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Supplement to Energy Transfer from Colloidal Nanocrystals to Strongly Absorbing Perovskites

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Electronic Supplementary Information

Energy Transfer from Colloidal Nanocrystals to Strongly Absorbing Perovskites

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Supplementary Methods

***In-situ* FTIR during ALD**. For these measurements, double-side-polished, float-zone grown Si (111) wafers (n-doped, ρ ~ 10-60 Ω cm) are cut into 3.8 x 1.5 cm^2 substrates to fit the sample holder in a home-built ALD reactor.[1] Substrates are cleaned and perovskite films grown as described in the main text. After cleaning and/or perovskite growth, the sample is loaded into the N_2-purged ALD reactor, with a base pressure of ~10^{-4} Torr. To monitor perovskite stability and characterize the ALD process, the sample is loaded into the reactor, heated to 80 ^oC under N_2 gas and reference spectra are collected. For stability measurements, IR spectra are collected at 80^oC as a function of time. For Al_2O_3 growth, 20 TMA/D_2O cycles are carried out. The precursor exposures are both 1s pulse for TMA (p = 390mTorr) and 1s pulse for D_2O (p = ~800 mTorr) at a deposition temperature of 80 ^oC with 10 min purges after each exposure, after which IR spectra are collected.

The IR absorption measurements are performed with a Thermo Nicolet 6700 infrared interferometer, equipped with a liquid-nitrogen cooled broadband mercury cadmium telluride (MCT-B) detector. A single-pass transmission at Brewster incidence (~74^o to normal) is used to minimize substrate phonon absorption in the low frequency region (<1000 cm^{-1}) and increase sensitivity of all components (parallel and perpendicular to the surface) of surface species. Manual gate valves are used to protect the potassium bromide (KBr) windows from the precursor gases during ALD cycles. The sample temperature is monitored with a K-type thermocouple spot-welded onto a tantalum clip firmly attached at the center of the long edge of the Si substrate.

Supplementary Figures

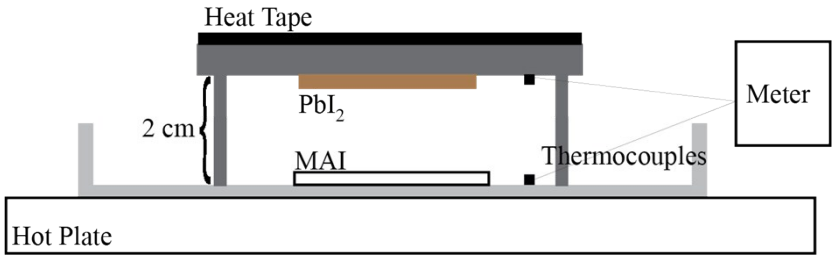

Fig. S1. Schematic of the home-built set-up for the conversion of PbI_2 to perovskite. A glass petri dish is paced on a hot plate on which a small amount of methyl ammonium iodide (MAI) is placed. The powder is surrounded by a 2 cm tall aluminum cylinder over which an aluminum plate is suspended. The PbI_2 film on glass is mounted to the bottom of the Al plate and centered over the MAI powder. Heat tape is attached to the top-side of the Al plate to control the substrate temperature. Thermocouples are attached to both the bottom glass plate and top aluminum plate to monitor the temperature. By adjusting the power to the hot plate and heat tape, the temperature of both plates was held at 160 ^{o}C during the conversion.

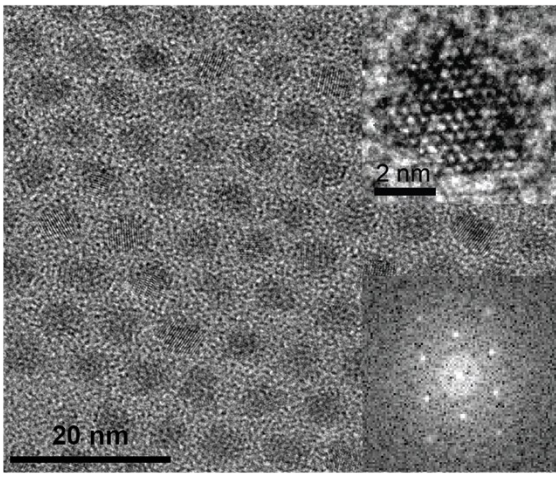

Fig. S2. TEM image of CdSe/ZnS NQDs. The upper inset is HRTEM image of a single NQD while the lower inset shows the FFT pattern of the NQD highlighting its crystallinity.

