

Two-Photon Photoemission Study of Competing Auger and Surface-Mediated Relaxation of Hot Electrons in CdSe Quantum Dot Solids

Philipp Sippel,^{†,#} Wiebke Albrecht,^{‡,#} Dariusz Mitoraj,[‡] Rainer Eichberger,[†] Thomas Hannappel,^{†,§} and Daniel Vanmaekelbergh^{*,‡}

[†]Helmholtz-Zentrum Berlin für Materialien und Energie, E – IF: Solar Fuels, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany [‡]Debye Institute for Nanomaterial Science, Utrecht University, Princetonplein 5, 3584 CC Utrecht, The Netherlands [§]Institut für Physik, Technische Universität Ilmenau, Postfach 100565, 98684 Ilmenau, Germany

(5) Supporting Information

ABSTRACT: Solids composed of colloidal quantum dots hold promise for third generation highly efficient thin-film photovoltaic cells. The presence of well-separated conduction electron states opens the possibility for an energy-selective collection of hot and equilibrated carriers, pushing the efficiency above the one-band gap limit. However, in order to reach this goal the decay of hot carriers within a band must be better understood and prevented, eventually. Here, we present a two-photon photoemission study of the $1P_e \rightarrow 1S_e$ intraband relaxation dynamics in a CdSe quantum dot solid that mimics the active layer in a photovoltaic cell. We observe fast hot electron relaxation from the $1P_e$ to the $1S_e$ state on a femtosecond-scale by Auger-type energy donation to the hole. However, if the oleic acid capping is exchanged for hexanedithiol capping, fast deep hole trapping competes efficiently with this relaxation pathway, blocking the Auger-type electron—hole energy exchange. A slower decay becomes then visible; we provide evidence that this is a multistep process involving the surface.



KEYWORDS: TR-2PPE, quantum dot solid, CdSe, capping, hot electron relaxation, ultrafast

S olids composed of colloidal nanocrystalline quantum dots (QDs) are auspicious candidates for light-absorbing active layers in thin-film solar cells and sensitive photon detectors.¹⁻⁴ The high quantum confinement characteristic of these systems has the advantages of a size-tunable band gap and a strong light absorption.

Quantum-dot systems with electron levels well separated in energy provide an opportunity for the energy-selective collection of hot carriers, for example, electrons in the 1Pe state in parallel to the collection of equilibrated $(1S_e)$ carriers.⁵ This would allow the efficiency to exceed the Shockley-Queisser one band gap limit. This promise has led to much excitement and scientific interest in the lifetime and decay dynamics of hot electrons. The decay of the electron from the $1P_{\rm e}$ state to the $1S_{\rm e}$ state in colloidal CdSe QDs was mostly studied by pump-probe transient absorption spectroscopy⁶⁻⁸ in which the occupation of the 1Se and 1Pe states was monitored. For CdSe, it was generally observed that the $1P_e \rightarrow$ 1Se decay, over an energy gap of 100-300 meV, has a decay time constant in the subps range. This is unexpectedly fast concerning the phonon-bottleneck model that has been proposed for nanometer-sized quantum dots, thus questioning our physical understanding of strongly confined quantum dots.⁵

Why the so-called "phonon bottleneck" is not active in preserving hot carriers in QDs with strong confinement has been an issue of extensive research in the last years. Several decay mechanisms that circumvent the phonon bottleneck have been proposed. The two most prominent ones are an Augertype energy donation of the hot electron to the valence hole, which afterward decays back via a dense spectrum of hole states,^{10–12} or a surface-mediated electron decay via energy transfer to the capping molecules.¹³ It was recently shown with CdSe quantum dots that the lifetime of the 1P_e state can be enhanced by more than 2 orders of magnitude by a core– multishell architecture.¹⁴ This was rationalized by the fact that in such systems, the exciton wave function shows less overlap with the capping or surface states.

