



Full paper

Perovskite-quantum dots interface: Deciphering its ultrafast charge carrier dynamics



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ABSTRACT

Understanding electron and hole (e,h) transport at semiconductor interfaces is paramount to developing efficient optoelectronic devices. Halide perovskite/semiconductor quantum dots (QDs) have emerged as smart hybrid systems with a huge potential for light emission and energy conversion. However, the dynamics of generated e-h pairs are not fully understood. Ultrafast UV–VIS transient absorption and THz spectroscopies have enabled us to unravel the processes of the e-h recombination within a hybrid film of methylammonium lead triiodide (MAPbI₃) interacting with different amount of PbS/CdS core/shell QDs. To accurately analyze the complex behavior, we applied a new model for e-h events in this hybrid material. The results obtained with sample having a high concentration of QDs (7.3 mass percentage) indicate: (i) a large population (92%) of the photogenerated charge carriers are affected by QDs presence. The main part of these carriers (85% of the total) in perovskite domain diffuse towards QDs, where they transfer to the interface (electrons) and QD's valence bands (holes) with rate constants of $1.2 \times 10^{10} \text{ s}^{-1}$ and $4.6 \times 10^{10} \text{ s}^{-1}$, respectively. 7% of these affected charged entities are excitons in the perovskite domain in close vicinity of the interface, and show a recombination rate constant of $3.7 \times 10^{10} \text{ s}^{-1}$. (ii) The carriers not affected by QDs presence (8%) recombine through known perovskite deactivation channels. Lowering the QDs mass percentage to 0.24 causes a decrease of electron and hole effective transfer rate constants, and disappearance of excitons. These results provide clues to improve the performance of perovskite/QD based devices.

1. Introduction

Over the past few years semiconductor colloidal quantum dots (QDs) and trihalide perovskites have been intensively studied [1–6]. The outstanding properties of semiconductor QDs, such as the tunability of the optical band gap across a wide range of energies and their high light absorption coefficient, make them attractive for heterojunction solar cells, light-emitting diodes (LEDs) and lasers [1–3,7,8]. Halide perovskites solar cells have achieved photoconversion efficiencies (PCE) higher than 22% [9], and the performance of LEDs, photodetectors and lasers based on halide perovskites has improved continuously over the past few years [4,10–17]. Beyond this scenario, a combination of materials with different natures could provide

interesting synergistic interactions that would produce advanced configurations enhancing the performance of related optoelectronic devices. In this sense, the composites of perovskite and semiconductor QDs have shown strong potential in lighting and photovoltaic conversion [18–27]. QDs solar cells showed a significant but lower efficiency than that of other photovoltaic devices due to the low charge carrier mobilities and high surface trap density [28–31]. By combining the efficient charge generation in QDs and the e-h high mobility in the perovskite, efficient colloidal QDs solar cells were fabricated [20–22].

The use of perovskite as a passivating agent for QDs surfaces led to materials that can act as a highly conductive matrix to increase the power conversion efficiency (PCE) of photovoltaic devices based on lead trihalides [19,27], as well as the efficiency of IR LEDs [25] and

Abbreviations: THz, terahertz; TRTS, time-resolved terahertz spectroscopy;; TAS, time-resolved transient absorption spectroscopy;; IRF, instrumental response function;; wt%, mass percentage; ph/cm², photons per cm²

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photodetectors [26]. Perovskite and small core/shell QDs have been combined to prepare voltage tunable LEDs that exhibit exciplex emission, which could be used for developing advanced solar cell configurations, such as intermediate band gap ones [23]. In addition to that PbS QDs have been used as seeds to grow perovskite solar cells with larger grain sizes, significantly increasing the performance of the solar cells [19,24]. These results clearly show the enormous potential of combining perovskite and QD materials to develop highly efficient advanced optoelectronic devices. However, detailed studies of the photoinduced processes that occur in these composites are lacking. Understanding the ultrafast events in perovskite/QDs interfaces, such as charge carrier transfer and recombination dynamics, is paramount to improving the overall efficiency of optoelectronic devices based on these materials. However, the real-time observation of the interfacial processes remains unexplored.

Herein, we report on photodynamics studies of thin polycrystalline films of methylammonium lead triiodide (MAPbI₃) matrix embedded with different concentrations of PbS/CdS (core/shell) QDs, using ultrafast time-resolved transient visible-NIR absorption and terahertz (THz) spectroscopies (TAS and TRTS, respectively). By photogenerating charge carriers over the band gap of MAPbI₃ (~1.55 eV) in the MAPbI₃/QDs hybrid material, we observed fast and efficient charge carrier deactivation due to their transfer to the QDs. The initial (< 1 ps) population and mobility of electrons and holes in the perovskite domain are not affected by the presence of QDs. To accurately elucidate the complex electrons and hole events within the material, we propose a new kinetic model. We found that: (i) the majority (~90%) of photoexcited electrons and holes diffuse towards QDs and is afterwards transferred to the interface and QDs, respectively, (ii) few percent of them fast recombine as excitons in the close vicinity of the interface, and (iii) a small part of the photoexcited charges is not affected by the presence of QDs, and therefore follows the typical perovskite deactivation channels. Lowering the QDs concentration increases the carrier diffusion time, and thus slows down their effective transfer to the interface and QDs, and decreases the concentration of excitons. These results show high collection efficiency of electrons and holes by these QDs in this hybrid material, and the relevance of MAPbI₃/QDs interface states in charge carrier transition/trapping processes. We propose that further optimization of perovskite/QD system requires a reduction of the interface traps. Not of less importance, the proposed kinetic model can be used to characterize the electron-hole events in other complex hybrid structures.