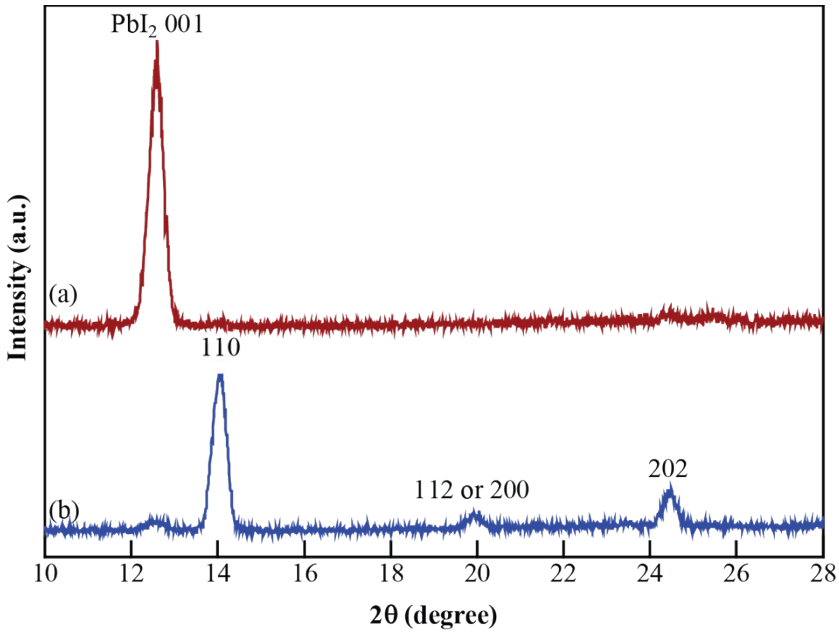

Fig. S3. XRD patterns of perovskite films after ALD at 80 ºC where (a) 160 cycles of TMA/H_2O and (b) 10 pulses of TMA followed by 160 cycles of TMA/H_2O were deposited. The peaks at 14º, 19º, and 24.5º correspond to the orthorhombic perovskite phase while the peak at 12.5º corresponds to the 001 phase of PbI_2.

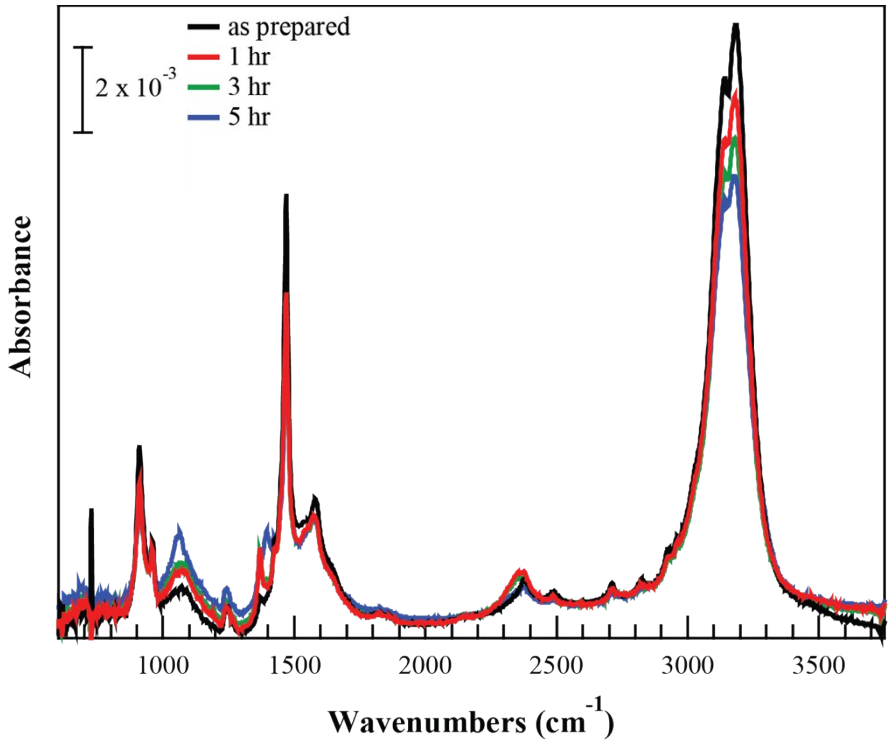

Fig. S4. FTIR spectra of the lead halide perovskite as a function of annealing time at 80 °C. A decrease in the intensity of the CH_x/NH_x stretching modes (2600 - 3570 cm^{-1}) is observed with time indicting sample degradation. After 3 hours at 80°C, the intensity of these modes decreased ~20% indicting that the majority of the sample remained in the perovskite phase.

