Type of presentation: Poster

MS-1-P-1856 Covellite nanocrystals and their evolution by addition of metals atoms: HRTEM and Exit Wave study

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Copper sulphides ($Cu_{2-x}S$) and related nanocrystals are promising candidates in optoelectronics device, due to their intrinsic p-type doping and tunability of their band-gap with stoichiometry.
In particular, the covellite structure (CuS) has one third of the Cu atoms in triangular coordination and two thirds of Cu atoms in tetrahedral coordination. At the same time, two thirds of S atoms form disulfide groups and one third are single sulfide ions.(1) At the tetrahedral sites, the Cu atoms are bound to the S atoms of the disulfide bonds. These different sites can be resolved in HRTEM (here we use negative C_3 imaging conditions) or Exit Wave reconstructions (EWR) from side views (as [100] or [210] orientations) of $Cu_{1.1}S$ nanocrystals (see Figure 1). Indeed, at opportune values of defocus ΔZ, the S-S disulfide layers connected appear bright in the image, permitting to directly visualize them.
Our group demonstrated how the evolution from $Cu_{1.1}S$ (covellite type) to Cu_2S (chalcocite) was accompanied by the red-shifting of the localized surface plasmon resonance (LSPR) generated by free holes generated in the valence band (and with a dominant in-plane mode).(2) The resonance gradually disappears as the Cu_2S stoichiometry is reached (*i.e.* no copper deficiencies left). These states seem then to be linked to the disulfide bonds present of the CuS covellite structure (see Figure 1). In general, we expect by adding M^{x+} atoms, the following transformation:

$Cu_{1.1}S + \gamma M^{x+} + \gamma e^- \rightarrow Cu_{1.1}M_\gamma S$,

in which S(-1) is reduced to S(-2), possibly by breaking the S-S bonds, and the metal keeps its (x+) oxidation state. In this presentation we focus on Pd(II) doped CuS nanocrystals synthesized by chemical methods. Pd is added by using Palladium(II)-acetylacetonate plus ascorbic acid. We see how by increasing the amount of Pd atoms, the CuS structure is progressively lost, as the number of disulfide layers is gradually reduced, as can be seen from the HRTEM images (see Figure 2). Consequently, the density of holes in the valence band is lowered and the plasmon resonance is consequently red-shifted and reduced.
This is indeed a demonstration of the tunability of the LSPR with the amount of metal atoms in Covellite type nanocrystals.

[1] Pattrick R.A.D. *et al.* Geochim. Cosmochim. Acta, 1997, 61 (10), pp. 2023–2036
[2] Xie Y. *et al.* J. Am. Chem. Soc., 2013, 135 (46), pp. 17630–17637

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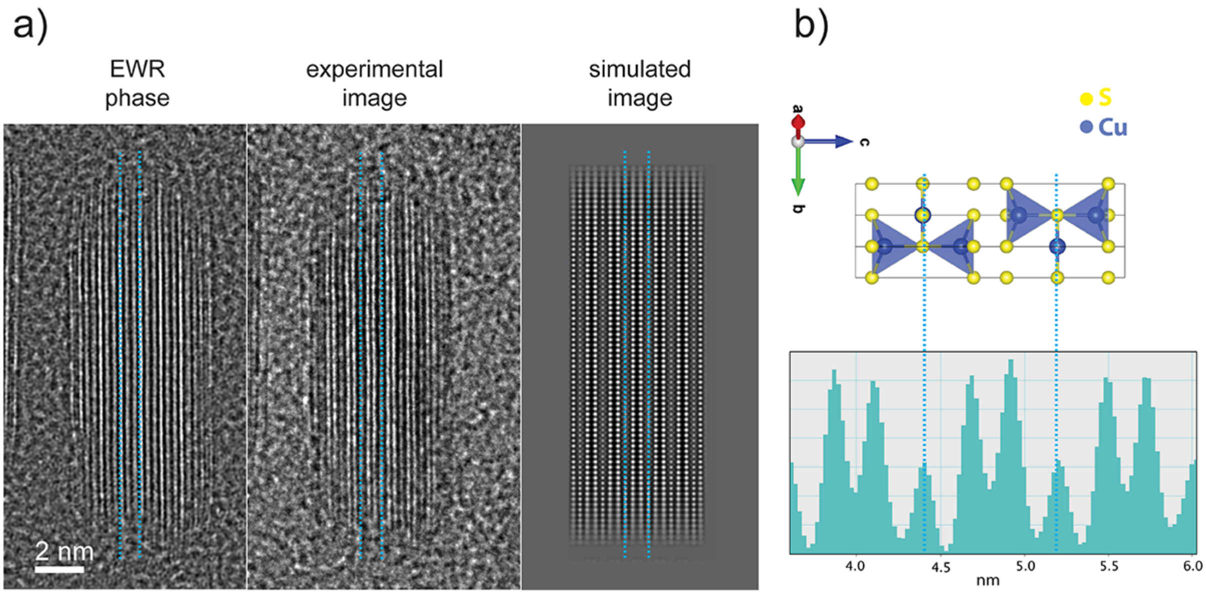

