Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting Information for: Inverse-designed semiconductor nanocatalysts for targeted CO_2 reduction in water

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Tetrapod geometry

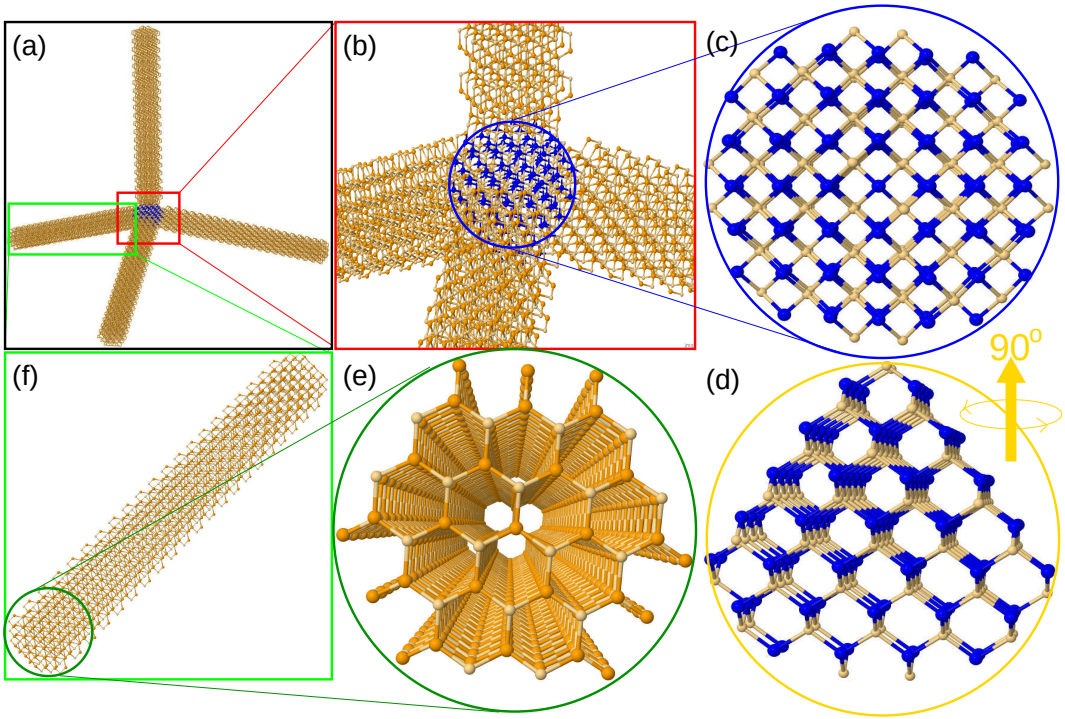

Figure S 1: Our CdTe/CdSe core/arm tetrapods (a) have a central zinc blende tetrahedral core with four (111) facets made of CdTe, (b)-(d), from which four wurtzite CdSe rod-like arms protrude, (e)-(f).

Band alignments: the CdTe/CdSe tetrapod and its constituent CdTe core and CdSe arms

