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Supplementary Information

Size-dependent critical transition in the origin of the light emission from core-shell Si-SiO_2 nanoparticles

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In the following, we describe our approach to estimate the variation of the PL maximum position as a function of nanocrystal size. The core idea underlying the simulation consists in reproducing the Gaussian curves of peaks *A* and *B* (for simplicity, peak B^* is neglected because it does not affect the PL maximum position), followed by their sum to obtain the "total" PL spectrum. To this end, it is required to know *a priori* the parameters that define the Gaussian curves of peaks *A* and *B* as a function of nanocrystal size, whose dependencies can be obtained from our experimental data. The size-dependence of the three parameters that define each Gaussian (peaks *A* and *B*) can be inferred from the data resulting from our fittings of the spectra (see examples for a few samples in Fig. 6 of the main manuscript). The data obtained from these fits for all samples are shown in Fig. S1.

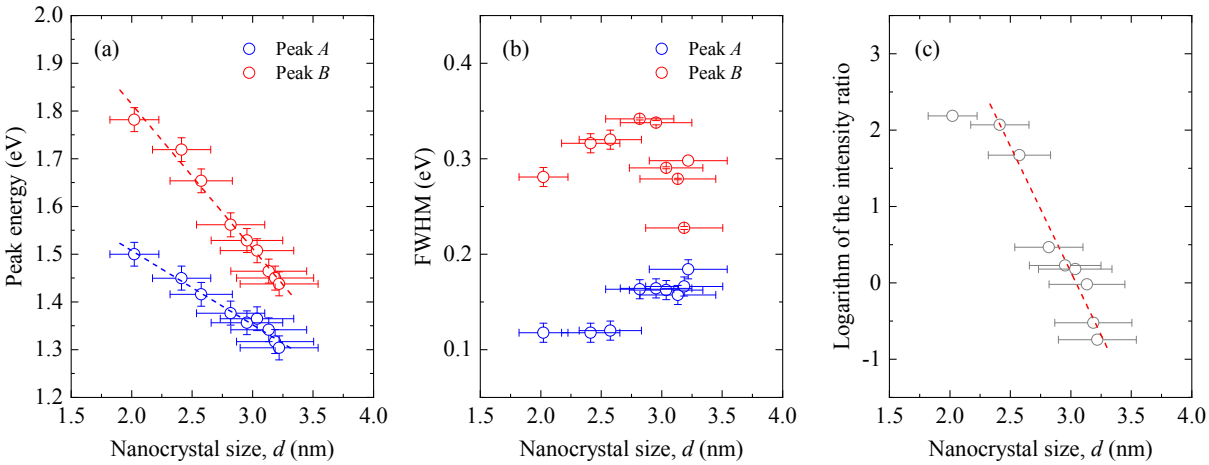

Fig. S1 Dependence of the Gaussian function parameters (a) peak energy, (b) full width at half maximum (FWHM), and (c) logarithm of the intensity ratio $(I_B + I_B^*)/I_A$ on the nanocrystal size. The dashed lines represent linear fits to the experimental data.

To describe the dependencies of each parameter on the nanocrystal size in a continuous way, we fitted the discrete data points with linear functions; these are represented as dashed lines in Figs. S1a and S1c. We note that, in the case of the intensity ratio we excluded the first data point from the fit shown in Fig. S1c. From the linear fits, we obtained the following functions for the energy of peaks *A* and *B*, respectively

$$E_A = 1.82 - 0.16d \quad \text{and} \quad E_B = 2.42 - 0.30d \ . \tag{1}$$

The intensity ratio is described by the relation

$$\log\left[I_{ratio}(d)\right] = 10.03 - 3.30d \ , \tag{2}$$

from which the intensities of peaks *A* and *B* are defined as

$$I_A(d) = 1 \quad \text{and} \quad I_B(d) = 10^{10.03-3.30d} \ . \tag{3}$$

The FWHM of peaks *A* and *B* is parameterized according to their mean value (see Fig. S1b), respectively, as

$$FWHM_A = 0.15 \quad \text{and} \quad FWHM_B = 0.30 \ . \tag{4}$$

The relations provided through Equations 1 – 4 are then used to reproduce the Gaussian functions associated to the peaks *A* and *B* for different nanocrystal sizes, whose sums give the simulated "total" spectra. This exercise was carried out over a broad range of nanocrystal size values ($1.7 < d < 3.6$), for which the PL maximum was estimated. The obtained data is represented in Fig. 8 of the main text as a black line. We note that the largest deviation between the PL maxima of the simulated and the experimental spectra is of the order of 20 meV, well within the error of the experimental spectra fittings.