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Supporting Information for: Tuning the Radiative Lifetime in InP Colloidal Quantum Dots by Controlling the Surface Stoichiometry

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Passivation procedure and parameters

The unsaturated bonds at the dot surface are passivated here using pseudo-hydrogenic, short-range potentials with Gaussian form,

$$v(\mathbf{r}) = \alpha e^{-(|\mathbf{r}-\mathbf{R}(\gamma)|/\sigma)^2} \tag{S1}$$

Each passivant is therefore characterized by (i) the amplitude α and (ii) the width σ of the Gaussian potential, and by (iii) the distance γd from the surface atom along the ideal bond line connecting it with the missing atom (d is the bond length and $\mathbf{R}(\gamma)$ is the ligand position).[1–3] As the electronic structure calculations are performed in reciprocal space, Eq. (S1) needs to be Fourier transformed into[3]

$$v(\mathbf{q}) = \alpha\pi^{1.5}\sigma^3 e^{i\mathbf{q}\cdot\mathbf{R}} e^{-(\sigma|\mathbf{q}|/2)^2} \tag{S2}$$

to obtain the relationship between real-space parameters and q-space ones (which are the actual input to the calculations): $a = \alpha\pi^{1.5}\sigma^3$, $b = \sigma/2$, and $c = \gamma$.

Table S 1: Passivation parameters used to passivate surface In and P atoms in this work compared with the parameters used by Fu and Zunger[2] and Graf *et al.*[3]

Passivation	cation						anion					
	1 dangling bond†			2 dangling bonds†			1 dangling bond†			2 dangling bonds†		
	a	b	c	a	b	c	a	b	c	a	b	c
This work	1.18	0.40	0.55	1.40	0.55	0.65	-1.20	0.40	0.25	-0.78	0.75	0.25
Fu & Zunger [2]	1.18	0.45	0.25	1.90	0.70	0.50	-0.93	0.50	0.25	-0.78	0.75	0.25
Graf *et al.*[3]	1.68	0.80	0.35	1.68	0.64	0.25	-1.68	0.33	0.25	-1.05	0.80	0.25

† Surface atoms with 3 dangling bonds were removed as they are unstable for dissociation.

Electronic configuration of the outer shell of the anions most commonly found in semiconductor NCs

Table S 2: Electronic configuration of the outer shell of the anions most commonly found in semiconductor NCs

Element	Electronic Configuration
P	$3s^2 3p^3$
As	$3d^{10} 4s^2 4p^3$
Sb	$4d^{10} 5s^2 5p^3$
S	$3s^2 3p^4$
Se	$3d^{10} 4s^2 4p^4$
Te	$4d^{10} 5s^2 5p^4$

