

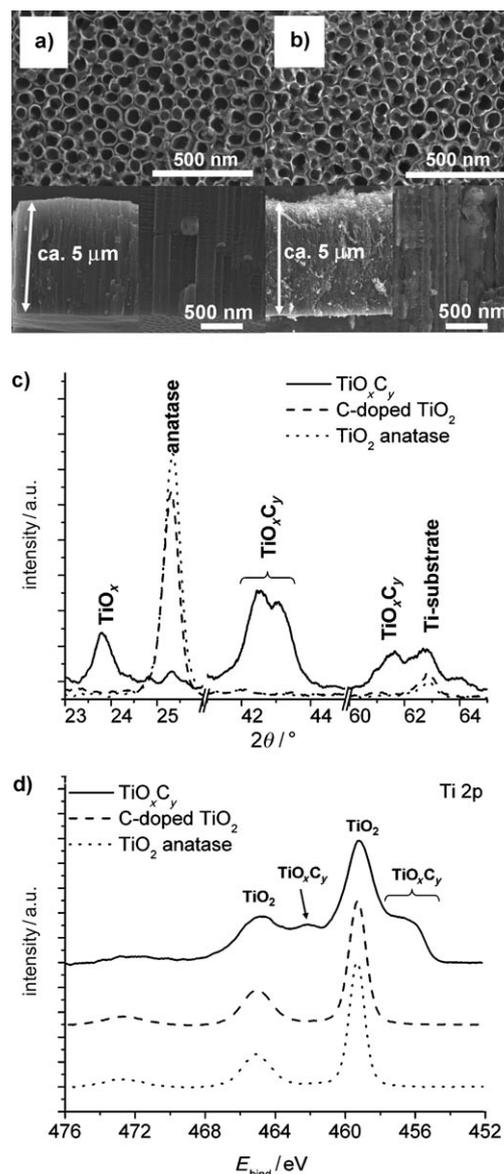
**Semimetallic TiO<sub>2</sub> Nanotubes\*\***

Robert Hahn, Felix Schmidt-Stein, Jarno Salonen, Stefan Thiemann, Yan Yan Song, Julia Kunze, Vesa-Pekka Lehto, and Patrik Schmuki\*

The highly defined morphology of self-organized anodic TiO<sub>2</sub> nanotube layers found in recent years has applications in fields such as biotechnology,<sup>[1,2]</sup> photo-catalysis,<sup>[3,4]</sup> or dye-sensitized solar cells.<sup>[5]</sup> While the semiconducting nature of TiO<sub>2</sub> is crucial for many of these applications, the limited conductivity prevents an even broader and efficient use in applications that require a fast electron transport, such as functional electrodes or as electrocatalyst supports. Herein we demonstrate how to overcome this limitation by using a robust carbo-thermal reduction treatment converting the TiO<sub>2</sub> into an oxy carbide compound that shows stable semimetallic conductivity. These TiO<sub>x</sub>C<sub>y</sub> nanotubes can be used, for example, as an inert electrode with substantial overpotential for O<sub>2</sub> evolution, or as a highly efficient support for electrocatalytic reactions, such as in methanol-based fuel cells.

To produce TiO<sub>2</sub> nanotube layers we use self-organizing electrochemical anodization,<sup>[6–9]</sup> a process leading to oxide nanotubes on a range of refractory metals (e.g. titanium,<sup>[10]</sup> zirconium, hafnium<sup>[11,12]</sup>). TiO<sub>2</sub> in its anatase or rutile form is a wide band-gap semiconductor material ( $E_g \approx 3.0\text{--}3.2$  eV) and as such particularly suitable for applications based on UV- or X-ray-induced interactions.<sup>[13]</sup> To achieve enhanced control over the electronic and optical properties of these semiconducting nanotubes, various doping approaches with suitable elements, for example, C<sup>[14,15]</sup> and N,<sup>[16–18]</sup> or various transition metals<sup>[19]</sup> were reported. However, for high-throughput electrodes, or electrocatalyst supports, the conventional doping approaches do not provide sufficient electrical conductivity. Herein we use a high-temperature treatment in acetylene that converts the semiconducting anatase phase into carbon rich (Magnéli-type) phases that show semimetallic conductivity. The process can be carried

out without loss of the ordered nanotubular morphology as illustrated in Figure 1. In this case self-organized TiO<sub>2</sub> nanotubes were grown with a diameter of 80 nm to a layer



**Figure 1.** SEM images of the nanotubes after a) anodization formation and b) after a thermal acetylene treatment at 850 °C for 10 min. The lower insets are the corresponding cross-sectional views. c) X-ray diffraction results for the acetylene-treated tubes and those of anatase TiO<sub>2</sub> nanotubes and highly C-doped TiO<sub>2</sub> nanotubes. d) XPS spectra showing the Ti2p peak of thermal-carbonized nanotubes and of anatase TiO<sub>2</sub> nanotubes and highly C-doped TiO<sub>2</sub> nanotubes.

