Type of presentation: Poster

IT-7-P-5919 Real-time observation of in-situ cation exchange in CdSe-PbSe nanodumbbells during epitaxial solid-solid-vapor growth

Yalcin A. O.[1], Goris B.[2], Bals S.[2], Van Tendeloo G.[2], Casavola M.[3], Vanmaekelbergh D.[3], Tichelaar F. D.[1], Zandbergen H. W.[1], van Huis M. A.[3]

[1]Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands, [2]Electron Microscopy for Materials Science (EMAT), University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium, [3]Debye Institute for Nanomaterials Science, Utrecht University, Princetonplein 5, 3584 CC Utrecht, The Netherlands

Email of the presenting author: a.o.yalcin@tudelft.nl

Both the synthesis and design of hetero-nanocrystals (HNCs) have undergone a rapid development, whereby PbSe and CdSe NCs are key materials acting as functional building blocks within a wide variety of heterogeneous nanostructures.[1,2] Heat treatment of HNCs can induce new interface designs, exemplified by the transformation of PbSe/CdSe core/shell systems into PbSe-CdSe bi-hemispheres.[2] Here, we report an in-situ heating-induced epitaxial PbSe NC domain growth at the solid-solid PbSe-CdSe nano-interface through cation exchange. We show that Pb replaces Cd at the PbSe/CdSe interface, resulting in growth of the PbSe phase at the expense of the CdSe phase.[3] In analogy with vapor-liquid-solid[4] and vapor-solid-solid[5] growth mechanisms, the currently observed process could be called solid-solid-vapor (SSV) growth as the Cd evaporates, either as neutrally charged Cd atoms or in a molecular complex such as Cd-oleate. **Figure 1** shows the elemental maps of CdSe-PbSe HNCs at each stage of the cation exchange during epitaxial SSV growth mechanism. As a result of the cation exchange from CdSe to PbSe, the crystal structure transformed epitaxially from hexagonal wurtzite (WZ) to cubic rock-salt (RS). **Figure 2** shows this transformation at atomic resolution. When the HNC was heated from 160 ^{0}C (**Figure 2a**) to 180 ^{0}C (**Figure 2b**), the brighter intensity corresponding to PbSe advanced into the CdSe region. The PbSe RS (200) lattice spacings started to appear along the nanorod domain instead of the CdSe WZ (0002) lattice spacings, as confirmed by the Fourier Transformation (FT) patterns shown in the insets. It is clear that the cation exchange takes place at the PbSe/CdSe interface and propagates epitaxially (layer by layer) along the WZ<0001> direction.

[1] Son, D. H. *et al. Science* **2004**, 306, 1009-1012.
[2] Grodzińska, D. *et al. J. Mater. Chem.* **2011**, 21, 11556-11565.
[3] Yalcin, A. O. *et al. Nano Lett.* **2014**, 14, 3661–3667.
[4] Gudiksen, M. S. *et al. Nature* **2002**, 415, 617-620.
[5] Persson, A. I. *et al. Nat. Mater.* **2004**, 3, 677-681.

Acknowledgement: This work is part of the research programme of the Foundation for Fundamental Research on Matter (FOM), which is part of the Netherlands Organization for Scientific Research (NWO).