Most of the studies have been performed on systems consisting of dispersions of noninteracting QDs. It is, however, of considerable interest to study the fate of hot electrons in a quantum dot solid with an architecture that resembles that in a quantum dot solar cell as close as possible. We have prepared thin films of QDs by drop casting of QD suspensions on a conducting substrate. The decay of the hot $1P_e$ electrons in such a system was measured by two-photon photoemission spectroscopy (2PPE) (Figure 1a) in which a pump-pulse resonantly excites hot $(1P_e, 1P_{3/2})$ excitons in the QD solid, followed by a probe pulse that lifts photoexcited electrons, for example, those present in the $1P_e$ or $1S_e$ states and also those in localized surface states, above the vacuum level. Subsequently,

Received:January 10, 2013Revised:March 15, 2013Published:March 18, 2013



Figure 1. Two-photon photoemission spectroscopy to study the $1P_e \rightarrow 1$ S_e decay in a CdSe QD solid. (a) Scheme of selective photogeneration with a pump pulse and energy-resolved measurement with a UV probe pulse. The pump pulse excites electrons directly into the $1P_e$ state of the QD and the time delayed UV probe pulse emits them above the vacuum level E_V where their kinetic energy is measured by the detector, resulting in an intensity peak in the spectrum. The peak at lowest kinetic energies is the secondary electron peak stemming from electrons that are inelastically scattered on their way to the surface. (b) Absorption spectrum of the CdSe quantum dots in suspension showing allowed interband transitions labeled following the common nomenclature.²⁷ (c) Optical transmittance of the CdSe QD solids on an ITO substrate; the black line is for the QDs capped with hexanedithiol. The slightly red-shifted optical absorption of HDT-capped QDs indicates successful ligand exchange.

the photoemitted electrons are collected and their kinetic energy is measured. We should emphasize here that twophoton photoemission spectroscopy is sensitive to all photoexcited electrons; in our case, this means electrons that are still in the original 1Pe state, but also the electrons that are already partially relaxed and located between the 1Pe and 1Se state, and finally the electrons in the long-lived 1Se state. Time-resolution in the femtosecond regime is obtained by variation of the delay between the pump and the probe pulse, which means that the dynamics of the $1P_e \rightarrow 1S_e$ relaxation can be accurately accessed as well. Thus, recording the kinetic energy spectra at different pump-probe delays allows for the simultaneous observation of the evolution of photoexcited electrons with energy and time resolution. The emitted electrons are replaced by carrier injection from the electric contact, hence mimicking the photocurrent flow in an illuminated solar cell.

In the past, 2PPE was mostly used to study the energetics and dynamics of well-defined single crystal surfaces $^{15-18}$ and adsorbed molecules on such surfaces.^{19,20} Only very recently 2PPE has been used in the field of quantum dots as a method to study multiexciton generation on PbSe nanocrystals.²¹ Excitons with very high excess energy (several times the band gap) were generated and the subsequent relaxation of the electrons was studied. The dynamics of electrons present in the 1Pe and 1Se states could, however, not be resolved. In the present study, by selectively exciting the $1P_{3/2}-1P_e$ dipole transition, we show the feasibility of two-photon photoemission spectroscopy for the study of hot electrons photogenerated in the quantum confined 1Pe state in a QD solid. We studied the energetics and $1P_e \rightarrow 1S_e$ relaxation dynamics in two types of quantum dot solids: systems consisting of oleic acid (OA) and 1,6-hexanedithiol- (HDT) capped 4.2 nm-sized CdSe QDs, respectively. We generally observe that QD solids with oleic acid-capped QDs may become weakly charged during prolonged 2PPE spectroscopy leading to a variable position of the energy levels; this is in sharp contrast to the

hexanedithiol-capped samples that show a constant position of the energy levels over many samples and prolonged experiments. Our kinetic results provide strong evidence for an Auger-type electron-to-hole energy transfer. In the case of hexanedithiol-capped QDs, fast hole trapping can block this process and a slower relaxation pathway then becomes visible in the data. We have developed a general kinetic model that provides excellent fits to the time-dependent collection of the highest energy electrons, that is, those emitted from the 1Pe states. Furthermore, the sensitivity of the 2PPE method for all photogenerated electrons allowed us to probe the slower decay pathway in detail; it is found that the electrons decay gradually to lower energy between the 1Pe and 1Se state with time, indicating a multistep relaxation pathway. A model that treats such a stepwise relaxation process is presented reproducing the energy dependent curves with high accuracy. Multistep relaxation from 1Pe to 1Se may involve surface states and/or capping-related states.

