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Temperature- and ligand-dependent carrier transport dynamics in photovoltaic PbS colloidal quantum dot thin films using diffusion-wave methods

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ABSTRACT

Solution-processed colloidal quantum dots (CQDs) are promising candidates for large-scale, low-cost, and lightweight photovoltaic and electronic devices. Carrier transport dynamics has a substantial impact on device efficiency optimization. Coupled with photocarrier radiometry (PCR) — a dynamic spectrally integrated frequency-domain photoluminescence (PL) modality, we report the derivation of a trap-state-mediated carrier hopping transport model for the extraction of multiple carrier transport parameters in PbS CQD thin films. These parameters, including effective carrier lifetime τ_E, hopping diffusivity D_h, trap-state-dependent carrier trapping rate R_T, diffusion length L_h, and carrier thermal emission rate e_i, were obtained for CQD thin films with different dot size and capping ligands: tetrabutylammonium iodide (TBAI), 1,2-ethanedithiol (EDT), and methylammonium lead triiodide perovskite ($MAPbI_3$). Consistent with the framework of phonon-assisted carrier hopping mechanism, τ_E, D_h, and L_h have demonstrated a monotonic dependence on temperature in the range from 100 K to 300 K. Perovskite-passivated PbS CQD thin films, especially those with larger dot sizes which are free of apparent defect induced PL emission and have higher τ_E and D_h at room temperature (ca. 0.51 μs and 1.80×10^{-2} cm^2/s, respectively) than their counterparts, demonstrate better photovoltaic material properties. Dot-size-dependent exciton binding energies (35.21–53.20 meV) were characterized using a dynamic PCR photo-thermal spectroscopy that also characterized the trap-state-mediated carrier hopping activation energies in the range from 100 meV to 280 meV. To test the reliability of the best-fitted results, computational fitting uniqueness was examined using a parametric theory.

1. Introduction

Solution-processed colloidal quantum dots (CQDs) have appealing electronic and optical properties such as size-tunable energy bandgap [1,2], multiple exciton generation [3–5], pathways for harvesting hot-electrons [6], and ambipolar (hole and electron) charge transfer [7,8]. Due to these unique granular electronic material features, CQDs have shown great potentials in various optoelectronic and electronic device applications, including thin films transistors [9–11], photodetectors [3,12–14], solar cells [15–18], and light-emitting diodes [19,20].

Understanding carrier transport dynamics and shedding light on energy dissipation mechanisms in optoelectronics is essential to device efficiency optimization. QD disorder in the form of energy and/or geometry, originating in dot shape, size, composition, surface chemistry, and capping ligands, as well as the degree of polydispersity and superlattice order in thin films, disrupts the formation of continuous energy band structures in CQD ensembles. Depending on the level of QD disorder, there are four possible carrier transport mechanisms [21]: (i) bulk crystal-like Bloch state electron transport, (ii) direct tunneling mechanisms without the help of phonons, (iii) over-the-barrier carrier activation, and (iv) phonon-assisted hopping. Phonon-assisted hopping in the form of, for example, nearest neighbor hopping (NNH) and Efros-Shklovskii variable range hopping (ES-VRH), is the most prevailing mechanism that has been widely applied in studying

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various QD systems [22–28] in which carriers hop from one dot to the next depending on the interdot distance, coupling strength, temperature, and the type of carrier. Moreover, strengthening the capping-ligand-controlled interdot coupling has been reported in PbSe QDs as originating in the Coulomb blockade dominated insulating regime and into the hopping conduction dominated semiconductor regime [22], and has also been found to assist exciton dissociation into free electrons and holes [29,30]. Furthermore, Lee et al. [31] and Liu et al. [24] have observed a monotonic increase in hole mobility with increasing QD size, while electron mobility exhibits a peak at QD diameter of 6 nm, which can be ascribed to the compromise between reduced activation energy (lower hopping energy barrier) and weakened interdot coupling strength amongst larger QDs. In addition, hopping conduction behavior has been manifested when carrier mobility drops exponentially with the increase of capping ligand length [24], showing consistency with the Shklovskii and Efros hopping mobility equation [32]. The phonon-assisted hopping transport mechanism predicts a temperature-dependent carrier mobility, diffusivity, lifetime, conductivity, and conductance of QD devices [18,22,23,25,27,28,33]. However, due to the large specific surfaces of QDs, even with the application of capping ligands, QD trap states still hinder the efficiency of CQD based electronic devices through acting as undesired radiative and nonradiative recombination centers [24,34–40]. Important as these effects are, a systematic study of trap-state-modified carrier transport is still lacking.

Despite the importance of carrier dynamics to QD optoelectronic and electronic device efficiency optimization, current characterization techniques are still not able to provide sufficient feedback information about carrier transport kinetics in QD substrates and devices. At present, carrier mobility can be characterized by linearly increasing voltage (CELIV) [39,41,42], time of flight (TOF) [41,43], transient photovoltage [39,44], and by using field effect transistors (FET) [39,45,46]. Nonetheless, these methods require thick QD films and a completed device. Although Zhitomirsky et al. [47] introduced photoluminescence (PL) quenching for carrier diffusion length measurement in CQD thin films, additional coating and/or embedding different types of CQDs are compulsory. Nowadays, carrier lifetime is measured mostly by V_{oc} (open-circuit voltage) transient decay [41] and transient PL [39,48,49] for devices and substrates, respectively. However, due to the fragile nature of materials comprising photovoltaic devices, especially organic and QD-based solar cells, most of these conventional techniques are suitable neither for industrial in-line mass manufacturing of electronic devices at any and all fabrication stages, nor for optoelectronic process analysis involving light-carrier interactions.

