Electronic Supplementary Information

Quantum Dots Protected from Oxidative Attack Using Alumina Shells Synthesized by Atomic Layer Deposition

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Experimental methods.

Films comprised of QDs were prepared by drop casting (Figures 1c and 1d of main text). Carboxyl-terminated CdTe QDs with nominal emission wavelength at 610 nm were purchased from Sigma-Aldrich (P/N: 777951) and used as-received without further purification. The diameter of these nanocrystals was estimated to be 3.6 nm from the peak of the photoluminescence wavelength.[1] Approximately 25 mg of nanocrystals were dispersed in 2 ml of a mixture of 1:1 isopropanol:water. The isopropanol was added first to the dry nanocrystals, followed by the water. The resulting mixture was an unstable colloidal suspension. The suspension was shaken vigorously, and then drop-casted immediately into a rubber mold that was secured to the microscope glass substrate. The nanocrystals settled out of solution onto the substrate before the isopropanol:water mixture had fully evaporated. The resulting film comprised of nanocrystals was sufficiently adherent to survive the subsequent processing steps:

photoluminescence testing, atomic layer deposition, stability testing, x-ray photoelectron spectroscopy and so forth.

Atomic layer deposition (ALD) was carried out in a custom hot wall reactor. The sample chamber consisted of a stainless steel tube, 1.5” inner diameter, approximately 2’ in length, which was inserted into a tube furnace equipped with a temperature controller. During deposition, argon was continuously flowing through the chamber at a rate of 30 standard cubic centimeters per minute (SCCM). The steady state pressure in the chamber with no precursor pulsing was approximately 0.5 Torr. The manifold upstream of the chamber was heated to 130 ^{o}C to prevent condensation and suppress physisorption of water. The temperature in the chamber during deposition was controlled in the range from 30 ^{o}C to 180 ^{o}C using the tube furnace. Samples were allowed to outgas for 10 minutes before deposition commenced. The trimethyl-aluminum (TMA) and water were sequentially pulsed through the reactor with purge steps in between. One cycle consisted of the following timing sequence: TMA-purge-H_2O-purge = 1-60-1-60, where the units are seconds. This timing sequence resulted in a maximum precursor partial pressure of approximately 0.4 Torr during the TMA pulse, and a maximum precursor partial pressure of approximately 1 Torr during the water pulse. The measured growth rate under these conditions depended slightly on the deposition temperature, but was approximately 0.1 nm per cycle. The thickness of the Al_2O_3 coating was verified by transmission electron microscopy.

The PL was measured before and after ALD for each sample using a modular system consisting of a 390 nm light-emitting diode as the excitation source and an Ocean Optics USB 2000 spectrometer for measuring the emission. The spectra were baseline corrected to eliminate the effect of stray light.

The stability measurements were performed by the following procedure. Both the uncoated and coated samples were placed side-by-side on a hotplate (IKA) covered with a black anodized aluminum foil (Thorlabs) at a measured temperature of 86 ^{o}C, inside of a light-sealed box. The temperature of the samples was measured by an infrared thermometer (Micro Epsilon). Both samples were continuously illuminated at 420 nm by an LED (Thorlabs) for the entire 17 hours of the experiment. The approximate intensity of illumination was 14 μW cm^{-2} as measured by a calibrated silicon photodiode (Thorlabs S120-UV) connected to a power meter (Thorlabs PM300). The samples were in contact with ambient laboratory air during the entire experiment. The PL was measured by a quantitative deep-cool CCD camera (FLI) with a CCD-47-10 (e2V) chip. The temperature of the detector was -38 ^{o}C and the exposure time was 200 ms. The camera was equipped with a Nikkor Ai-S 28 mm f2.8 focusing lens (Nikon) and a 550 nm long pass filter to reduce interference from the 420 nm excitation source. Images were acquired periodically to establish the trends in time using μManager data acquisition software. The emitted intensity for each sample was measured by integrating the intensity from the area of the image occupied by a given sample using Image J. The baseline intensity was subtracted from this raw intensity to determine the PL intensity. The baseline was determined by calculating the average intensity in the image for the area surrounding a given QD sample.

