Electronic Supplementary Material

Supporting Information for

Quantum Rate Spectroscopy as a Spectroscopic Methodology for Measuring the Electronic Structure of Quantum Dots

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SI.1. Response of the capacitance of interface for the gold, L-cysteine monolayer, and the assembly of CdTe QDs
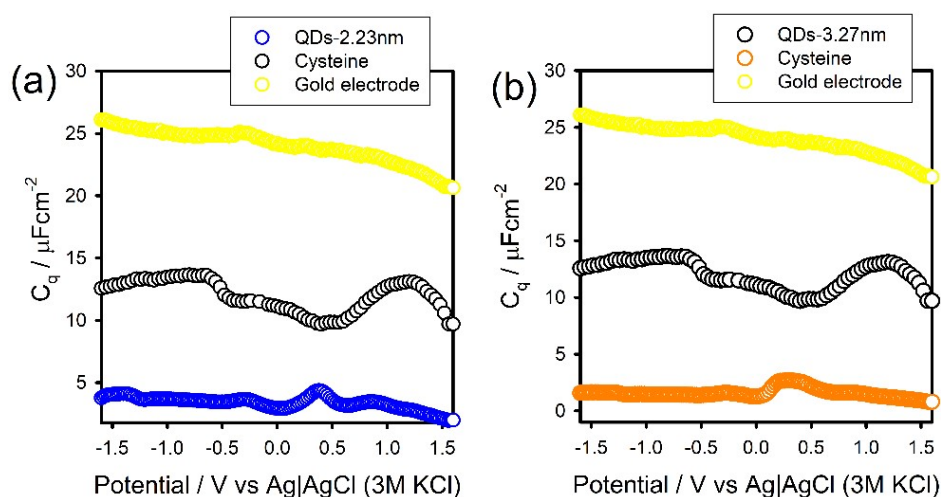
Fig. S1. Comparison between the responses of capacitance attained for the gold electrode, the L-cysteine monolayer (without QDs), and the assemblies of CdTe QDs (with QDs immobilized over the molecular monolayer) of nanoparticle size: (a) 2.23 nm (blue curve) and (b) 3.27 nm (orange curve). The responses for the gold electrode and the L-cysteine monolayer occur at a larger capacitance value and have quite different behavior (as expected) compared to those recorded for the immobilized QDs.

SI.2. Compared response of the quantum capacitance regarding scan potential directions
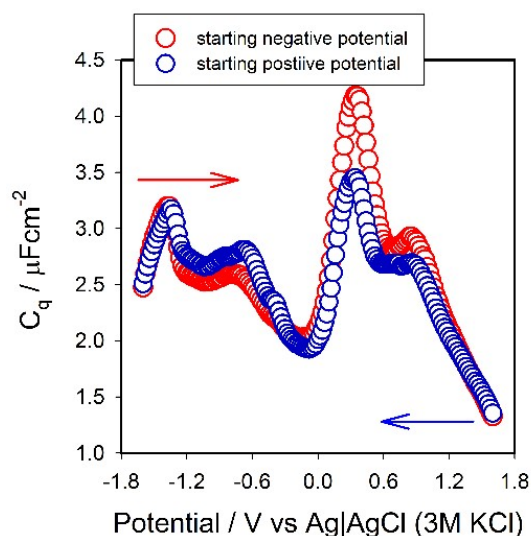
Fig. S2. Comparison between the responses of the quantum capacitance attained for CdTe QDs (size of 2.23 nm) regarding scan potential directions. As noticed, the shape is quite similar although there are some differences in the intensity of the peaks.