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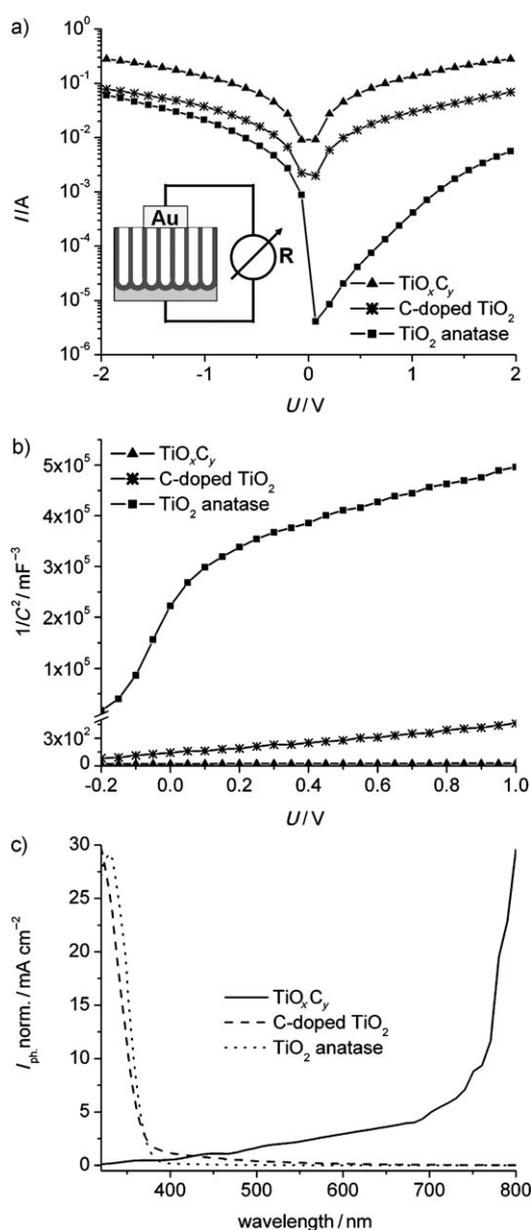
thickness of 5  $\mu\text{m}$  using an anodization process, and annealed in air at 450°C to form anatase crystal structure (details are given in the Supporting Information). These layers were then treated in acetylene at 850°C to trigger the desired carbonization reaction. After the treatment (Figure 1b) the nanotube layers only show some minor morphology changes, that is, the tubular shape is well maintained during the carbonization process. Figure 1c shows the most significant peaks of the X-ray diffraction (XRD) patterns (the full spectrum is given in the Supporting Information) before and after acetylene treatment.

The observed diffraction peaks can be attributed to the formation of titanium oxy carbide ( $\text{TiO}_x\text{C}_y$ ), which is a solid solution of TiO in TiC and various  $\text{TiO}_2$  suboxides. This result is also consistent with some TEM observations shown in the Supporting Information. These titanium oxy carbide species have been observed as intermediates, in addition to various suboxides ( $\text{Ti}_4\text{O}_7$ ,  $\text{Ti}_3\text{O}_5$ , and  $\text{Ti}_2\text{O}_3$ ), during the reduction of  $\text{TiO}_2$  to form TiC.<sup>[20,21]</sup>

In addition, after acetylene treatment, a significant hardening of the layers through the carbon uptake was observed. To illustrate the differences to a conventional  $\text{TiO}_2$  carbon-doping process<sup>[22]</sup> we included for comparison XRD data of  $\text{TiO}_2$  nanotubes that were only C-doped by an acetylene treatment at 500°C.<sup>[15]</sup> When using this classic, simple doping, clearly the characteristic  $\text{TiO}_x\text{C}_y$  peaks at  $2\theta \approx 42.5^\circ$ ,  $61.5^\circ$  are completely absent. The significant difference between C-doping and  $\text{TiO}_x\text{C}_y$  conversion also becomes evident from the X-ray photoelectron spectra (XPS) data (Figure 1d). Clear changes can be seen in the Ti 2p peak. The peak shifts show the formation of oxy carbides and the partial reduction of  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$ .<sup>[23]</sup> An evaluation of the total composition of Ti:O:C revealed changes from an atomic ratio of 1:2.2:0.25 for the anatase nanotubes produced in an organic electrolyte to 1:1.6:3.8 after the high-temperature acetylene reaction. Further differences between doping and conversion are also evident in the XPS C1s and O1s peaks (see Supporting Information). An evaluation of the oxy carbide amount based on the O1s region yields a ratio of oxy carbide to oxide of approximately 2.5:1. Solid-state electrical measurements are shown in Figure 2a for the anatase tubes, the C-doped  $\text{TiO}_2$  tubes and  $\text{TiO}_x\text{C}_y$  nanotube layers. Results for different metal contacts (using sputter evaporated Al or Pt dots) are shown in the Supporting Information.