Fig. 1: a) EWR phase together with the experimental image (ΔZ = -34 nm, C_3 = -26 um) and the simulated image from [210] side view of a CuS nanodisk. At about -30/+20 nm defocus the intensity is transferred to the planes with Cu-S in tetrahedral coordination, giving a direct visualization of S disulfur planes (see the intensity profile in b).

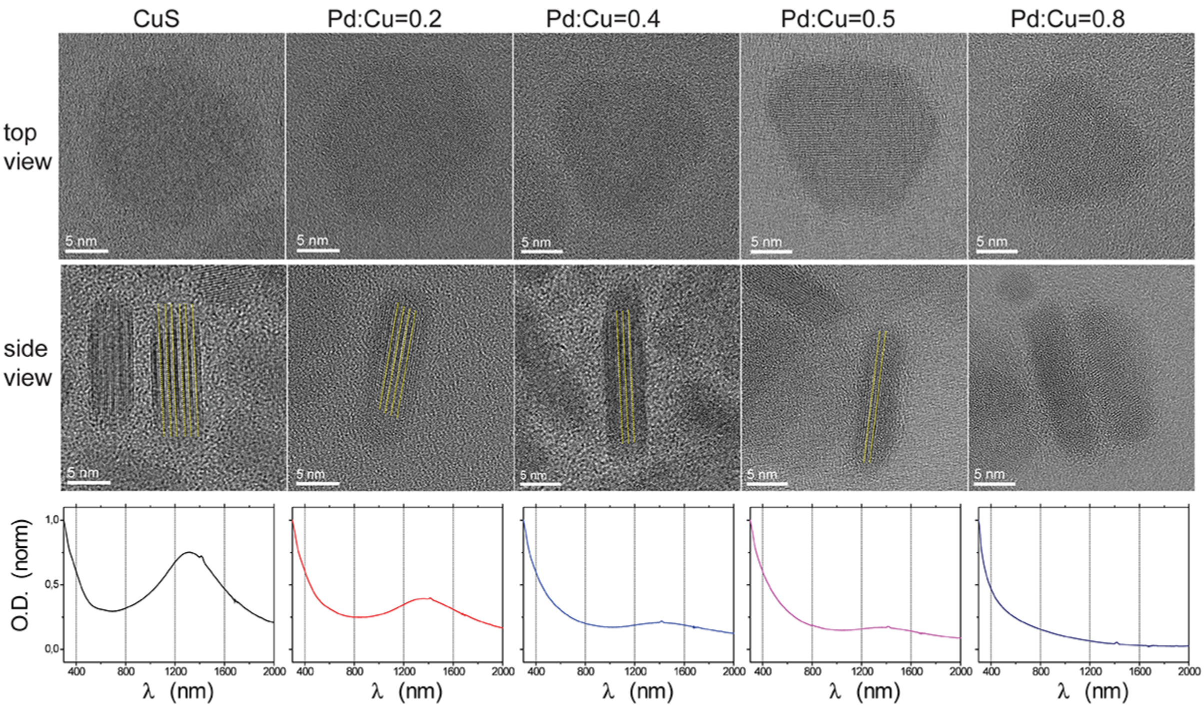

Fig. 2: The nanocrystals maintain their hexagonal shape while adding Pd metal atoms. However, the number of S-S layers is progressively reduced as Pd increases, as well as the LSPR is reduced in intensity and red shifted.