Supporting information:

Size dependent electron transfer from PbSe quantum dots to SnO_2 monitored by picosecond Terahertz spectroscopy

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Preparation of PbSe QDs

Oleic acid-capped PbSe QDs were prepared following the recipe of Talapin and Murray[1]. Lead(II) oleate was prepared from 2.16 g lead(II) acetate trihydrate and 7.3 mL oleic acid by heating a mixture of these chemicals in 40 mL octadecene under vacuum. Under nitrogen, a 14.2 mL sample of the resulting Pb-oleate stock solution was heated to the required temperature (100 to 150 ^{o}C , depending on the required size) at which point 5.4 mL of 1.0 M selenium in trioctyl phosphine was injected by syringe. The QDs were allowed to grow from 30 seconds to 10 minutes, resulting in monodisperse, quasi-spherical QDs. The QD diameters were determined from the energy of the first exciton absorption and the calibration provided in in the litherature[2]. The QDs were precipitated twice by the addition of a butanol-methanol mixture (2:1 v/v) and collected by centrifugation.

Preparation of QD PbSe sensitized SnO_2 films

The oxide films were prepared from commercial SnO_2 powders (ref# 5549657, Sigma Aldrich) with average grain sizes <100nm. 1gr from these powders was mixed in a mortar with 0.8gr of NH_4OH and 4.5ml of Ethanol obtaining a paste which was treated during 10min

with ultrasounds bath. The resulting SnO_2 paste was spread by the doctor blading technique on fused silica substrates (LG Optical Ltd.). The films were dried at 115°C for 30 minutes and subsequently annealed in air at 450°C for 3hours. The resulting films were immersed for 3h in a solution of 2ml of acetonitrile containing 0.2ml of mercapto propionic acid (MPA). Afterwards, the films were washed thoroughly with acetonitrile and toluene and immersed in a suspension of PbSe QDs in toluene for 12h.

Description of THz-TDS setup and measurements

A detailed layout of the THz time-domain spectrometer is shown in figure S1.

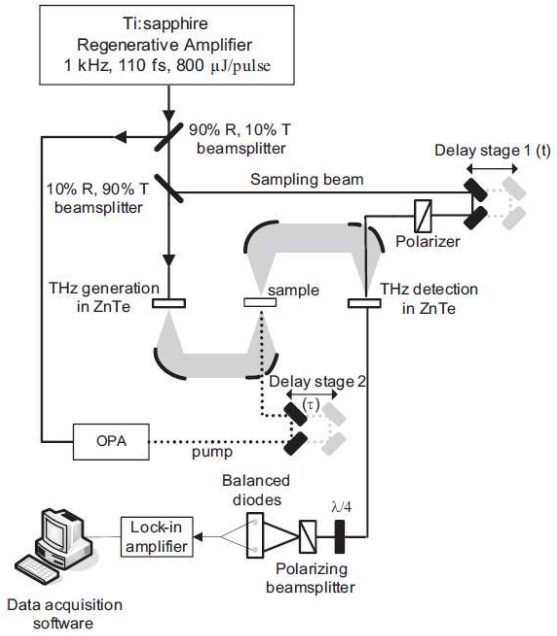


Figure S1: Layout of the THz time domain spectroscopy setup.

The light source used to operate the spectrometer is a pulsed laser system that is based on a Coherent Legend regenerative amplifier (Regen), seeded by a Coherent Verdi (790 nm central wavelength, 110 fs pulse duration FWHM, 80 MHz repetition rate, 500 mW output power). The Regen is pumped by a Coherent Evolution system (527 nm central wavelength, 20 ns pulse duration FWHM, 1 KHz repetition rate, 23 W output power). The amplified output of the Regen is centered at 800 nm and has pulse duration of 110 fs FWHM and a repetition rate of 1 KHz. Of the 2.5 W output power of the Regen, ~ 900 mW is used to run the pump-probe THz-TDS setup. For the THz generation and detection, 10% of the incoming laser beam is

used (90 mW). THz radiation is generated in a phase-matched manner by optical rectification[3] in a ZnTe crystal (<110> orientation, 10x10x1 mm thickness, purchased from MaTeck). The ZnTe generation crystal is pumped with a slightly focused beam (~ 3 mm diameter) of 800 nm light (80 mW power). The THz light exits the ZnTe generation crystal slightly divergent and is first collimated and subsequently focused on the sample using a pair of off-axis parabolic mirrors. The transmitted THz pulses are recollimated and focused on a second ZnTe detection crystal by another pair of parabolic mirrors, where the instantaneous THz field strength is detected through electro-optical sampling[4].