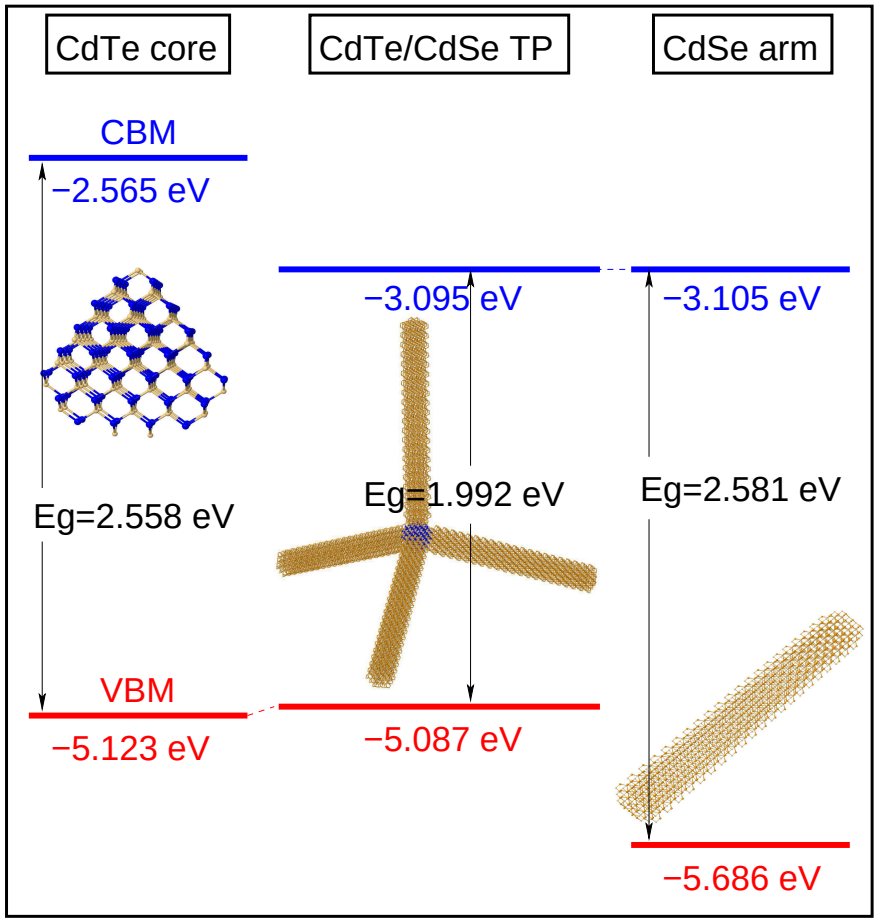

Figure S 2: Valence and conduction band edge energies, calculated with respect to vacuum, for a CdTe core (left), a CdTe/CdSe core/arms TP (centre), and a CdSe arm (right), with $D = 2.1$ nm and $L = 14$ nm, showing the origin of the TP's band edges to be the core (for the VBM) and the arm (for the CBM). [The slight difference in the position of the VBM in core and TP is due to the fact that, in the latter, the confinement provided by the CdSe arms is weaker than that provided by the capping groups in the core only case]. As a consequence, the band gap in type II heterostructures can be smaller than that of both core and arm.

