

SUPPORTING INFORMATION

Modulation of Charge Recombination in CsPbBr₃ Perovskite Films with Electrochemical Bias

Rebecca A. Scheidt,^{1,2,#} Gergely F. Samu,^{2,3,#} Csaba Janáky^{3,4,*} and Prashant V. Kamat^{1,2,*}

¹Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana, 46556, United States

²Department of Chemistry and Biochemistry, University of Notre Dame

³Department of Physical Chemistry and Materials Science, University of Szeged, Rerrich Square 1, Szeged, H-6720, Hungary

⁴ELI-ALPS Research Institute, Szeged, Dugonics sq. 13, 6720, Hungary

Contributed equally to this work

*Address correspondence to these authors: pkamat@nd.edu, janaky@chem.u-szeged.hu twitter: @kamatlabND

Experimental

Materials

The blocking TiO₂ layer was obtained by using titanium diisopropoxide bis(acetylacetonate) (Sigma-Aldrich, 75 wt. % in isopropanol) and 1-butanol (Sigma-Aldrich, 99.8%). A homemade TiO₂ paste was the basis of the mesoporous TiO₂ layer, which was treated with titanium-tetrachloride (TiCl₄ - Alfa Aesar, 99.6%) in a subsequent step. Details about the preparation procedure of the TiO₂ paste can be found in previously published literature¹.

CsPbBr₃ nanocrystals (NCs) were synthesized using lead (II) bromide (PbBr₂ - Alfa Aesar, 99.999%), cesium carbonate (Cs₂CO₃, Alfa Aesar, 99.9%), oleic acid (OAc, Sigma Aldrich, 90% technical grade), oleylamine (OAm - Sigma Aldrich, 70% technical grade), 1-octadecene (ODE, Sigma-Aldrich, 95%), acetone (Fischer Scientific, HPLC grade), *n*-hexane (Sigma-Aldrich, 95% anhydrous), *n*-heptane (Sigma-Aldrich, 99% spectrophotometric grade), and ethanol (KOPTEC, 200 proof, anhydrous).

All electrochemical experiments were performed in dichloromethane (DCM – Sigma Aldrich, anhydrous, ≥99.8%, contains 40-150 ppm amylene as stabilizer) with 0.1 M tetrabutyl ammonium-hexafluorophosphate (Bu₄NPF₆ – Sigma Aldrich, for electrochemical analysis, ≥99.0%) as the conducting electrolyte. Bu₄NPF₆ was dried prior to use in a vacuum oven at T=180 °C for t=6 hours.

