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2016

Li, M., Bhaumik, S., Mhaisalkar, S., Mathews, N., & Sum, T. C. (2016). Carrier dynamics in low-dimensional perovskites. 2016 IEEE International Nanoelectronics Conference (INEC). doi:10.1109/INEC.2016.7589434

<https://hdl.handle.net/10356/141298>

<https://doi.org/10.1109/INEC.2016.7589434>

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Carrier Dynamics in Low-dimensional Perovskites

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Abstract — Low-dimensional organic-inorganic halide perovskites (*e.g.*, nanocrystals (NCs) and nanoplatelets (NPLs)) are the new kids on the block for potential nanoelectronic applications. Herein, the recombination dynamics of the photoexcited species in methylammonium lead bromide (MAPbBr₃) NCs and NPLs are probed using time-resolved photoluminescence spectroscopy. They exhibit distinct recombination lifetimes as a consequence of their dimensionality, thereby offering new possibilities for altering perovskites' optoelectronic properties for nanoelectronic applications.

Keywords—organic-inorganic perovskites, nanocrystals, nanoplatelets, ultrafast spectroscopy and carrier dynamics

I. INTRODUCTION

Organic-inorganic halide perovskites have garnered immense research interests because of their outstanding optoelectronic properties for applications ranging from photovoltaics, light emission, lasing and even radiation detection. In particular, ultrafast optical spectroscopy [1] (*e.g.*, transient photoluminescence and transient absorption *etc.*) had played a pivotal role in the discoveries of long balanced electron-diffusion lengths, slow hot-hole cooling and ultralow threshold lasing in these materials [2, 3]. Low-dimensional halide perovskites (*e.g.*, nanocrystals, nanoplatelets *etc.*) present new exciting possibilities for tuning the optoelectronic properties for nanoelectronic applications. Key to the development of such applications is through a clear understanding of the carrier dynamics of these emerging systems [4]. In this work, we utilize time-integrated and time-resolved photoluminescence spectroscopy to probe the recombination dynamics in methylammonium lead bromide (MAPbBr₃) nanocrystals (NCs) and nanoplatelets (NPLs).

II. EXPERIMENTAL

A. Nanostructure Synthesis

Methylammonium lead bromide (MAPbBr₃) nanocrystals (NCs) were synthesized by the ligand-assisted re-precipitation (LARP) method as reported elsewhere [5]. At first in a glass vial 0.16 mmol of MABr, 0.2 mmol of PbBr₂ were mixed in 5 mL dimethylformamide (DMF) solution. Later 50 μ L of oleylamine (OAm) and 0.5 mL oleic acid (OAc) were also mixed in the DMF solution to form the final precursor solution. Another round bottom glass flask

containing 5 mL of toluene was heated at 60°C in an oil bath. Then 250 μ L of as prepared precursor solution was swiftly injected into toluene under vigorous stirring condition. The solution turned into green color, confirming the formation of MAPbBr₃ NPs. The reaction was continued for 5 min and then transferred into a centrifuge tube. The NPs were purified by centrifugation method that centrifuged at different speeds for 10 min. The average NCs diameter is around 8 nm.

MAPbBr₃ perovskite nanoplatelets (NPLs) were synthesized using a modified ligand-assisted precipitation method [6]. A 200 μ L solution containing 0.1 mmol lead bromide, 0.16 mmol octylamine, 0.24 mmol methylamine, and 0.5 mmol hydrobromic acid in DMF was added into 3 mL acetone at room temperature to produce the colloidal solution. The yellow product was collected and air-dried after centrifugation at 4400 rpm for 10 min. The perovskite nanoplatelets obtained can be redispersed into toluene or acetone to form a colloidal solution again. Typically, the NPLs are of several hundreds of nm².

B. Optical Studies

The optical measurements were performed on the NCs and NPLs samples dispersed in toluene solution at room temperature with femtosecond laser excitation (1 kHz, 50 fs). The 400 nm laser pulses were generated by frequency doubling the 800 nm fundamental from the output of a Coherent LibraTM regenerative amplifier system. Time-integrated photoluminescence (TIPL) was collected at a backscattering angle by a spectrometer (Acton, Spectra Pro 2500i) and CCD (Princeton Instruments, Pixis 400B); while time-resolved photoluminescence (TRPL) was collected in the same geometry using an Optronis Optoscope streak camera system, which has an ultimate temporal resolution of 6 ps.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the TIPL spectra of NCs (red curve) and NPLs (blue curve). The emission peak of NCs is located at ~517 nm. For NPLs, there is one main peak located at ~533 nm, and several weak shoulders at higher energy side (located at ~490, 476 and 455 nm, respectively). In contrast to the reported 570 nm emission peak for bulk MAPbBr₃ single crystals [7], the obvious blue-shift for both samples can be attributed to quantum confinement effects in our

samples. The multiple peaks at higher energies in NPLs sample probably originate from the NPLs with smaller number of layers, their weak emission intensities can be explained by the re-absorption by the thicker NPLs with emission at ~ 533 nm. Figure 1(b) shows the TRPL curves of two samples in a log-log representation measured by a streak camera system. For the NCs, the PL decay is nearly single-exponential with a fitted lifetime of ~ 12 ns. Together with the high PL quantum yield (PLQY $\sim 85\%$) observed for these NCs, this suggests the presence of low defects in the NCs. On the other hand, the transient PL of the NPLs (at their main emission peak at ~ 533 nm) exhibits bi-exponential decay kinetics with a short lifetime component (40 ns with 60% amplitude) and a long lifetime component (500 ns with 40% amplitude). With a lower PLQY of $\sim 35\%$, this suggests a higher defect concentration in the NPLs.

Fig 1 (a) TIPL spectra of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ nanocrystals (red) and nanoplatelets (blue) in toluene solution. (b) TRPL decay transients of the two samples following excitation at 400 nm (1 kHz, 150 fs) with pump fluence of $0.5 \mu\text{J cm}^{-2}$.

IV. CONCLUSIONS

In summary, the recombination dynamics in methylammonium lead bromide (MAPbBr_3) nanocrystals (NCs) and nanoplatelets (NPLs) were investigated using time-integrated and time-resolved photoluminescence spectroscopy. The NCs exhibits a single exponential PL decay with a lifetime of ~ 12 ns with low defect densities; while the NPLs exhibits a bi-exponential PL decay with lifetimes of ~ 40 ns and ~ 500 ns. Such low-dimensional

perovskites offer new opportunities for modulating the optoelectronic properties of perovskites in nanoelectronics.

ACKNOWLEDGMENT

Financial support from Nanyang Technological University start-up grants M4080514 and M4081293, the Ministry of Education AcRF Tier 1 grants RG184/14, RG101/15 and RG115/15; and Tier 2 grants MOE2013-T2-1-081 and MOE2014-T2-1-044; the NTU-A*STAR Silicon Technologies Center of Excellence Program Grant 11235100003 and from the Singapore National Research Foundation (NRF) through the Singapore-Berkeley Research Initiative for Sustainable Energy (SinBeRISE) CREATE Program and the Competitive Research Program NRF-CRP14-2014-03 is gratefully acknowledged.

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