

STEM imaging and concomitant EDS mapping of in situ cation-exchange at solid state between diverse nanoparticles populations: how it actually works.

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A cation exchange (CE) reaction occurs whenever a cationic species in a crystalline structure is partially or completely replaced, leaving the anionic lattice unmodified. CE is usually performed as a fast reaction occurring in liquid between inorganic colloidal nanoparticles (NPs) and cationic species, but the liquid environment and the fast reaction kinetics hinder the possibility of directly imaging the process. In the recent past we showed that an *in situ* Transmission Electron Microscopy (TEM)/Scanning TEM (STEM) approach at solid state gives a way to overcome these limitations [1]. In fact, when heated, spherical Cu₂Se NPs having cubic crystalline phase expel free Cu species, forming Cu-vacancies in the cation sublattice with subsequent variations in their stoichiometry (to about Cu_{1.8}Se). Such a thermally-driven expulsion of free Cu species can be exploited to perform *in situ* CE reactions at solid state between the cubic Cu₂Se NPs and CdSe nanowires (NWs) deposited on a common heated substrate, as shown in Figure 1. When reached by the free Cu species, CdSe NWs suffer a pervasive chemical and structural transformation, revealing the substitution of Cd species with Cu. This leads to Cu₂Se constituting the final, completely substituted NWs.

While in the past we showed how this phenomenon occurs at 400°C for starting CdSe NWs with a hexagonal crystalline phase, here we show that it also occurs with a lowered activation temperature of less than 150°C for NWs with a cubic phase. In fact, the activation temperature is higher in the case of CE occurring to hexagonal CdSe NWs, due to the higher energy required to complete the hexagonal-to-cubic phase transition. This means that this temperature, acting as a threshold for CE, is strongly dependent on the crystalline phase of the CdSe acceptor nanostructures. Moreover, further insights were found by studying *via in situ* STEM-Energy Dispersive Spectrometry (EDS) this phenomenon: first, the free copper, before entering the CdSe NWs and then giving rise to the CE reaction, surrounds the wires; second, it moves along the NWs' axis with different speeds in the two opposite directions, as shown in Figure 2. Then, the application of the *in situ* STEM heating approach, combined with the slower kinetics of solid state CE reactions, allows to direct image the transient states leading to the final products of CE, which conversely would be the only observable step in the corresponding CE reactions occurring in liquid state.

Besides, in order to establish insight into the CE reaction mechanism, we have performed *ab initio* molecular dynamics simulations, using the Vienna Ab-initio Simulation Package, developing models for the CdSe NWs with both hexagonal and cubic phase, and taking also into account the possibility that lattice defects are present. Then, these CdSe models are put in contact with Cu to monitor the CE reaction. The differences observed between both the defect-free and defective CdSe NWs are compared to the experimental situation.

References

[1] Casu, A. [...] and Falqui, A. *Cu₂Se and Cu Nanocrystals as Local Sources of Copper in Thermally Activated In Situ Cation Exchange*. ACS Nano **2016**, 10 (2), 2406-2414. DOI: 10.1021/acs.nano.5b07219

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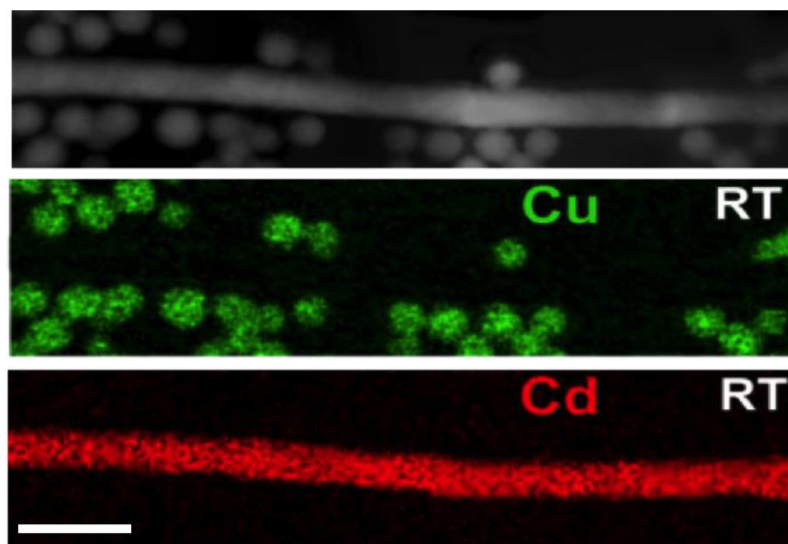


Figure 1. Top panel: low magnification STEM image of a CdSe NW (with cubic crystal phase) with Cu_2Se spherical NPs as deposited at room temperature (RT) on the common silicon nitride substrate that will act as heating plate. Middle panel: corresponding STEM-EDS Cu map. Bottom panel: corresponding STEM-EDS Cd map. Scale bar is 50 nm.

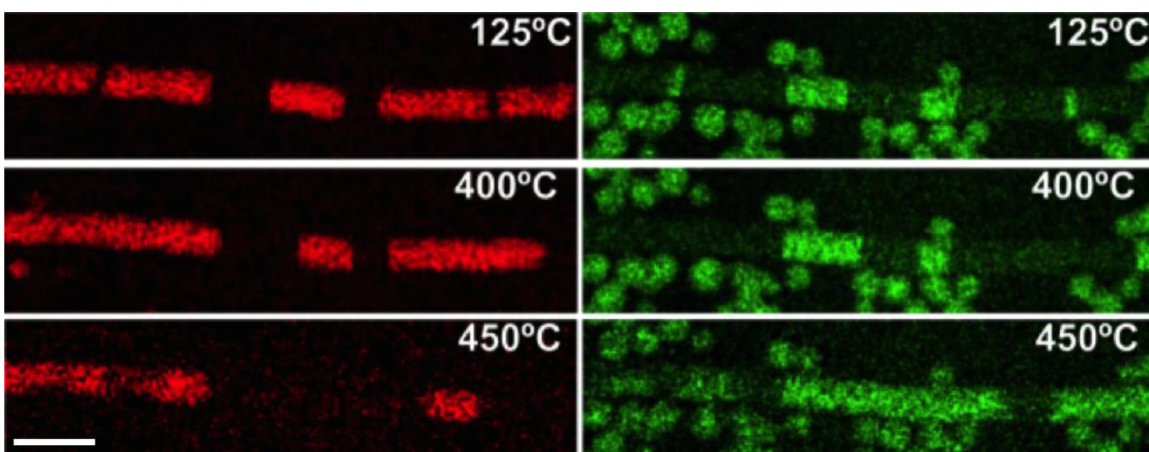


Figure 2. Thermal evolution of Cd (left column) and Cu (right column) distribution when the initial CdSe NW and Cu_2Se NPs are heated at 125°C, 400°C and 450°C, respectively. At 125°C (top panels) a uniform, thin layer of copper surrounds the CdSe NW, where also some CdSe has been transformed into Cu_2Se domains. At 400°C (middle panels) the largest domain of Cu_2Se has grown following a preferential direction, from left to right, while the smallest ones have been transformed back into CdSe. At 425°C (bottom panels) most of the initial wire has been transformed into Cu_2Se , still indicating the same preferential growth direction followed by its domains. Scale bar is 50 nm.