

A. Potential windows in aqueous solution

Due to the semi-conducting and redox properties of TiO_2 , a prerequisite to any electrochemical measurement performed with TiO_2 modified electrodes is to determine the potential window in which the electrode response to solution-phase redox probes is not affected by the TiO_2 thin film. Figure A shows the CV curves recorded with the bare FTO, the TiO_2 -gel-FTO and the TiO_2 -anatase-FTO electrodes in a blank electrolyte solution at pH 4.1.

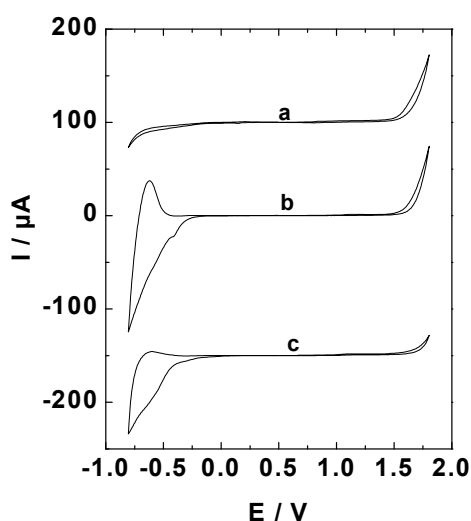


Figure A. Cyclic voltammetric curves recorded in a blank electrolyte solution (0.05 M hydrogen phthalate at pH 4.1) using (a) bare FTO, (b) TiO_2 -gel-FTO, and (c) TiO_2 -anatase-FTO electrodes; film thickness of about 160 nm (b, c); scan rate: 50 mV s^{-1} .

Voltammetric potential limits for the bare electrode were -0.8 V and $+1.7 \text{ V}$, respectively in the cathodic and anodic regions. When covered with a TiO_2 -gel or a TiO_2 -anatase film, the anodic limit remained unchanged whereas the cathodic one was restricted to -0.4 V (TiO_2 -gel) or -0.5 V (TiO_2 -anatase). These limits were a little bit lower when working in phosphate buffer at pH 6.8 (-0.5 V for TiO_2 -gel and -0.6 V (TiO_2 -anatase). As the electroactive probes used in this study are charac-

terised by Voltammetric signals located

within these potential ranges, one can consider the TiO_2 films as inert barriers in between the FTO surface and the external solution. No charge transfer reactions are expected to occur on TiO_2 surfaces, in agreement with a recent report dealing with the oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ on FTO electrodes covered with TiO_2 nanoparticles, indicating that electron transfer occurred on the fraction of the electrode not covered by the TiO_2 nanocrystals and exposed to the electrolyte.^{1a} Note that participation of the TiO_2 thin film to electron transfer reactions may occur in case of electron injection into the sub-bandgap states of the metal oxide film,^{1b} but

this was restricted to rather low potential values (<-0.5 V) that were not investigated in the present studies. One can therefore consider the TiO_2 thin films as an electrochemically inert barrier for all CV experiments carried out hereafter.

B. Cyclic voltammetry with Meldola's Blue

Comparison between amorphous and nanocrystalline mesoporous titania thin films has been completed by studying the CV response of the positively-charged Meldola's Blue (MB), a well-known charge transfer mediator displaying a reversible behaviour on most electrodes. Indeed, on a bare FTO electrode, MB was characterised by well-defined oxidation-reduction peaks separated by a ΔE value equal to 58 mV (Fig. B, curve "a"), in good agreement with the

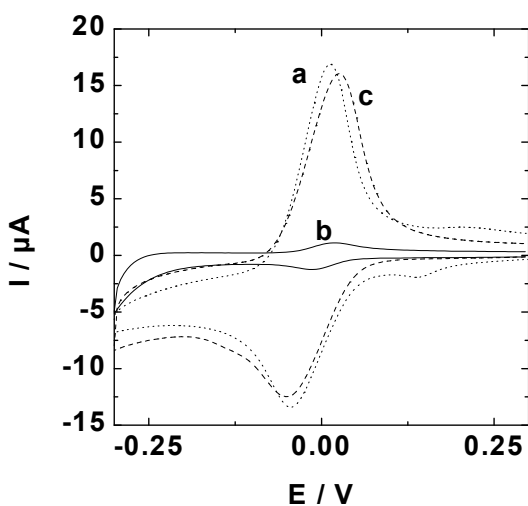


Figure B. Cyclic voltammograms recorded in 0.1 mM Meldola's Blue (in 0.05 M hydrogen phthalate solution at pH 4.1) using (a) bare FTO, (b) TiO_2 -gel-FTO, and (c) TiO_2 -anatase-FTO electrodes; film thickness of about 90 nm (b, c); scan rate: 50 mV s^{-1} .

expected value for one electron transfer.

