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Colloidal $Cu_{2-x}(S_ySe_{1-y})$ Alloy Nanocrystals with Controllable Crystal Phase: Synthesis, Plasmonic Properties, Cation Exchange and Electrochemical Lithiation

Enrico Dilena[a§], Dirk Dorfs[a,b§], Chandramohan George[a§], Karol Miszta[a], Mauro Povia[a], Alessandro Genovese[a], Alberto Casu[a], Mirko Prato[a] and Liberato Manna[a]*

[a] *Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy, tel. +39 010 71781502; Email: liberato.manna@iit.it*
[b] *Institut für Physikalische Chemie und Elektrochemie, Leibniz Universität Hannover, 30167 Hannover, Germany*
[§] These people contributed equally to this work.

Corresponding Author
* liberato.manna@iit.it

Supporting Information

TEM analyses

Cu-based NCs. NCs structural data, obtained from HRTEM observations, exhibited lattice cells compatible with cubic and hexagonal symmetries according the synthesis route. Cubic NCs displayed berzelianite-like structure, as confirmed from d-spacing measurements and angular relationships of lattice sets in direct space and from vector and angular relationship of diffraction spots in Fourier space (Figure 1a). For what concern the NCs with hexagonal symmetry both the lattice sets d-spacing measurements carried out in the direct space and the vector and angular relationships of diffraction spots carried out in the Fourier space exhibited chalcocite-like structure (Figure 1b).