2. Materials and methods

2.1. synthesis of PbS/CdS core-shell QDs

Core/shell quantum dots (QDs) were synthesized according to a previously reported procedure [24,32]. Briefly, a mixture of 0.9 g (4 mmol) of PbO, 2.7 g (9.6 mmol) of oleic acid (OA) and 36 ml of 1-octadecene (ODE) in a three-necked round-bottom flask was heated to 150 °C under N₂ to form Pb-oleate moieties. The solution was degassed for 30 min under vacuum, then opened to N₂, and 3 ml (6.7 mmol) of trioctylphosphine (90%) was injected. A mixture of 0.42 ml (2 mmol) of hexamethyldisilathiane (HMDS) and 4 ml of ODE was quickly injected to the flask when the temperature dropped to 110 °C. The solution was left to cool to room temperature. The reaction product was cleaned three times with ethanol/acetone (1:1, v/v), centrifuged (3000 rpm for 10 min) and dispersed in toluene (100 mg/ml).

For the growth of the CdS shell, a flask containing 0.34 g (2.6 mmol) of CdO, 1.85 g (6.5 mmol) of OA and 40 ml of ODE was heated to 220 °C in air to dissolve CdO, cooled to 150 °C and then degassed for 1 h under vacuum. After that, the temperature was reduced to 70 °C. 5 ml of the as-prepared PbS QD suspension (100 mg/ml in toluene) was rapidly injected to the flask. The reaction was kept at 70 °C for 5 min then stopped by adding the non-solvent mixture (ethanol/acetone, 1:1, v/v).

The product was washed following the same procedure used for PbS nanocrystals and dispersed in octane for the ligand exchange. We got PbS/CdS QDs of 3.0 ± 0.3 nm in size, and which distribution was characterized by TEM (Fig. S1).

2.2. Ligand exchange and perovskite, perovskite/QDs solution preparation

1.5 ml (10 mg/ml) of PbS/CdS core-shell QDs in octane was mixed with 0.5 ml of dimethylformamide (DMF) containing 58.3 mg of PbI₂ and 25 mg of methylammonium iodide (MAI). The as-mixed solution separated into 2 phases: at the top, QDs in octane (brown) and (PbI₂ + MAI) in DMF at the bottom (yellow). After stirring for 30 min, the QDs transferred from the top octane phase to the bottom DMF phase, resulting in a color change: transparent at the top and dark at the bottom. The octane solution was removed and the QD solution was washed three more times using the same solution to remove the organic residue. Subsequently, the QDs were precipitated adding toluene. After removing all the liquids, the QDs were dried under vacuum and dispersed in perovskite solution (0.4 M) to form a MAPbI₃/QDs solution. The amount of C_{QDs} was varied from 2 to 200 mg/ml. The 0.4 M MAPbI₃ reference solution (without QDs) was prepared by dissolving 0.438 mmol of PbI₂ and 0.438 mmol of MAI in a mixture of 1 ml of DMF and 95 μl of dimethyl sulfoxide (DMSO). Further details have been published elsewhere [24].

2.3. Perovskite and perovskite/QDs film preparation

Glass substrates were cleaned with soap, sonicated in distilled water, ethanol and isopropanol for 15 min and then treated with an UV–O₃ lamp for 15 min. MAPbI₃ or MAPbI₃/QD films were spin coated at 9000 rpm from 50 μl of MAPbI₃ or MAPbI₃/QD solution, respectively. Diethyl ether was poured on a film after the spin coater was running for 4 s. The films were annealed for 1 min at 65 °C, then for 2 min at 100 °C. The deposition was carried out inside a glovebox filled with N₂.

2.4. SEM and XRD measurement

The morphology and structural properties of the films were analyzed using a field emission scanning electron microscope (JSM7001F, JEOL) and a Bruker AXS D4 X-ray diffractometer using Cu Kα radiation.

2.5. UV–VIS–NIR absorption spectroscopy

The UV–VIS–NIR absorption spectra of the MAPbI₃, MAPbI₃/QDs and QDs were measured using a standard spectrophotometer (JASCO V-670). To eliminate the contribution of the scattered light, we carried out diffuse reflectance measurements using a 60-mm integration sphere (ISN-723).

2.6. Femtosecond transient absorption spectroscopy

The used femtosecond (fs) transient UV–VIS–NIR absorption setup has been described elsewhere [33]. Briefly, it consists of a Ti:sapphire oscillator (TISSA 50, CDP Systems) pumped by a 5 W diode-laser (Verdi 5, Coherent). The oscillator output pulses (30 fs, 480 mW at 86 MHz) centered at 800 nm were guided to a regenerative amplifier (Legend-USP, Coherent) and used as a seeding signal. The amplified fundamental beam (50 fs, 1 W at 1 kHz) was then directed through an optical parametric amplifier (OPA, CDP Systems) for wavelength conversion and an additional 1-mm BBO crystal for frequency doubling to obtain 400, 600, 700 and 740 nm pulses. The pump intensities ranged from ~40–250 μW. The transient absorption measurements were performed in the spectral ranges of 450–780 nm. All the spectra analyzed in the visible-NIR region were corrected for the chirp of the white light continuum. To avoid sample degradation, the samples were moved during the measurement using the XY translational stage. The instrument

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