Electrode preparation methods

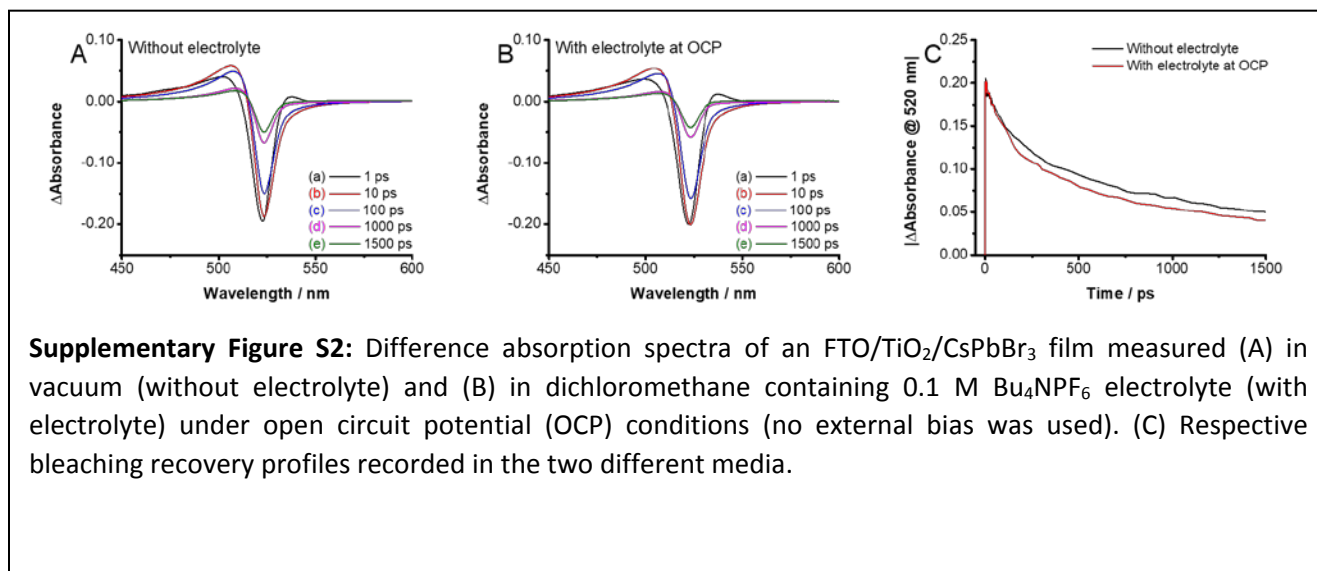
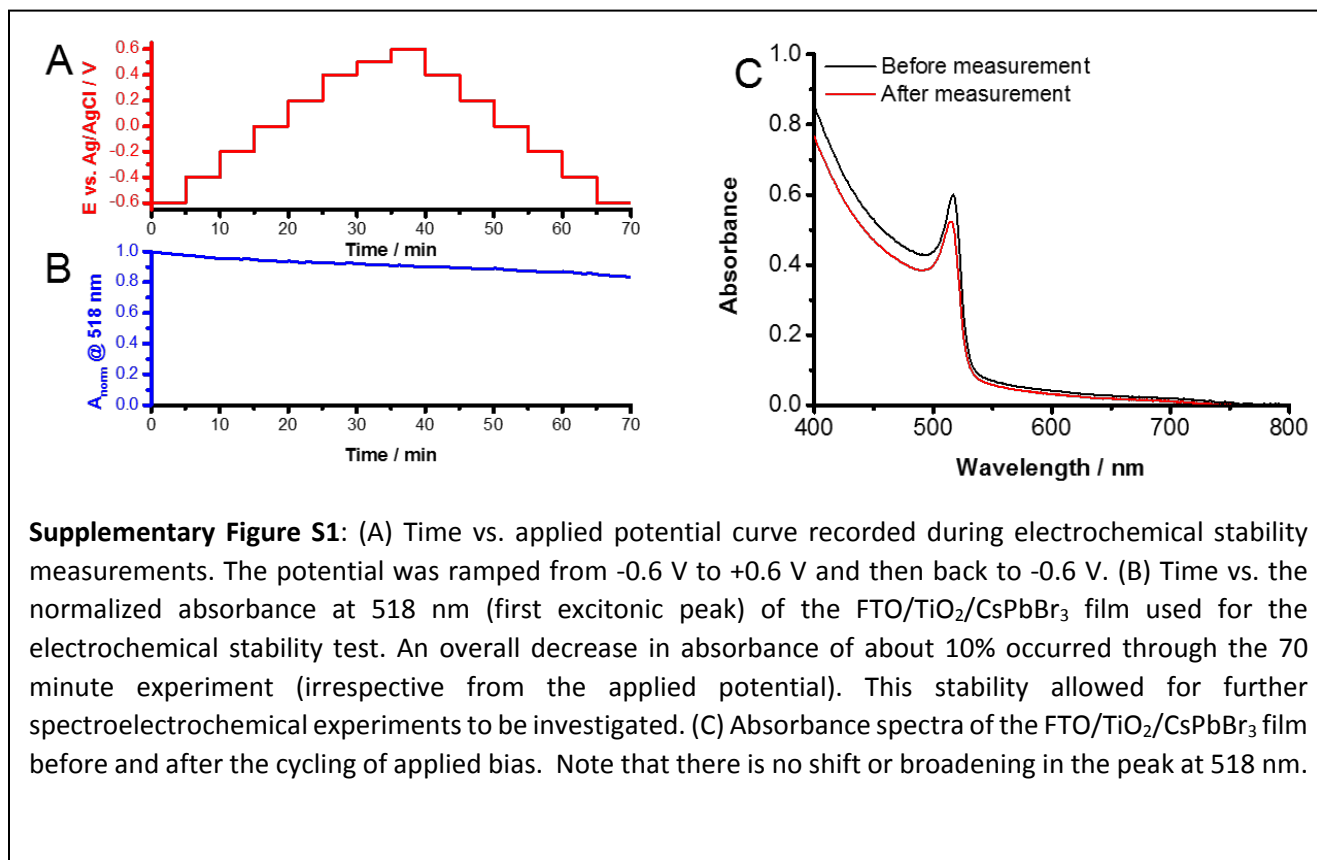
The FTO substrates were washed with soap, rinsed with DI water, sonicated in ethanol for 20 minutes and finally plasma-cleaned prior to use. A TiO₂ blocking layer was spin-coated onto these substrates from a 0.15 M titanium diisopropoxide bis(acetylacetonate) solution in 1-butanol. These layers were immediately transferred to a hotplate and heat treated for 5 minutes at T=125°C, under glovebox conditions (N₂ atmosphere, H₂O < 0.1 ppm, O₂ < 0.1 ppm). A mesoporous TiO₂ layer was then spin-coated from an ethanol based suspension (c=0.12 g cm⁻³), and subsequently calcined for 1 hour at T=550 °C in air. This step was followed by a TiCl₄ treatment, carried out in a 20 mM TiCl₄ solution at T=90 °C for 10 minutes. A final calcination step was then performed at T=500 °C in air for 30 minutes.