X-ray photoelectron spectroscopy (XPS) depth profiling was performed on a Physical Electronics® 5000 VersaProbe II Scanning ESCA (XPS) Microprobe system with a base pressure below 1×10^{-9} Torr. An argon ion gun operating at 2 kV and 500 V was used to etch through the coated sample and uncoated sample in 30 s intervals, respectively. XPS data were acquired using the 1486.6 eV line from a monochromated Al Kα source at 150 W with a multichannel detector set to a pass energy of 23.5 eV for the high-resolution scans. Acquisition times were approximately 30 min per step, depending on the energy region being probed. The expected peak positions and chemical shifts were taken from the National Institute of Standards and Technology (NIST) X-ray Photoelectron Spectroscopy Database. The peaks were baseline-subtracted and integrated to obtain the composition profiles.

Transmission electron microscopy (TEM) was performed using a JEOL 2100F field emission microscope using an accelerating voltage of 200 kV. Samples were prepared by drop-casting a small amount of QDs on the specimen support. The specimen support consisted of lacey carbon fibers and an ultrathin 3 nm continuous carbon film deposited on a 400 mesh copper grid. The TEM specimen, comprised of QDs supported by the TEM grid, was coated by atomic layer deposition using the same conditions as those used to prepare the ALD-coated sample for stability testing (10 nm at 50 °C, and 10 nm at 150 °C).

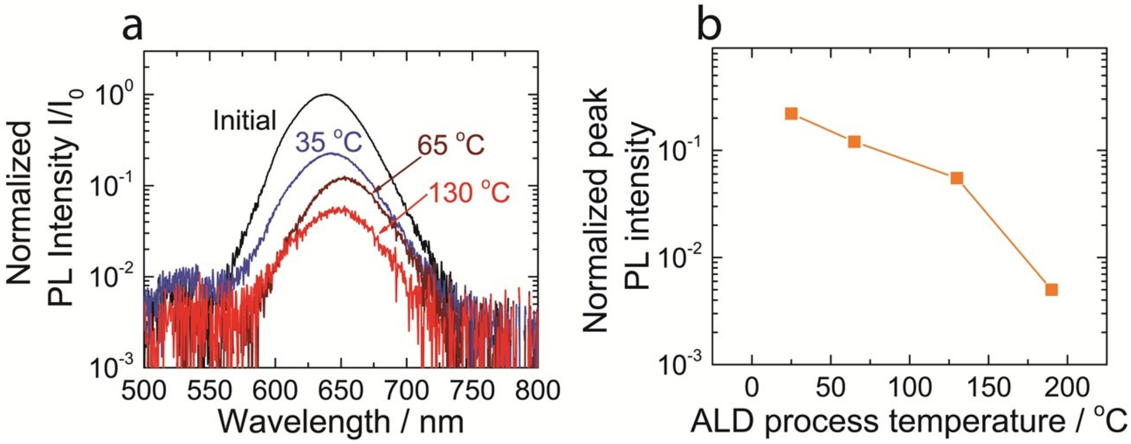

Figure S1. Normalized PL intensity for samples coated with 20 nm of Al_2O_3 by ALD at different process temperatures. The intensity was normalized by the initial peak intensity before ALD coating. In other words, each spectra in (a) corresponds to the PL measured after ALD coating at the indicated temperature, divided by the peak intensity before ALD coating. Panel (b) is the peak value of the spectra in (a) plotted as a function of ALD process temperature. The ALD process time for each of the samples in (a) and (b) was the same, approximately 6.8 hours.

