

SUPPORTING INFORMATION

A Dual Band Electrochromic Device Switchable across Four Distinct Optical Modes

Synthesis of pure TiO₂ and V-modified TiO₂ nanoparticles. Two batches of pure TiO₂ and V-modified anatase NCs were prepared by reproducing a previously reported synthetic procedure [17]: bare TiO₂ nanoparticles were first synthesized by sol-gel and then crystallized by solvothermal treatment in oleic acid. In detail: 0.75 g of TiCl₄ was reacted with 10 mL of methanol (MeOH), followed by water addition in a H₂O:Ti molar ratio of 16. Then 2 mL of the resulting solution was injected into 10 mL of n-dodecylamine at room temperature. The resulting slurry was then heated at 100 °C for 1 h, followed by extraction of the white precipitate and purification with acetone and solvothermal crystallization at 250 °C for 2 h, that has been carried out upon re-dispersing the TiO₂ nanoparticles in 10 mL of oleic acid. To obtain the V-modified nanoparticles, a 0.5 mL drop of vanadium chloromethoxide solution was added to the sol just before initiate the solvothermal treatment. The vanadium chloromethoxide was prepared in an analogous way to the Ti precursor. In detail, 10 mL of MeOH was slowly added to 0.75 g of VCl₄ in glovebox (Braun, LabStar). A greenish suspension was thus obtained.

TEM analysis of the VTO NCs. Transmission electron microscopy analysis of the V-modified TiO₂ nano-powders was carried out with a field-emission gun microscope Jeol 2010F working at 200 kV.

XRD analysis. X-ray diffraction were performed on a Panalytical diffractometer working with the Cu K α radiation ($\lambda=1.5406$ Å) using a Bragg-Brentano geometry. The XRD results were analyzed by Rietveld refinement, using the Fullprof software. Rietveld fitting of the XRD profile of the VTO film was realized by including both a single anatase structure (which revealed a Goodness of Fit, GoF= 3.485) and a combination of TiO₂ anatase and V₂O₅ structures (which revealed indeed a GoF of 3.007). The formation of a thin superficial layer of vanadium oxide (that was thus reasonably identified as V₂O₅) was also indirectly inferred by the analysis of the unit cell volume (UCV): VTO sample exhibited a UCV of 135.5 Å³, a bit smaller than the UCV of the nanocrystalline anatase (ICSD #154602), that's of 137.34 Å³.

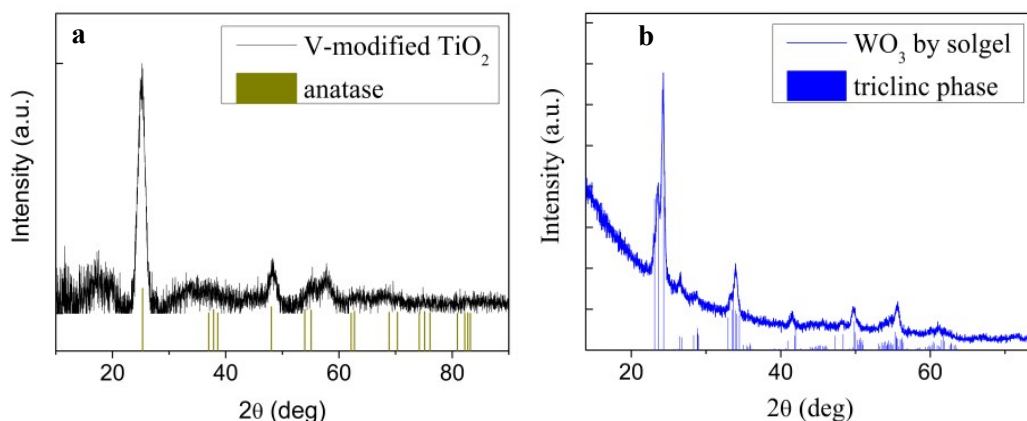


Figure S1. XRD spectra of the a) VTO and b) WO₃ electrode respectively

Fabrication of VTO nanocrystalline electrodes. VTO NCs were used to prepare a viscous paste that were subsequently deposited by screen-printing onto a set of ITO-coated glass substrates. Pristine colloidal NCs suspended in toluene were turned into printable viscous pastes upon the addition of a proper amount of ethyl cellulose (30-70 mPa*s from Sigma Aldrich) dissolved in terpineol (0.65g of polymer in 5mL of solvent). The low boiling solvents were made slowly evaporating through a R-300 Rotavapor®. Mesoporous electrodes were obtained by depositing the V-TiO₂-based paste by screen-printing and then subjecting the films to a thermal annealing in air at 420°C for 60 min. The deposition process was repeated several times until the desired thickness was achieved. A representative number of films were selected to be observed at high magnification through a FEI Helios 600i electron beam system.

Fabrication of WO₃ nanocrystalline electrodes. WO₃ nanocrystalline electrodes were also realized by sol-gel synthesis and subsequent screen-printing deposition. In this case the WO_x-NC-based viscous slurry was obtained from a hydrolysis and condensation of tungsten hexachloride (WCl₆) in isopropanol: 600 mg of WCl₆ in 20 mL of isopropanol for 8 hours at room temperature. Then, 0.65 g of ethylcellulose (30-70 mPa*s) dissolved in 5mL of α -terpineol were added to the reacting sol along with a small amount of acetic acid (0.5mL in 15mL of isopropanol). The mixture was then subjected to vigorous stirring for 12 hours at 60°C to allow the residual isopropanol to evaporate. The so obtained viscous ink was thus used to realize a batch of WO_x-NPs-containing films, which have been finally turned into nanoporous WO₃ electrodes upon thermal annealing in air at 390°C for 30 min. The deposition process was repeated several times until the desired thickness was achieved.

