

Electronic Supplementary Information (ESI)

Octapod synthesis and decoration procedures.

CdSe@CdS octapods were prepared according to a recently developed protocol based on the anisotropic growth of CdS arms on CdSe seeds obtained from Cu₂Se seeds by cation exchange. Cu_{2-x}Se seeds were obtained by reaction at 300 °C under inert atmosphere between a solution of CuCl and oleylamine in 1-octadecene and a Se precursor solution prepared by dissolving Se in oleylamine. The resulting Cu_{2-x}Se nanocrystals was purified and dispersed in tri-n-octylphosphine (TOP). In order to promote CdSe@CdS octapod formation, Cu_{2-x}Se nanocrystals in TOP were mixed with a suspension of S in TOP and injected at 380°C in a mixture containing CdO, CdCl₂, n-Octadecylphosphonic acid, n-hexylphosphonic acid, tri-n-octylphosphine oxide, and TOP. After the injection, the reaction was run for 10 min and then the solution cooled to room temperature. The resulting product was purified by repeated washings with toluene and methanol and dispersed in toluene.

We then proceeded to deposit Pt domains on CdSe@CdS octapods. A mixture of 1,2-hexadecanediol, oleylamine, and oleic acid in diphenyl ether were mixed in a 25 mL three-neck-flask connected to a Schlenk line and first heated at 80° under vacuum for 30 min while refluxing, and then placed under flowing nitrogen and heated up to 200° C. At this temperature, a mixture containing a given amount (with an overall volume 2 mL) of pre-formed CdSe@CdS octapods and platinum acetylacetonate in dichlorobenzene was rapidly injected into the flask. While the amount of octapods was kept fixed (~0.9 mg), the amount of platinum precursor was varied (0.2 mg and 1 mg for the Pt-tipped and Pt-covered samples, respectively). After 30 min the reaction was quenched and the Pt-CdSe@CdS heterostructures were collected and purified by repeated cycles of precipitation by addition of excess ethanol and dispersion in toluene. Pt-free CdSe@CdS octapods were also subjected to the same procedure, without the addition of platinum acetylacetonate, in order to reproduce the same surface modifications that may occur in Pt-decorated samples.

Nanocrystal characterization.

X-ray diffraction (XRD) patterns of the nanocrystals were collected using a Panalytical Empyrean diffractometer equipped with a X'Celerator linear detector using Cu K α radiation operating at 40 kV/40 mA and a Ni filter on the incident beam. The scans were collected under sample spinning in Bragg-Brentano geometry within the range of 20°-80° (2 θ) using a step size of 0.016, 149.86 sec per step. Samples for XRD measurements were prepared by depositing few drops of concentrated nanocrystal suspensions on a low background Si sample holder and then allowing the solvent to evaporate.

Transmission electron microscopy (TEM) images were recorded on a Hitachi H-7000 microscope equipped with a W thermionic electron source operating at 125 KV. Samples for TEM analysis were prepared by depositing few drops of diluted nanocrystal suspensions on a carbon-coated copper grid and then allowing the solvent to evaporate at room temperature.

UV-Visible absorption spectra were recorded with two spectrophotometers, a UV-Vis Varian Cary 50 equipped with a Xenon flash lamp and a Si-based detector and a Perkin Elmer Lambda 950. All spectra were recorded on toluene-based suspensions in quartz cuvette with a 1 cm path length.

Transient absorption spectroscopy experimental setup.

The laser source employed for this experiments was a Ti:Sapphire regenerative amplifier (Quantronix Integra C) operating at a repetition rate of 1 kHz and emitting at 786 nm in wavelength. The absorption spectrum was probed with white-light continuum 150 fs-long laser pulses, 450-700 nm in spectrum, generated by focusing the output of the regenerative amplifier, attenuated to approximately 1 μ J energy per pulse, on a 1 mm sapphire plate. Probe pulses had a variable delay with respect to pump pulses (394 nm wavelength, 150 fs-long). Pump and probe beams were focused on a 1 mm quartz cuvette filled with nanocrystals dispersed in toluene. The cumulative effect of spectral chirp and wavefront distortion of laser pulses resulted in a 200-fs time-delay resolution. The concentration of nanocrystals was chosen to keep the optical density of the whole cuvette around 0.3 at 400 nm in wavelength, guaranteeing the best compromise between

