

Electronic Supplementary Information for

Surface Modification of Metal Oxide Nanocrystals for Improved Supercapacitors

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SYNTHESIS

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For the synthesis of the TiO₂ nanocrystals, we followed a previously established protocol with slight modifications.¹ Briefly, for the preparation of the starting solutions, methanol (10 mL) was slowly added to TiCl₄ (0.75 g) previously weighed in a glove-box, with evolution of white smokes and heat. After 1 hour from methanolysis, water was slowly dropped to the colorless solution, with no precipitation. The H₂O:Ti molar ratio was 16. For processing the solutions, n-dodecylamine (DA) (10 mL) was poured into a glass vial. Then the TiO₂ starting solution (2 mL) was added, and a white slurry was immediately formed. The vial was then inserted into an oven and heated for 1 hour at 100 °C for enhancing the product formation. Then, the white precipitate was recovered by centrifugation, washed in acetone and redispersed in oleic acid (10 mL). The resulting slurry was poured into a Teflon bottle, which was sealed with a silicone tape and inserted in an oven, where it was heated at a rate of 5 °C min⁻¹ up 250 °C, and kept for two hours. After cooling, the product was recovered by addition of methanol and centrifugation, washed in acetone and finally dried at 90 °C. An off-yellow powder was obtained. For preparing the TiO₂-VO_x sample, a solution of hydrolyzed vanadium chloroalkoxide (0.5 mL) was poured into the titania slurry before the heating step at 250 °C. The V solution was prepared as described elsewhere.²

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MATERIAL CHARACTERIZATION SETUP

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X-ray diffraction (XRD) on the dried powders was carried out with a Panalytical X'Pert PRO-MPD diffractometer working with the Cu K α radiation ($\lambda = 1.5406$) using a Bragg-Brentano geometry. High-resolution Transmission Electron Microscopy (HRTEM) observations studies were carried out with a field emission gun microscope Jeol 2010F, which works at 200 kV and has a point-to-point resolution of 0.19 nm. X-ray Photoelectron Spectroscopy (XPS) was performed using a PHI ESCA-5500 equipment working with the Al K α radiation (1486.6 eV). The powders were fixed on the sample holder with a biadhesive film, giving them a certain amount of surface charging on all of the peak positions of the main narrow scan spectra acquired: V2p3/2, O1s, C1s. They were all properly corrected with respect to the adventitious C1s present on the surface with respect to the tabulated and literature value of 284.6 eV. Induced Couple Plasma (ICP) analysis was carried out in a Perkin Elmer Optima 7300 DV ICP-OES equipment. The protocol used to dissolve the samples was a chemical attack in an aqueous solution with 2% HF, under microwave treatment for 10 min at 700 W. Results of solid NMR-MAS of ⁵¹V were obtained using a Varian Infinity 400 spectrometer operating at 400 MHz in a nominal field of 9.395 T, using a probe of 4 mm coil. The spectra can be acquired efficiently with standard single pulse sequence. Each pulse was 3.5 μ s duration. The delay between scans was 1 s and 50000-60000 scans were collected for each spectrum. The vanadium NMR spectra were referenced against ammonium metavanadate as external standard. This compound is shifted (-572 ppm) against the shift of the conventional standard for vanadium, VOCl₃ (0 ppm). ⁵¹V (I=7/2) has a Larmor frequency of 105,152 MHz.

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ELECTROCHEMICAL CHARACTERIZATION SETUP

Electrochemical measurements were acquired with a Biologic VMP3 potentiostat using deaerated aqueous 0.1 M K_2SO_4 electrolytes. Three electrode configurations used Ag/AgCl as reference electrode and a platinum mesh as counterelectrode. Charge/discharge experiments were performed in symmetric configurations in Swagelok[®] cells. The electrodes were prepared by pressing at 500 Kg cm^{-2} pastes of active material:carbon black:PTFE with 75:15:10 wt% on nickel foam (1.6 mm thick, 95% purity and porosity, Goodfellow) current collectors.

SAED PATTERNS FROM HRTEM ANALYSIS

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For having a more detailed insight on the crystalline structure of the nanoparticles here reported and the possible influence of the addition of VO_x on the TiO_2 lattice structure, SAED patterns were extracted from HRTEM analysis. The results, shown in table S1 below, identify TiO_2 nanocrystals with anatase phase, while no obvious changes in the initial anatase lattice parameters are measured after VO_x addition.

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Table S1. Comparison of experimental crystal lattice parameters of different planes extracted from SAED patterns of figure 2, for pure TiO_2 and TiO_2-VO_x (last two columns on the right, respectively) to theoretical values of the most closely matched compounds (first three columns on the left).

