

Role of Surface Reduction in the Formation of Traps in n -Doped II–VI Semiconductor Nanocrystals: How to Charge without Reducing the Surface

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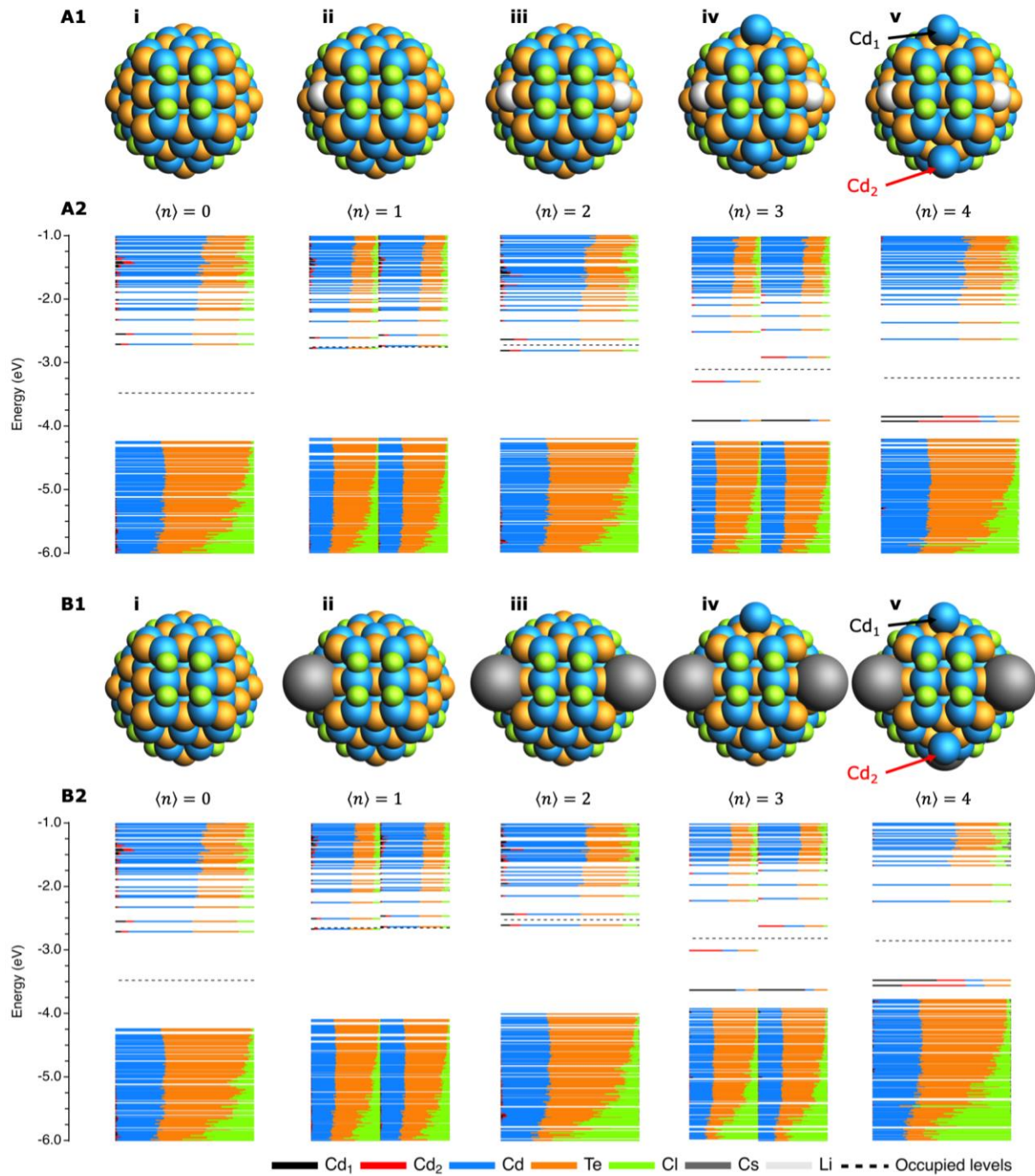


