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Ultrafast selective extraction of hot holes from cesium lead iodide perovskite films

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ABSTRACT

Lead halide perovskites have some unique properties which are very promising for optoelectronic applications such as solar cells, LEDs and lasers. One important and expected application of perovskite halide semiconductors is solar cell operation including hot carriers. This advanced solar cell concept allows overcoming the Shockley–Queisser efficiency limit, thereby achieving energy conversion efficiency as high as 66% by extracting hot carriers. Understanding ultrafast photoexcited carrier dynamics and extraction in lead halide perovskites is crucial for these applications. Here, we clarify the hot carrier cooling and transfer dynamics in all-inorganic cesium lead iodide (CsPbI₃) perovskite using transient absorption spectroscopy and Al₂O₃, poly(3-hexylthiophene-2,5-diyl) (P3HT) and TiO₂ as selective contacts. We find that slow hot carrier cooling occurs on a timescale longer than 10 ps in the cases of CsPbI₃/Al₂O₃ and CsPbI₃/TiO₂, which is attributed to hot phonon bottleneck for the high photoexcited carrier density. An efficient ultrafast hole transfer from CsPbI₃ to the P3HT hole extracting layer is observed. These results suggest that hot holes can be extracted by appropriate selective contacts before energy dissipation into the halide perovskite lattice and that CsPbI₃ has a potential for hot carrier solar cell applications.

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1. Introduction

Organic–inorganic hybrid perovskite (CH₃NH₃PbI₃ (MAPbI₃)) solar cells have attracted more and more attention in recent years, because the perovskite can be simply prepared using solution process at low temperatures (≤ 100 °C) and the record power conversion efficiency (PCE) has been reported to be over 22% [1–22]. The high efficiency results from some unique properties of MAPbI₃ such as a high optical absorption coefficient [23,24], small exciton binding energy [25], long photoexcited carrier lifetimes [26,27] and very small Urbach energy [28]. However, there are some critical issues for perovskite solar cells such as improving the material stability and understanding the degradation mechanisms. All-inorganic cesium lead halide (CsPbI₃) perovskite is nowadays a basic ingredient entering the composition of stable photovoltaic devices [29–34]. In addition, very recently, it was found that phase

stabilization could even be reached in pure CsPbI₃ quantum dot solar cells [35].

To further improve the photovoltaic properties, it is very important to understand the basic processes of photoexcited carrier relaxation. Especially, for advanced applications such as hot carrier solar cells [36] and electrically pumped lasers [37,38], ultrafast photoexcited carrier dynamics is the first key. Very recently, we studied hot carrier cooling dynamics in CsPbI₃ using transient absorption (TA) spectroscopy, finding that it becomes slower as the photoexcited carrier density increases. The cooling time is longer than 10 ps when the photoexcited carrier density is larger than 1×10^{18} cm⁻³, which is attributed to hot phonon bottleneck for high photoexcited carrier densities [39]. Similar slow hot carrier cooling phenomena for larger photoexcited carrier densities were also observed in MAPbI₃ and FAPbI₃ perovskites [40,41]. Therefore, our findings indicate that the inorganic cation Cs has a similar effect on the hot carrier cooling as organic cations (MA or FA) in a perovskite lattice. For hot carrier solar cell applications, the second key is to extract hot carriers before they relax to the band edges. In this study, we clarify the hot carrier extraction from CsPbI₃ perovskite using the TA technique. Due to the small thicknesses of

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halide perovskite thin films, slow cooling dynamics gives a unique opportunity to achieve hot carrier extraction before relaxation to the band edges. For that purpose, Al_2O_3 , poly(3-hexylthiophene-2,5-diyl) (P3HT) and TiO_2 are used as selective contacts to elucidate how hot hole and hot electron can be transferred from the CsPbI_3 perovskite to contact layers. The ultrafast efficient extraction of hot holes to P3HT within a few 100 fs, appears as the most striking result of the present work.

2. Experimental

CsPbI_3 perovskite samples were deposited on Al_2O_3 ($\text{Al}_2\text{O}_3/\text{CsPbI}_3$) without and with a P3HT hole extraction layer ($\text{Al}_2\text{O}_3/\text{CsPbI}_3/\text{P3HT}$) [29]. First, mesoporous Al_2O_3 scaffold films were deposited on glass substrates. The alumina solution was diluted in 2-propanol (2:3 by vol.) and spin coated at 2000 rpm for 60 s. Subsequently, the Al_2O_3 substrates were heated at 60 °C for 10 min and 130 °C for 30 min. The Al_2O_3 substrates were then transferred into a glove box and CsPbI_3 films deposited using a one-step solution deposition method [29]. A mixture of CsI and PbI_2 (wt. ratio 1:1) dissolved in DMF with a concentration of 20 wt% was prepared at 60 °C for that purpose until complete dissolution. The Al_2O_3 substrates were pre-heated at 60 °C for 15 min, and an aliquot of the CsPbI_3 solution was spin-coated at 2000 rpm for 30 s, followed by thermal annealing on a hot plate at 60 °C and then 350 °C for 30 min each. Fig. S1 shows the SEM images of the surfaces of the Al_2O_3 substrate and the CsPbI_3 layer, from which we can observe clearly that both the Al_2O_3 substrate and the CsPbI_3 layer are uniform. The hole extraction material, P3HT, was then spin coated from an aliquot at 1000 rpm for 10 s onto the perovskite films at room temperature. The concentration of the P3HT in *o*-dichlorobenzene was 17 mg/mL. The solution was heated for several hours at 60 °C. The substrates were kept in a petri dish overnight in the dark to allow the solvent to evaporate. The films were then annealed at 130 °C for 10 min. Finally, the substrates were encapsulated with polymethylmethacrylate (PMMA) on a spin coater at 3000 rpm for 60 s in order to isolate the sample from air and keep them stable.