The FTO/TiO₂/CsPbBr₃ electrodes were prepared with a method using subsequent cycles of NC deposition and annealing. This procedure is thoroughly detailed elsewhere². As a first step a Cs-oleate precursor (0.306 g Cs₂CO₃, 2.8 cm³ of OAc, and 3 cm³ ODE) was injected into a PbBr₂ precursor solution (0.808 g PbBr₂, 6 cm³ OAc, 6 cm³ ODE, and 6 cm³ OAm) at a 170 °C. Highly luminescent, yellow colored CsPbBr₃ NCs were formed immediately after injection. The NCs were cooled to room temperature, purified via centrifugation, carefully washed with acetone, and re-suspended in 3 cm³ of a 95/5 V/V% *n*-hexane/*n*-heptane mixture. Deposition of the NCs on the substrate was followed by annealing at 250 °C for 3 minutes, and this cycle was repeated until bulk films were formed with the desired optical density of A_{518nm} ~ 0.8. The CsPbBr₃ coated electrodes were kept under glovebox conditions (N₂ atmosphere, H₂O < 0.1 ppm, O₂ < 0.1 ppm) after preparation and used immediately.

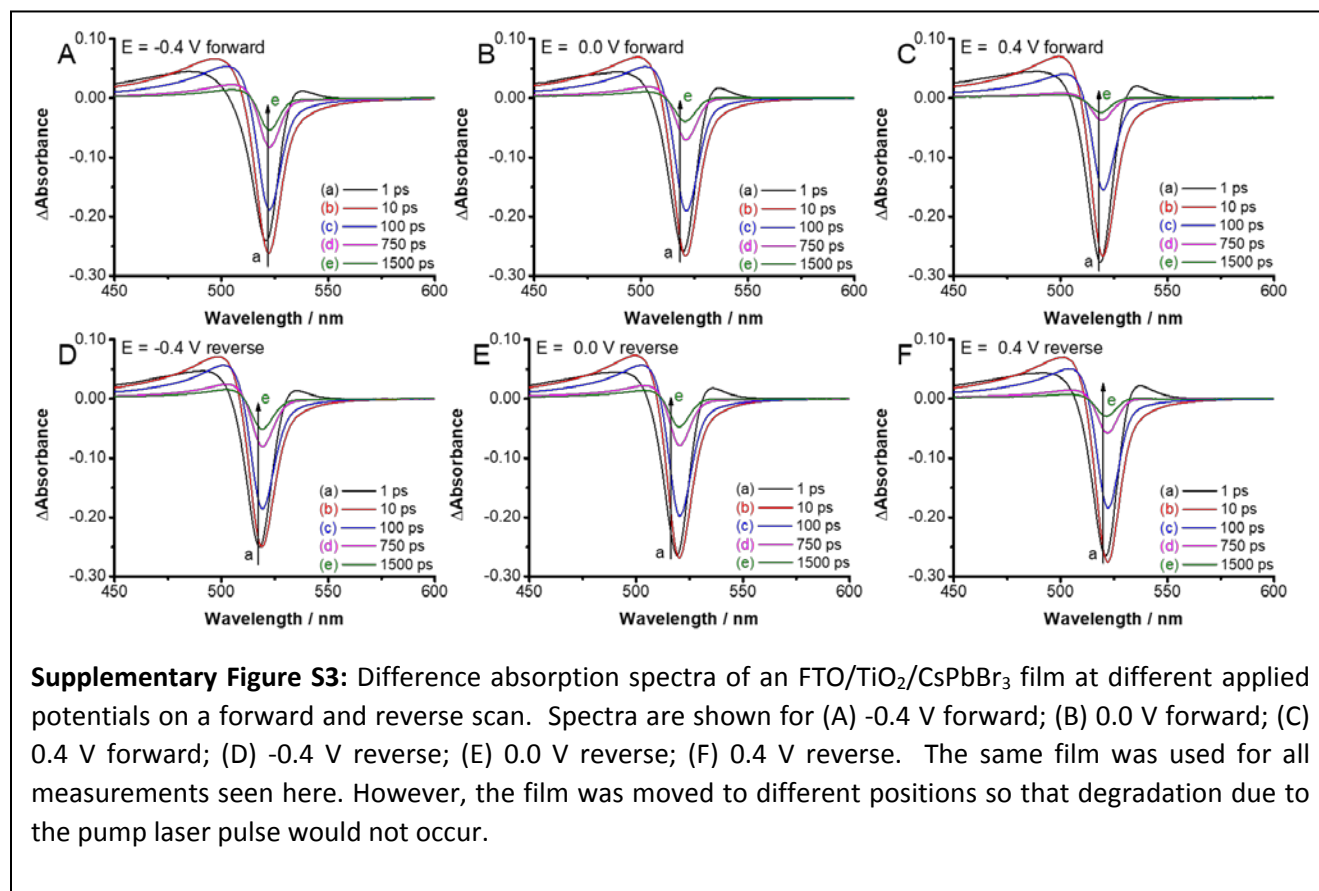
Characterization methods

Steady state UV-vis absorption spectra of the CsPbBr₃ coated electrodes were recorded with a Cary 50 Bio spectrophotometer (Varian). A Gamry potentiostat was used to perform the electrochemical measurements. These were carried out in a standard three electrode setup, where the prepared FTO/TiO₂/CsPbBr₃ electrodes functioned as the working electrode, a Pt mesh as the counterelectrode, and a Ag/AgCl wire as a pseudoreference electrode. The reference electrode was calibrated towards the ferrocene/ferrocenium (Fc/Fc⁺) redox couple (measured $E_{\text{Fc}/\text{Fc}^+} = 0.45 \pm 0.04$ V). All cells were assembled in a glovebox (N₂ atmosphere, H₂O < 0.1 ppm, O₂ < 0.1 ppm) and sealed hermetically to ensure inert conditions.

