Solar Energy Materials & Solar Cells 151 (2016) 102–112

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Time-resolved fluorescence anisotropy study of organic lead halide perovskite

Yajie Jiang [a], Xiaoming Wen [a,*], Aleš Benda [b], Rui Sheng [a], Anita W.Y. Ho-Baillie [a], Shujuan Huang [a], Fuzhi Huang [c], Yi-Bing Cheng [c], Martin A. Green [a]

[a] *Australian Centre for Advanced Photovoltaics, University of New South Wales, Sydney 2052, Australia*
[b] *Biomedical Imaging Facility, Mark Wainwright Analytical Centre, University of New South Wales, Sydney 2052, Australia*
[c] *Department of Materials Science and Engineering, Monash University, Victoria 3800, Australia*

ARTICLE INFO

Article history:
Received 2 October 2015
Received in revised form
3 March 2016
Accepted 3 March 2016
Available online 22 March 2016

Keywords:
Time-resolved
Fluorescence anisotropy
Perovskite
Solar cell

ABSTRACT

The photoluminescent polarization properties of organic halide perovskites are of great importance for the fundamental understanding and for device fabrication, while limited relevant work has been published. In this work we investigate the fluorescence polarization properties of the $CH_3NH_3PbI_3$, $CH_3NH_3PbI_{3-x}Cl_x$, and $CH_3NH_3PbBr_3$ perovskites which have been used in some of the highly efficient solar device to date. Time-resolved fluorescence anisotropy measurements were conducted on these perovskites fabricated by different methods, and with or without the capping hole transport layer. We demonstrate that $CH_3NH_3PbBr_3$ perovskite exhibits isotropic fluorescence polarization while $CH_3NH_3PbI_3$ and $CH_3NH_3PbI_{3-x}Cl_x$ perovskites exhibit anisotropic fluorescence polarization. The composition influences significantly fluorescence anisotropy dynamics while fabrication has relatively weaker influence. The hole transport capping layer can accelerate the decay of the fluorescence anisotropy. The symmetry of perovskite structure is proposed to be the key factor to impact the fluorescence anisotropy.

1. Introduction

A new solar cell technology based on organic halide perovskites emerges unprecedentedly over the last few years [1–4]. The perovskites exhibit exceptional electrical [5], structural [6,7], optical [8,9] and ferroelectric [10] properties enabling excellent photovoltaic energy conversion efficiency. Perovskite is the common name of the mineral $CaTiO_3$, but this term is used in collectively designating ABX_3 structures. For the purpose of photovoltaic devices, A is generally methyl ammonium ($CH_3NH_3^+$ or MA), B is a metal ion such as Pb or Sn, and X represents a halogen ion such as I, Cl or Br. A distinct advantage of $MAPbX_3$ perovskite is that the band gap can be easily tuned from 1.2 to 2.3 eV by different compositions of cations and anions [11–14]. Most inorganic perovskites exhibit spontaneous electric polarization, arising from the breaking of centro-symmetry [15]. The polarization is expected to be more significant in organic–inorganic perovskite because the atomic structures are more complicated due to the non-centrosymmetric of organic cation. The strong polarization of the lattice is generally benefit for photovoltaic application by the enhanced charge separation and open circuit voltages above the band gap [16]. The interesting roles that different halide elements play in photovoltaic device performance have also been discussed [17,18].

To date, the fluorescence anisotropy has been nearly unexplored for perovskite based solar cells [19]. The anisotropic behavior of the perovskite dielectric response has been theoretically confirmed previously [20]. The behavior is ascribed to the existence of oriented permanent dipoles close to the perovskite/oxide interface [21], and spontaneous electric polarization in hybrid halide perovskite [22]. Furthermore, the presence of hysteresis in the current–voltage characteristic is sometimes attributed to the reorientation of the permanent dipoles $CH_3NH_3^+$ and ferroelectric domains with the applied electric field in addition to the resistance of PbI_3^- lattice [23–26]. However, few works reported on the fluorescence polarization of perovskites, although it may be a strong determinant of many key photovoltaic enabling properties. Recently, Watson et al. investigated annealing effect on the orientation of transition dipole moments in $CH_3NH_3PbI_3$ perovskite using two-photon total internal reflectance microscopy [27]. An enhanced in-plane transition moment orientation was observed as the increase of thermal annealing time, while the underlying mechanism still requires further confirmation.

Fluorescence techniques have been commonly used in the study of recombination [28] and carrier extraction in perovskite solar cell research [29]. Apart from time-resolved and steady state

---

* Corresponding author.
E-mail address: x.wen@unsw.edu.au (X. Wen).

http://dx.doi.org/10.1016/j.solmat.2016.03.002
0927-0248/© 2016 Elsevier B.V. All rights reserved.

photoluminescence, the spatially-resolved intensity of the emitted fluorescence can also be used to study the morphology and defects of a perovskite film [30] which aids the understanding of the underlying mechanisms for recombination and carrier extraction.

Time-resolved fluorescence anisotropy measurements are based on excitation by linearly polarized light and the detection of fluorescence emission at different polarization angles [31,32]. Such measurements allow determination of the extent of sample polarization. Every emitted photon has electric and magnetic vectors oscillating along a particular axis. Their orientations reflect the nature of the intrinsic fluorescence process, the structure and the properties of the material, but also depend on the type and polarization of the excitation beam. The crystals whose absorption transition dipoles moments aligning in parallel with the electric excitation vectors of the laser are preferably excited [33]. Time-resolved fluorescence anisotropy can be determined by measuring the excited state fluorescence decays of the vertically and horizontally polarized emissions. Time dependent polarization typically originates from the existence of transition moments for absorption and emission that lie along specific directions. It reveals the fluorophore dynamics, which resulted in numerous applications in biochemical research [33,34]. It also provides information on the processes of thermal and spin relaxation of electrons and holes in semiconductor crystals [35]. Moreover, fluorescence anisotropy is a powerful technique in many disciplines characterizing rotational characteristics of molecules [36], protein–protein interactions [37], crystallographic properties [38,39], and membrane fluidity [40].