Figure S1. The effect of charging fully passivated CdTe nanocrystals (NCs) on their structure and density of states (DOS), using (A) Li^+ and (B) Cs^+ as counterion. (A1) and (B1) Structure of the NCs when respectively 0, 1, 2, 3 and 4 electrons are injected. The total system is kept neutral by the addition of (A1) a lithium or (B1) a cesium cation for each added electron. (A2) and (B2) DOS

for each of the NCs, where every line corresponds to a molecular orbital (MO). The length of a colored line segment indicates the contribution of the corresponding atom or element to that MO. MOs above the dotted line are empty, whereas the ones below are occupied. In this and the ensuing figures, if the total number of electrons is odd ($n = 1, 3$), the spin-up and spin-down orbitals are plotted separately on the left- and right-hand side of the graph. Each MO is then occupied by a single electron.

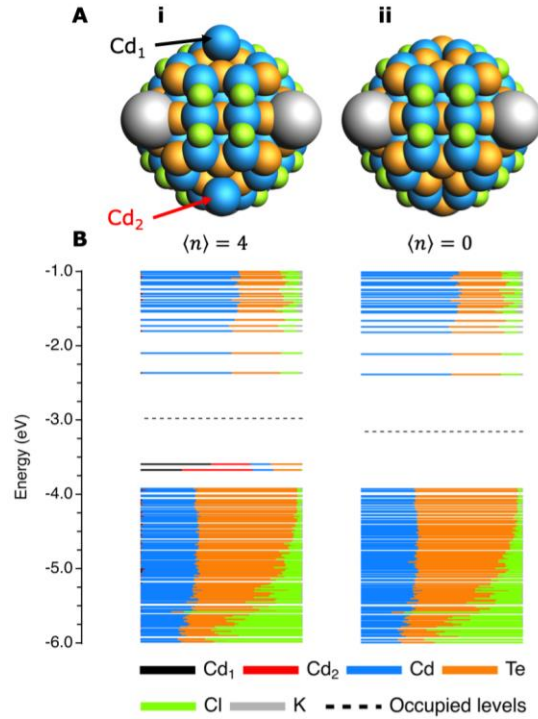


Figure S2. The effect of removing the Cd^0 atoms from a charged NC on its structure and DOS. (A) Structure of the NCs. i) The NC is charged with four electrons, which is compensated by the presence of four potassium cations. As also shown in Figure 1-v in the main text, Cd_1 and Cd_2 are reduced to Cd^0 and ejected from the lattice. ii) The Cd^0 sites (Cd_1 and Cd_2) are removed from the structure. (B) DOS of the two NCs. The DOS in i) shows two in-gap levels that are highly localized on Cd_1 and Cd_2 . Removal of these two Cd^0 atoms in ii) also removes the related trap states.

