

SUPPORTING INFORMATION

Modification of charge trapping at particle/particle interfaces by electrochemical hydrogen doping of nanocrystalline TiO₂

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Electrochemical and photoelectrochemical measurements

Measurements were performed at room temperature in a standard three-electrode electrochemical cell. All potentials were measured against and are referred to an Ag/AgCl/KCl (3M) electrode (BASi). A Pt wire was used as the counter electrode. Measurements were performed with a computer-controlled Autolab PGSTAT302N potentiostat. The current and charge densities are given on the basis of the geometric electrode area. A 450 W Xe arc lamp (Thermo Oriel) equipped with a water filter was used for UV/Vis irradiation of the electrode from the electrolyte side. The applied light irradiance was measured with an optical power meter (International Light, IL1400A) equipped with a bolometer (SEL623/U) being $500 \text{ mW}\cdot\text{cm}^{-2}$. In all experiments, a 0.1 M solution of HClO_4 in ultrapure water was used as working electrolyte and was purged from oxygen by bubbling with N_2 . Methanol (1 M) was added to the electrolyte to act as a hole scavenger when the porous film was operated as a photoanode. Methanol, however, has no effect on the electrochemical response of the electrodes in the absence of UV light as verified by experiments conducted in the pure electrolyte. Cyclic voltammograms (CVs) were recorded between 0.8 and -0.6 V at a scan rate of $20 \text{ mV}\cdot\text{s}^{-1}$.

