

## Thermally Driven Cation Exchange at Solid State between $\text{Cu}_2\text{Se}$ and $\text{CdSe}$ Nanocrystals: an *In-Situ* TEM Study.

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Cation exchange (CE) reactions in crystals concern the partial or the complete substitution of a cation species, while the anion one keeps its place in the crystalline structure and is essentially preserved in the reaction [1]. CE is commonly based on the very rapid direct reaction occurring in liquid solution between inorganic colloidal nanocrystals (NCs) and cationic species. Due to the highly dynamic nature of the phenomenon as well as to the liquid environment in which it takes place, its direct imaging looks very hard to perform. Copper chalcogenides have been found to be inclined to CE reactions, since in these materials the formation of a great number of copper vacancies offers effective pathways for cation interdiffusion and exchange [2]. Between copper chalcogenides,  $\text{Cu}_2\text{Se}$  (NCs) nanocrystals are colloidal nanomaterials well known for their semiconducting, optoelectronic and thermoelectric properties. In particular, antifluorite  $\text{Cu}_2\text{Se}$  phase becomes superionic when heated above a threshold temperature, so that Cu cations are able to diffuse randomly with liquid-like mobility around the rigid Se sublattice.

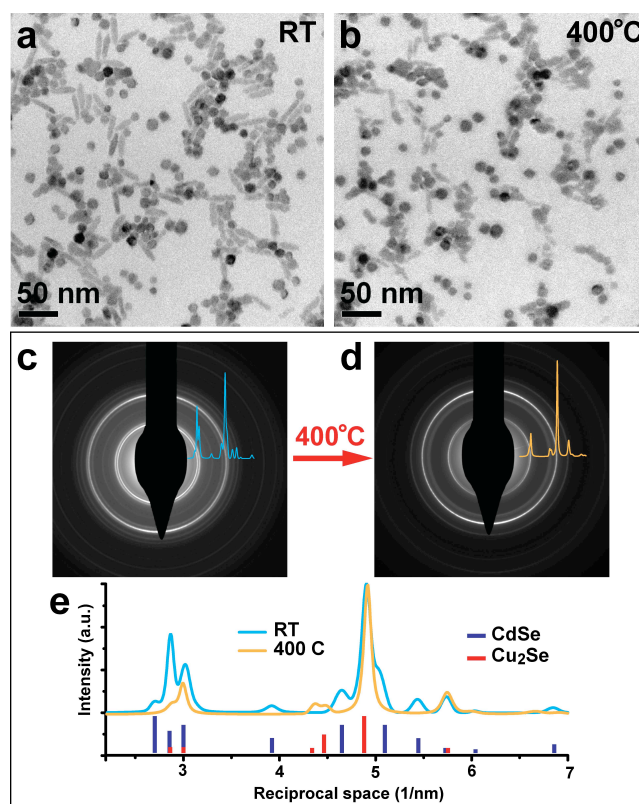
Using an *in-situ* TEM approach, our work first shows what happens to only  $\text{Cu}_2\text{Se}$  NCs when the temperature is increased at  $400^\circ\text{C}$ :  $\text{Cu}_2\text{Se}$  NCs expel free Cu species, forming then Cu-vacancies in cation sublattice, with consequent change of stoichiometry into  $\text{Cu}_{2-x}\text{Se}$ , and with both a concomitant small decrease of the cubic lattice constant and a modification of the electronic structure. Besides, this change in the electronic structure of Cu-depleted  $\text{Cu}_{2-x}\text{Se}$  can be correlated to the appearance of a plasmon absorption band in the electron energy loss (EEL) spectrum, showing a peak at about 1.1 eV, detected only by high-resolution EEL Spectrometry. *Ab-initio* simulations of the EEL spectrum have also confirmed the appearance of this low-loss energy feature as a consequence of the Cu vacancies formation in the  $\text{Cu}_2\text{Se}$  cation sublattice.

Furthermore, we report that the free Cu species expelled from  $\text{Cu}_{2-x}\text{Se}$  NCs at  $400^\circ\text{C}$  can be exploited to perform solid state CE reactions at local scale by simple thermal activation. In particular, we present the results of thermally driven CE between cubic  $\text{Cu}_2\text{Se}$  NCs and wurtzite  $\text{CdSe}$  nanorods (NRs) or nanowires (NWs), when deposited on the same amorphous substrate (constituted either by thin carbon film or  $\text{Si}_3\text{N}_4$  membrane). After this *in-situ* heating at  $400^\circ\text{C}$ ,  $\text{Cu}_{2-x}\text{Se}$  NCs show again the Cu-depletion already observed when they were put as only species on the TEM grid and heated at the same temperature. Moreover,  $\text{CdSe}$  NRs or NWs undergo a pervasive chemical transformation, revealing a total loss of Cd species with concomitant substitution with Cu. Total exchanged- $\text{CdSe}$  NRs and NWs experience also a complete structural transformation from wurtzite to antifluorite crystal structure, preserving the close-packing direction of Se atoms in the structures, namely  $[0001]_{\text{hcp}}$  and  $[111]_{\text{fcc}}$ .

These studies evidence that: a) the shape features of both the nanosized species are basically preserved during the CE reaction, but with CdSe NRs/NWs length decrease; b) in absence of  $\text{Cu}_2\text{Se}$  NCs, CdSe NRs or NWs do not undergo any transformation in the same thermal range; c) the CE reaction occurs also in regions not irradiated by the electron beam, indicating to be a simple thermally driven process; d) the CE reaction likely happens due to a migration of the Cu species expelled from the  $\text{Cu}_2\text{Se}$  NCs on the amorphous substrate irrespective of its chemical nature, until reaching the CdSe NRs or NWs. Finally, we show how by using the in-situ heating approach, it is feasible following a CE process that, when happening in a liquid environment, is so fast that only the ultimate and stable reaction's product can be studied and directly imaged.

## References

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**Figure 1.** Mixture of the  $\text{Cu}_2\text{Se}$  NCs and CdSe NRs: a) at RT, before heating; b) at RT, after heating at  $400^\circ\text{C}$ ; Electron Diffraction patterns of a representative region featuring  $\text{Cu}_2\text{Se}$  NCs and CdSe NRs at RT pre- (c) and post- (d) thermal treatment at  $400^\circ\text{C}$  with superposition of 1D profile of electron diffraction signal, as obtained by integration over the full round angle in the reciprocal space; e) comparison between these integrated linear profiles collected at RT pre- (magenta) and post- (orange) treatment at  $400^\circ\text{C}$ , revealing the phase transformation occurred to the CdSe NRs component of the original mixture. The RT pre-heating electron diffraction profile is indexed as a combination of a cubic  $\text{Cu}_2\text{Se}$  and wurtzite CdSe, while after  $400^\circ\text{C}$  heating only cubic  $\text{Cu}_{2-x}\text{Se}$  phase is found.