Energy separation in the conduction band of CdTe/CdSe tetrapods

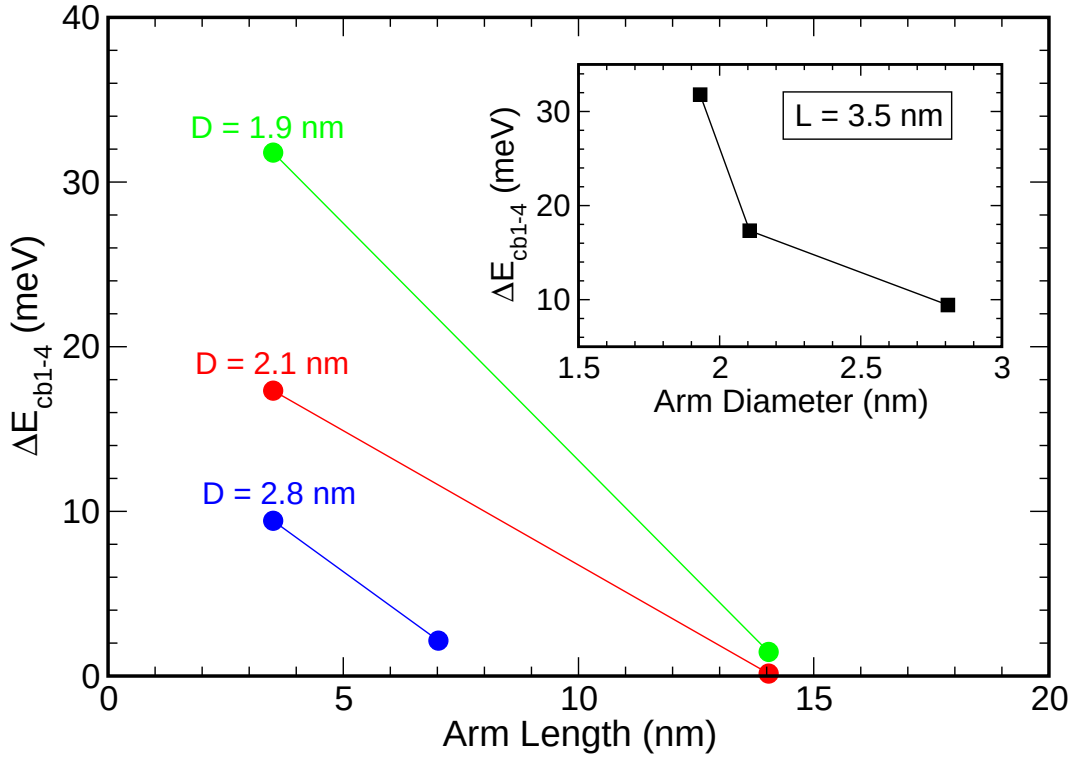

Figure S 3: Energy separation $\Delta E_{\mathrm{cb}_{1-4}}$ between the first (cb_1 = CBM) and the fourth (cb_4 = CBM+3) electron state as a function of TP size: arm length L, for different values of the diameter $D = 1.9$ nm (green symbols), 2.1 nm (red symbols) and 2.8 nm (blue symbols) - mainframe; arm diameter D, for $L = 3.5$ nm (black symbols) - inset.

Auger Recombination: Schematics

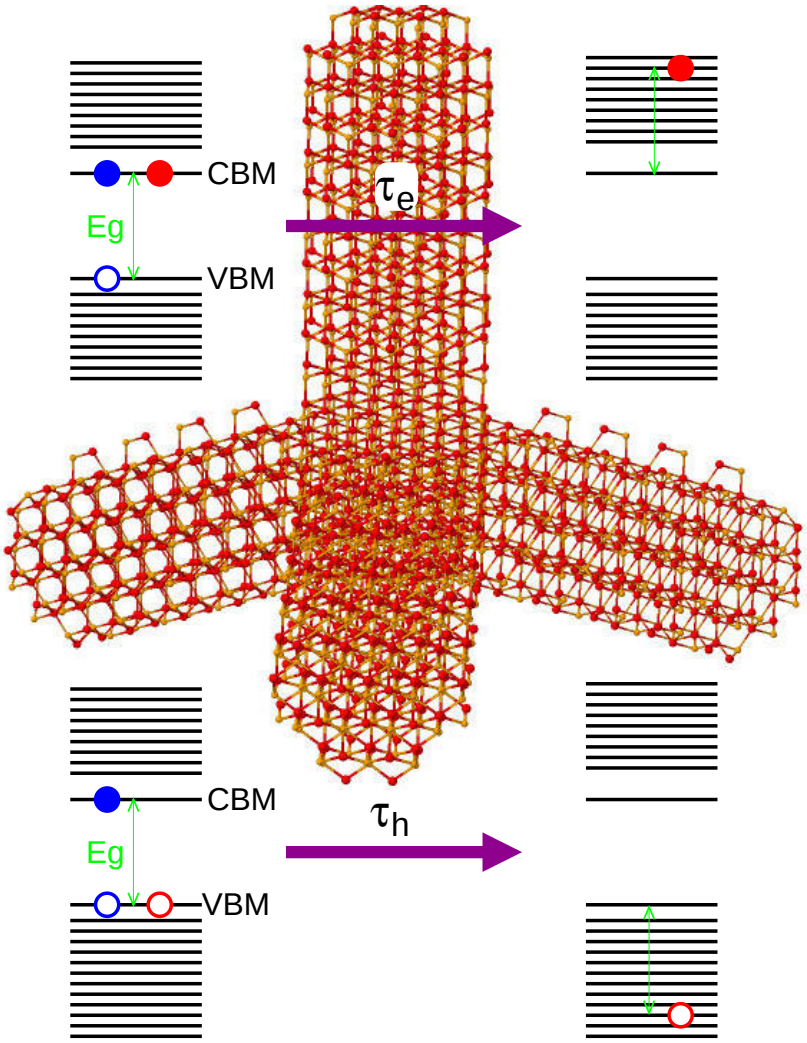

Figure S 4: Schematics of the Auger Recombination processes in the presence of an excess electron (top panels) or an excess hole (bottom panels).[1]