Clearly, the carbon-modified tubes show an ohmic I–V behavior for which the resistance is several orders of magnitude lower than for the carbon-doped or pure-anatase  $\text{TiO}_2$  nanotubes. A rough estimate yields approximate conductivity values of  $3 \times 10^5 \text{ S m}^{-1}$  for  $\text{TiO}_x\text{C}_y$ ,  $9 \times 10^4 \text{ S m}^{-1}$  for C-doped  $\text{TiO}_2$ , and  $10^3 \text{ S m}^{-1}$  for anatase  $\text{TiO}_2$  nanotubes.

A clear difference between semiconducting and semi-metallic behavior is also evident using liquid electrolyte contacts. Capacity measurements at 1 kHz in 0.1 M  $\text{Na}_2\text{SO}_4$  are plotted in Figure 2b according to a Mott–Schottky approach.<sup>[24]</sup> Also in these measurements, the anatase and the C-doped nanotubes reveal a voltage dependence of the capacity which is typical for the space charge layer controlled capacity of a n-type semiconductor in contact with an electrolyte. The evaluation of flatband potentials yields

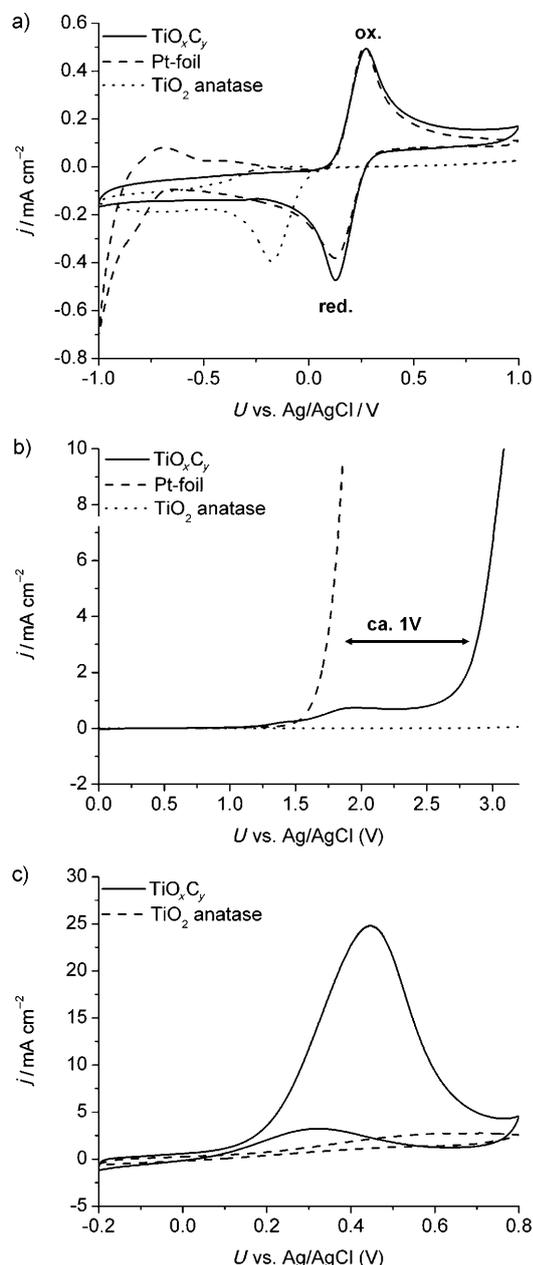


**Figure 2.** a) I–V characteristics of 2-point solid-state measurements of carbonized tubes and of anatase  $\text{TiO}_2$  nanotube layers and C-doped layers. Inset: a simplified sketch of the 2-point measurement arrangement. b) Potential-dependent capacity measurements of the different nanotube layers in 0.1 M  $\text{Na}_2\text{SO}_4$  solution at 1 kHz and plotted in a Mott–Schottky graph. c) Electrochemical photocurrent measurement of the nanotube layers in 0.1 M  $\text{Na}_2\text{SO}_4$  at 500 mV versus Ag/AgCl.

values of  $-270 \text{ mV}$  (anatase) and of  $-490 \text{ mV}$  (C-doped material). In contrast, the capacity of the  $\text{TiO}_x\text{C}_y$  electrode system has metallic behavior with only a weak dependence of the capacitance on the applied voltage, that is, a capacitance solely determined by the Helmholtz layer at the solid–liquid interface and therefore no reasonable flatband potential can be extracted. Moreover, from the photocurrent data in Figure 2c it is evident that for the anatase and C-doped materials a typical response of a semiconductor is observed whereas for the semimetal a completely different optical behavior (with a strong IR response) is obtained.

