Supporting Information for

Cation exchange synthesis and optoelectronic properties of type II CdTe-Cu_{2-x}Te nano-heterostructures

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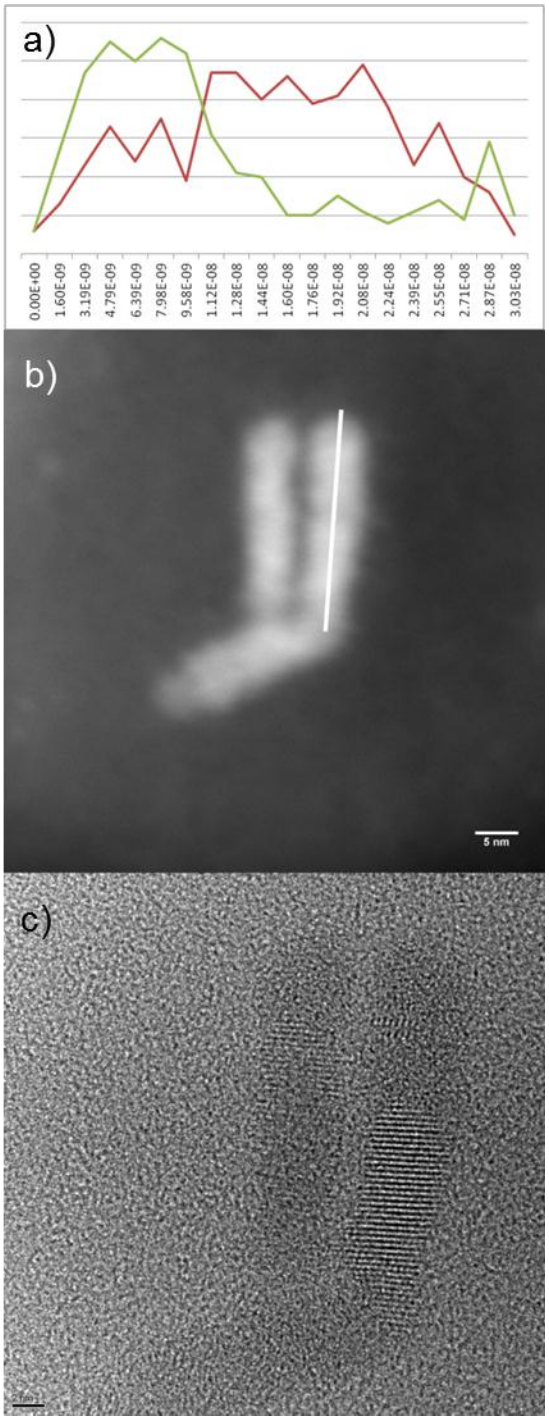

Fig. S1 a) EDX spectrum (red: Cd, green: Cu) of the CdTe-$Cu_{2-x}Te$ nanorod whose STEM image is shown in (b). The EDX spectrum of the nanorod in (b) is obtained along the indicated white line, from top to bottom. c) HRTEM image of the same nanorod. Here it is clearly visible the degradation of the $Cu_{2-x}Te$ sub-unit, namely the transformation from crystalline into amorphous, upon electron beam exposure.