Similarly to what was observed for $\text{Ru}(\text{bpy})_3^{2+}$ (Fig. 2 of the paper) the voltammetric curve recorded for MB on the titania film electrode after thermal treatment at 500°C and concomitant crystallisation of the TiO_2 gel in anatase (Fig. B, curve "c"), was nearly the same as that obtained on the bare FTO electrode, except that peak potential separation rose to 75 mV and peak currents slightly decreased (by less than

5%). Once again, this was due to structure openings perpendicular to the electrode surface, enabling fast diffusion of electroactive species to the FTO substrate. Varying potential scan rates from 10 to 1000 mV s^{-1} resulted in peak currents evolving linearly with the square root of the scan rate, indicating that the redox processes were diffusion-controlled.

This time, however, a well-defined electrochemical signal, yet much less intense (by 90 %), was observed with the FTO electrode modified by a mesoporous titania thin film treated at only 300°C (contracted cubic structure having orthorhombic symmetry). The CV curve (Fig. B, curve “b”) was characterised by an anodic-to-cathodic peak separation of 34 mV (i.e., less than the theoretical value for diffusion-controlled one-electron transfer), suggesting the contribution of a thin-layer behaviour. This was also sustained by the variation of peak currents with the potential scan rate, which was now in between the expected linear relationships with the square root of scan rate (purely diffusional behaviour) and the direct proportionality with the scan rate (typical of confined species on the electrode surface). It seems thus that the planar geometry of MB enables its entrapment in the contracted cubic mesoporous structure of the thin film treated at 300°C, giving rise to a non negligible electrochemical response, contrarily to the more bulky $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Ru}(\text{bpy})_3^{2+}$ that are not likely to penetrate in such confined environment and, therefore, electrochemically silent.

C. Copper electrodeposition and anodic stripping voltammetry (ASV)

The electrochemical reduction of metal ions was also investigated to evaluate the effectiveness of metal electrodeposition in these mesoporous matrices. Again, distinction was made between the films treated at 300°C and 500°C. Figure C depicts the linear sweep voltammograms obtained after 1 min electrolysis at -0.3 V from a 1 mM Cu(II) solution. Clearly, large currents ($>50 \mu\text{A}$) were observed in the -0.3 to -0.1 V potential region when using the TiO_2 -anatase-FTO electrode treated at 500°C (Fig. C, curve “b”), consistent with the extremely open structure of the nanocrystalline titania layer, enabling the copper(II) ions to diffuse freely to the FTO surface to be reduced and re-oxidised in a well-defined stripping

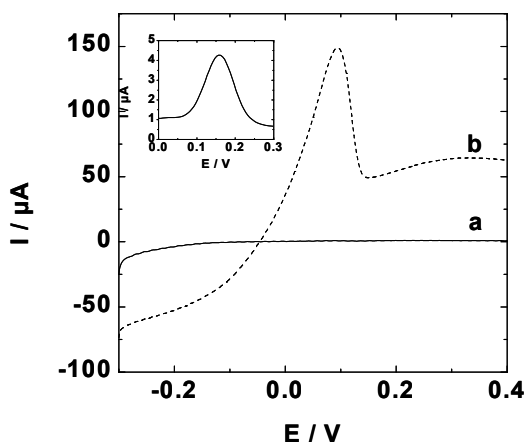


Figure C. Linear sweep anodic stripping voltammetric curves obtained after 60 s electrolysis at -0.3 V (vs. Ag/AgCl) in 10^{-2} M HNO_3 solution containing 1 mM Cu^{2+} species at (a) TiO_2 -gel-FTO and (b) TiO_2 -anatase-FTO electrodes; film thickness of about 125 nm; scan rate: 50 mV s^{-1} . Inset: differential pulse anodic stripping voltammetric curve obtained for case (a) in the same conditions as above; modulation time: 0.05 s; modulation amplitude: 50 mV; step potential: 5 mV; interval time: 0.5 s.

peak at +0.1 V. At the opposite, no detectable stripping peak can be found on the linear sweep ASV curve recorded in the same conditions using the TiO_2 -gel-FTO electrode (i.e., thin film treated at only 300°C), as shown on Figure C (curve “a”). It was only possible to detect a small peak by recording the ASV curve in the more sensitive differential pulse mode (inset in Fig. C). This confirms that very little amount of Cu(II) species has really reached the FTO surface

when covered by a contracted cubic TiO_2 film. From the electroanalytical point of view, it is of course evident that considerable advantage is provided by the 3D nanocrystalline mesoporous structure ensuring fast mass transfer processes, as otherwise demonstrated for functionalized mesoporous silica modified electrodes.²

- 1 (a) K.-R. Meier, M. Grätzel, *ChemPhysChem* (2002) 371. (c) S. Cosnier, C. Gondran, M. Grätzel, N. Vlachopoulos, *Electroanalysis* 9 (1997) 1387. (b) E. Topoglidis, A. E.G. Cass, B. O'Regan, J.R. Durrant, *J. Electroanal. Chem.* 517 (2001) 20. (b) K.-R. Meier, M. Grätzel, *ChemPhysChem* (2002) 371. (c) S. Cosnier, C. Gondran, M. Grätzel, N. Vlachopoulos, *Electroanalysis* 9 (1997) 1387.
- 2 A. Walcarius, M. Etienne, S. Sayen and B. Lebeau, *Electroanalysis* 15 (2003) 414.