.5 mA cm^{–2}), the only comparably small IR drop for RuO₂-C/TiNTs reflects the excellent electrical conductivity of samples; this is consistent with the four point measurements (ESI†).

In order to evaluate the cycling stability of the RuO₂-C/TiNTs we performed a 1000 cycle charge–discharge test. From Fig. 3c, it is apparent that the first five cycles and last five cycles within the charge–discharge test remain symmetrical with triangular

Fig. 3 (a) Specific capacitance of TiNTs/C/TiNTs, RuO₂-TiNTs and RuO₂-C/TiNTs at the scan rate of 5, 10, 20, 30, 40, 50, 80, 100, 200, 500 mV s^{–1}. (b) Charge–discharge for RuO₂-C/TiNTs measured at different current density. (c) Stability test of RuO₂-C/TiNTs at 0.5 mA cm^{–2} for 1000 cycles.

shape and maintain almost the same characteristics. Over the entire cycling, the specific capacitance decreased from 88.20 F g⁻¹ to 84.32 F g⁻¹, *i.e.* the sample shows good capacity retention of 95.6% of the initial value.

The achieved enhancement in the capacitance performance can be ascribed on the one hand to the improvement of electrical conductivity of carbon clad RuO₂-TiO₂ nanotubes. On the other hand, the use of C-chemistry enables a defined loading and uniform dispersion of RuO₂ NPs on the tube walls. As a result, the formation of nanosized RuO₂ particles with higher efficiency per particle, *i.e.* a maximum utilization of decorated RuO₂ with fast and reversible faradaic processes on the electrode surfaces becomes possible.

The present work introduces a novel concept of fabricating uniformly graphitized TiO₂ nanotubes and provides an example of a highly beneficial use in fabricating a 3D-RuO₂ based supercapacitor structure. In general, the feasibility to functionalize C/TiO₂ nanotubes using classic graphitic chemistry to attach functionality to TiO₂ NTs opens wide possibilities to enhance the performance of TiO₂ NT devices. Particularly, the strong improvement of the electron conductivity of these tubes is promising in view of any electron conducting devices, such as batteries or other electrode materials.

This work was supported by the National Natural Science Foundation of China (No. 21322504, 11174046, 21275026), the Fundamental Research Funds for the Central Universities (N140505001, N140504006).

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