I. Experimental Part/Background. The laser pulses stem from a Ti:sapphire laser system with two noncollinear-opticalparametric amplifiers^{22,23} and in the case of the probe beam subsequent second harmonic generation leads to the desired photon energies. Time delay is achieved using an electronically controlled delay stage to vary the optical path of one of the beams. While the probe beam photon energy was kept at 4.59 eV, the photon energy of the pump beam could be tuned independently over the optical range to match the optically allowed $1P_{3/2}-1P_e$ and $1S_{3/2}-1S_e$ transitions. The photon flux per pulse of pump and probe beam is below 5×10^{13} cm⁻² and 2×10^{10} cm⁻², respectively, ensuring that the average number of electron hole pairs is far below 1 per QD. To achieve a satisfactory time resolution the pulses were compressed using prism pairs resulting in a cross correlation of sub-40 fs. The kinetic energy of the photoemitted electrons is measured with a homemade time-of-flight spectrometer.²⁴ The substrates are attached by metal clamps to a metal sample holder which is



Figure 2. Temporal evolution of 2PPE spectra measured at two types of CdSe QD solids. (a,b) The results for a solid with oleic acid-capped quantum dots for $1P_{3/2}-1P_e$ excitation: (a) as measured (only probe pulse background subtracted) and (b) after subtraction of the long-lived contribution, that is, the spectrum I (E_{kin} , $t_d = 30$ ps). (c,d) The results obtained with a solid of hexanedithiol capped quantum dots: (c) for $1P_{3/2}-1P_e$ excitation and (d) reference experiment with $1S_{3/2}-1S_e$ excitation (in both cases the long-lived contribution has been subtracted). The excitation and decay pathways are visualized in the schemes on the right-hand side.

connected to ground, thus ensuring the refilling of photoexcited electrons. All measurements are conducted under room temperature and ultrahigh vacuum (UHV) conditions (pressure below 1×10^{-10} mbar). The samples were prepared in a glovebox with nitrogen atmosphere and via a specially build transfer system brought directly to the UHV chamber and thus not exposed to air. The colloidal CdSe QDs were synthesized following the hot injection method,²⁵ leading to CdSe nanocrystal suspensions with a small size dispersion capped with oleic acid. Ligand exchange to hexanedithiol has been done using the dipcoating technique. Two types of substrates have been used, indium tin oxide (ITO) and highly ordered pyrolytic graphite (HOPG). Absorption, emission, and transmission electron microscopy measurements (shown in Figure S1 in the Supporting Information) verified the quality of the samples with a size dispersion of 5%. The absorption spectra also yielded the appropriate pump energy in the 2PPE measurements required to address the $1P_{3/2}-1P_e$ and $1S_{3/2}-1P_e$ 1S_e optical transitions. Figure 1b shows the absorbance for the QD solution revealing the good quality of the sample. In order to ensure an equally good quality for the QD arrays on a substrate, transmittance measurements were conducted shown in Figure 1c. The $1S_{3/2}-1S_e$ dip is slightly red shifted for the HDT-capped QDs in respect to the oleic acid-capped QD arrays. This is in agreement with previous reports and indicates that the ligand exchange was successful.²⁶

II. Results and Discussion. Figure 2a shows 2PPE results recorded at 4.2 nm CdSe QDs capped with oleic acid pumped with a photon energy which is tuned to address the $1P_{3/2}-1P_e$ transition. In the transmission spectra shown in Figure 1c, the dips related to the $1P_{3/2}-1P_e$ and $3S_{1/2}-1S_e$ cannot be distinguished, thus impeding to selectively address only the $1P_{3/2}-1P_e$ transition. To be sure to excite $1P_e$ electrons, we tune the peak photon energy of the ~20 nm broad excitation pulse to the maximum of the broad structure around $\lambda \sim 500$ nm, which is due to both transitions. Hence, besides quantum dots with an electron in $1P_e$ directly after excitation.

