

# Photoluminescence Dynamics of Colloidal CuInS<sub>2</sub> Nanocrystals

Miriam Karpińska, Magdalena Duda, Małgorzata Szymura,  
Bożena Sikora, and Łukasz Kłopotowski

*Institute of Physics Polish Academy of Sciences, Al. Lotników 32/46,  
02-668 Warsaw, Poland*

CuInS<sub>2</sub> (CIS) colloidal nanocrystals (NCs) have recently instigated great interest as non-toxic materials with easily controllable properties that can be tuned by the synthesis conditions and concentration of compounds used as precursors. These semiconductors have thus a potential to be used in applications such as solar concentrators [1], where negligible overlap between absorption and photoluminescence (PL) spectra and possibility of bandgap tuning in a wide energy range are indispensable.

CIS NCs exhibit PL peaks that originate from the radiative recombination of a delocalized electron in the conduction band with a hole localized in the trap state just above the valence band edge (VBE). These states are related to the copper ions. The PL linewidth is much larger compared to, e.g., CdSe NCs, where only excitonic recombination occurs [2]. The origin of this considerable broadening is currently a subject of intense debate. On the one hand, it was assumed, that the positions of traps related to copper with respect to VBE vary in individual NCs [3]. On the other hand, the broadening mechanism may be due to the varying degree of electron-phonon coupling resulting in exciton self-trapping [4]. In order to gain more insight into the origin of the PL linewidth, we conducted the measurements of time-resolved PL as a function of the photon energy.

The analyzed colloidal CIS NCs of three different diameters were synthesized based on previously reported protocol [5]. All the experiments were performed at room temperature. The absorption edge exhibits the blueshift with decreasing NC radius, a phenomenon reflecting the size effect of the nanoscale objects. The PL shows a large Stokes shift between the absorption edge and PL peak. The obtained results of time-resolved PL reveal the clear dependence of lifetimes on the energy of emitted photons. Namely, the PL lifetime increases by a factor of 3 to 5 upon decreasing the detection energy across the PL spectrum. If the broadening mechanism were related to the exciton self-trapping, PL decay times should be independent of the PL energy. Therefore, our observations suggest that the copper ions introduce trap states located at distinctive energy positions above VBE. The PL decay results then from two competing processes: the radiative recombination of electrons with holes, and hopping of holes to the lower energy states before recombination.

The research was partially supported by National Centre of Science (Poland), grant number 2013/08/A/ST3/00297.

- [1] W. van der Stam, A. C. Berends, C. de Mello Donega *ChemPhysChem* **17**, 559 (2016)
- [2] L. Qu and X. Peng *J. Am. Chem. Soc.* **124**, 2049 (2001)
- [3] A. C. Berends, F. T. Rabouw, F. C. M. Spoor, E. Bladt, F. C. Grozema, A. J. Houtepen, L. D. A. Siebbeles, C. De Mello Donega *J. Phys. Chem. Lett.* **7**, 3503 (2016)
- [4] P. J. Whitham, A. Marchioro, K. E. Knowles, T. B. Kilburn, P. J. Reid, D. R. Gamelin *J. Phys. Chem. C* **120**, 17136 (2016)
- [5] L. Li, A. Pandey, D. J. Werder, B. P. Khanal, J. M. Pietryga, V. I. Klimov, *J. Am. Chem. Soc.* **133**, 1176 (2011)