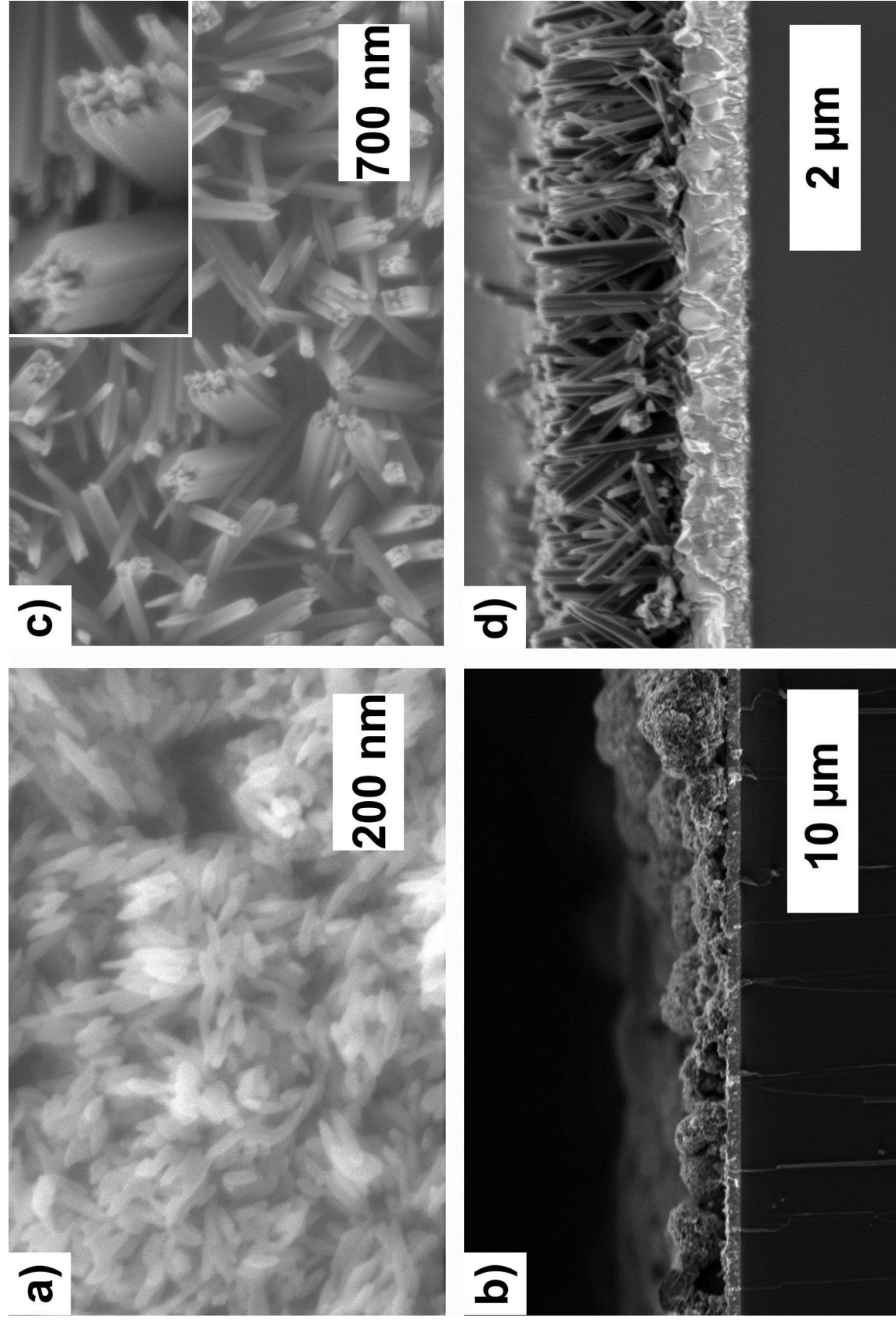


Figure S1: Scanning electron micrographs of rutile TiO_2 electrodes: top view (a, c) and cross section (b, d) of NP (a, b) and NC (c, d) films. The inset in Figure S1c shows a magnification of nanocolumn top regions.

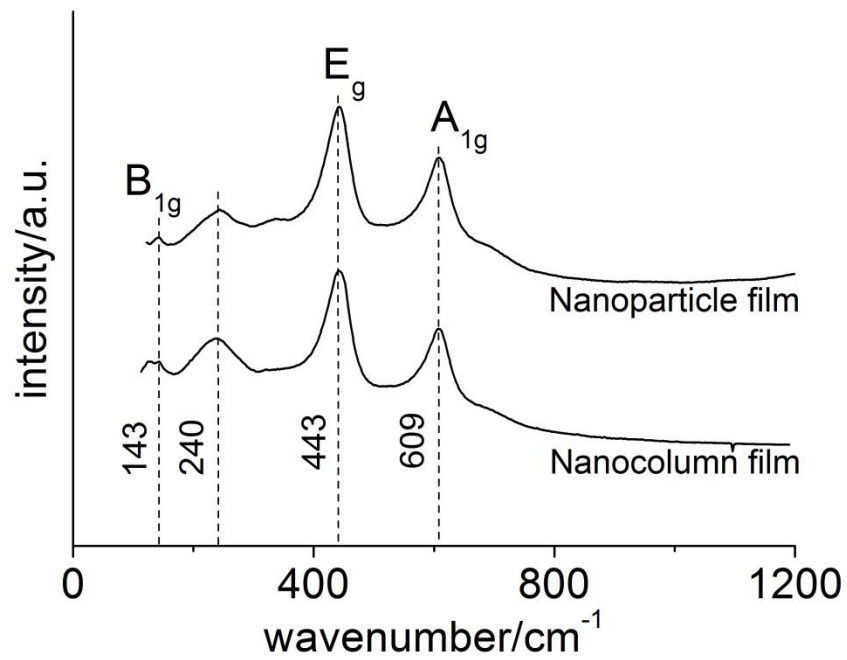


Figure S2: Raman spectra of rutile TiO_2 NP and NC films. Rutile specific bands are indicated by dashed lines.

