Electronic Supplementary Information

Atomic Models for Anionic Ligand Passivation of Cation-Rich Surfaces of IV-VI, II-VI, and III-V Colloidal Quantum Dots

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Computational Details

All first-principles density functional theory (DFT) calculations were carried out using all-electron-like projector-augmented wave (PAW) potentials and Perdew-Burke-Ernzerhof (PBE) exchange correlation functional, as implemented in Vienna Ab-Initio Simulation Package (VASP).¹⁻⁴ For a plane-wave basis set, we employed a kinetic energy cutoff of 400 eV. Our pseudopotentials have the following valence electron configurations: Pb: $6s^26p^2$, S: $3s^23p^4$, Cd: $4d^{10}5s^2$, Se: $4s^24p^4$, In: $4d^{10}5s^25p^1$, As: $4s^24p^3$. All atomic forces and electronic energies were fully relaxed to less than 0.020 eV/Å and 10⁻⁵ eV, respectively. Surfaces were simulated in surface slab models with a vacuum separation of ~15 Å. Nonpolar surface slabs have the same atomic structure for front and back surfaces, but polar surface with pseudohydrogen passivation. For the rock-salt PbS (111) surface, we can construct a symmetric slab, but for zinc-blende polar surfaces, we have to use an asymmetric slab with the back-surface passivation.

To quantify a thermodynamic trend of the ligand-surface coordination, we calculated a surface stabilization energy, which represents how much a given surface could be stabilized by ligand coordination. If we know an absolute surface energy of bare surfaces, adding the stabilization energy to the bare surface energy will give the surface formation energy for ligand-coordinated surfaces. For the anion-passivated PbS (111) surface, the surface stabilization energy can be defined as

 $E_{\text{stabilization}} = [E(PbL_2) + E(\text{surface}) - E(PbL_2/\text{surface})] / A$,

where E is DFT total energy, L is anion, and A is surface area. For acetate-passivated CdSe and InAs polar surfaces, the surface stabilization energy can be defined as

 $E_{\text{stabilization}} = [nE(AA-H) + E(\text{surface}) - E(nAA/\text{surface}) - (n/2)E(H_2)] / A$,

where AA is acetate, AA-H is acetic acid, and n represents the number of acetates participating the anion-passivation. For amine-halide co-passivation, we defined the surface stabilization energy as

 $E_{\text{stabilization}} = [(n/2)E(\text{Cl}_2) + mE(\text{MA}) + E(\text{surface}) - E(n\text{Cl}/m\text{MA/surface})] / A$,

where *n* and *m* represents the number of chlorides (Cl) and methylamine (MA) groups in the simulation cell, respectively. The reference states for AA-H, H_2 , Cl_2 and MA are all used for free gas molecule.



Fig. S1 (top) Top views of ball-and-stick models for bare (a) (100) and (b) (110) surfaces of PbS CQD, and side views of ball-and-stick models for bare (110) surfaces of (c) CdSe and (d) InAs CQDs. (bottom) Electronic band structures of respective non-polar surfaces showing a clear band gap opening due to the self-passivation effect. The coordinates of high symmetry **k**-points are $X=(0,\frac{1}{2})$, $\Gamma=(0,0)$, and $M=(\frac{1}{2},\frac{1}{2})$ for PbS b(100) surface; $Y=(0,\frac{1}{2})$, $\Gamma=(0,0)$, $X=(\frac{1}{2},0)$, and $S=(\frac{1}{2},\frac{1}{2})$ for PbS b(110), CdSe b(110) and InAs b(110) surface. The zero energy indicates the Fermi level. (surface Pb, black; Pb, grey; S, yellow; surface Cd, brown; Cd, orange; Se, pale yellow; Surface In, dark green; In, pale green; As, pink).



Fig. S2 (top) Top views of ball-and-stick models for (a) acetate-passivated (*lp*) (100) (1x1), (b) self-passivated (*sp*) (100) (2x1), (c) acetate-passivated (111) (2x1), and (d) amine-halide co-passivated (*cp*) (111) (2x1) surfaces of CdSe CQD, and (bottom) their respective electronic band structures with the band gap opening. The coordinates of high symmetry **k**points are X=(0,¹/₂), Γ =(0,0), and M=(¹/₂,¹/₂) for CdSe *lp*(100) (1x1) surface; Y=(0,¹/₂), Γ =(0,0), X=(¹/₂,0), and S=(¹/₂,¹/₂) for CdSe *sp*(100) (2x1) surface; X=(¹/₂,¹/₂), Γ =(0,0), and S=(¹/₂,0) for CdSe *lp*(111) (2x1) and CdSe *cp*(111) (2x1) surfaces. The zero energy represents the Fermi level (C, cyan; O, red; H, white; N, blue; Cl, green).



Fig. S3 (top) Top views of ball-and-stick models for (a) acetate-passivated (100) (2x1), (b) amine-halide co-passivated (100) (2x1), (c) acetate-passivated (111) (2x2), and (d) amine-halide co-passivated (111) (2x2) surfaces of InAs CQD, and (bottom) their respective electronic band structures. The coordinates of high symmetry *k*-points are $Y=(0,\frac{1}{2})$, $\Gamma=(0,0)$, $X=(\frac{1}{2},0)$, and $S=(\frac{1}{2},\frac{1}{2})$ for InAs *lp*(100) (2x1) and InAs *cp*(100) (2x1) surfaces; $M=(\frac{1}{2},0)$, $\Gamma=(0,0)$, and $K=(\frac{2}{3},\frac{1}{3})$ for InAs *lp*(111) (2x2) and InAs *cp*(111) (2x2) surfaces. To reduce the dangling bonds in the (2x1) (100) surface unit, the (100) surface undergoes the In-In dimerization. The zero energy in electronic band structure represents the Fermi level.

References

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