SI.3. Absorption and photoluminescence spectra of CdTe quantum dots

Absorption spectra were acquired employing a spectrophotometer (Shimadzu, UV-2450/2550), with a spectral resolution of 1.0 nm, and a slit width of 1.0 nm, in the 200–700 nm region. UV-Vis absorption spectra were acquired employing a spectrophotometer (Shimadzu, UV-2450/2550), with a spectral resolution of 1.0 nm, and a slit width of 1.0 nm. PL spectra were registered with a spectrofluorometer (Shimadzu, RF-5301 PC) equipped with a 150 W Xenon lamp. The spectral resolution utilized was 1.0 nm, the excitation and emission slits were both set to 3.0 nm and the excitation wavelength to 355 nm. All the spectroscopical studies were performed with 10.00 mm quartz cuvettes (Shimadzu) at room temperature.
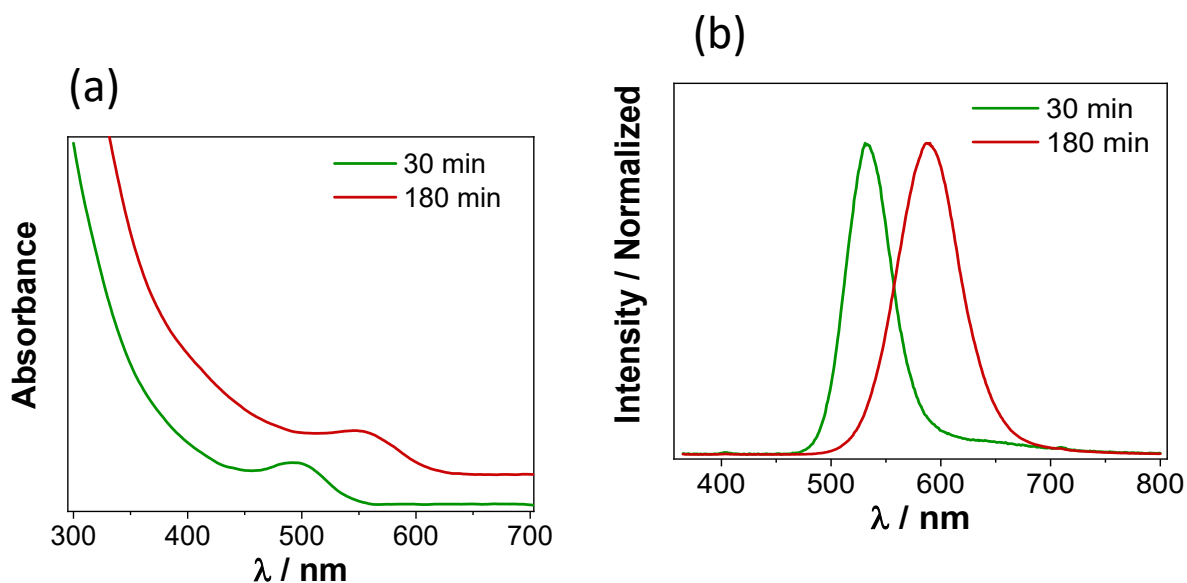
**Fig. S3.** (a) UV-Vis and (b) PL spectra of different-sized QDs.

Fig.S3 shows the absorption and PL spectra of MPA-capped CdTe QDs at different reaction times. The UV-Vis absorption spectra (Fig. 3a) were characterized by one well-defined absorption band at 496 and 553 nm for 30 and 180 min samples, respectively, attributed to the first excitonic absorption ($1S_e \rightarrow 1S_{3/2}$).[1] Due to the strong quantum confinement regime presented by the CdTe QDs, this absorption shifts to longer wavelengths as well as the maximum of PL spectra, since the size of the quantum dot increases with the synthesis time. Furthermore, the PL spectra FWHM were sharp indicating that this method produced MPA-capped CdTe QDs of narrow size dispersion.[2]

SI.4. Determination of band gap and particle size for CdTe QDs in solution

The QDs bandgap energy can be estimated based on the maximum absorption of the excitonic band (see Fig.S3), or easily at the local minimum of the 2nd order derivative absorption spectra showed in Fig.S2 by using the equation below:

$$E_g = \frac{h\upsilon}{\lambda_{abs}} = \frac{1240}{\lambda_{abs}}$$

where E_g is the optical bandgap of the QDs with the maximum absorption at the wavelength λ_{abs}.
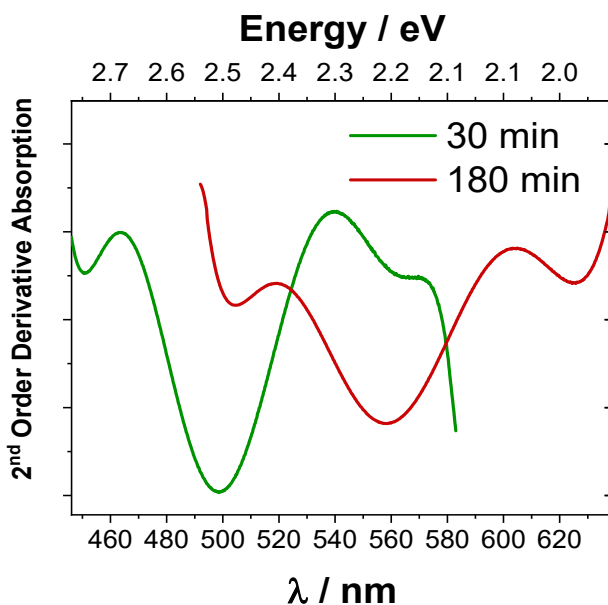
Fig. S4. Second-order derivative absorption spectra for the different sized QDs.

The mean diameter (D) of a given CdTe QDs sample can also be estimated from absorption spectra using the following equation:[3]

$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - (194.84)$$

where D (nm) is the mean diameter of the QDs and λ (nm) is the wavelength of the first excitonic absorption peak, which was obtained by adjusting a Gaussian function on the experimental data. The bandgap energy (E_g), and the mean particle size of the QDs calculated from the UV-Vis/ PL spectra are shown in Table S1.

QDs sample	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift (meV)	FWHM (meV)	E_g (eV)	Size (nm)
30 min	496	533	174	209	2.50	2.23 ± 0.22
180 min	553	589	119	242	2.24	3.27 ± 0.33

Table SI.1. Spectroscopical parameters obtained from UV-Vis/PL spectra and calculated mean sizes and bandgap energies.

