From Binary Copper Chalcogenide to Multicomponent Semiconductor Nanocrystals via Cation Exchange

Vladimir Lesnyak

Physical Chemistry, TU Dresden, Zellescher Weg 19, 01069 Dresden, Germany

vladimir.lesnyak@tu-dresden.de

Copper chalcogenide-based nanocrystals (NCs) are a suitable replacement for toxic Cd/Pb chalcogenide NCs in a wide range of applications including photovoltaics, optoelectronics, and biological imaging. However, despite rigorous research, direct synthesis approaches of this class of compounds suffer from inhomogeneous size, shape, and composition of the NC ensembles, which is reflected in their broad photoluminescence (PL) band widths. A partial cation exchange (CE) strategy, wherein host cations in the initial binary copper chalcogenide are replaced by incoming guest cations to form ternary/quaternary multicomponent NCs, offers a valuable alternative.

A straightforward synthesis of binary copper chalcogenide NCs[1] provides a perfect basement for obtaining fairly monodisperse multicomponent particles by replacing a part of host copper ions by guest cations of choice. This partial CE allows for a precise control of the composition of the exchanging NCs by simple tuning the ratio between host particles and incoming cation precursors, while preserving the size, shape, and crystal structure of template NCs.[2] Host copper ions can easily be replaced by a range of different metal cations, making copper chalcogenides a universal platform to prepare different metal chalcogenide structures, otherwise inaccessible from direct synthesis, including 2D nanomaterials and more complex anisotropic structures.[3] Partial Cu^{+}-to-In^{3+} CE yields Cu-In-S[4] and Cu-In-Se[5] NCs with a uniform distribution of all elements over individual particles. At the same time, the simultaneous incorporation of In^{3+} and Zn^{2+} into $Cu_{2-x}Se$ NCs results in gradient alloyed Cu-Zn-In-Se NCs with a Zn-rich surface.[6] Without an additional shell growth these NCs exhibit near-infrared PL with narrow bands, reaching quantum yields of 20%. These results evidence that synthetic approaches that help to eliminate inhomogeneities in the NC ensembles can lead to narrower PL spectra. The large Stokes shift inherent to these materials, their absorption in the solar range, as well as their near-infrared PL within the biological window make them suitable candidates for applications in the area of solar energy harvesting and bioimaging.

References

[1] a) P. L. Saldanha, R. Brescia, M. Prato, H. Li, M. Povia, L. Manna, V. Lesnyak, *Chem. Mater.* **2014**, *26*, 1442; b) V. Lesnyak, R. Brescia, G. C. Messina, L. Manna, *J. Am. Chem. Soc.* **2015**, *137*, 9315.

[2] V. Lesnyak, C. George, A. Genovese, M. Prato, A. Casu, S. Ayyappan, A. Scarpellini, L. Manna, *ACS Nano* **2014**, *8*, 8407.

[3] a) V. Shamraienko, D. Spittel, R. Hübner, M. Samadi Khoshkhoo, N. Weiß, M. Georgi, K. B. L. Borchert, D. Schwarz, V. Lesnyak, A. Eychmüller, *J. Mater. Chem. C* **2021**, *9*, 16523; b) A. Bora, A. Prudnikau, N. Fu, R. Hübner, K. B. L. Borchert, D. Schwarz, N. Gaponik, V. Lesnyak, *Chem. Mater.* **2022**, *34*, 9251; c) A. Bora, N. Fu, A. Saha, A. Prudnikau, R. Hübner, H. Bahmani Jalali, F. Di Stasio, N. Gaponik, V. Lesnyak, *Nanoscale* **2025**, *17*, 2577.

[4] Q. A. Akkerman, A. Genovese, C. George, M. Prato, I. Moreels, A. Casu, S. Marras, A. Curcio, A. Scarpellini, T. Pellegrino, L. Manna, V. Lesnyak, *ACS Nano* **2015**, *9*, 521.

[5] J. F. L. Lox, Z. Dang, V. M. Dzhagan, D. Spittel, B. Martín-García, I. Moreels, D. R. T. Zahn, V. Lesnyak, *Chem. Mater.* **2018**, *30*, 2607.

[6] A. Bora, J. Lox, R. Hübner, N. Weiß, H. Bahmani Jalali, F. Di Stasio, C. Steinbach, N. Gaponik, V. Lesnyak, *Chem. Mater.* **2023**, *35*, 4068.