Electronic Supporting Information

# Semimetallic $TiO_2$ Nanotubes: New Interfaces for Bioelectrochemical Enzymatic Catalysis

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*Experimental*

All chemicals and horse heart cyt c have been purchased from Sigma-Aldrich (Taufkirchen, Germany). All solutions have been prepared in 18 MΩ□ Millipore water (Eschborn, Germany).

Titan dioxide nanostructured surfaces have been prepared and modified according to previously reported procedures.[1, 2] After usage they have been stored in potassium phosphate buffer. sGDH (*Acinetobacter calcoaceticus*) has been provided by Roche Diagnostics GmbH. The enzyme is recombinant expressed in *E. coli*. PQQ has been purchased from Wako Pure Chemical Industries. sGDH has been dissolved in 5mM MES buffer in the presence of 1mM $CaCl_2$ and pH 5 has been adjusted. According to Olsthoorn et al.[3] the apoGDH has been reconstituted by a PQQ/GDH ratio of 1. For this purpose sGDH and PQQ have been incubated for one hour at room temperature in the dark. Aliquots have been stored at -20°C. Human SO has been expressed from E. Coli TP1000 cells as described previously by Temple.[4] All measurements with SO have been carried out in potassium phosphate buffer at pH 7. All electrochemical measurements were done in a 1 ml sell using Ag/AgCl/ 1M KCl reference (Biometra, Germany) and a Pt-wire counter electrode. The working electrodes were $TiO_2$ nanostructures. Cyclic voltammetric experiments have been carried out with the Autolab PGSTAT 30 device (Metrohm, Germany).

1. R. Hahn, F. Schmidt-Stein, J. Salonen, S. Thiemann, Y. Y. Song, J. Kunze, V. P. Lehto and P. Schmuki, *Angew. Chem.-Int. Edit.,* 2009, **48**, 7236.
2. J. M. Macak, H. Hildebrand, U. Marten-Jahns and P. Schmuki, *J. Electroanal. Chem.,* 2008, **621**, 254.
3. A. J. J. Olsthoorn and J. A. Duine, *Arch. Biochem. Biophys.,* 1996, **336**, 42.
4. C. A. Temple, T. N. Graf and K. V. Rajagopalan, *Arch. Biochem. Biophys.,* 2000, **383**, 281.

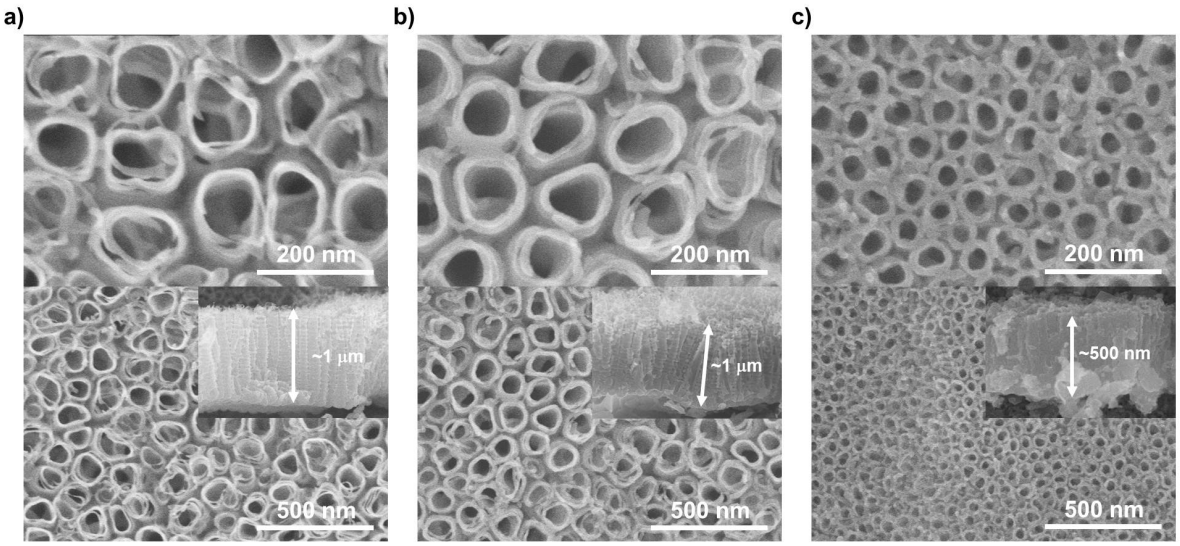



Figure S1. SEM images of the used nanotubular electrodes (high and lower magnification top-views, insets: corresponding cross-sectional views): a) C-doped $TiO_2$ nanotubes, b) $TiO_xC_y$ nanotubes with 100 nm diameter, c) $TiO_xC_y$ nanotubes with 50 nm diameter. Anatase $TiO_2$ nanotubes (not shown here) have a similar morphology to a).