uniformity of excitation and magnitude of the transient absorption signal. Optical spectra were recorded with a CCD camera (Andor Newton, 16 bit resolution, used in vertical binning) coupled to a grating spectrometer (Acton SP2300i, equipped with a grating 300 groves/mm). Sample transmission was measured by dividing the spectrum of white light pulses sent through the sample by the spectrum of similar pulses split before reaching the sample. Differential transmission $\Delta T/T = (T_{\text{on}} - T_{\text{off}})/T_{\text{off}}$ was obtained by recording sequential transmission spectra with (T_{on}) and without (T_{off}) pump pulses illuminating the sample. Typical sensitivity to differential transmission changes in our set-up was about 10^{-4} with few seconds acquisition time. Absorption and differential absorption spectra could be traced back through the relation linking absorption A and transmission T , when reflection and scattering are neglected: $A=1-T$.

Time-resolved photoluminescence experimental setup.

Samples were optically excited with the same laser used for transient absorption, frequency-doubled to 392 nm in wavelength and focused to a 150 μm spot. The optical emission was collimated using a 100-mm focal-length achromatic doublet. Transient emission measurements were performed using a 300-mm spectrometer (Acton SpectraPro 2300i equipped with a 50 groves/mm grating) coupled to a picosecond streak camera (Hamamatsu C5680) providing ~ 20 ps temporal resolution in operating conditions.

Effects of Pt decoration procedure on nanocrystal surface.

We measured time-resolved photoluminescence and transient absorption in octapod nanocrystals before and after the treatment at 200 °C simulating the decoration procedure. The results show that differential transmission dynamics is not affected, meaning that no new traps for electrons are created. The shortening of the differential transmission decay in Pt-decorated nanocrystals, discussed in the main text, can therefore be safely attributed to electron capture by Pt.

On the other hand, the photoluminescence lifetime increases significantly following the treatment. Since we attribute the photoluminescence lifetime to hole trapping, we infer that the treatment alter the amount of surface traps for photoexcited holes and their depth.

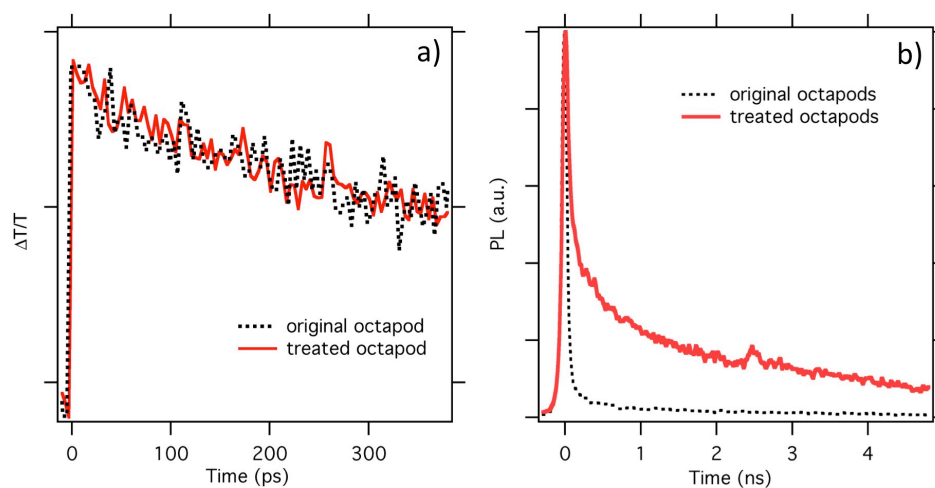


Fig. S1 (a) Comparison of differential transmission signals in Pt-free nanocrystals before and after the 200 °C treatment; the spectral integration window is 460-520 nm. (b) Comparison of time-resolved photoluminescence signals in Pt-free nanocrystals before and after the 200 °C treatment; the spectral integration window is 400-600 nm.