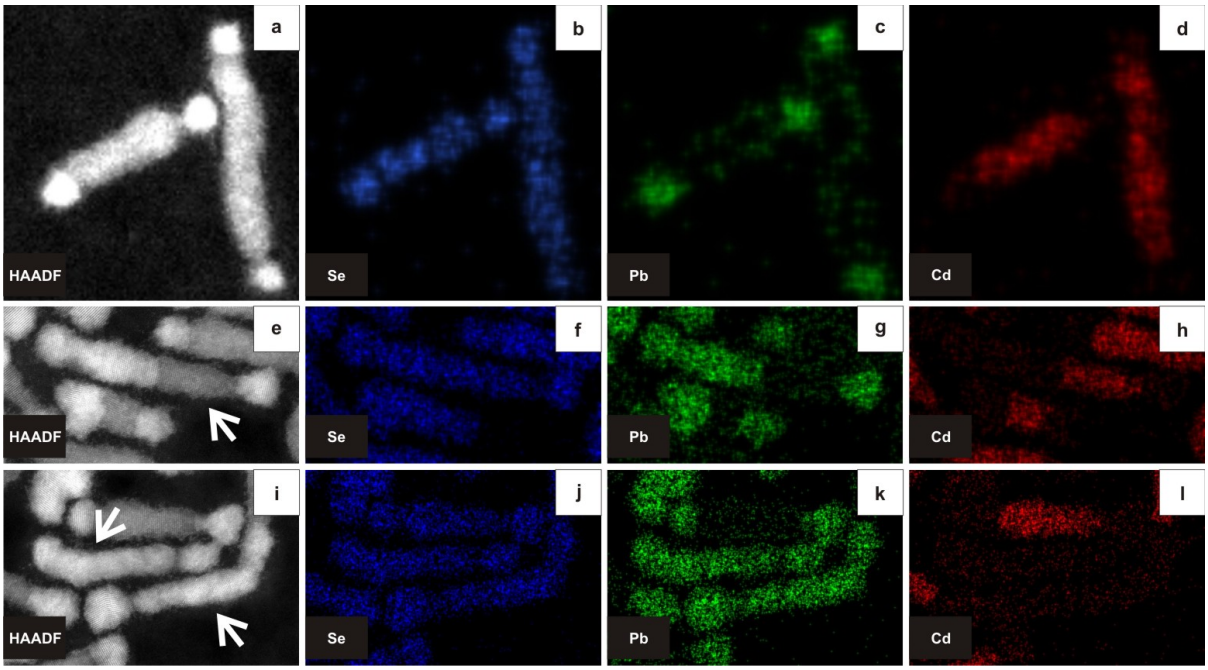

Fig. 1: HAADF-STEM images and chemical maps of CdSe-PbSe HNCs at (a-d) 100 ºC (initial configuration), (e-h) 170 ºC, and (i-l) 200 ºC. In (e-h), a partially transformed nanorod is present. In (i-l), two PbSe-CdSe HNCs became full PbSe domains. The Se remains in place during the transformation. Reprinted with permission from Ref. [3].

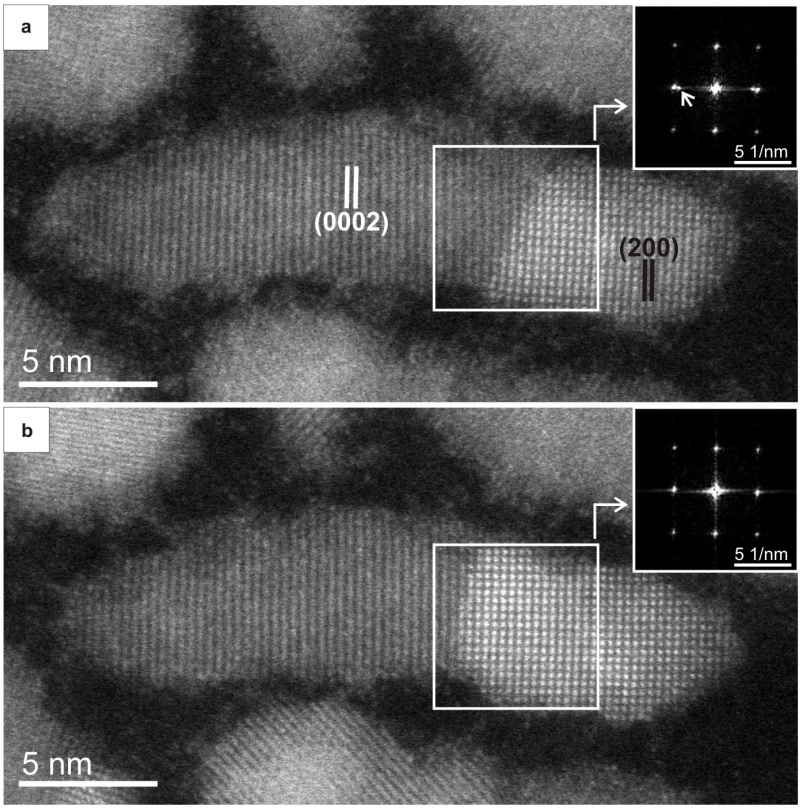

Fig. 2: HAADF-STEM images of CdSe-PbSe HNC. With heating from 160ºC (a) to 180ºC (b), WZ CdSe nanorod started to transform to RS PbSe. The spot depicted with an arrow in the inset FT in Fig. 2a corresponds to WZ CdSe(0002) spacing. It disappeared in the inset FT of Fig. 2b, confirming the WZ to RS transformation. Reprinted with permission from Ref. [3].