Supporting Information to

Some Aspects of the Charge Transfer Dynamics in Nanostructured WO₃ Films

by

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Figure S1. Cross sectional view of a transparent WO_3 colloidal electrode (6 subsequent depositions) spin coated onto FTO



Figure S2. (A) Absorption spectrum of WO₃ colloidal electrode (6 subsequent depositions) spin coated onto FTO (transmission mode); (B) Reflectance spectrum of anodically grown WO₃. Inset: spectrum in Kubelka-Munk units.



Figure S3. JV curves of a colloidal WO_3 electrode in the presence of different sulphate based electrolytes.



Figure S4. Photocurrent transients as a function of the applied voltage in different supporting electrolytes: (1): colloidal electrode in 0.1 M H_2SO_4 ; (2) anodic electrode in 0.1 M H_2SO_4 ; (3) colloidal electrode in 0.1 M LiHSO₄; (4) colloidal electrode in 0.1 M TBAHSO₄



Figure S5. Linear sweep voltammetry (20 mV/s) in the dark of anodically grown WO_3 electrodes in 0.1 M H₂SO₄ (red) and in 0.1 M TBAHSO₄ (black).



Figure S6. EPR spectrum obtained after few seconds photoirradiation ($\lambda > 420$ nm) of aqueous suspension of WO₃ containing H₂SO₄ (0.1 M) and pbn (5 x 10⁻² M)



Figure S7. [pbn-OH]· intensity as a function of irradiation time (λ > 420 nm) of aqueous suspensions of WO₃ containing pbn (5 x 10⁻²M) and H₂SO₄ (0.1M, squares) or TBAHSO₄ (0.1M, circles).



Figure S8. EPR spectrum obtained after ca 100s seconds photoirradiation ($\lambda > 420$ nm) of aqueous suspension of WO₃ containing TBAHSO₄ (0.1 M) and pbn (5 x 10⁻² M). X indicates the resonances of the carbon centred radical trapped by pbn



Figure S9. Experimental Impedance response of type C photoelectrodes held at 0.36 V vs SCE under 1 sun illumination in 0.1 M H_2SO_4 ; (a) complete scan (10⁵-10⁻¹ Hz) outlining the charge transfer arc; (b) high frequency scan showing the first small semicircle which is barely perceptible in (a).



Figure S10. Experimental Impedance response of type A photoelectrodes held at 0.36 V vs SCE under 1 sun illumination in 0.1 M H_2SO_4 . In type A electrodes the first high frequency semicircle was often difficult to observe.



Figure S11. Relationship between the inverse of charge transfer resistance (circles and triangles) and dynamic (20 mV/s) i-V derivatives (continuous lines) in different electrolytes in the absence (red) and in the presence (blue) of MeOH. 1-3-5 Colloidal electrode; 2-4-6 Anodic electrode.



Figure S12 Time evolution of difference absorption spectra of WO₃ polarized at -20 mV (1) and -50 mV (2) vs SCE in H_2SO_4 for 20 minutes. The spectral contribution of electrons trapped in conduction band or in surface states of the semiconductor is negligible in the 400-500 nm interval.



Figure S13. Dependence of the 430 nm absorption as a function of the applied voltage (vs SCE) in H_2SO_4 (1) and in TBAHSO_4 (2). In the case of TBAHSO_4 the potential dependence of both the initial (red) and the long component (blue) which appears constant on the 20 µs time scale of the 430 nm transient are reported.



Figure S14. (1) J-V curves in organic electrolytes containing 0.1 M TBAHSO₄: Methanol (black) and 1:1 Ethylene/propylene carbonate (red); (2) Nyquist plots recorded at 0.4 V vs SCE for methanol (black) and at 0.5 V vs SCE for Ethylene/propylene carbonate (red). The solid lines are fits to the experimental points.