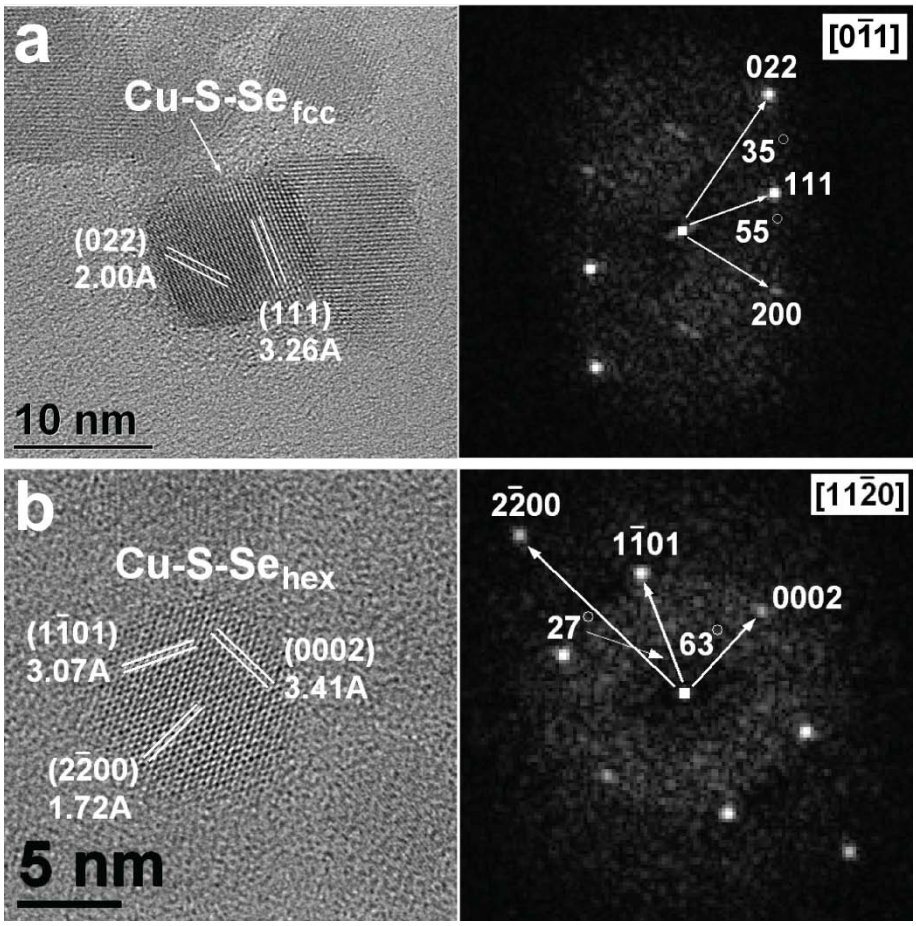

Figure S1. *a) HRTEM image cubic Cu-based NC showing the (022) and (111) lattice sets with measured d-spacings of 2.00Å and 3.26Å, respectively and its corresponding 2D-FT pattern consistent with a fcc diffraction pattern along [0 1 -1] zone axis. b) HRTEM image of hexagonal Cu-based NC displaying the (1-101), (0002) and (2-200) lattice sets with d-spacing of 3.07Å, 3.41Å and 1.72Å, respectively; the corresponding 2D-FT pattern is consistent with the [11-20] zone axis of chalcocite-like structure where the [2-200]^[1-101] angle is 27° and [1-101]^[0002] is 63°.*

Cd-based NCs. The total Cd-exchanged NCs exhibited the same symmetry of the corresponding pristine Cu-based NCs, i.e. cubic and hexagonal. Figure 2a,b report two reference NCs deriving from the cubic and hexagonal Cu-based NCs respectively. Also here, the measurements of lattice sets d-spacing in the direct space and the vector and angular relationships of diffraction spots in the Fourier space, display berzelianite-like and chalcocite-like structures for cubic and hexagonal Cd-based alloys, respectively.