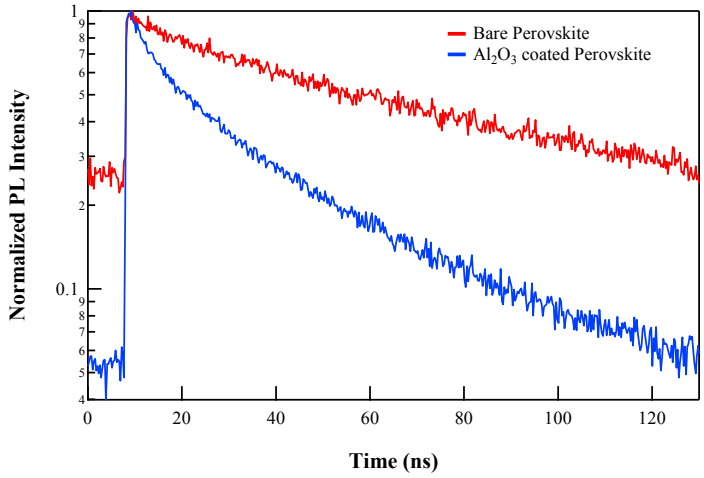

Fig. S5. PL lifetimes of perovskite with and without an Al_2O_3 overlayer.

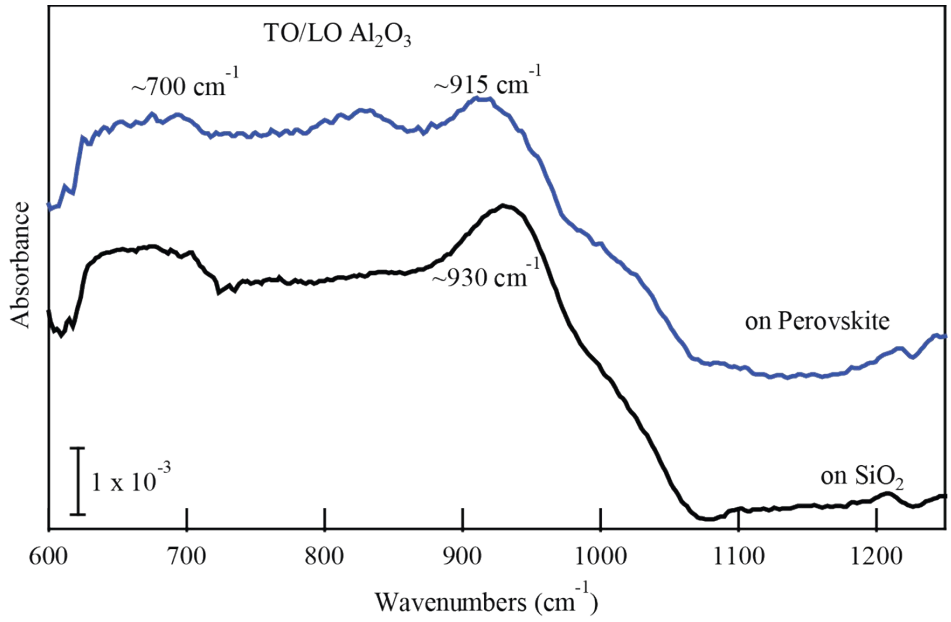

Fig. S6. Transmission IR spectra of Al_2O_3 grown from 10 pulses TMA followed by 20 TMA/D_2O cycles on perovskite and SiO_2 substrates. The total absorbance after 20 cycles is calculated by referencing the last spectra to the starting substrate. After 20 cycles, the appearance of the TO/LO phonon modes are visible indicative of Al_2O_3 growth. Note that the LO mode for the Al_2O_3 grown on the perovskite is at slightly lower frequency (915 rather than 930 cm^{-1}) than for Al_2O_3 on SiO_2, indicating poorer uniformity (smaller domains) on the perovskite presumably due to the perovskite surface roughness. However, the integrated areas of the TO/LO phonon modes for both samples are within 5% of each other indicating that Al_2O_3 grew at the same average rate on both SiO_2 and perovskite surfaces.