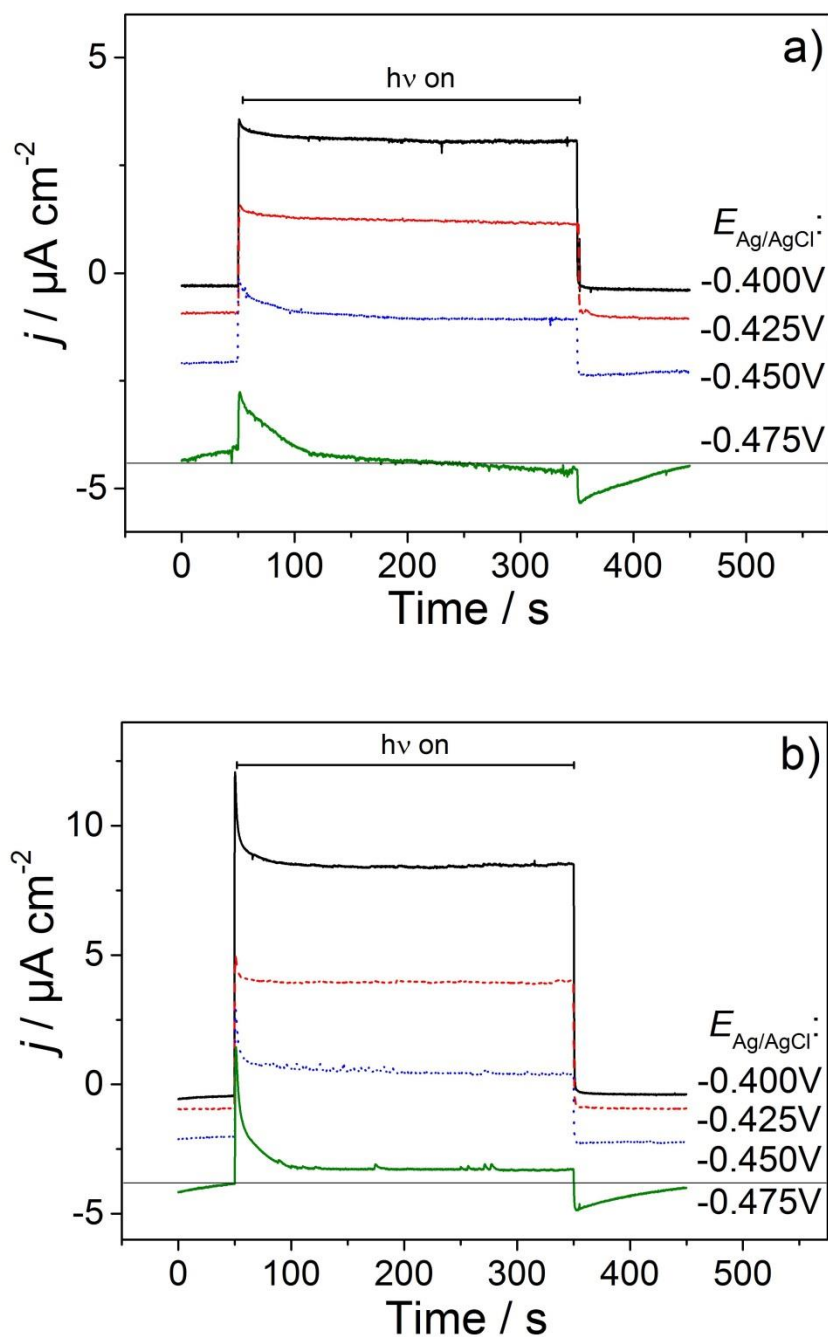


Figure S3: Photocurrent transients at different potentials $E_{\text{Ag/AgCl}}$ under polychromatic illumination (a) for pristine rutile TiO_2 NP electrodes and (b) for NP electrodes after electrochemical doping ($E^{\text{dop}} = -0.6 \text{ V}$, $t^{\text{dop}} = 3 \text{ h}$). Electrolyte: N_2 -flushed 1 M methanol/0.1 M HClO_4 aqueous solution. Irradiance: $500 \text{ mW}\cdot\text{cm}^{-2}$.