In this study we investigate the fluorescence polarization properties via time-resolved fluorescence anisotropy of various perovskite thin films with different compositions, fabrication methods, and with or without the capping hole transport materials (HTM) layer. We demonstrate that perovskite materials exhibit fluorescence polarization properties that are influenced by the type of halide, fabrication methods and the presence of the capping layer.

2. Experimental methods

The perovskite samples used in this study include $CH_3NH_3PbI_3$ by conventional spin coating and gas-assisted fabrication [41], $CH_3NH_3PbI_{3-x}Cl_x$ by conventional spin coating [42], and $CH_3NH_3PbBr_3$ by vapor-assisted deposition [43]. Some of which are capped with a spiro-OMeTAD layer. The details of sample fabrications are described in Appendix A.

The time-resolved fluorescence anisotropy was measured by time correlated single photon counting technique on MicroTime 200 microscope (PicoQuant). The system configuration used in this study is a pulsed linearly polarized 470 nm laser with variable repetition and pulse width of 50 ps, two single photon counting detectors, photon counting unit PicoHarp 300 (PicoQuant,), 50 μm pinhole, 536/40 nm or 750/40 nm emission bandpass filters and polarizing beam splitter. The sample is illuminated by focused laser beam with optical axis perpendicular to the sample surface and polarized along the x axis. The emitted fluorescence is collected by the same objective, is spatially filtered by the pinhole, spectrally filtered by the emission bandpass filters and split into two beams with orthogonal polarizations (x and y axis) by the polarizing beam splitter. Each of the beams is then focused onto its single photon counting detector and detected photons for both polarizations are simultaneously registered by the photon counting unit using the Time-tagged time resolved (TTTR) data format (Table 1).

The morphology of each sample was characterized by either fluorescence imaging or scanning electron microscopy (SEM) in Appendix B (Figs. A1-A3). The fluorescence spectra of $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ perovskites were measured by a Si-CCD spectrometer and excited at 405 nm. Fig. 1(a) shows the absorption and fluorescence spectra of conventional spin coated and gas-assisted deposited $CH_3NH_3PbI_3$, while Fig. 1(b) shows those of vapor-assisted deposited $CH_3NH_3PbBr_3$. The absorption and fluorescence spectra of $CH_3NH_3PbI_{3-x}Cl_x$ are similar to those of $CH_3NH_3PbI_3$, and therefore not shown. The emission spectra of $CH_3NH_3PbBr_3$ and $CH_3NH_3PbI_3$ show peaks at 770 nm and 536 nm respectively, in good agreement with the expected optical bandgaps [1].

Table 1
Perovskite samples examined in this study.

Sample no.	Composition	Fabrication method	Capping layer
S1	$CH_3NH_3PbI_3$	Conventional spin coating [41]	None
S2	$CH_3NH_3PbI_3$	Gas assisted [41]	None
S3	$CH_3NH_3PbI_3$	Gas assisted [41]	Spiro-OMeTAD
S4	$CH_3NH_3PbI_{3-x}Cl_x$	Conventional spin coating [42]	None
S5	$CH_3NH_3PbI_{3-x}Cl_x$	Conventional spin coating [42]	Spiro-OMeTAD
S6	$CH_3NH_3PbBr_3$	Vapor assisted [43]	None

The fluorescence anisotropy in perovskite is illustrated schematically in Fig. 2. Perovskite samples are excited with a linearly polarized laser at 470 nm. Fluorophore is usually regarded as an oscillating dipole with an absorption probability related to the polarization angle between its absorption dipole and the excitation light. The possibility of a photon being absorbed by a dipole is proportional to $\cos^2\theta$, where θ is the angle between the polarization of the incident photons and the dipole. The absorption dipoles parallel to the polarization plane of the exciting light are preferentially excited, while those whose dipoles aligned perpendicular to the plane are not excited. This polarization based photo-selection excites a selected population of properly oriented dipoles (molecules). The emitted fluorescence light is usually depolarized compared to the excitation light. The sources of depolarization are the different orientations of excitation and emission dipoles, the rotation of the dipole and/or the energy transfer between molecules (dipoles). The depolarization results in a partially oriented fluorescence emission as illustrated in Fig. 2. The time-resolved anisotropy measurements allow the quantification of depolarization and the time scale in which the depolarization happens.

The extent of polarization is normally quantified in terms of fluorescence anisotropy r as a function of measured fluorescence intensities of polarization along different axes:

$$r = \frac{I_{/\!/} - G \bullet I_{\perp}}{I_{/\!/} + 2 \bullet G \bullet I_{\perp}} \tag{1}$$

Here $I_{/\!/}$ and $I_{\perp}$ are the intensities of the parallel and perpendicular polarized emissions, when the sample is excited with linearly polarized light. G represents the instrument correction factor accounting for the polarization bias of the detection system. The G factors for 770 nm and 536 nm emissions were determined by calibrating the system with standard dyes (Alexa 488 and Alexa 593) in solution, see Appendix D. Time-resolved anisotropy $r(t)$,

$$r(t) = r_{\infty} + r_0 \exp(t/\tau) \tag{2}$$

are obtained by measuring anisotropy as a function of time, where the initial anisotropy r_0 refers to the mutual orientations of absorption and emission dipoles; the residual anisotropy r_{∞} describes the level of lost anisotropic characteristics due to dipole reorientation or energy transfers. The depolarization time t