The 2PPE spectra have been recorded at specific time delays between the pump and probe pulse, hence they represent the relaxation dynamics of the electrons that were pumped into the 1Pe state. A background correction was done by subtracting a spectrum at negative time delays with the probe pulse arriving ~ 10 ps before the pump pulse since in this case no photoinduced signal is expected. This is necessary as the probe beam itself causes a background when it pumps and probes within its own pulse duration, thus exciting higher states in the dot and ligand. Because of its much lower photon energy, the pump pulse is less probable to cause an emission of electrons. The big sharp peak at low energies around 0.3 eV is the secondary electron peak stemming from electrons that are inelastically scattered on their way to the surface and subsequently have lost most of their excess energy and barely succeed in leaving the sample. A clear feature can be seen at around 1.75 eV (marked by an arrow) indicating the intensity decrease of the electrons with highest kinetic energy for increasing pulse time delays.

Since the kinetic energy of the electrons coming from different states is resolved in the 2PPE spectra a clear distinction can be made between electrons originating from the $1S_e$ and $1P_e$ state: the electrons with the highest kinetic energy can only stem from the $1P_e$ electronic state since the pump energy is adjusted to match the $1P_{3/2}-1P_e$ transition and energetically higher lying electron states cannot be reached with the used photon energy.

The temporal and energetic behavior of these $1P_e$ electrons can be distinctly accentuated by subtracting the contribution of any long-living electrons. The latter consists of the $1S_e$ electrons excited directly by the pump pulse and of already relaxed $1P_e$ electrons. This is done by subtracting the signal that remains for pump-probe time delays longer than 30 ps. Figure 2b shows the resulting spectra obtained from the data of Figure 2a. The peak at 1.7 eV stems from electrons emitted from the $1P_e$ states. This peak has a fwhm of ~0.4 eV originating both from the limited resolution of the apparatus and the absolute position of the $1P_e$ states in the sample. First, we have an



Figure 3. (a) Transient occupation of the $1P_e$ levels in OA (red) and HDT capped (black) samples. Symbols represent the 2PPE data; solid lines are fits based on the models shown in (b,c), respectively. (b) Scheme of a rate model for the Auger-type relaxation process in OA capped samples. (c) Scheme of a rate model for the relaxation process in HDT-capped samples involving the Auger-type process, hole trapping, and an alternative relaxation mechanism in which the valence hole is not involved. VB marks the valence band, which for simplicity is here drawn as continuum.

energy resolution of about 0.1 eV of the TOF-spectrometer and a 0.1 eV broadening due to the spectral width of the probe pulse. Second, partially due to a distribution in size and strong confinement and partially due to inhomogeneous charging, the absolute energy of the $1P_e$ state in the sample may vary over about 100 meV. Third, electron tunneling spectroscopy in an STM has shown that there is a strong intrinsic broadening of the electron states due to electron–phonon coupling.²⁸ Finally, we should also consider that in contrast to a single crystalline sample²⁹ QD solids have a rough surface, possibly also with variations of the surface potential that may alter the kinetic energy of the emitted electrons.

The intensity of the $1P_e$ electrons drops significantly with increasing time delays and after 0.6 ps only a small fraction is left that is completely gone after 10 ps. In comparison, for QD solids with HDT-capped CdSe quantum dots, the $1P_e$ peak still shows a significant intensity after 0.6 ps indicating a longer decay time compared to oleic acid-capped samples.