In view of these facts, this paper introduces an all-optical, fast, and non-destructive technique, photocarrier radiometry (PCR)—a dynamic spectrally integrated frequency-domain PL modality, to the characterization of CQD thin films. A trap-state-mediated carrier hopping transport model was developed and applied for the extraction of multiple carrier transport parameters of different ligand-capped PbS CQD thin films. The temperature-dependent carrier transport dynamics was investigated in perovskite-passivated PbS CQD thin films. Furthermore, sample homogeneity was examined through PCR-based lock-in carrierography (LIC) imaging [50]. The energy band structure and carrier transport activation energies of our CQD thin films were analyzed using static PL and photo-thermal spectroscopy (PTS) [51], respectively. Combined with a carrier hopping transport model, PCR was shown to exhibit great potential in QD materials characterization for fundamental physics research of carrier transport dynamics, in addition to being an all-optical, nondestructive and promising technique for industrial device quality control.

2. Carrier hopping transport model

Fig. 1(a) and (b) exhibit the schematic of surface-passivated and laser-illuminated PbS CQDs in a ligand matrix. Upon laser excitation,

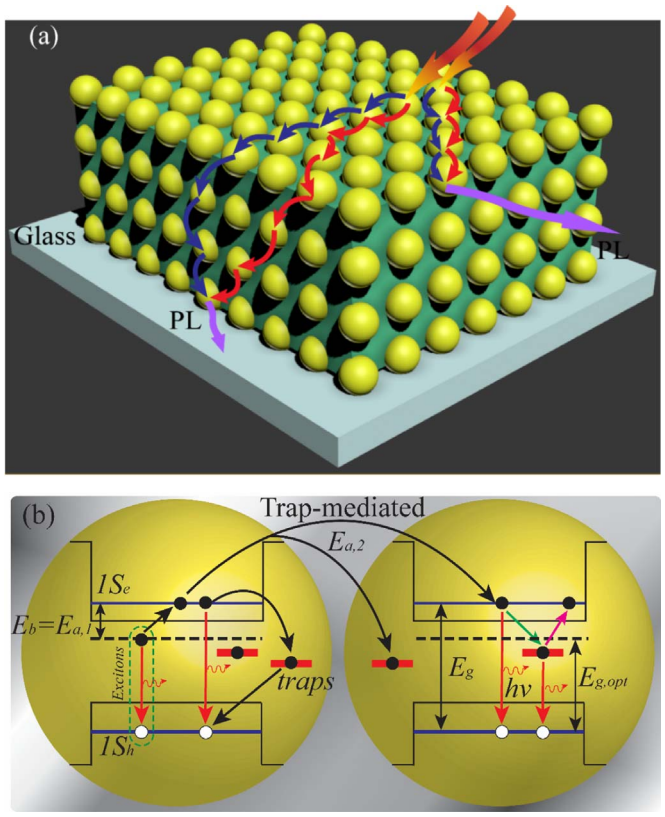

Fig. 1. (a) Schematic of carrier hopping transport in PbS CQD thin films embedded in a surface-passivation ligand matrix when excited by a frequency-modulated laser source. (b) Illustration of carrier generation, dissociation, hopping transport, and trapping processes in a CQD assembly. S_e and S_h are the ground states for electrons and holes, respectively. $E_{a,1}$ and $E_{a,2}$ are the activation energies associated with exciton binding energy (E_b) and trap-mediated transition process, respectively. E_g and $E_{g,\ opt}$ are, respectively, the electronic and optical band gap energy.

excitons will firstly form within the CQDs and diffuse away through a carrier hopping mechanism [Fig. 1(a)], during which process, excitons may dissociate into free charge carriers. All these particles, including excitons and their dissociated charge carriers can recombine radiatively, or be bound to or trapped in trap states and recombine radiatively or non-radiatively [Fig. 1(b)]. The rate equation for the population $N_i(x, t)$ of charge carriers in quantum dot i [52] must include the presence of trap states acting as thermal emission and capture centers. Such trap states have been reported in thiol-capped PbS QDs [53], and in glass-encapsulated PbS QDs [54], also several trap-related emission bands have been reported for PbS QDs in polyvinyl alcohol [55]. Taking into consideration that those trap states acting as thermal emission and capture centers, the carrier rate equation can be expressed as:

$$\frac{\partial N_i(x,t)}{\partial t} = -\sum_j P_{ij}N_i(x,t) + \sum_j P_{ji}N_j(x,t) + \sum_{k=1}^{m}\{e_{ik}(T)n_{Tk}(x,t) - C_{ik}N_i(x,t)[N_{Tk} - n_{Tk}(x,t)]\} - \frac{N_i(x,t)}{\tau} + G_0(x,t) \quad (1)$$

where k denotes trap level, e_{ik} is the thermal emission rate of charge carriers from the trap level k, C_{ik} is the charge carrier capture coefficient, τ is the carrier lifetime, N_{Tk} is the trap density of level k, n_{Tk} is the trapped carrier density, P_{ij} (P_{ji}) is the hopping probability from the i_{th} (j_{th}) QD to the j_{th}(i_{th}) QD. Here, $C_{ik}N_{Tk}$ is defined as the carrier-trapping rate R_{Tk}. G_o is the photocarrier generation rate. In the PbS CQD system under consideration, all the trap states at different levels are considered to have the same effects on carrier transport behavior,