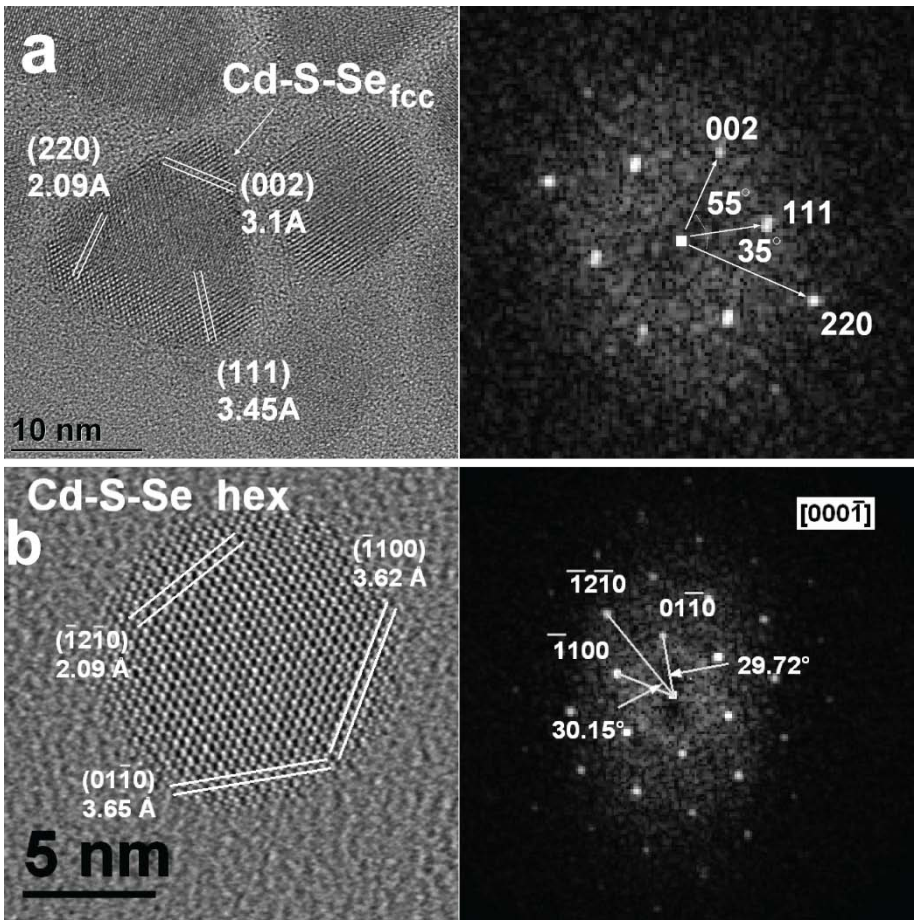

Figure S2. *a) HRTEM image of cubic Cd-exchanged NC showing the (220), (002) and (111) lattice sets with measured d-spacings of 2.09Å, 3.1Å and 3.45Å, respectively and its corresponding 2D FT consistent with a fcc diffraction in the [-1 1 0] zone axis. b) HRTEM image of hexagonal Cd-exchanged NC showing the (-12-10), (-1100) and (01-10) lattice sets with measured d-spacing of 2.09Å, 3.62Å and 3.65Å respectively; the corresponding 2D-FT pattern is comapatible with a [000-1] zone axis projection of a chalcocite-like structure where the [01-10]^[-12-10] and [-1100]^[-12-10] experimental angles are very closed to 30°.*

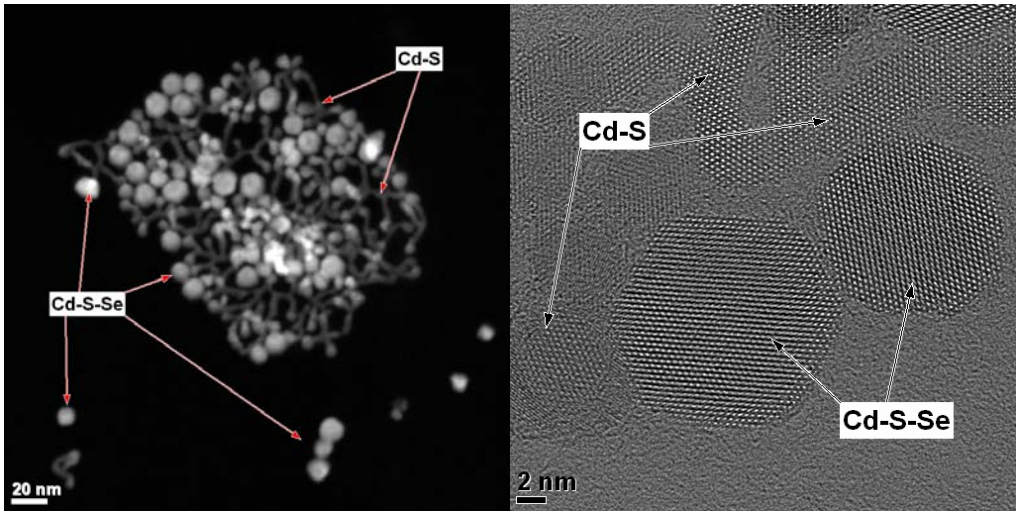

Figure S3. *(a-b)HAADF-TEM and HRTEM of hexagonal $Cd(S_ySe_{1-y})$ NCs showing two phases : worm-like CdS NCs and spherical-like $Cd(S_ySe_{1-y})$ alloyed NCs.*

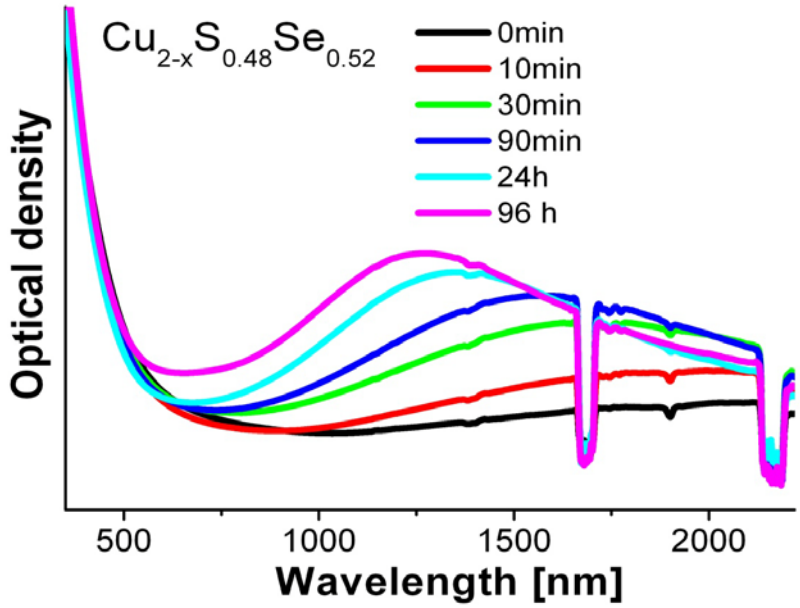

Figure S4. *Plasmon peaks upon oxidation over the period of four days in toluene of the hexagonal $Cu_{2-x}S_{0.48}Se_{0.52}$ alloy nanocrystals.*