As a reference experiment, the pump pulse center energy was adjusted to the $1S_{3/2}-1S_e$ transition of the HDT-capped QDs (Figure 2d), which should leave the $1P_e$ states unpopulated. It is clear that then no change in signal is measured in the energy range between 1 and 2 eV in the entire time window. Hence, this proofs that the time-dependent intensities in Figure 2b,c can be safely attributed to the $1P_e$ electrons. It should also be noticed, that the kinetic energy of the $1S_e$ electrons cannot be identified since a $1S_e$ peak (expected 0.3 eV below the $1P_e$ signal) is not visible in the spectra. Instead, a rather broad and time-independent shoulder is observed in the region between the secondary electron peak and the $1P_e$ peak.

We attribute the broad structure to secondary electrons stemming from $1S_e$ electrons that have lost a part of their energy by inelastic scattering before leaving the sample. The QDs with their surrounding ligands are complex systems and charges or dipoles on the surface can alter the kinetic energy of the photoemitted electrons. For the measurements with $1P_{3/2}$ -

 $1P_e$ excitation also secondary electrons stemming from $1P_e$ are expected to overlap energetically with the signal from $1S_e$ electrons. Because $1P_e$ electrons would provide a signal that decreases in time and the $1S_e$ electrons would provide a signal that rises approximately with the same time constant, it can be understood that the broad feature arising from inelastic scattered electrons of both states does not show a clear time-dependence in the measurement window of the apparatus up to 40 ps.

The visibility of feeding of electrons in the 1S_e state is further hindered since it is overlapped with the background signal belonging to 1S_e electrons directly excited by the pump pulse by the $3S_{1/2}-1S_e$ transition. In addition, the "backward process" occurring at lower kinetic energy regions around $t_d = 0$ fs in which the roles of the laser pulses are exchanged masks the signal in the 1S_e energy range in the first \sim 200 fs. This is shown in Figure S2 in the Supporting Information. Since the probe pulse is in the UV range, it excites states with high excess energy and the pump pulse "probes" these states. This can be seen as the reverse process of "normal" 2PPE and thus a corresponding decay is observed at negative time delays. However, this process also influences the first ~200 fs of positive time delay as there is still a temporal overlap of pump and probe pulses leading to a very high photoexcitation intensity compared to the rest of the signal.

Energetic differences between oleic acid and HDT-capped QDs can be addressed via the work function. A good estimate for the work function can be obtained from the position of the secondary electron edge in the kinetic energy spectra (compare Figure 1a). It was observed that the oleic acid-capped QD solids show a work function that varied between 3.2 and 3.5 eV when the laser spot was scanned over a given sample, or when different QD solids were measured. In contrast, the samples consisting of HDT-capped QDs all have a constant work function of 3.5 eV. The work function is sensitive to surface dipoles and charges. Other groups also observed that



Figure 4. (a) 2PPE-transients of the HDT capped samples at different kinetic energies near the $1P_e$ peak signal. Black squares represent the experimental data; the black lines are simulated curves, based on the model described in the text. The red, blue, and green lines show the individual contributions of $1P_{e^j}$ intermediate and $1S_e$ state, respectively. For all transients the remaining signal above $t_d = 30$ ps was subtracted (long-living electron background) and the resulting curves were normalized by dividing by their particular value at $t_d = 350$ fs. (b) Scheme of a simple rate model, describing the decay from $1P_e$ to $1S_e$ via an intermediate state. (c) Simulated curves of $1P_{e^j}$ intermediate state and $1S_{e^j}$ according to the model shown in (b) with time constants $\tau_{p\rightarrow interm} = 1$ ps and $\tau_{interm\rightarrow s} = 5$ ps.