Some examples of the strongly enhanced performance of the carbonized nanotubes as a conductive electrode material for electrochemistry are shown in Figure 3.

The cyclic voltammetry results in Figure 3a show the behavior of carbon modified tubes with a flat platinum foil and conventional anatase TiO<sub>2</sub> nanotubes in a defined redox electrolyte. The TiO<sub>x</sub>C<sub>y</sub> nanotube electrode clearly shows similarly defined oxidation and reduction peaks as a pure



**Figure 3.** Electrochemical characterization: a) cyclic voltammetry results of carbonized nanotubes, anatase TiO<sub>2</sub> nanotubes, and a flat Pt foil in 5 mM [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> solution. b) Polarization curves of the samples in 1 M H<sub>2</sub>SO<sub>4</sub> illustrating the high overpotential for O<sub>2</sub> evolution. c) Cyclic voltammogram for the electrocatalytic oxidation of methanol from a 1 M CH<sub>3</sub>OH + 1 M H<sub>2</sub>SO<sub>4</sub> solution by using TiO<sub>x</sub>C<sub>y</sub> and anatase TiO<sub>2</sub> loaded under same conditions with Pt/Ru nanoparticles (500 μg cm<sup>-2</sup>).

platinum electrode with electron-transfer kinetics that are orders of magnitude higher than for semiconducting anatase TiO<sub>2</sub>. In fact, the anatase TiO<sub>2</sub> nanotube electrode shows only negligible reactions at these anodic overvoltages owing to the blocking character that is an inherent characteristic for an n-type semiconductor under anodic bias.<sup>[25]</sup>

The oxy carbide electrodes also showed a high cycling stability as shown in the Supporting Information in Figure S4.

The electrodes have a large overpotential to oxygen evolution (Figure 3b). The small current increase between 1.5 V and 2.5 V may be ascribed to minimal oxide formation on oxy carbide phases.<sup>[26]</sup>

To give another example for an electrochemical reaction that requires an enhanced “potential window” we selected a reaction relevant to methanol-based fuel cells, that is the Pt/Ru catalyzed oxidation of methanol (usually performed on carbon substrates).<sup>[27,28]</sup> While previous work demonstrated that conventional anatase TiO<sub>2</sub> nanotubes can serve as a very beneficial support for methanol oxidation,<sup>[29]</sup> we show in Figure 3c that the use of conductive TiO<sub>x</sub>C<sub>y</sub> enhances (under the same catalyst loading conditions) the catalytic activity for methanol oxidation by 700%. Furthermore, for the semi-metallic support the oxidation peak is much more defined. This simply reflects the strongly enhanced electron transfer across the support.

Overall, herein we demonstrate the successful conversion of TiO<sub>2</sub> in a nanotube array into a highly conductive and stable TiO<sub>x</sub>C<sub>y</sub> phase by a simple, one step, high-temperature treatment in acetylene. We obtain a highly functional and robust nanotubular electrode material with a very well defined and controllable morphology. The combination of semimetallic conductivity with a high overpotential for O<sub>2</sub> evolution makes the material, among other applications, suitable as a catalytic support for methanol fuel cells or other applications that require high electron conductivity.

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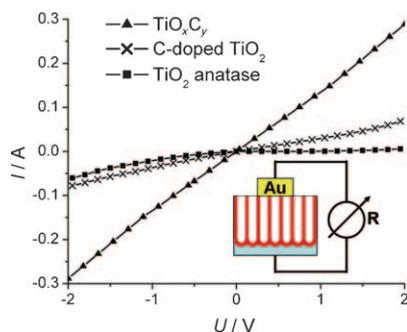
## Communications



### Conductive $\text{TiO}_2$

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Semimetallic  $\text{TiO}_2$  Nanotubes



**Orchestrating conductors:** A carbo-thermal reduction treatment of a  $\text{TiO}_2$  nanotube layer in acetylene converts the tube walls into highly conductive and stable oxy carbide compounds. The resulting semimetallic  $\text{TiO}_2$  nanotube layers ( $\text{TiO}_x\text{C}_y$ ) are electrode materials with properties that differ from other  $\text{TiO}_2$  nanotubes (see picture). They have a high oxygen overpotential and can be used as a catalyst support, for example, for methanol oxidation.