Spectro-electrochemical characterization. Cyclic voltammetry (CV) were performed using a 1M LiClO₄ solution in propylene carbonate in a three-electrode electrochemical cell. Ag/AgCl in saturated LiCl in anhydrous propylene carbonate and Pt foil were used as a reference and counter electrode respectively. All potentials were referred to the Ag/AgCl electrode. All the data were acquired using an Autolab PGSTAT 302N. The transmittance spectra of the films in the three-electrode configuration were measured by appropriately positioning the electrochemical cell (a cubic quartz cell purchased from Hellma®) in a Varian Cary 5000 spectrophotometer.

Fabrication of dual-band EC devices. A batch of ITO-coated glass samples (size: 3 x 2 cm², thickness: 1.1 mm, resistivity: 20 Ω /sq, from XIN YAN TECHNOLOGY LTD) was used as substrates. They were initially cleaned up via three subsequent sonication steps in deionized water, acetone and isopropanol. VTO and WO₃ electrodes (both with an active area of 1cm²) were assembled together to form a sandwich cell by using a thermoplastic gasket (DuPont™ Surlyn®). A liquid electrolyte was then used to fill the gap through a hole, which had been previously made on one of the glasses. Several different electrolyte formulations were tested over the duration of this study. The electrolyte used to fill the here reported DB-EC cell is composed of 1 M LiClO₄ + 0.05 M LiI in DMSO. The hole was finally capped with two-part curable epoxy resin.

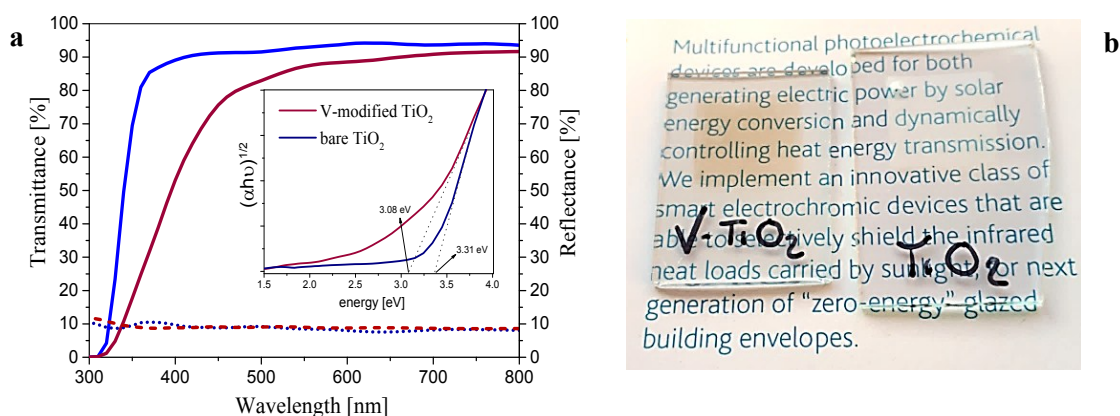


Figure S2. a) Transmittance spectra of bare TiO₂ and V-modified TiO₂ films (thickness 700nm) deposited on bare glass. Tauc plots are traced out in the inset graph. b) Optical images of the corresponding samples.

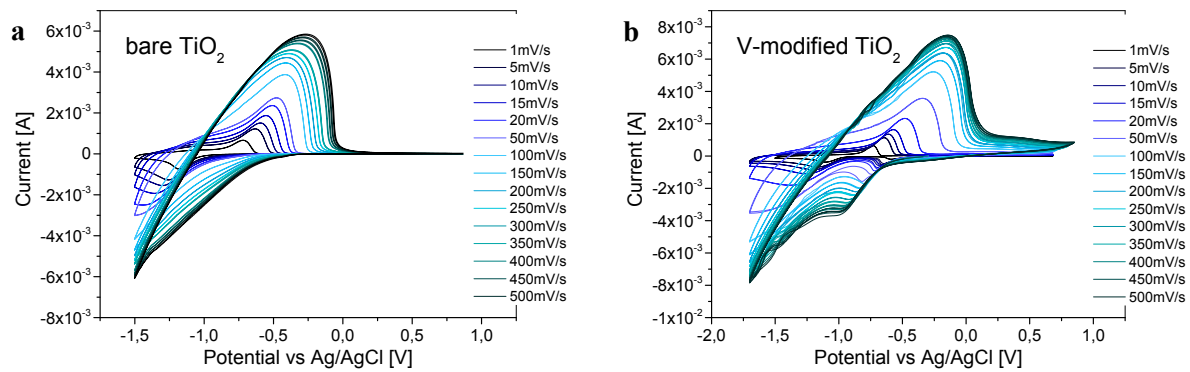


Figure S3. CV plots of a) bare TiO_2 and b) V-modified TiO_2 recorded in 1M LiClO_4 in PC at different scan rates (from 1 to 500 mV/s)