exchanging ligands shifts the energy levels relative to the vacuum level and also the vacuum level itself.^{30,31} This was attributed to a dipole creation between the ligand anchor group and the surface of the QD. We believe that the variation of the work function with oleic acid-capped QDs can be attributed to a residual charging by photogeneration and photoemission. Because of the photoemission of electrons out of the sample it becomes locally positively charged and could remain so if the valence band holes are not sufficiently rapidly replenished by carrier injection from the back-contact and transport. Because of the long oleic acid molecules around the QDs, the tunneling barriers between the QDs in the sample are considerable, and transport may not be fast enough. In contrast, HDT is a much shorter molecule and by improved carrier transport, the empty states in the valence band are sufficiently fast refilled.^{32–34}

To evaluate the temporal evolution of the electrons in the 1Pe state, the mean intensity of photoemitted electrons at kinetic energies corresponding to the 1P_e peak (compare Figure 2b,c) is averaged over 0.2 eV and plotted for different pulse time delays. The resulting transient populations of 1Pe state electrons are shown in Figure 3a for oleic acid and HDTcapped samples. To minimize contributions other than 1Pe electrons, the transients shown here represent only the intensity of photoemitted electrons from the high energy edge of the 1Pe-related signal. The oleic acid-capped sample shows a much faster decay than the HDT capped one; the curve can be fitted with a monoexponential decay and a constant offset for positive pump-probe delays. We ascribe the fast decay with a time constant of $\tau = 220$ fs to an Auger-like process, where the electron relaxes to 1Se by transferring its excess energy to the hole. This process is visualized in Figure 3b. Similar time constants observed by transient absorption spectroscopy were also ascribed to an Auger-like relaxation.^{7,35} The offset stays constant for at least 40 ps, which is the

measurement limit of the used setup. It is also present at the HDT-capped sample but not visible after normalization of the transients, since the actual signal is much bigger than for the OA-capped samples. The bigger signal for HDT-capped samples probably stems from the better refilling of photoemitted electrons through the back contact. Although, in principle, injection of hot electrons into the electrode can form an alternative decay path parallel to the $1P_e$ -to- $1S_e$ relaxation,³⁶ it can be neglected here since the nanocrystalline film is about 50–100 nm in thickness and hot electron transfer between the nanocrystals is much slower than the measured decay. Thus, substrate effects are not seen in the conducted 2PPE measurements.

The 1Pe electron decay curve of the HDT-capped sample shows a more complex decay, involving much slower components on a picoseconds time scale. This forms a strong indication that the Auger process is suppressed. We argue that that this suppression is due to trapping of the hole in a localized state in the band gap. This is in line with studies by Wuister et al.³⁷ who showed by photoluminescence measurements that the hole can be trapped by thiol ligand states located inside the band gap. Transient absorption studies for CdSe nanocrystals by different groups showed that the lifetime of 1Pe-electrons is considerably increased into the picoseconds time scale after hole capture, similar to our findings.^{12,13} In fact, this decay is still much faster than one would expect in terms of the phonon bottleneck⁹ and points to the existence of an alternative relaxation mechanism. Previous works have proposed that this non-Auger process is mediated by surface states or capping molecules.14

We have used a generalized kinetic scheme (Figure 3c) that accounts for the Auger pathway and the alternative relaxation pathway in case trapping of the hole occurs. Directly after photoexcitation (top left in the scheme) the electron is in the $1P_e$ state, while the hole is in $1P_{3/2}$. Because of the small energy spacings between the valence band states that are in the range of the phonon spectrum, the hole relaxes extremely fast.¹¹ Then, two competing processes take place; the electron can relax to 1Se by the Auger-like process with a time constant $au_{ ext{auger}}$ or the hole can be trapped by the HDT ligand states with a time constant τ_{htrap} , impeding the Auger-like process. In this state of the system (bottom left in the scheme), relaxation of the electron to $1S_e$ is still possible via the alternative relaxation pathway (time constant τ_{alt}) mediated by the surface or the capping molecules. A fit based on this model (Figure 3a) is in good agreement with the data. The time constants of the fit are $\tau_{\rm auger}$ = 290 fs, $\tau_{\rm htrap}$ = 350 fs and $\tau_{\rm alt}$ = 1.7 ps. The Auger time constant is slightly larger than for the oleic acid-capped sample. The trapping time of 350 fs is comparable with transient absorption measurements of Klimov et al. providing a hole trapping time constant of about 400 fs for pyridine-capped samples.12