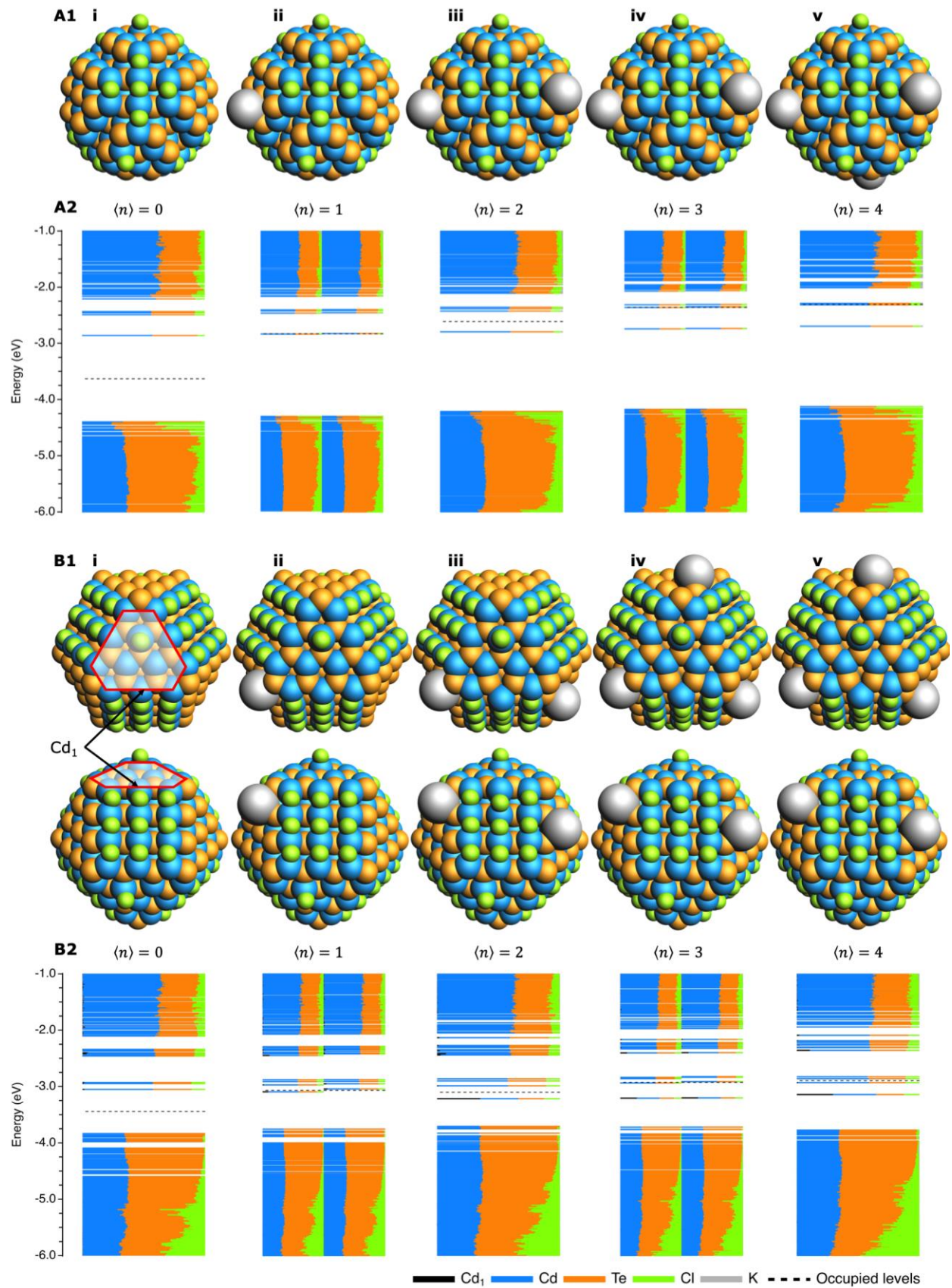


Figure S3. The effect of charging larger fully passivated NCs of different sizes. (A1) Structure and (A2) DOS of $\text{Cd}_{152}\text{Te}_{135}\text{Cl}_{34}$ NCs when respectively 0, 1, 2, 3 and 4 electrons are injected. Note that the NCs are stable under these conditions and that no trap states are formed. (B1) Structure of $\text{Cd}_{176}\text{Te}_{147}\text{Cl}_{58}$ NCs when 0 to 4 electrons are injected. The top row shows the top-view of the (111) facet indicated in the lower row. Note that here, charging leads to the expulsion of Cd_1 from the (111) plane. (B2) DOS for each of the NCs. In all cases, the total system is kept neutral by the addition of a potassium cation for each added electron.