Radiative lifetimes for different surface stoichiometries

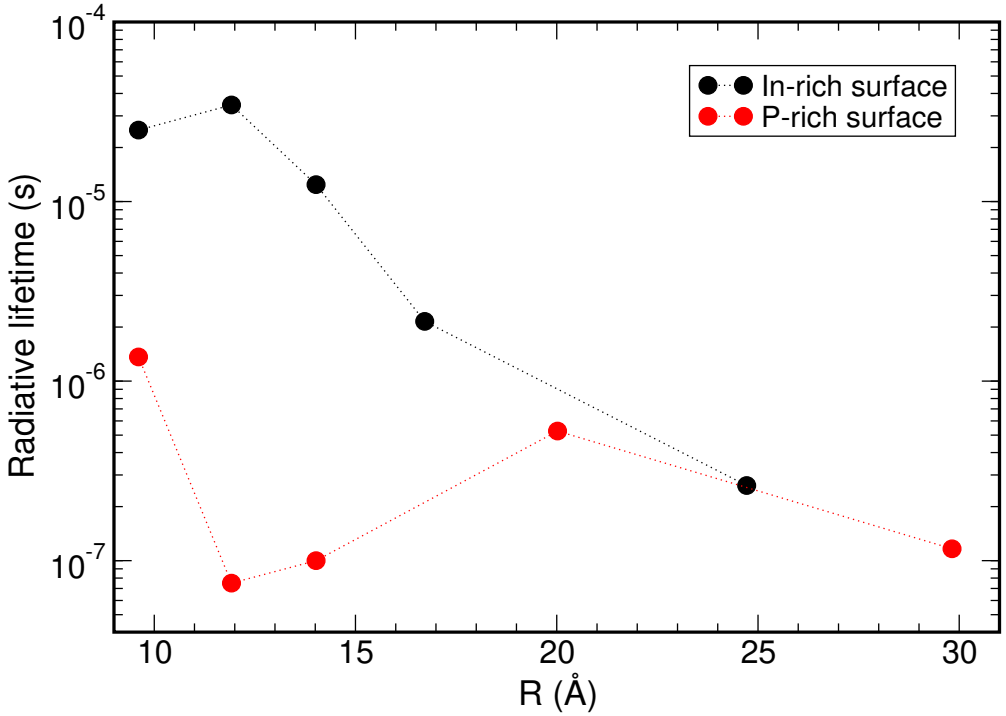

Figure S 1: Comparison between radiative lifetimes calculated in NCs with P-rich (red circles) and In-rich (black circles) surfaces.

Calculated Auger Cooling times

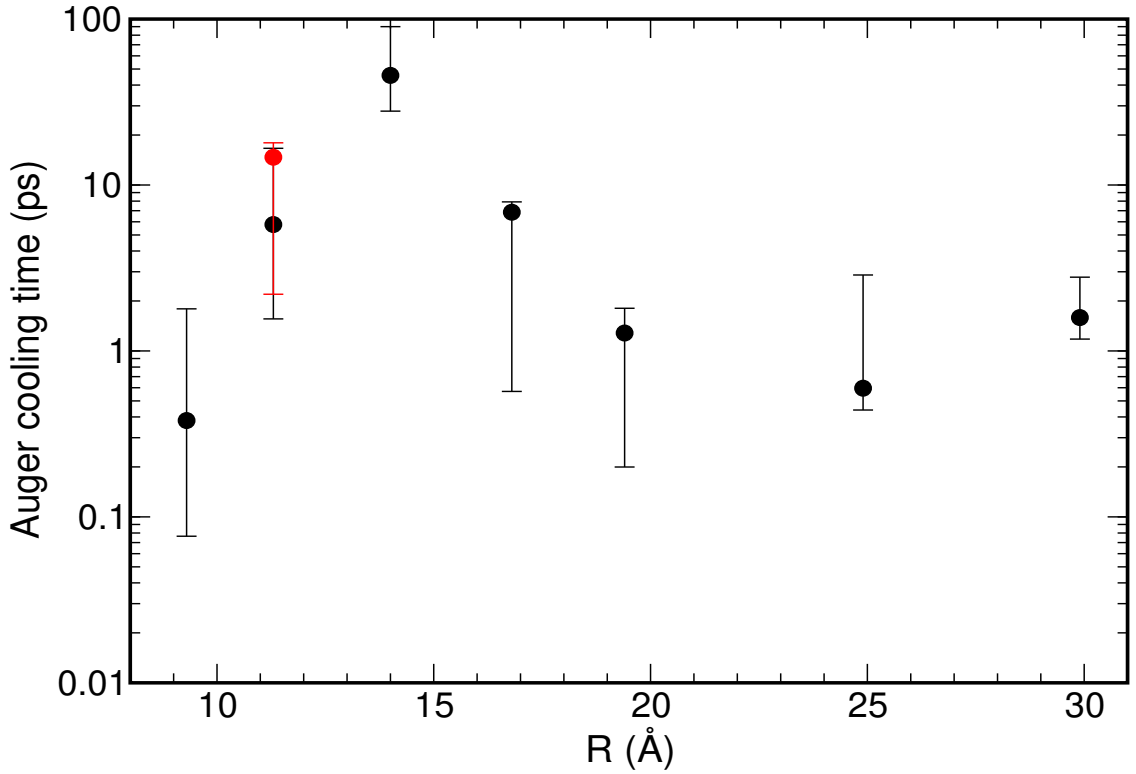

Figure S 2: Auger Cooling lifetimes as a function of QD radius. The red circle represents the result obtained after the addition of 6 P atoms, one on each of the equivalent (100) facets of the NC. The error bars are obtained using a procedure similar to that followed in ref. [4], by varying the s-p splitting in the conduction band over a range of energies corresponding to a 10% size distribution.

References

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