Ring	$d_{theor. TiO_2}$ Anatase [nm] / {hkl}	$d_{theor. TiO_2}$ Rutile [nm] / {hkl}	$d_{theor. TiVO_2}$ Karelianite [nm] / {hkl}	d Pure TiO_2 [nm]	d TiO_2-VO_x [nm]
1	0.3517 / {101}	0.3248 / {110}	0.3708 / {102}	0.352	0.346
2	0.2378 / {004} 0.2333 / {112}	0.2488 / {101} 0.2297 / {200}	0.2728 / {114} 0.2527 / {110}	0.234	0.232
3	0.1893 / {200}	0.2054 / {120}	0.1854 / {224}	0.190	0.191
4	0.1667 / {211}	0.1687 / {211}	0.1610 / {131}	0.167	0.167
5	0.1481 / {204}	0.1480 / {002}	0.1495 / {124}	0.146	0.146

EDS SPECTRA DURING TEM CHARACTERIZATION

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For proving the presence of V in the TiO_2-VO_x samples, we acquired the elemental maps during TEM characterization using EDS. The results, shown in Figure S1 below, detect V with an atomic content of 7%.

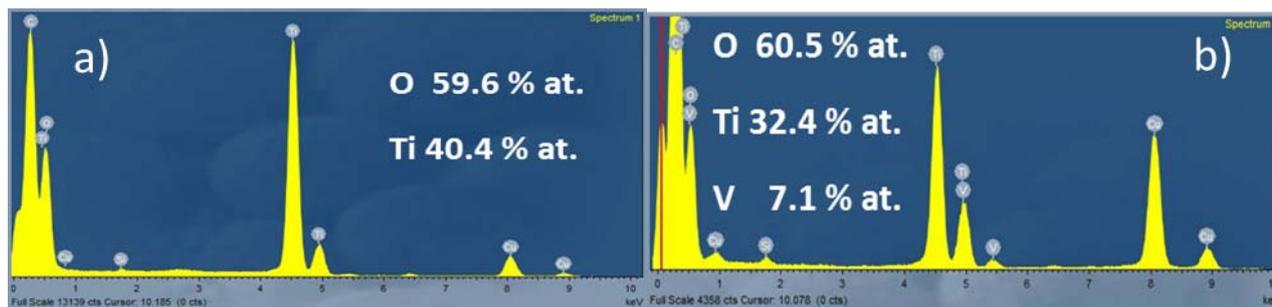


Figure S1. EDS compositional analysis acquired during TEM characterization of: (a) Pure TiO_2 ; and (b) TiO_2-VO_x nanocrystals.

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SUPPORTING XRD CHARACTERIZATION RESULTS

For having a more detailed insight on the attachment of the surface species present in TiO_2-VO_x nanocrystals, we annealed them at 500 °C, as at that temperature any loosely bound VO_x species would likely form V_2O_5 nanocrystals. The XRD characterization shown in Figure S2 only presents peaks which can be attributed to anatase and a small peak at 30° which we attribute to rutile, but no VO_x phases.

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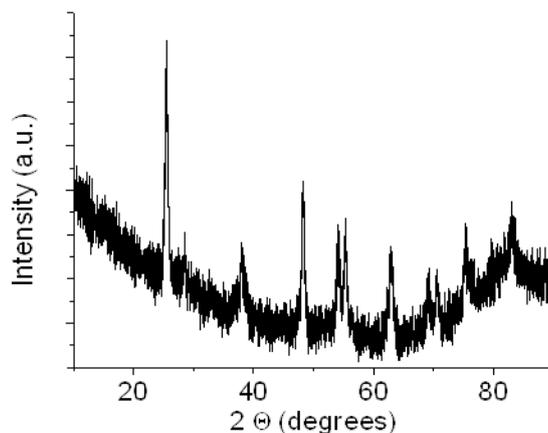
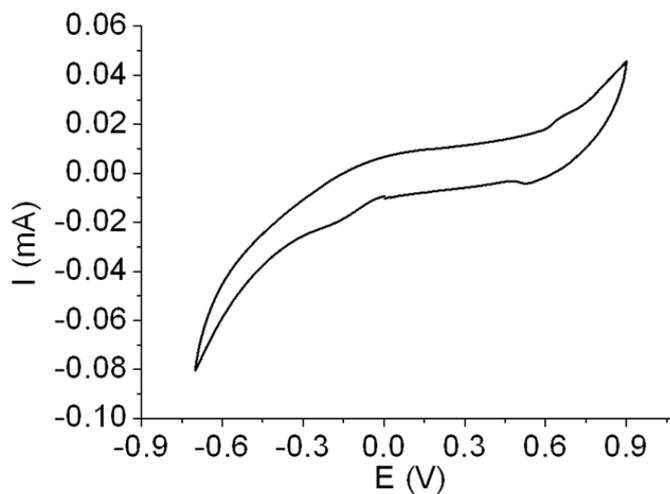


Figure S2. XRD spectrum of the TiO₂-VO_x nanocrystals after annealing at 500 °C.

SUPPORTING ELECTROCHEMICAL CHARACTERIZATION RESULTS

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Initial experiments on TiO₂ nanocrystals comprised cycling voltammograms in three electrode configuration to establish the electrochemical window which will afterwards preserve a good cycling stability of the electrodes, avoiding any irreversible process which may degrade them during charging/discharging experiments. The results, shown in Figure S3, establish a <1.2V electrochemical window.



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Figure S3. Cyclic voltammogram of TiO₂ in 0.1 M K₂SO₄ at 5 mV s⁻¹.

References

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