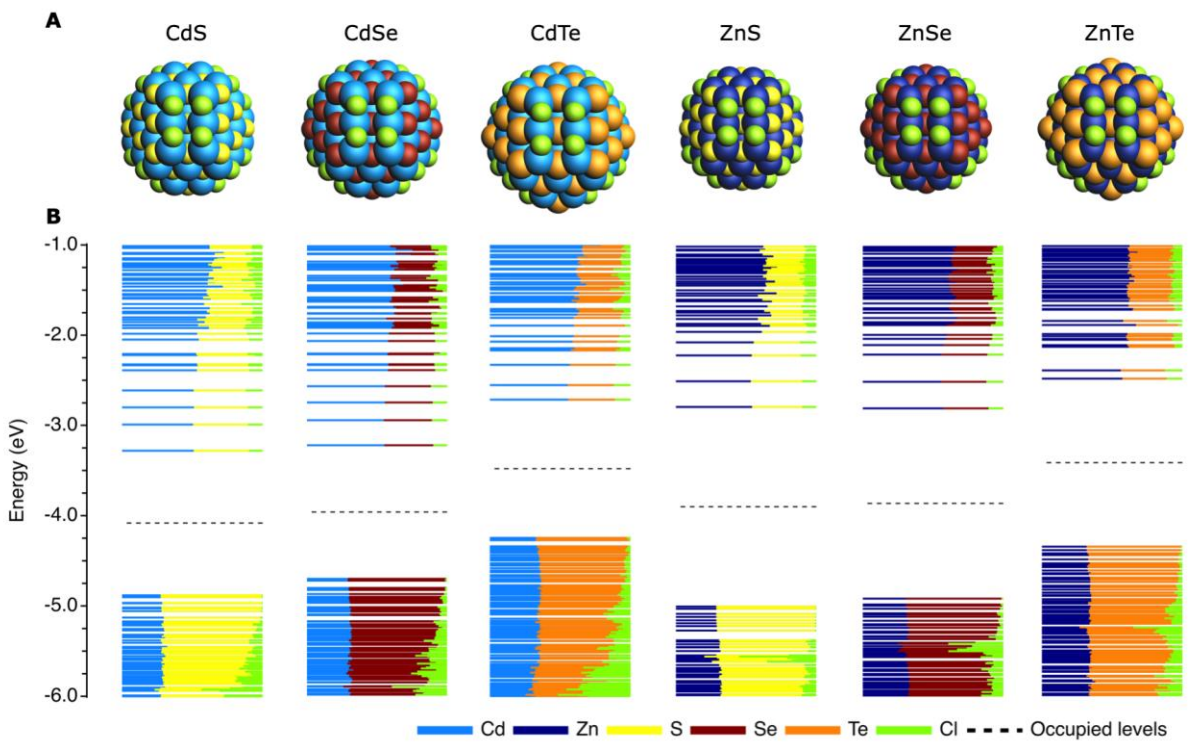


Figure S4. The structure and DOS of different fully passivated neutral $M_{68}X_{55}Cl_{26}$ ($M = Cd, Zn$; $X = S, Se, Te$) zincblende NCs. (A) Structure and (B) DOS of the NCs.

