Carrier Doping and Assembly Control of Colloidal Quantum Dot Solids for Energy Harvesting Devices

RIKEN-Center for Emergent Matter Science, Japan [1], Tokyo Institute of Technology, Japan [2]

°Satria Zulkarnaen Bisri [1,2]

E-mail: satria.bisri@riken.jp

Colloidal quantum dot solids (QDs) are solution-processable thin-films that exploit the quantum confinement properties of the constituent nanocrystals. The quantum confinement effect occurred in this materials generate energy bandgap value variations by size, which are strikingly different from their bulk counterpart, and the quasi-atom-like discrete energy levels.[1] These two important properties of the QDs, in addition to their solution-processability, are intriguing for applications in different kinds of energy-converting, -storage and -harvesting devices. The tunable absorption and the possibility to have multiple exciton generations in these systems are attractive for highly efficient photodetectors and solar cells, to overcome the Shockley-Quisser limit.[2] On the other hands, the discrete energy levels with sharp peaks of the density of states, together with the variations of the QD assemblies, are prospective for developing new thermoelectric materials[3]. Investigation of carrier transport and electronic properties of highly-crosslinked QD assemblies is vital for the uses of these class of materials in diverse emerging applications.

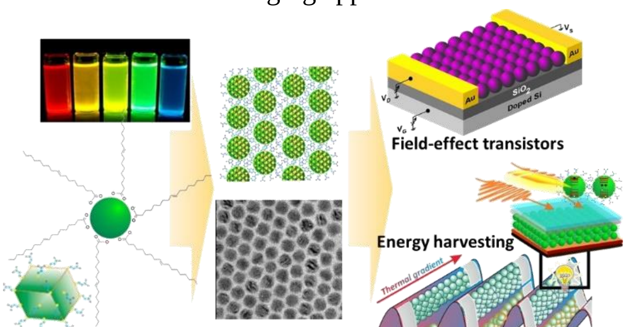

Figure 1 Colloidal semiconductor quantum dots allow us to build LEGO™-like material assemblies, with some distinct features beneficial for energy harvesting device applications. Controlling the QD assemblies, and their doping levels are crucial to ensure efficient charge carrier transport that is prerequisite for many of their application prospects.

Here charge carrier control in thin film assemblies of colloidal semiconductor QDs will be discussed. We will explain how to control the assembly morphology by various deposition techniques and how to crosslink the colloidal QDs, either by replacing the insulating native ligands with different organic and inorganic molecules,[4] or directing the facets of the individual QDs by selective ligand stripping. The demonstration of various approaches of carrier doping into lead chalcogenide QD assemblies will be explained, which involve either chemical approach (e.g. ligand modification, etc.) or physical approach (field-induced doping). The implications of having a large surface area to volume ratio in the QD system towards the possible origins of charge carrier trap states will be shown in the context on how to overcome using doping controls. We will show that the use of state-of-the-art electric double layer gating[4] allows us to perform field-induced doping with a tremendous amount of accumulated charge carrier that allowed not only the passivation of charge carrier traps,[5] but also the band fillings of QD energy states. Knowledge of how many electrons can sit for each QD discrete energy levels is vital to strategize the other means of doping.[6] Through this, clear preservation of quantum confinement merit of QD system can be demonstrated despite the assemblies are highly crosslinked. In addition to recent success in controlling both the intrinsic hole and electron transports in the QDs using proper selections of organic molecular ligands.[7] the implications of carrier control on the usage of QD assemblies for energy harvesting will be explained, in particular within photovoltaic and thermoelectric contexts, which efficient charge carrier transport are the prerequisites.

Refs: [1] M.V. Kovalenko, et al. *ACS Nano* 9, 1012 (2015); [2] M.C. Beard, et al. *Acc. Chem. Res.* 46, 1252 (2013); C. Piliego, et al. *Energy & Env. Sci.* 6, 3054 (2013) [3] J.J. Urban, *Nature Nanotech.* 10, 997 (2015); [4] S.Z. Bisri, et al., *Adv. Mater.* 25, 4309 (2013) [5] *Adv. Mater.* 27, 2107 (2015) [6] *Adv. Mater.* 26, 5639 (2014); *Adv. Mater.* 29, 1607054 (2017); [7] L. Liu, et al. *ACS Appl. Nano Mater.*, 1, 5217 (2018); [8] S.Z. Bisri, et al. *submitted*; *Pat. fil.* WO2018012009. I acknowledge the contributions of RIKEN-affiliated co-workers toward parts of this work, which are: Ms L. Liu, Ms R. Miranti, Mr R. D. Septianto, Mr D. Shin, Mr I. Watanabe, Dr I. Johnson, Dr M. Wheeler, Dr D. Balazs, Dr Y. Ishida, Prof T. Aida, and Prof Y. Iwasa. Collaboration supports by Dr J. Burroughes, Dr F. Iskandar, Dr M. Ibanez, Prof N. Matsushita, Prof M.A. Loi, and Prof M.V. Kovalenko are highly appreciated.