Supporting Information for:

Shape Evolution and Single Particle Luminescence of Organometal Perovskite Nanocrystals

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Figure S1. Standard XRD patterns of (CH₃NH₃)_nPbI_m phases.



Figure S2. Standard XRD patterns of (CH₃NH₃)_nPbBr_m phases.



Figure S3. TEM images of bulk CH₃NH₃PbBr₃ particles immediately after (left) and a few (3-5) minutes after (right) exposure to the TEM electron beam of an FEI-Tecnai 2-F20 STEM operating under 200 kV.



Figure S4. Relationship between photoluminescence maxima (PL_{max}) and optical absorption onsets for bulk and nanostructured CH₃NH₃PbI₃ (a) and CH₃NH₃PbBr₃ (b) perovskites. The appearance of PL_{max} values above the band edge in similar samples has been explained by introducing a Urbach tail at the absorption edge.{Tan, 2014 #96}



Figure S5. Photoluminescence decay lifetimes of solutions containing crystalline CH₃NH₃PbI₃ particles of different sizes and morphologies ($\lambda_{exc} = 638$ nm). A biexponential model was employed to the analyze PL decay of the different materials. The long component is characteristic of the intrinsic recombination rate of the exciton or free carriers, while the faster component can be attributed to recombination through surface states. In bulk CH₃NH₃PbI₃, the fast carrier trapping through surface states is the dominant channel of recombination, resulting in a short lifetime of 9.1 ns consistent with the low QY. The long component becomes more important in anisotropic CH₃NH₃PbI₃ nanostructures, resulting in a longer lifetime 30.4 ns for 1500 nm × 34 nm CH₃NH₃PbI₃ nanowires and 65.6 ns 810 nm × 54 nm CH₃NH₃PbI₃ nanorods. The shorter lifetime displayed by the longer CH₃NH₃PbI₃ nanowires is likely caused by the presence of more nonradiative surface states due to a larger surface-to-volume ratio compared to the shorter CH₃NH₃PbI₃ nanorods.⁵⁸



Figure S6. Single particle photoluminescence as a function of time for a single, dot-like $CH_3NH_3PbI_3$ nanocrystal ($\lambda_{exc} = 540$ nm, $\lambda_{PL} = 700$ nm, scale bar = 1 µm) (see Movie S1).



Figure S7. Single particle photoluminescence as a function of time for a single, dot-like $CH_3NH_3PbI_3$ nanocrystal ($\lambda_{exc} = 540$ nm, $\lambda_{PL} = 700$ nm, scale bar = 1 µm).



Figure S8. Single particle photoluminescence as a function of time for a single, dot-like $CH_3NH_3PbI_3$ nanocrystal ($\lambda_{exc} = 540$ nm, $\lambda_{PL} = 700$ nm, scale bar = 1 µm).



Figure S9. Single particle photoluminescence as a function of time for a single, wire-like $CH_3NH_3PbI_3$ nanocrystal ($\lambda_{exc} = 540$ nm, $\lambda_{PL} = 700$ nm, scale bar = 1 µm) (see Movie S2).



Figure S10. Single particle photoluminescence as a function of time for a single, wire-like $CH_3NH_3PbI_3$ nanocrystal ($\lambda_{exc} = 540$ nm, $\lambda_{PL} = 700$ nm, scale bar = 1 µm).



Figure S11. Single particle photoluminescence as a function of time for a single, wire-like $CH_3NH_3PbI_3$ nanocrystal ($\lambda_{exc} = 540$ nm, $\lambda_{PL} = 700$ nm, scale bar = 1 µm).



Figure S12. Single particle photoluminescence as a function of time for a single, wire-like $CH_3NH_3PbI_3$ nanocrystal ($\lambda_{exc} = 540$ nm, $\lambda_{PL} = 700$ nm, scale bar = 1 µm).



Figure S13. Single particle photoluminescence as a function of time for a single, plate-like $CH_3NH_3PbI_3$ nanocrystal ($\lambda_{exc} = 540$ nm, $\lambda_{PL} = 700$ nm, scale bar = 1 µm) (see Movie S3).



Figure S14. Single particle photoluminescence as a function of time for a single, plate-like $CH_3NH_3PbI_3$ nanocrystal ($\lambda_{exc} = 540$ nm, $\lambda_{PL} = 700$ nm, scale bar = 1 µm).



Figure S15. Selective Area Electron Diffraction (SAED) pattern of a sample containing several nanowires shows main diffraction spots with an interplanar spacing of 3.14 Å, which is characteristic of the (220) planes in tetragonal CH₃NH₃PbI₃.



Figure S16. Infrared (IR) spectra of bulk (polycrystalline, no surfactant) $CH_3NH_3PbI_3 vs.$ n-octylammoniumiodide-produced (C8-capped) $CH_3NH_3PbI_3$ nanowires (1500 nm × 34 nm) collected as NaCl pellets (solids). Peak assignments: (a) corresponds to N-H stretching (3200-3100 cm⁻¹), and is present in both samples; (b) corresponds to asymmetric CH_2 stretching (2940-2915 cm⁻¹) and is present in the C8-capped nanowires; (c) corresponds to antisymmetric CH_3 deformation (bending, 1470-1435 cm-1) or CH_2 deformation (scissoring, 1480-1440 cm₋₁), and is present in both samples; and (d) corresponds to symmetric CH_3 deformation and is weaker in the C8-capped nanowires.

Table	S1.	d-Spacings	between	main	lattice	planes	in	CH ₃ NH ₃ PbI ₃	and		
CH ₃ NH ₃ PbBr ₃ .											
CH ₃ NH ₃ PbI ₃					CH ₃ NH ₃ PbBr ₃						
(Tetragonal)					(Orthorhombic)						
	hkl		d (Å)		1	nkl		<i>d</i> (Å)			
(002		6.34		(001		5.90			
	110		6.27		()11		4.17			
(004		3.17		(002		2.95			
	220		3.14		(021		2.64			
	114		2.83		2	211		2.41			
-	222		2.81		()22		2.09			
-	224		2.23		(003		1.97			
(040		2.22								

Table S2. Comparison between TEM and XRD ensemble sizes measured for CH₃NH₃PbI₃ nanocrystals.^{*a*}

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Parameter	Len	igth (nm)	Diameter (nm)			
Measurement Type	TEM	XRD (110 - 220)	TEM	XRD (002 - 004)		
Nanowires	1500	110 - 58	34	32 - 48		
Nanorods	810	95 - 65	54	77 - 59		
Aggregated dots	20	23 - 17	20	16 - 20		

^{*a*}In solution-made colloidal semiconductors, it is relatively common to find that the XRD sizes (or Scherrer sizes, see below) of the single crystalline domains are smaller than the total particle sizes observed by TEM. This is often explained by the presence of stacking or twinning faults within each nanocrystal (or rod or wire, see for example: Ruberu, T. P. A. *et al. ACS Nano* **2012**, *6*, 5348–5359 & *ACS Nano* **2011**, *5*, 5775–5784, and Kuno, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 620–639). However, the Scherrer equation is limited to nano scale particles and is not applicable to grains larger than 0.1-0.2 μ m. The XRD (Scherrer) diameters calculated here are within this limit, and are roughly comparable with the TEM diameters. In contrast, the XRD (Scherrer) lengths calculated here are expected to be much less reliable than the TEM lengths because the nanorods and nanowires are significantly longer than the Scherrer limit.