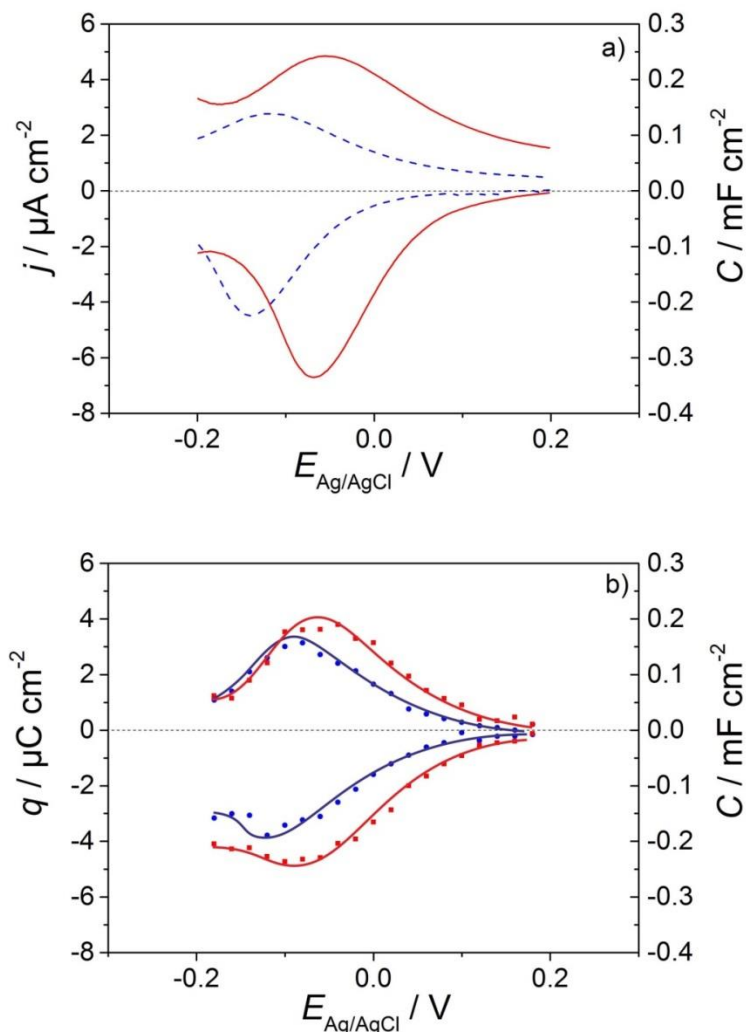


Figure S4: Chemical capacitance C (right axes) corresponding to deep traps on rutile TiO_2 NP electrodes before and after the electrochemical doping at $E_{\text{Ag/AgCl}} = -0.6$ V for 3 h (blue and red lines, respectively). The capacitance was determined (a) from the CVs in Figure 1a by dividing the capacitive current density j (left axis) by the scan rate $\nu = 20 \text{ mV} \cdot \text{s}^{-1}$ and (b) from long lasting charging/discharging measurements: For this purpose, we measured the capacitive currents (Figure S5) upon stepping the electrode potential in potential steps $\Delta E_{\text{Ag/AgCl}} = 0.02$ V first from 0.2 V to -0.2 V (charge accumulation) and then from -0.2 V back to 0.2 V (charge extraction). After every step the potential was kept constant for 60 s and the accumulated/ extracted charge density associated with each potential step (left axis in Figure S4b) was determined by integration of the resulting current transient (Figure S5). To obtain the chemical capacitance associated with grain boundary traps the charge was then referred to $\Delta E_{\text{Ag/AgCl}}$. The continuous lines in (b) are a guide to the eye. Electrolyte: N_2 -flushed 1 M methanol/0.1 M HClO_4 aqueous solution.

