Modulation of Charge Recombination in CsPbBr₃ Perovskite Films with Electrochemical Bias

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ABSTRACT: The charging of a mesoscopic TiO₂ layer in a metal halide perovskite solar cell can influence the overall power conversion efficiency. By employing CsPbBr₃ films deposited on a mesoscopic TiO₂ film, we have succeeded in probing the influence of electrochemical bias on the charge carrier recombination process. The transient absorption spectroscopy experiments conducted at different applied potentials indicate a decrease in the charge carrier lifetimes of CsPbBr₃ as we increase the potential from −0.6 to +0.6 V vs Ag/AgCl. The charge carrier lifetime increased upon reversing the applied bias, thus indicating the reversibility of the photoresponse to charging effects. The ultrafast spectroelectrochemical experiments described here offer a convenient approach to probe the charging effects in perovskite solar cells.

Ultrafast spectroelectrochemical measurements that elucidate the influence of electrochemical bias on the bimolecular charge recombination are discussed.

Although a few studies exist to probe the fate of charge carriers under solar cell operation conditions, there is a need to better understand how the electron storage in the ETL influences the charge carrier recombination in perovskite films. Such effects can be well studied by utilizing the principles of semiconductor photoelectrochemistry. However, the difficulty in applying electrochemistry principles to perovskite films arises from stability issues. Careful choice of organic solvent and electrolyte is needed to conduct electrochemical and spectroelectrochemical experiments.

To further clarify the charging of TiO₂ films and its influence on the excited state behavior of perovskite films, we have now probed the charge carrier recombination of CsPbBr₃ films deposited on a mesoscopic TiO₂ layer at different electrochemical biases. By employing a narrow electrochemical window between −0.6 and +0.6 V vs Ag/AgCl we were able to conduct spectroelectrochemical experiments with good reversibility. Ultrafast spectroelectrochemical measurements that elucidate the influence of electrochemical bias on the bimolecular charge recombination are discussed.

The CsPbBr₃ nanocrystals prepared by hot injection method were spin-cast on bare and TiO₂-coated fluorine doped tin oxide (FTO) glass slides using a previously reported method. Full experimental details can be found in the Supporting Information.

Establishing the Electrochemical Stability Window: The stability of CsPbBr₃ films in Bu₄NPF₆/dichloromethane (DCM) solution has enabled us to conduct electrochemical and spectroelectrochemical measurements on this system. Figure 1 shows the cyclic voltammograms recorded separately with anodic and cathodic scans using two different electrodes. The CsPbBr₃ exhibits a reduction peak at −1.4 V vs Ag/AgCl corresponding to the reduction of Pb⁺² to Pb⁰ and an oxidation peak at +0.85 V vs Ag/AgCl corresponding to the oxidation of Br⁻ ions. The irreversibility of these peaks suggests that these
peaks arise from the cathodic and anodic corrosion, and thus partial decomposition, of the perovskite material. It is interesting to note that similar reduction and oxidation peaks were used to estimate the conduction and valence band energies of colloidal perovskite nanocrystals and organic semiconductors. Given the irreversibility of these peaks, it raises an important question of whether one can consider anodic and cathodic corrosion potentials to represent band energy positions. The expanded current scale shows the onset potentials that induce corrosion (oxidation and reduction onset seen around +0.65 and −1.2 V vs Ag/AgCl, respectively). The inactivity of CsPbBr3 (oxidation and reduction onset seen around +0.65 and −1.2 V vs Ag/AgCl, respectively) shows very little changes (Figure S1).

Effect of Electrochemical Bias on the Charge Carrier Recombination. To further probe the effect of electrochemical bias on the charge carrier recombination in CsPbBr3 films we monitored the bleaching recovery (520 nm) at several different potential values from −0.6 to +0.6 V vs Ag/AgCl. The bleaching recovery follows simple second order decay. The contribution of trapped charge carriers at high excitation intensity becomes negligible. We also maintained similar magnitude of bleaching (ΔA = −0.25 at 520 nm) so that the initial charge carrier concentration is the same for all sets of measurements. The bleaching recovery profiles recorded at different applied potentials and the fitting of the data to second order kinetics (1/ΔA versus time) are shown in Figure 3A, respectively. Because the initial carrier concentrations were kept similar in all these bleaching recovery experiments, we can directly compare the slopes to obtain relative pseudo-first-order rate constants or apparent lifetimes of charge carriers.

The pseudo-first-order rate constants measured at different applied potentials showed an interesting trend as we increase the applied bias from −0.6 to +0.6 V in steps (Figure 3C). At 0.0 V and more negative potentials, the rate constant of charge carrier recombination showed only a small variation. The apparent rate constant κ (pseudo-first-order) obtained from the slope was ~2 × 10^9 s^{-1} at −0.6 V and ~2.5 × 10^9 s^{-1} at 0 V, respectively. On the other hand, we observe an increase by a factor of 3 in the bleaching recovery rate constant as we increased the applied bias from 0 V to +0.6 V. Because electrons are depleted from the TiO2 layer under anodic bias, one can expect an additional pathway for photogenerated electrons to participate in the charge injection into TiO2 film (κET). The competing charge injection process thus renders faster bleeding recovery at anodic bias. These observations are consistent with the mechanism of charge injection from excited molecular sensitizer into TiO2 that is influenced by applied bias.

Figure 2. Time-resolved transient spectra recorded following 387 nm laser pulse excitation (4 μJ cm⁻²) of FTO/TiO2/CsPbBr3 electrode in a spectroelectrochemical cell with deaerated DCM containing 0.1 M Bu₄NPF₆ electrolyte. The spectra were recorded at applied potentials of (A) +0.4 V; (B) −0.4 V; (C) +1.0 V, and (D) −1.2 V vs Ag/AgCl.