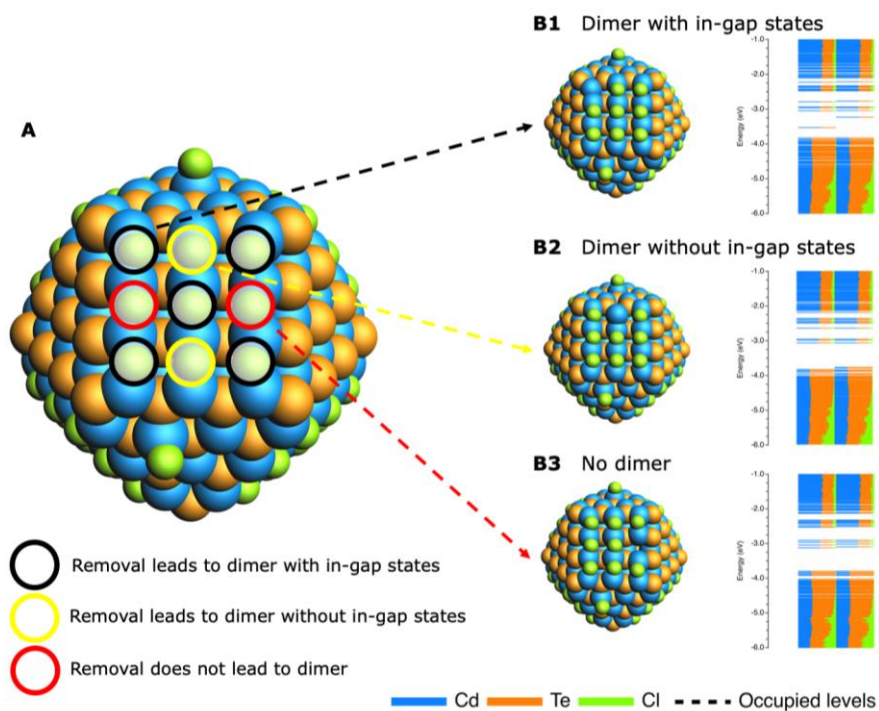


Figure S5. The effect of charging with one electron when a chloride (Cl^-) has been removed from different sites on the (100) plane of a larger CdTe NC on its structure and DOS. Note that this is isoelectric with removing a chlorine, Cl^0 . (A) Structure of the NC and the different chlorine atoms that have been removed. A black circle indicates that removal of the chlorine leads to Cd-Cd dimerization and trap-formation. Yellow circles indicate that removing the chlorine leads to the formation of a dimer, but that no new state in the bandgap is formed. Removal of the chlorine atoms that are circled in red does not lead to a dimer. (B1-3) gives the structure and DOS of the NCs in these respective cases and shows the heterogeneity of the sites on the (100) facet. The DOS of the perfectly passivated NC can be seen in **Figure S3B2-i**.

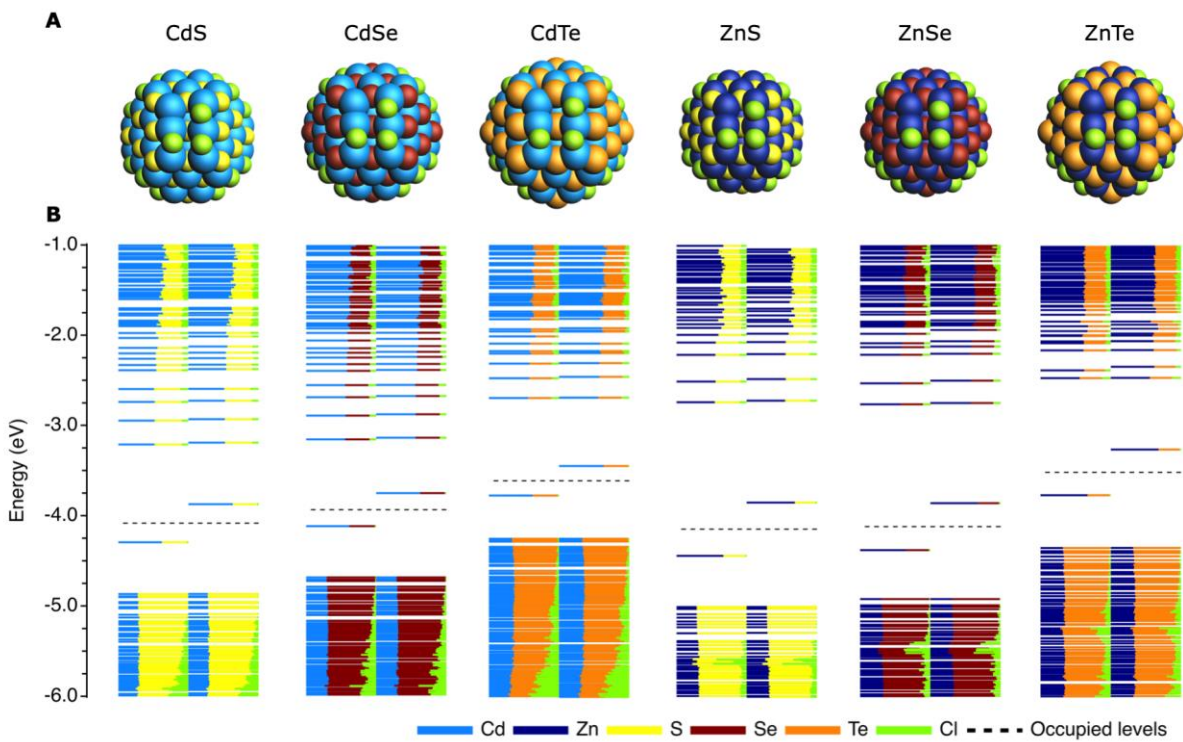


Figure S6. The effect of charging different $M_{68}X_{55}Cl_{26}$ ($M = Cd, Zn$; $X = S, Se, Te$) zincblende NCs with one electron, when a chloride (Cl^-) has been removed from the (100) surface. (A) Structure and (B) DOS of the NCs. The perfectly passivated NCs were already shown in **Figure S4**.