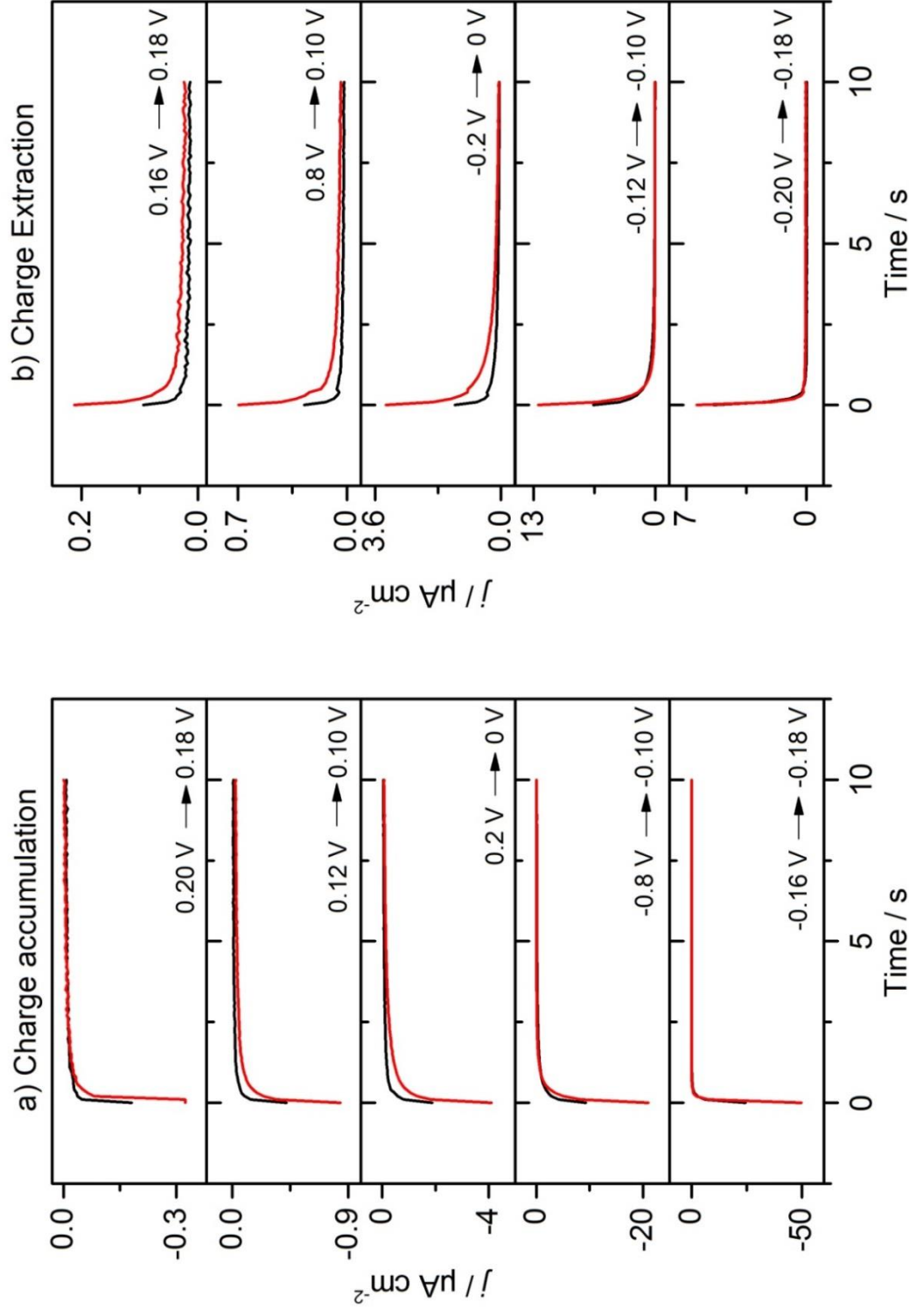


Figure S5: Selected current transients measured upon stepping the electrode potential in potential steps $\Delta E_{\text{Ag/AgCl}} = 0.02 \text{ V}$ first from 0.2 V to -0.2 V (charge accumulation) (a) and then from -0.2 V back to 0.2 V (charge extraction) (b). After every step the potential was kept constant for 60 s . For the sake of clarity only the first 10 s are shown here in each case. Black lines: pristine rutile TiO_2 NP electrodes, red lines: NP electrodes after electrochemical doping ($E^{\text{dop}} = -0.6 \text{ V}$, $t^{\text{dop}} = 3 \text{ h}$). Electrolyte: N_2 -flushed 1 M methanol/ 0.1 M HClO_4 aqueous solution.