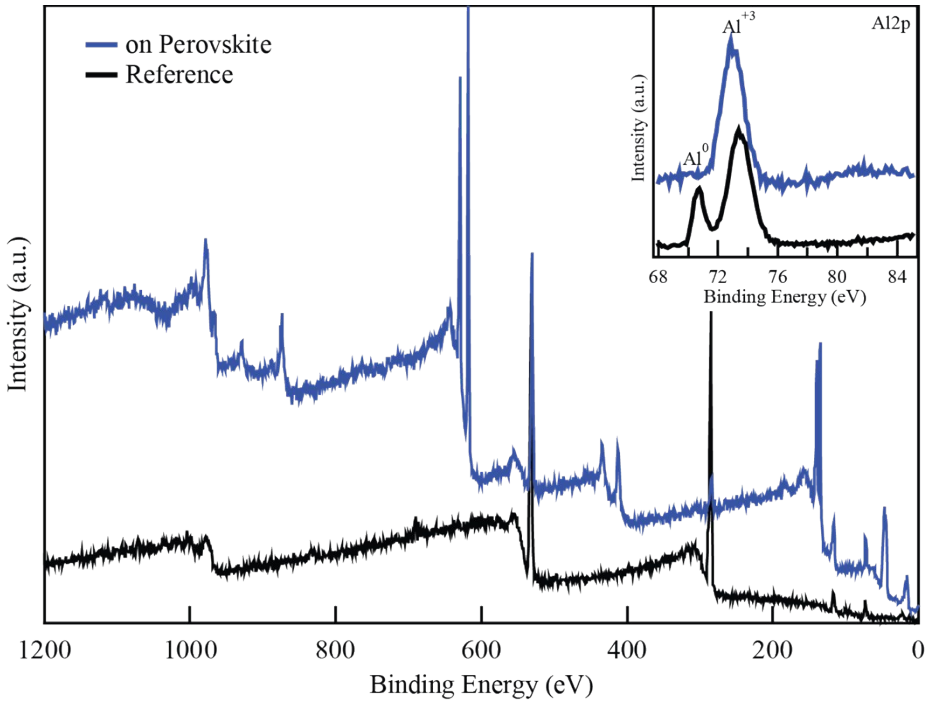

Fig. S7. XPS spectrum of Al_2O_3 grown from 20 cycles TMA and D_2O on the perovskite (blue). A reference Al_2O_3 spectrum taken from the native oxide layer on aluminum (black). Inset, Al2p region in which the reference sample confirms the presence of Al^{3+}. In addition to the Al and O peaks due to the Al_2O_3, other peaks are visible in the perovskite sample corresponding to the presence of Pb, I, and C from perovskite layer since Al_2O_3 layer is very thin.

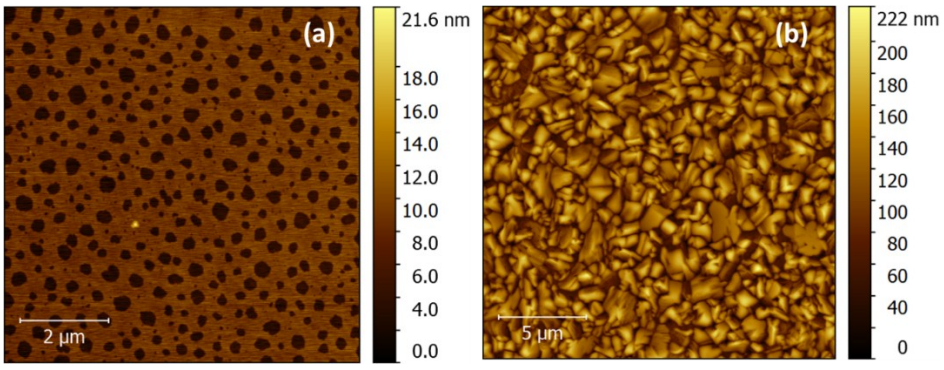

Fig. S8. AFM image of (a) a monolayer of NQD spun-cast on glass and (b) perovskite prepared at 160 °C for 90 min. The perovskite film has a root mean square roughness of ~32 nm.

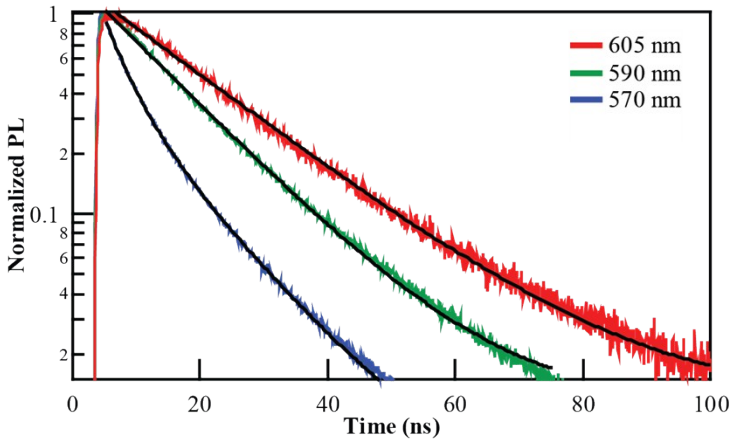

Figure S9. PL lifetimes of a close packed monolayer of NQDs as a function of wavelength. Due to spectral diffusion due to ET between neighboring NQDs of different sizes, NQDs with longer emission wavelengths exhibit slower decays.

Supplemental References

1. J. Kwon, M. Dai, M. D. Halls, E. Langereis, Y. J. Chabal and R. G. Gordon, *J. Phys. Chem. C*, 2009, **113**, 654-660.