When monitoring the carrier dynamics in our PbSe+SnO2 samples we used a 800 nm pump for the selective excitation of the PbSe QDs. The area probed by the pump was roughly 16mm^2 and typical fluences of 125μJ/cm^2 were employed. Our THz probe beam, comprises frequencies between 0– 2 THz (0-8meV) which is well below the electronic transitions of bulk and quantum-confined semiconductors. The THz probe will only interact strongly with free charge carriers in the samples (more likely those populating the oxide CB). Changes in the amplitude of the transmitted THz field can be monitored with picosecond resolution by changing the delay between pump and probe beams (see fig. S1). These changes are related to the real conductivity, which gives information about the number and mobility of free carriers in the samples.

Carrier dynamics of dropcast PbSe QDs vs oxidized PbSe+SnO_2 sample

In figure S2 is shown a comparison for the carrier dynamics of oxidized dropcast PbSe QDs (red line) and PbSe+SnO_2 samples (black line). As shown in figure S2(a), the carrier dynamics for both systems are almost identical within the first 50 ps. This result strongly suggests that the monitored fast decay component in the QD sensitized samples is coming from the presence of free carriers located within QD clusters. On the other hand, for long time scales (fig. S2(b)), the dynamics of both systems are different. For the clustered QDs an exponential decay is resolved which is compatible with the presence of QD surface trapping within the QD aggregates. Instead, for the oxidized QD+SnO_2 sample a DC offset in the carrier dynamics is obtained. Taking into account that the measured carrier dynamics from different phases are expected to be additive, the flat response at long time scales is not compatible with the presence of QD clusters in the QD sensitized sample. Two different scenarios explaining the origin of the monitored fast recombination processes are discussed in the letter.

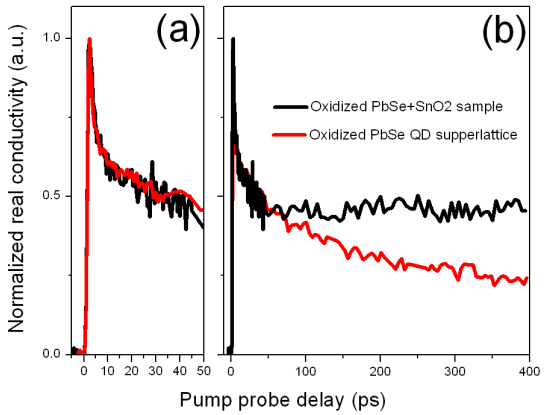


Figure S2: comparison for the carrier dynamics of oxidized dropcast PbSe QDs (red line) and oxidized PbSe+SnO_2 samples (black line).

THz-TDS fluence dependent measurements on oxidized PbSe+SnO_2 sample

In figure S3 is shown the pump fluence dependent carrier dynamics on a PbSe+SnO_2 sample exposed to air (20h). From the data is clear that the detected component τ_2 is related with a second order process. Accordingly we fitted the plots (blue trace in figure S3) following the equation:

$$N(t) = \frac{N_2}{1 + N_2 k_2 t} + y_1 \qquad \text{Eq. I}$$

Where $N(t)$ represents the amount of free carriers in the samples as a function of time, $(1/k_2)=\tau_2$ is the second order lifetime recombination and y_1 is a DC offset representing the contribution from the τ_1 mechanism (fig. 1 and 2). The obtained values for τ_2 as a function of fluence are shown in the inset of figure S3. A lifetime dependence on the inverse of the carrier density is obtained ($\tau_2 \propto 1/n$) indicating that the detected signal is related with a trap assisted Auger recombination process.

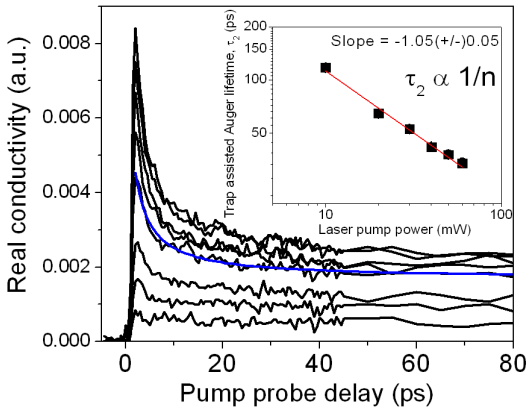
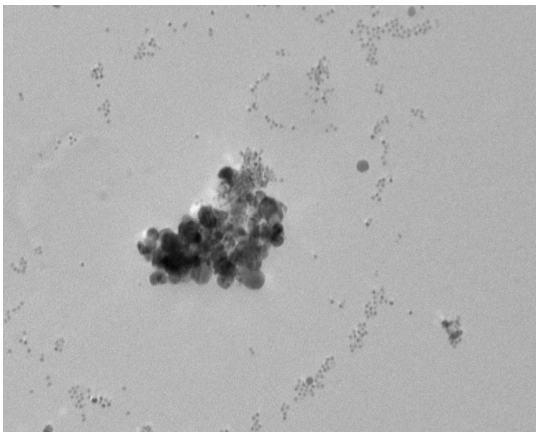
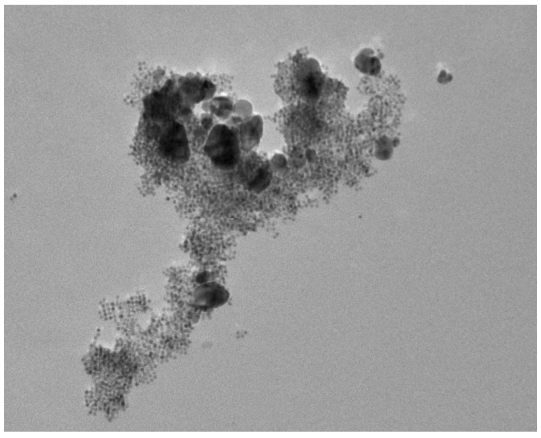