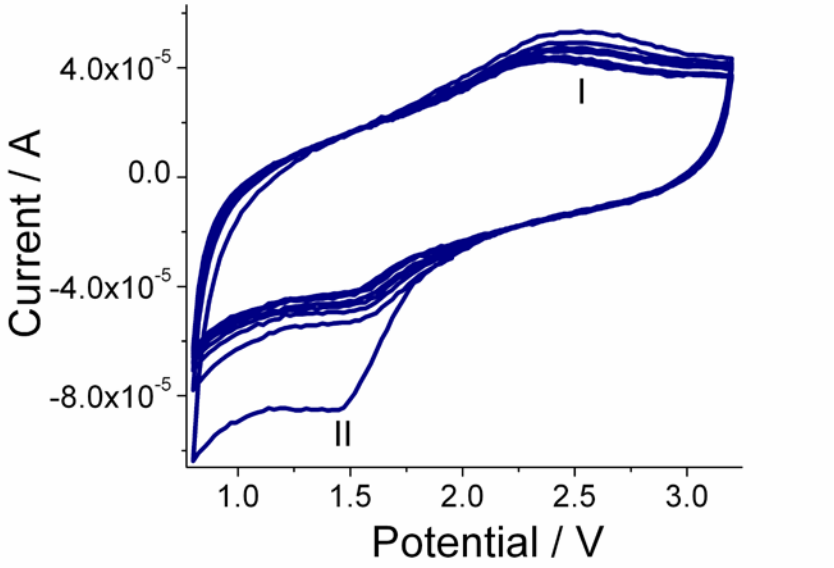

Figure S5. *a) CV cycles of $Cu_{2-x}(S_ySe_{1-y})$ ($S_{0.5}$:$Se_{0.5}$) nanocrystal electrodes at 5 mV/S VS Li*

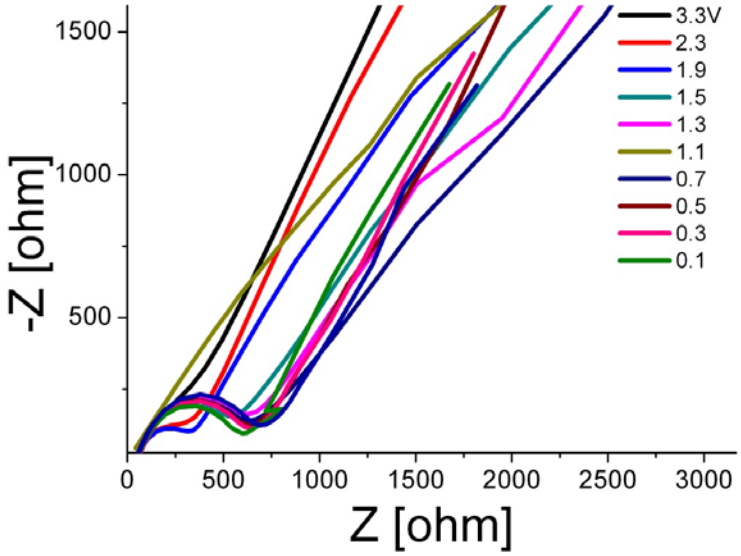

Figure S6. *a) EIS spectra of $Cu_{2-x}(S_ySe_{1-y})$ ($S_{0.5}$:$Se_{0.5}$) depicting the lithitaion process from later cycles.*

Additional References

(1) Fultz, B.; Howe, J. M. *Transmission electron microscopy and diffractometry of materials,2nd ed.* ; Springer-Verlag: Berlin Heidelberg, 2002.

(2) Egerton, R. F. *Electron energy loss spectroscopy in the electron microscope, 2nd edition*; Plenum Press: New York, 1996.