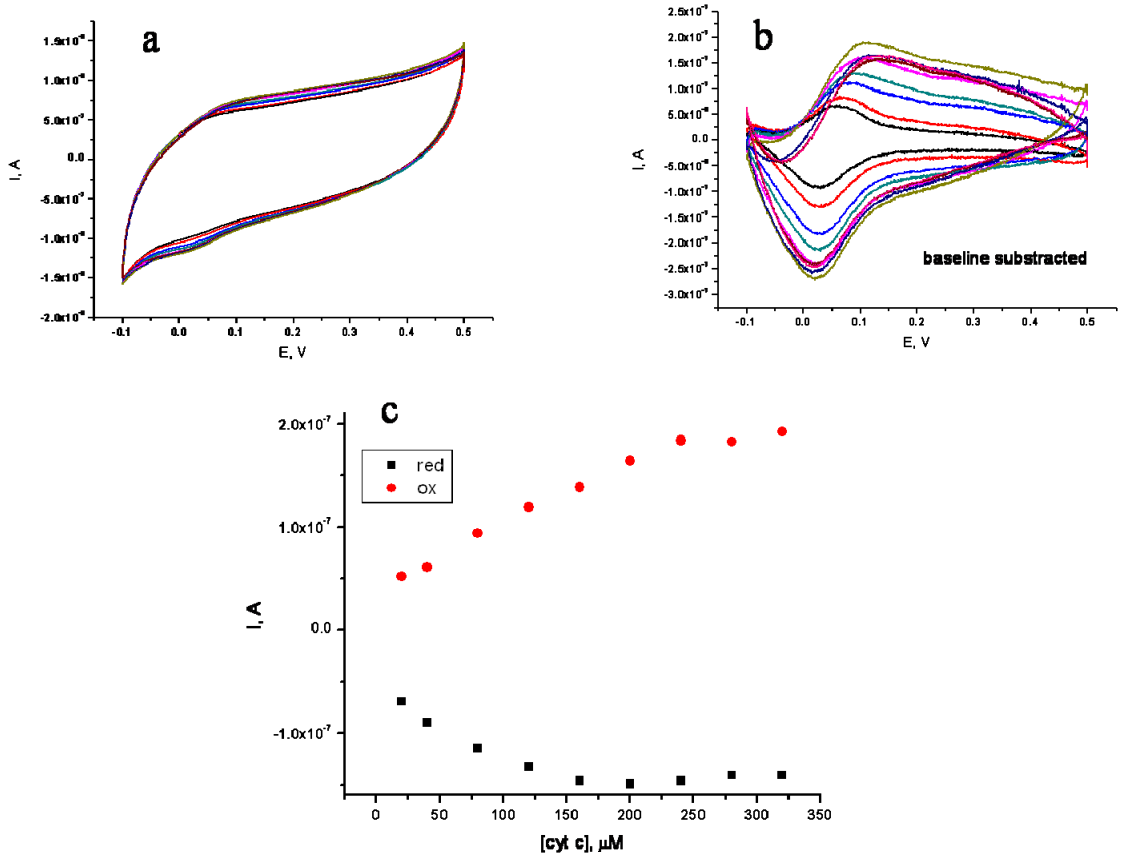
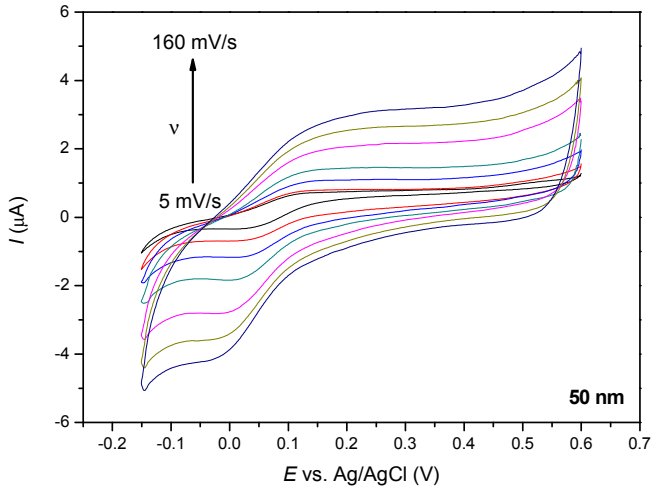