Auger Recombination: comparison of the lifetimes calculated using two different approaches for the screening

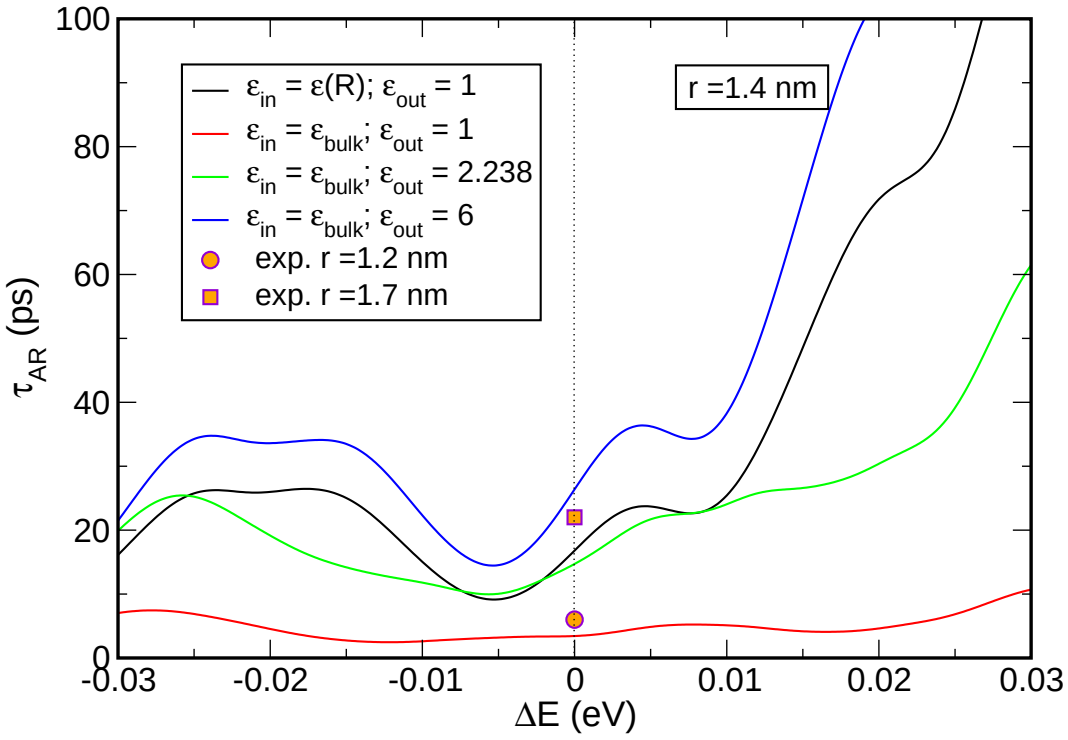

Figure S 5: Comparison of the Auger Recombination lifetimes calculated, as a function of the energy variation around the calculated single-particle gap (corresponding to $\Delta E = 0$), in a CdSe spherical nanocrystal with $r = 1.4$ nm, using the 'regional screening' approach of Wang *et al.*[1] (coloured lines), and the 'size-dependent screening' approach of Franceschetti *et al.*[2] (black line). Experimental data relative to CdSe spherical dots with $r = 1.2$ nm (circle) and $r = 1.7$ nm are also included for comparison. In the 'regional screening' approach the dielectric constant inside the dot (ϵ_{in}) is assumed equal to the bulk dielectric constant. The variation to the external dielectric constant ϵ_{out} occurs via a smoothly decaying sine-like function.[1] The 'size-dependent screening' approach assumes ϵ_{in} to be size- and position-dependent[2] and $\epsilon_{out} = 1$.

References

(1) Wang, L.-W.; Califano, M.; Zunger, A.; Franceschetti, A. Pseudopotential Theory of Auger Processes in CdSe Quantum Dots. *Phys. Rev. Lett.* **2003** *91*, 056404.

(2) Franceschetti, A.; Fu, H.; Wang, L.-W. & Zunger, A. Many-body pseudopotential theory of excitons in InP and CdSe quantum dots. *Phys. Rev. B* **1999**, *60*, 1819-1829.