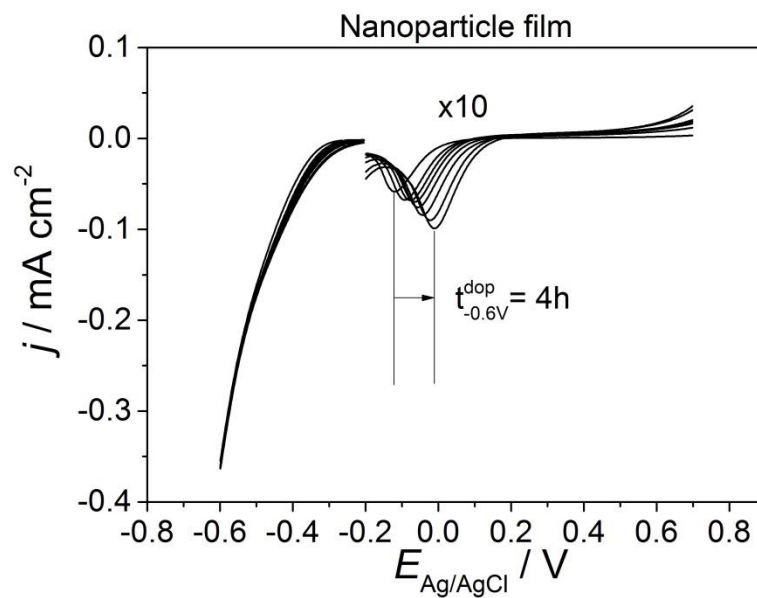


Figure S6: Linear voltammograms for a rutile TiO_2 NP electrode before and after electrochemical doping ($E^{\text{dop}} = -0.6 \text{ V}$, $t^{\text{dop}} = 20, 40, 60, 80, 120, 180, 240 \text{ min}$). Electrolyte: N_2 -flushed 0.1 M HClO_4 aqueous solution.

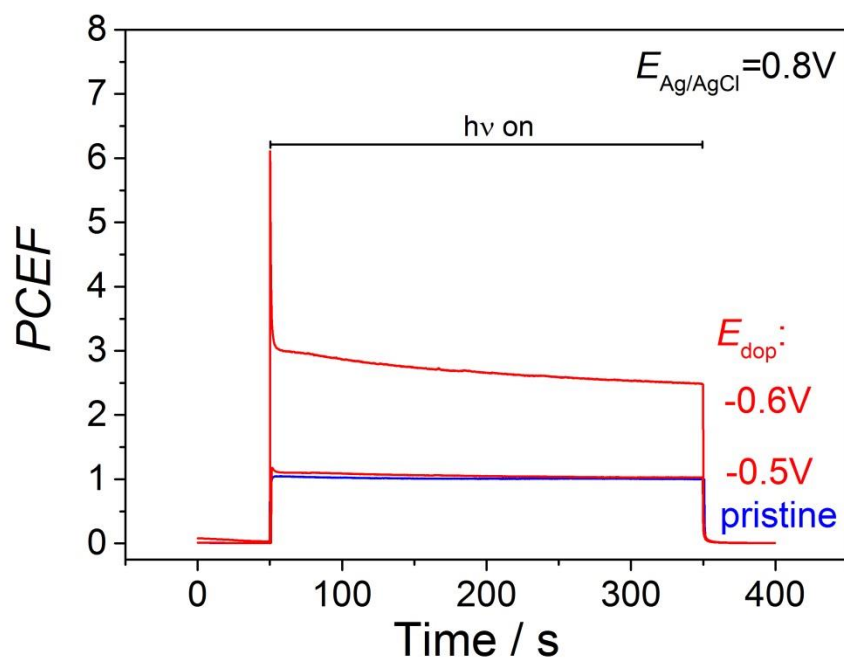


Figure S7: Photocurrent transients recorded upon UV exposure of a rutile TiO_2 NP electrode before and after electrochemical doping for $t^{\text{dop}} = 20$ min at different doping potentials (E_{dop}). Electrolyte: N_2 -flushed 1 M methanol/0.1 M HClO_4 aqueous solution. Irradiance: $500 \text{ mW} \cdot \text{cm}^{-2}$.