A Clark MXR-2010 laser system (775 nm fundamental, 1 mJ/pulse, FWHM=150 fs, 1 kHz repetition rate) was used to perform the ultrafast transient spectroelectrochemistry measurements. The data was collected using a Helios software from Ultrafast Systems. The fundamental was separated in an intensity ratio of 95/5, where the 95% was doubled in frequency to generate the 387 nm excitation pump. The remaining 5% was used to generate a white light continuum via a CaF₂ crystal. This light was used as the probe for all measurements. The intensity of the excitation pump was modulated so that the maximum change in absorbance remained constant in all measurements ($\Delta A_{520\text{nm}} \sim -0.25$), which corresponded to a pump excitation of about 12 $\mu\text{J cm}^{-2}$. This was done to ensure that similar amounts of charge carriers were generated in each measurement. A three-armed electrochemical cell with a fused silica cuvette body was placed at the spatial overlap of the pump and the probe. The electrode was kept at a constant potential while the transient absorption spectra were recorded. The sampling spot was adjusted between every measurement to ensure the sampling of a fresh electrode area.



Transient absorption spectra recorded at different applied potentials



References

- (1) Neale, N. R.; Frank, A. J. *J. Mater. Chem.* **2007**, *17*, 3216.
- (2) Hoffman, J. B.; Schleper, A. L.; Kamat, P. V. *J. Am. Chem. Soc.* **2016**, *138*, 8603–8611.