$\text{CsPbI}_3/\text{TiO}_2$ samples were prepared by using mesoporous TiO_2 scaffold films. The TiO_2 substrates were prepared with 20 nm of compact TiO_2 blocking layer by atomic layer deposition and 400 nm of mesoporous TiO_2 (mp- TiO_2) by spin coater. The mp- TiO_2 solution was diluted in α -terpineol (1:3 by vol.) for spin coating at 6000 rpm for 30 s. These films were sintered at 470 °C for 30 min. Once the scaffold layers were synthesized, the substrates were transferred into a glove box. Then, CsPbI_3 perovskites were prepared on the TiO_2 films using the method as mentioned above.

A femtosecond TA setup was used to study the photoexcited carrier dynamics, especially the hot carrier cooling dynamics in CsPbI_3 [42–45]. The laser source was a titanium/sapphire laser (CPA-2010, Clark-MXR Inc.) with a wavelength of 775 nm, a repetition rate of 1 kHz, and the pulse width is 150 fs. The light was separated into two parts. One part was incident on a sapphire plate to generate white light for the probe beam. The other part was used to pump an optical parametric amplifier (OPA) (a TOAPS from Quantronix) to generate light pulses to excite the sample. In this study, the pump light wavelength was 470 nm (2.6 eV) and the pump light intensity was 23 $\mu\text{J}/\text{cm}^2$. Time-resolved TA spectra were obtained from 530 nm (2.34 eV) to 750 nm (1.65 eV) with a temporal resolution of about 100 fs. For all measurements, the pump and probe beams were incident on the glass ($\text{Al}_2\text{O}_3/\text{CsPbI}_3$ or $\text{TiO}_2/\text{CsPbI}_3$) side of the samples and the TA measurements were carried out at room temperature.

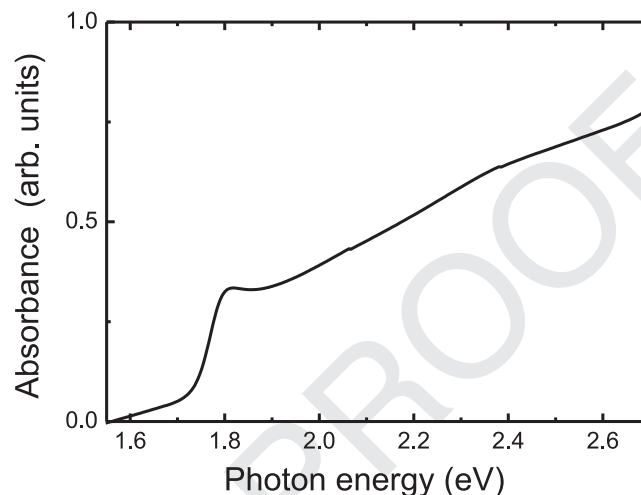


Fig. 1. Typical optical absorption spectrum of CsPbI_3 .

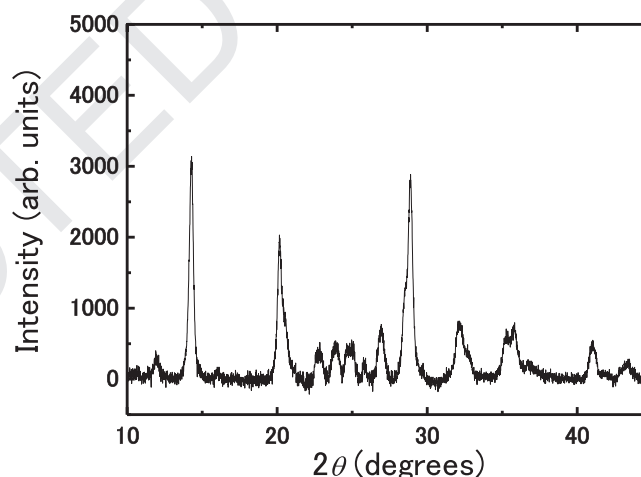


Fig. 2. XRD pattern of CsPbI_3 .

3. Results and discussion

Fig. 1 shows a typical optical absorption spectrum of the CsPbI_3 perovskite. A clear optical absorption shoulder can be observed at 1.8 eV, which corresponds to the excitonic transitions [41,46]. Fig. 2 shows the X-ray diffraction (XRD) pattern of the CsPbI_3 perovskite, which confirms that the crystal structure of the CsPbI_3 is cubic phase. Special care was taken to ensure stability of the crystal phase in the CsPbI_3 perovskite films, as described in details in our previous paper [39]. Thin films of a polymer poly(methyl methacrylate), PMMA, were coated on the sample surfaces in order to encapsulate the samples from air.

For the TA measurement, the pump light wavelength is 470 nm and its photon energy is 2.6 eV, which is larger than the bandgap 1.8 eV of CsPbI_3 . Fig. 3(a) shows the normalized TA spectra of $\text{CsPbI}_3/\text{Al}_2\text{O}_3$ for times from 0.3 ps to 4.4 ps, where photoexcited carrier density is $1.3 \times 10^{18} \text{ cm}^{-3}$. Since no electrons or holes are expected to be transferred from CsPbI_3 to Al_2O_3 , the intrinsic hot carrier relaxation dynamics in CsPbI_3 can be studied first. The detailed analyses of the TA spectra have been carried out in our previous paper [39]. The bleaching peak at 1.8 eV corresponds to the optical absorption peak of CsPbI_3 . The negative TA peak just below the bandgap (1.75 eV) is due to the interplay between bandgap renormalization and the hot-carrier distribution [39]. We have shown that the distribution of the carriers for times longer than

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