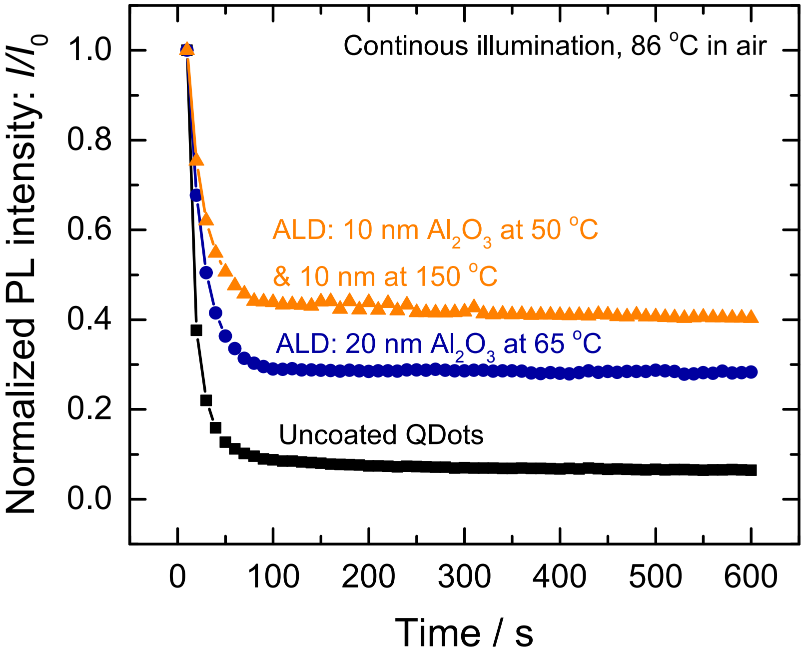

Figure S2. Normalized PL intensity as a function of time for samples held at 86 °C in air under continuous illumination at 420 nm**.** The intensity was baseline subtracted, and normalized to the initial value at time = 0. The black curve corresponds to uncoated CdTe QDs. The blue curve corresponds to QDs coated with 20 nm of Al_2O_3 at 65 °C. The orange curve corresponds to QDs coated with 10 nm of Al_2O_3 at 50 °C, and 10 nm of Al_2O_3 at 150 °C.

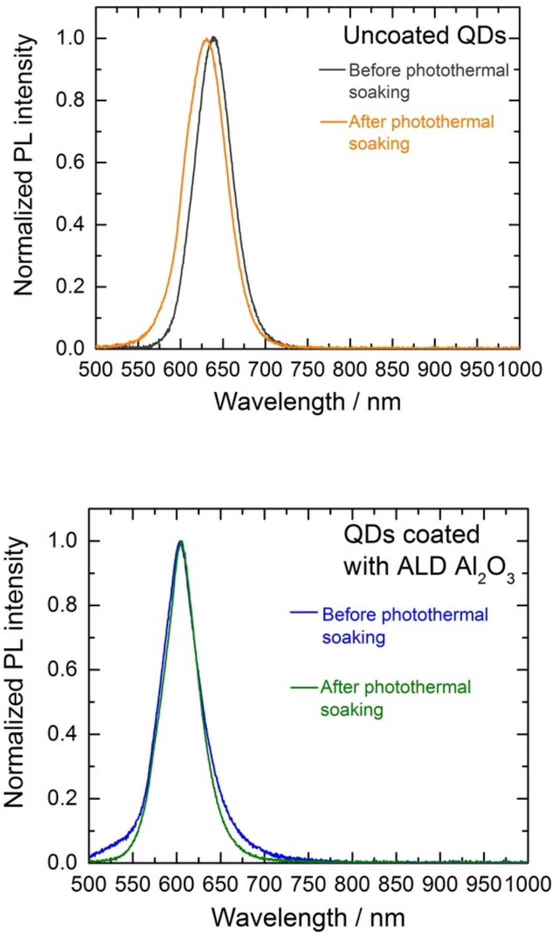

Figure S3. PL emission spectra, under excitation by a 390 nm LED lamp, of the same two samples characterized in Figures 2 and 3 of the main text, before and after photothermal soaking. (top) uncoated CdTe QDs and (bottom) CdTe QDs coated with 10 nm of Al_2O_3 at 50 ^oC and 10 nm Al_2O_3 at 150 ^oC.

References.

1. Yu, W. W.; Wang, Y. A.; Peng, X., Formation and Stability of Size-, Shape-, and Structure-Controlled CdTe Nanocrystals: Ligand Effects on Monomers and Nanocrystals. *Chem. Mater.* **2003,** *15* (22), 4300-4308.