The Stokes shift as well as the FWHM values were close to the values reported in similar works for the same systems.[4] These FWHM values are increasing with the reaction time, due to the widening of size dispersion as the reaction evolves.

SI.5. Characterization of trap states

In CdTe QDs, the presence of surface defects can lead to trap-states within the bandgap, resulting in larger stokes shifts and an asymmetry on the emission spectra or even in a second emission band at lower energy, as is evident for the 30-minute QDs in the Fig. S1b. This can be easily evidenced by plotting the PL spectra on a logarithmic scale, as shown in Fig. S3.
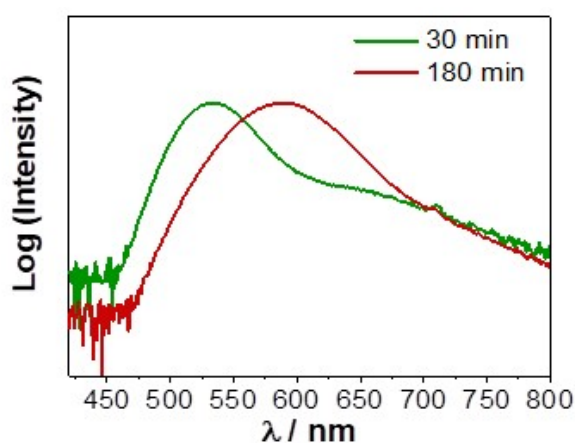

Fig. S5. PL Spectra (plotted on a logarithmic scale) of the different-sized QDs.

In the spectra (Fig. S3), it can be observed that besides the main excitonic emission peak, a second emissive electronic state is evidenced at 626 nm (1.98 eV), ascribed to emission from energy levels of the surface traps, becoming more prominent for the smaller sized QDs.[5] Since the smaller sized

QDs have a higher surface-to-volume ratio, they are more susceptible to surface defects creating trap states for the charge carriers.[6] It is reasonable to evaluate the surface states in terms of energy difference to the band-edge as depicted in Fig. S4.
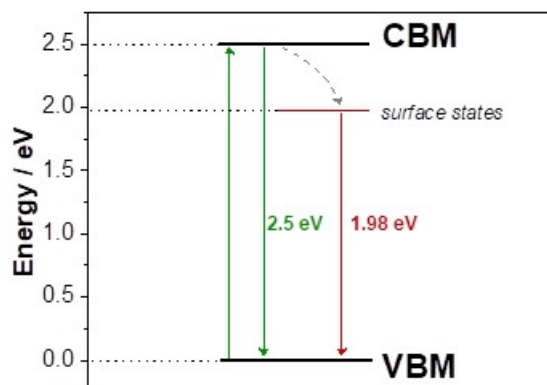
Fig. S5. Scheme of the energy band structure of a CdTe semiconducting nanoparticle considering the presence of the trap states as indicated by the photoluminescence spectrum.

SI.6. X-diffraction analysis

Powder X-ray diffraction (XRD) was performed on a diffractometer (XRD-6000, Shimadzu) using CuKα radiation with a 0.3 mm divergence slit. The diffraction angle was varied from 10 to 60 degrees (2θ) with a rate of 1°min−1 and a step of 0.02º. X-ray diffraction (XRD) analyses of the QDs samples are shown in Fig.S5, confirming that the crystal structure of the obtained QDs can be assigned to the cubic-zinc-blend phase (JCPDS #93942).[6]
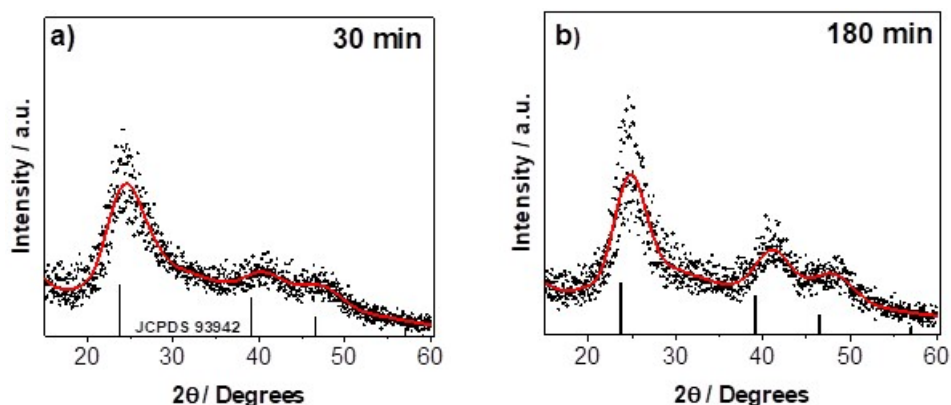
Fig. S6. Powder X-ray diffractograms of (a) 30 min, and (b) 180 min reacted CdTe QDs. The red lines are the smoothed data, and the bar plot below the data refers to the diffraction pattern of bulk CdTe (JCPDS #93942).

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