Figure S3: Carrier dynamics on a oxidized PbSe+SnO2 sample as a function of pump fluence. The blue trace is an example of fitting following eq. I. In the inset is shown the evolution of the Auger recombination lifetime as a function of fluence.

Structural characterization of PbSe QDs sensitizing SnO_2.

The samples were tested by TEM by drop casting scratched QD sensitized films dissolved in toluene onto a TEM metal grid. The results are shown in fig. S4. The top figures show how we detect an excess of QDs in our samples which are not linked to the oxide. This excess of QDs are apparently aggregated and agree with the presence of clustered phases in our samples as inferred from THz-TDS measurements (see fig. S2). In the bottom of figure S4 are shown two examples of how 6nm diameter PbSe QDs are linked to the oxide surface. We didn't observe any remarkable dispersion on QD sizes when comparing isolated and linked QDs. These results are in agreement with our observed single exponential ET dynamics (fig. 3) as explained in the text.





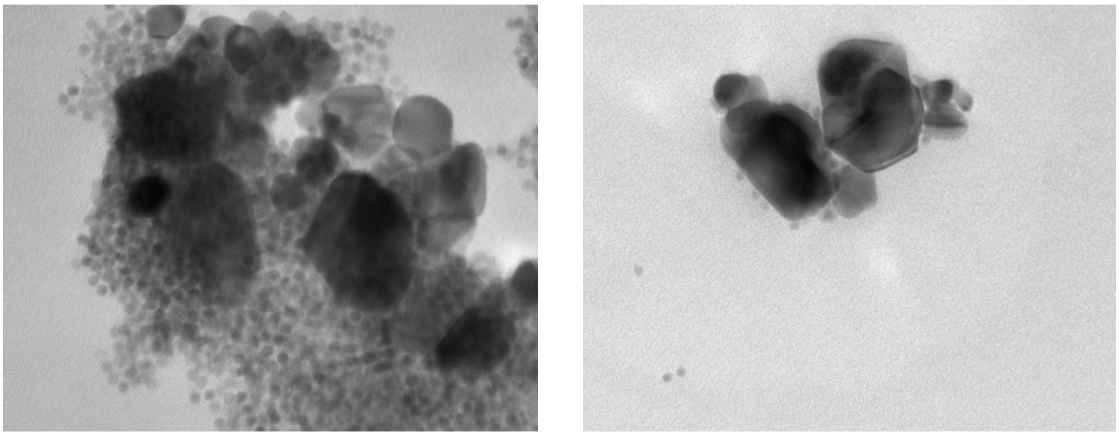


Figure S4: TEM characterization of 6nm diameter PbSe QDs sensitizing SnO_2

THz-TDS measurements on different sample's spots for a PbSe+SnO_2 sample

All the samples were measured in 5 different spots in order to check their homogeneity. Different amplitudes for all the components (from τ_0 to τ_2) were found, indicating a spatial inhomogeneous distribution of free carriers populating the oxide. In figure S4 is shown the characteristic results obtained for one of the samples under study (normalized to the value at 500ps). From the figure is clear that the strength for the Auger recombination contribution (τ_2) is not directly correlated with the ET from the dot to the oxide (τ_0) and/or surface defect related injection (τ_1).

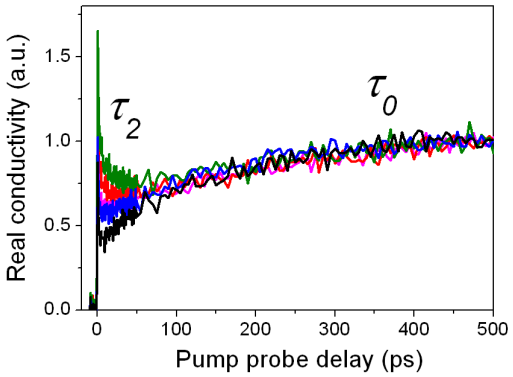


Figure S5: Carrier dynamics monitored in 5 different spots for a sample consisting on PbSe QDs sensitizing SnO_2 mesoporous film (normalized to the plateau value at 500ps). τ_2 refers to Auger recombination and τ_0 to the ET transfer from the donor to the acceptor species.

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