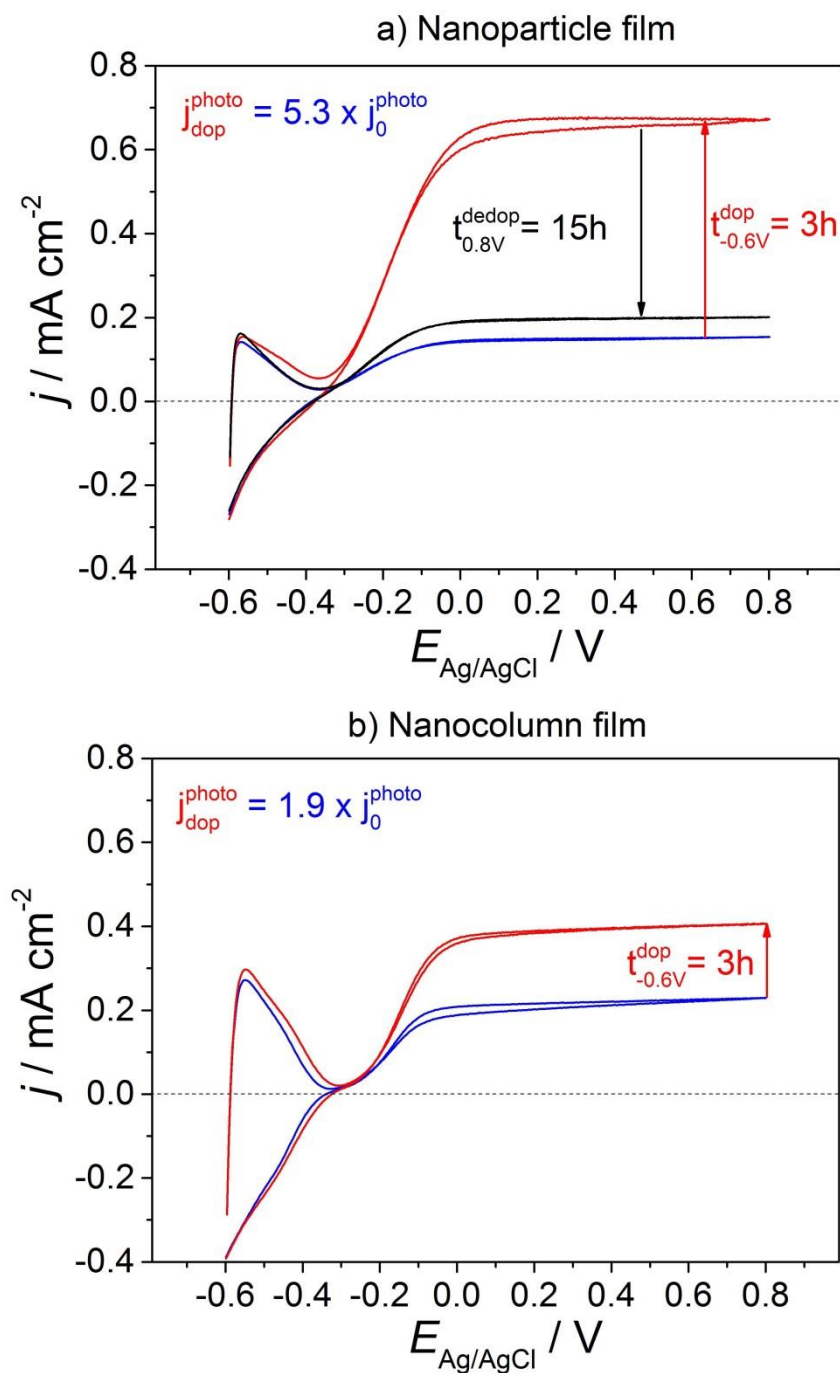


Figure S8: CVs recorded upon UV exposure for rutile TiO₂ NP (a) and NC (b) electrodes before and after an electrochemical doping at $E_{\text{Ag/AgCl}} = -0.6 \text{ V}$ for $t_{\text{dop}}^{-0.6\text{V}} = 3 \text{ h}$. For the NP electrode the effect of subsequent polarization for 15 h at 0.8 V (undoping) is also shown. Electrolyte: N₂-flushed 1 M methanol/0.1 M HClO₄ aqueous solution. Irradiance: 500 mW·cm⁻².