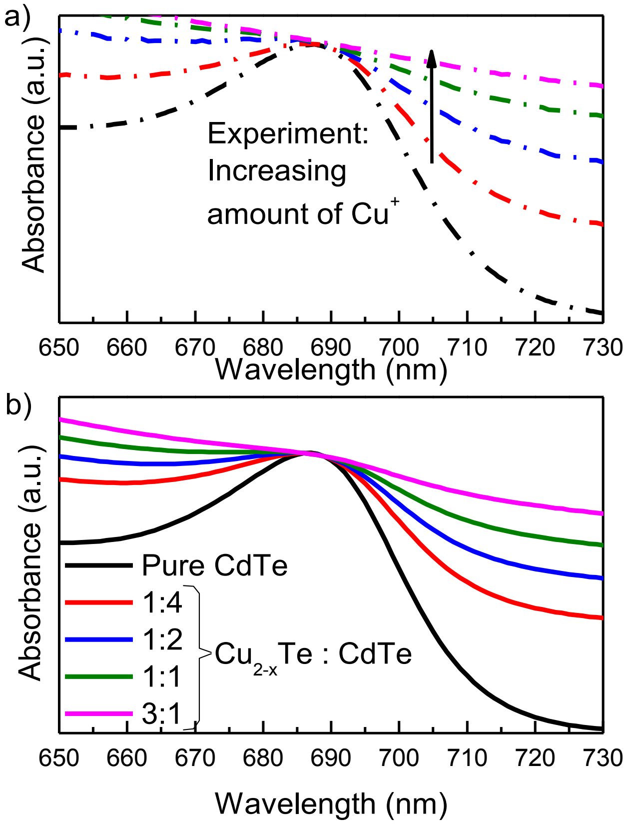

Fig. S2 Broadening of the excitonic peak as observed in the experiment with increasing the fraction of Cu$_{2\text{-}x}$Te in the CdTe-Cu$_{2\text{-}x}$Te heterostructures (a), and through the linear combination of the absorption spectra of the pure CdTe and Cu$_{2\text{-}x}$Te nanorods in different Cu$_{2\text{-}x}$Te:CdTe ratios (1:4, 1:2, 1:1, 3:1) (b). All spectra are normalized to the exciton peak.

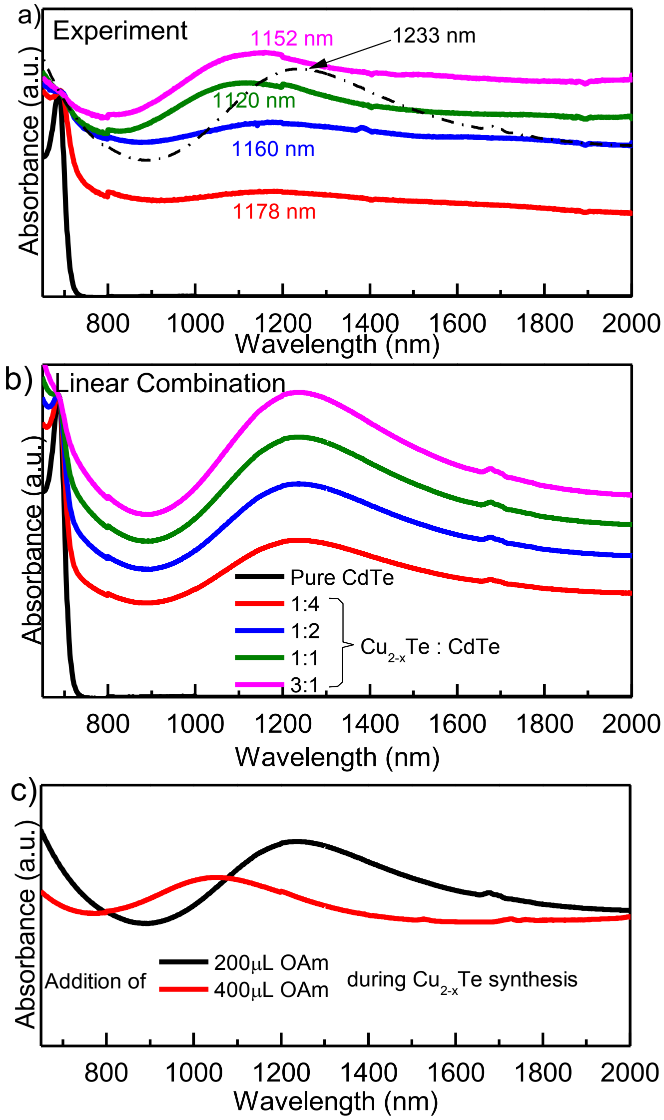

Fig. S3 a) Experimental spectra of pure $Cu_{2-x}Te$ and CdTe-$Cu_{2-x}Te$ NRs normalized to the exciton peak. The spectra show the region of the localized surface plasmon resonance (LSPR). In the heterostructures (red, blue, green and pink curves, with increasing the volume of Cu^+ added in the same order) the NIR plasmon resonances remain at a "relatively similar" position. However, the plasmon resonance in the completely exchanged sample ($Cu_{2-x}Te$ NRs, black curve) is significantly more red-shifted (1233 nm). b) Linear combination of the experimental absorption spectra of the pure CdTe and $Cu_{2-x}Te$ nanorods with different ratios. In all cases the plasmon resonance stays at a constant position. c) Effect of surface ligands on the position of the plasmon resonance in completely exchanged $Cu_{2-x}Te$ nanorods. The blue shifted NIR resonance in $Cu_{2-x}Te$ (red curve *vs.* black curve) may result from an increased ligand (oleylamine, OAm) addition (400 μL *vs.* 200 μL, respectively). In both cases OAm was added during the cation exchange process to preserve colloidal stability (see Experimental section in the manuscript for details). The observed blue-shift is in agreement with recent works, where a blue-shift in the LSPR has been observed for $Cu_{2-x}S$ NCs upon ligand exchange with OAm, and explained by the replacement of coordinated carboxyl groups on the NCs' surface by OAm, leading to a reduction in the NCs' carrier density and thus, to an LSPR red-shift. [1] In line with this argumentation, in our case it can be that in the sample where the lowest amount of OAm was added (black curve in Fig. S2c), the replacement of surface-grafted ligands[a] was incomplete, or at least less complete than in the sample with the highest amount of OAm added (red curve in Fig. S2c). This partial ligand replacement could result in a mixture of OAm and the ligands originally present on the CdTe NRs' surface that may give rise to a lower carrier density in the NCs, and thus, to a more red-shifted LSPR (black curve) when compared to the likely better ligand-exchanged sample (red curve).