Reversibility of Bleaching Recovery Kinetics to Applied Bias. In another, separate experiment we recorded transient absorption spectra under a forward scan (−0.6 to +0.5 V) followed by a reverse scan (+0.5 to −0.6 V). The lifetimes derived from the inverse slope of 1/ΔA versus time plots are taken as a measure for comparison. These apparent lifetimes obtained at set potentials during forward and reverse scans are presented in Figure 4A.

The decay profiles recorded at a set potential during forward and reverse scans showed the same trend of dependence on the FTO/TiO2/CsPbBr3 electrode recorded without applied bias is shown in the Supporting Information (Figure S2). The disappearance of the excitonic band, as indicated by the bleaching at 520 nm, represents charge separation. With increasing time, the bleaching at 520 nm recovers as the photogenerated electrons and holes combine. The time-resolved spectra recorded at −0.4 and +0.4 V show very similar features to those recorded in the absence of applied bias. Thus, qualitatively, the applied bias has no effect on the spectral evolution of transients in this potential regime. On the other hand, the spectra recorded at extreme cathodic (−1.2 V) and anodic (+1.0 V) potentials show variation in the spectral features with recovery time. In addition, the maximum bleaching intensity is significantly diminished. Thus, at these extremes a major fraction of the perovskite has degraded and become nonresponsive to excitation. These discrepancies in the transient absorption reaffirm the instability of the perovskite film at these electrochemical bias potentials (in close agreement with cyclic voltammetry).
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Figure 3. (A) Bleaching recovery profiles, (B) kinetic fit $1/\Delta A$ vs. time, and (C) relative pseudo-first-order rate constants determined from the slope of plots in panel B with the dashed line to guide the eye (the magnitude of bleaching was kept constant at $-0.25$ for all of these experiments so that initial charge carrier concentration is the same in all experiments). The applied potentials ranged from $-0.6$ to $+0.6$ V vs. Ag/AgCl. Experimental conditions were the same as in Figure 2.

Figure 4. Dependence of bleaching recovery lifetime determined from the inverse slope of the kinetic fit of $1/\Delta A$ vs. time. Measurements were carried out with (A) FTO/TiO$_2$/CsPbBr$_3$ and (B) FTO/CsPbBr$_3$ electrodes in deaerated DCM containing 0.1 M Bu$_4$NPF$_6$ electrolyte. The electrodes were biased at set potentials in the range $-0.6$ to $+0.5$ V vs. Ag/AgCl and excited with 387 nm laser pulse to record time-resolved transient absorption spectra.

The Influence of TiO$_2$ Layer on Bleaching Recovery Lifetime. The results presented in Figures 3 and 4 show the decrease in bleaching recovery time as we subject the FTO/TiO$_2$/CsPbBr$_3$ electrode to anodic (positive) bias. Because the bleaching recovery lifetime decreases, it represents the charge recombination lifetime. Hence, one can relate the measured lifetime to electron survivability following bandgap excitation of the perovskite film. The band energy diagram in Figure 5 shows a possible scenario of Fermi level changes during open circuit and electrochemical bias conditions. The mesoscopic TiO$_2$ layer, which is in contact with perovskite films, responds to anodic bias by capturing electrons under negative bias or depleting electrons under positive bias. Earlier studies carried out with TiO$_2$ films alone or dye sensitized SnO$_2$ films have shown the electron accumulation under negative bias.$^{2,4}$ If the TiO$_2$ film has excess electrons, as in the case of negative applied bias, we see suppression of electron transfer from excited perovskite to TiO$_2$. Hence charge carrier recombination is the only process dictating the carrier lifetime.

On the other hand, under anodic bias, the electron transfer from excited CsPbBr$_3$ to TiO$_2$ is greatly favored and this process now competes with recombination with holes. As a result, the bleaching recovery rate constant increases (or lifetime decreases) as the FTO/TiO$_2$/CsPbBr$_3$ electrode is subjected to positive bias.

The role of mesoscopic TiO$_2$ films in perovskite solar cells is an intrigue. Perovskite solar cells can perform well without the presence of a TiO$_2$ mesoscopic layer. For example, planar MAPbI$_3$ based solar cells with a different ETL (e.g., fullerenes) can deliver efficiencies in the range of 20%. Yet, the champion cells that utilize mesoscopic metal oxide architecture exhibit superior performance. Thus, the role of TiO$_2$ as an ETL that captures electrons from excited CsPbBr$_3$ seems to play an important role in delivering superior device performance. The influence of electron accumulation (or depletion) on the charge recombination rate is a good indication why higher efficiencies are observed in photovoltaic devices containing mesoscopic TiO$_2$ films.

It has been a common practice to manipulate the J-V characteristics through light soaking or applying cathodic bias. The perovskite solar cells show higher efficiency as the cells pretreated with cathodic bias (or light soaking) exhibit lower photovoltage. Under these pretreatment conditions, electron accumulation occurs in the TiO$_2$ film as reflected from a small increase in photovoltage. In fact, in our previous report on best practices in solar cell characterization, we were able to demonstrate the improvement in power conversion efficiency measurement of a poorly performing solar cell through electrochemical transient absorption measurement.
excited perovskite film to the ETL and thus allow a convenient evaluation tool for different perovskite/ETL pairs.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b10958.

Experimental methods, film preparation, spectroscopic and spectroelectrochemical measurements (PDF)

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## REFERENCES