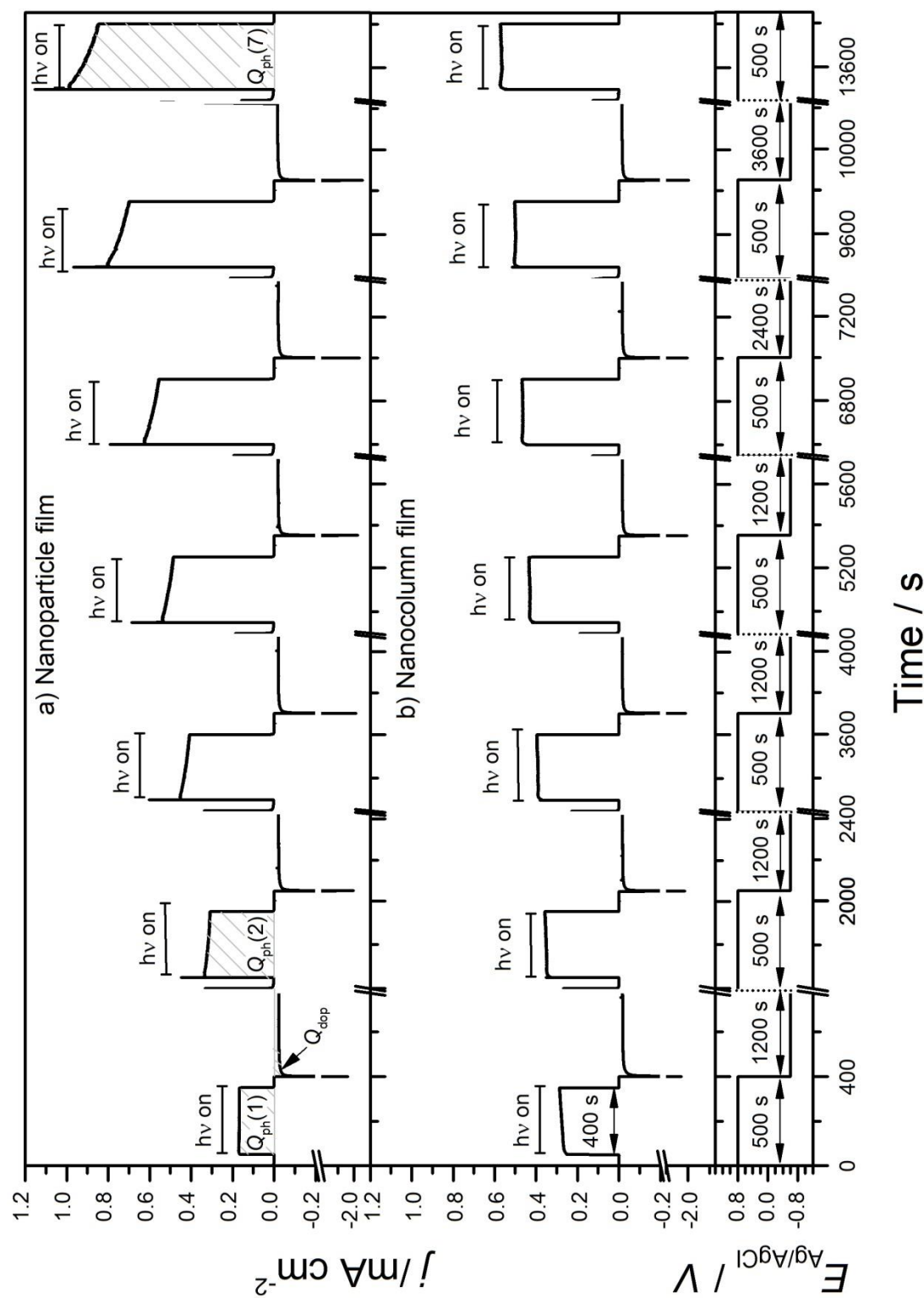


Figure S9: Chronoamperometric profiles highlighting the photocurrent evolution for rutile TiO_2 NP (a) and NC (b) electrodes following a progressive electrochemical doping of the films. The sequence of potentials applied to the electrodes is shown in the lower panel. Photocurrent transients were recorded at $E_{\text{Ag/AgCl}} = 0.8 \text{ V}$, electrochemical doping was performed at $E_{\text{dop}} = -0.6 \text{ V}$. Electrolyte: N_2 -flushed 1 M methanol/ 0.1 M HClO_4 aqueous solution. Irradiance: $500 \text{ mW}\cdot\text{cm}^{-2}$. (a) Following electrochemical doping, the additional charge transferred upon UV exposure from the TiO_2 film to the conducting substrate (e.g. $Q_{\text{ph}}(2) - Q_{\text{ph}}(1) = 45 \text{ mC}\cdot\text{cm}^{-2}$, $Q_{\text{ph}}(7) - Q_{\text{ph}}(1) = 222 \text{ mC}\cdot\text{cm}^{-2}$) exceeds by far the charge injected from the conducting substrate into the TiO_2 film during the doping step in the dark ($Q_{\text{dop}} = -27 \text{ mC}\cdot\text{cm}^{-2}$).