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[a] Note that, among other ligands we also employed n-tetradecylphosphonic acid (TDPA, a carboxylic acid, see Experimental section) for the synthesis of the CdTe NRs. Thus, it could be that some TDPA molecules stabilize the CdTe NRs' surface as well, and thus could play a role here.

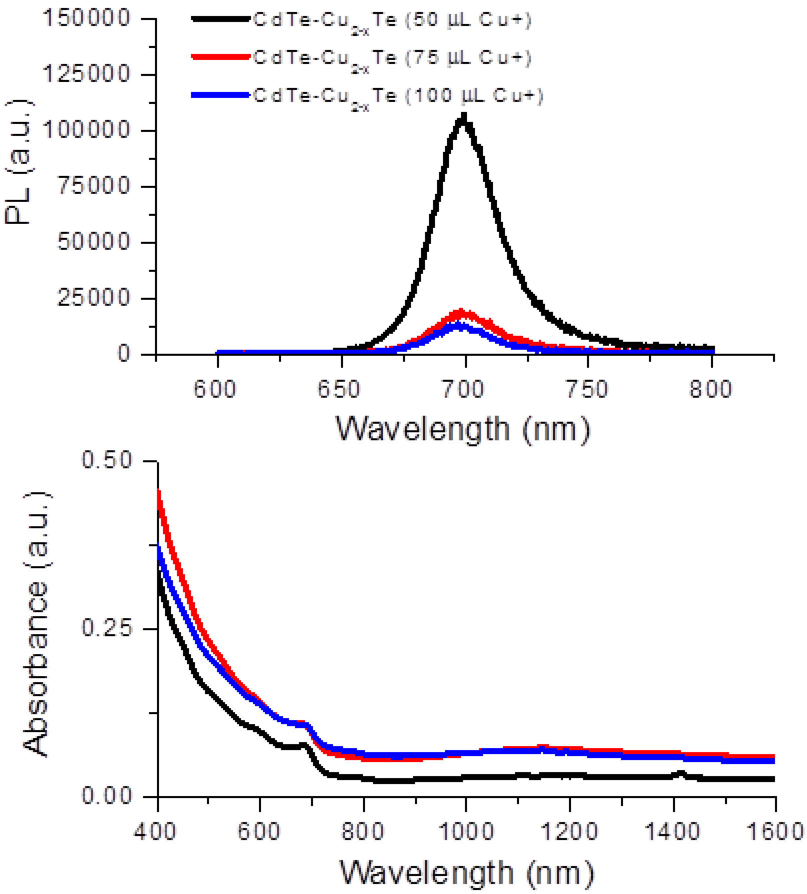

Fig. S4 Top: photoluminescence spectra of three CdTe-Cu$_{2-x}$Te NRs prepared by cation exchange upon addition of increasing amounts of Cu$^+$ from black to blue, as indicated in the labels. There is a significant quenching and blue-shift of the PL maximum with increasing the amount of Cu$^+$. These optical changes may be due to the formation of the Cu$_{2-x}$Te sub-units, but also to an altered surface chemistry of the NRs upon cation exchange. Bottom: corresponding absorption spectra of the CdTe-Cu$_{2-x}$Te NRs whose PL spectra are shown in the top panel.

References

[1] Liu, X., et al., *Size-Controlled Synthesis of Cu$_{2-x}$E (E = S, Se) Nanocrystals with Strong Tunable Near-Infrared Localized Surface Plasmon Resonance and High Conductivity in Thin Films*. Advanced Functional Materials, 2013. **23**(10): p. 1256-1264.