Figure S2. Electrochemical behavior of cyt c at $TiO_xC_y$ nanostructures: a) CVs of increasing concentrations of cyt c, b) baseline (bare $TiO_xC_y$ surface) subtracted CVs, c) concentration dependence of peak current. Experimental conditions: 5 mM potassium phosphate buffer, pH 7, [cyt c] has been variied between 10 µM and 325 µM.

a)




b)

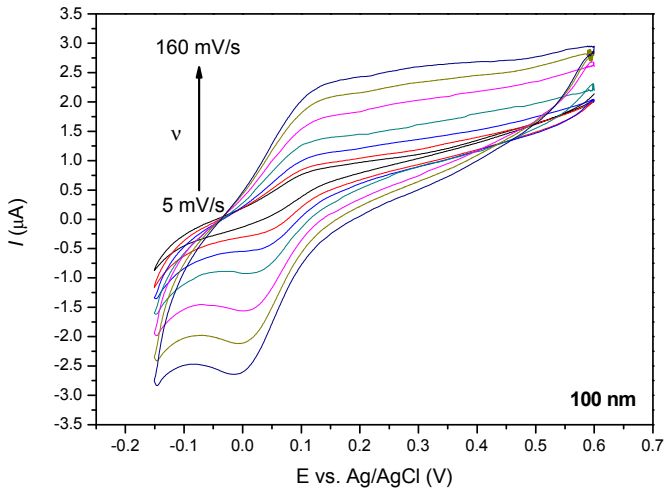
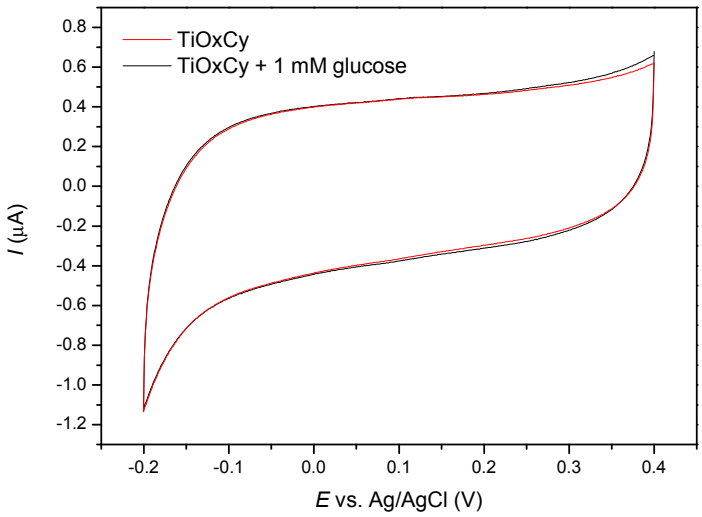



Figure S3. Selected CVs of a) 50 nm and b) 100 nm $TiO_xC_y$ nanotube electrodes taken at different scan rates in 240 μM cyt c (5mM potassium phosphate buffer, pH 7). The scan rates are variied between 20 and 160 mV/s.

a)




b)

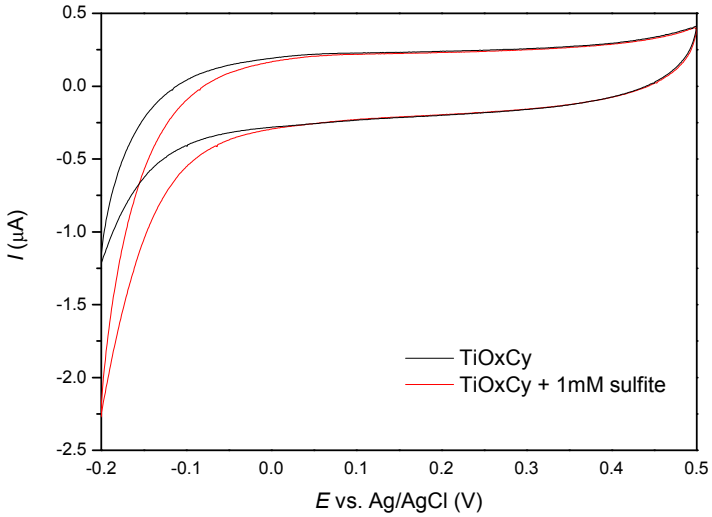



Figure 4S. CVs of $TiO_xC_y$ nanotube electrode: a) in the absence and the presence of 1 mM glucose, b) in the absence and the presence of 1 mM sulfite. Experimental conditions: Experimental conditions: a) [PQQ:GDH] = 10 μM, 5 mM MES buffer containing 1mM $CaCl_2$, pH 7; c) [SO] = 1 μM, 5mM potassium phosphate buffer, pH 7