The mechanism behind hot electron relaxation in CdSe quantum dots in the state with a trapped hole (bottom left in Figure 3c) is still a matter of discussion. We note that all previous results on that matter rely on transient absorption measurements that monitor the populations of $1S_e$ and $1P_e$ states but in contrast to 2PPE are unable to detect electrons in states between the $1P_e$ and $1S_e$ state in a direct way. The time constant of $\tau_{alt} = 1.7$ ps, which remains after hole trapping, must be ascribed to a relaxation mechanism that does not involve the hole. Pathways that have been proposed are via energy transfer to vibrational states of the capping molecules or via surface/interface/ligand related states which are energetically located between $1S_e$ and $1P_e$.

2PPE is sensitive for electrons in surface^{16–18} and molecular adsorbate states.^{19,40} Therefore, we performed a detailed analysis of the dynamic behavior in the energy range just below the $1P_e$ signal. In Figure 4a, transients are shown that correspond to different regions in the kinetic energy spectrum shown in Figure 2c.

The fast (Auger) component during the first few 100 fs remains nearly constant when monitored for different energy windows. The same behavior is also observed for the OAcapped sample (see Figure S3 in the Supporting Information). In contrast, the slow component of the decay curve for HDTcapped QDs shows a strong dependence on the kinetic energy window monitored. Only at 0.2 eV above E_{kin} (1P_e) we observe a time constant of τ_{alt} = 1.7 ps reported above. At 0.4 eV above the maximum of the 1Pe peak, where the signal is already very small, we see a decay of $au_{
m alt} pprox 1$ ps. The transients at lower kinetic energies, however, show a slower and more complex decay in the first few picoseconds, all ending in a slow monoexponential tail with a time constant of around 5 ps. These results point to a stepwise relaxation involving additional states between $1P_e$ and $1S_e$. We attribute the slow tail of 5 ps to electrons in states between 1Se and 1Pe that are photoemitted by the probe beam before being able to relax further.

In order to support this interpretation we compare our experimental data to calculations based on a rate equation model shown in Figure 4b that accounts for electron trapping of the 1P_e state and subsequent further relaxation to 1S_e. As time constants we use $\tau_{p \rightarrow interm} = 1$ ps for the relaxation from 1P_e to the intermediate state and $\tau_{interm \rightarrow s} = 5$ ps for the relaxation from the intermediate state to 1S_e. These are the time constants obtained by fitting the decay of the transient 0.4

eV above E_{kin} (1P_e) and by a single-exponent approximation for the slow tail of the transients at lower energy, respectively.

The simulated transient populations of 1P_e, the intermediate state, and 1S_e in Figure 4c are $p_{1Pe}(t_d)$, $p_{interm}(t_d)$ and $p_{1Se}(t_d)$, respectively. The calculated energy dependent 2PPE signal is finally a linear combination of all three contributions

$$I(E_{kin}, t_d) = A_{1Pe}(E_{kin}) \cdot p_{1Pe}(t_d) + A_{interm}(E_{kin}) \cdot p_{interm}(t_d) + A_{1Se}(E_{kin}) \cdot p_{1Se}(t_d)$$

with the energy dependent coefficients $A_{1Pe}(E_{kin})$, $A_{interm}(E_{kin})$, and $A_{1Se}(E_{kin})$. We achieve good agreement between the calculated curves and the measured data, by using a set of values for these coefficients that reflects the expected energy dependence: a dominating contribution of $1P_e$ state electrons for the transients at the high energetic side and a growing contribution of intermediate and $1S_e$ state electrons toward lower energies. It has to be noted that the constant offset at long delay times related to directly photoexcited $1S_e$ electrons has to be treated as an additional parameter and is also varied to get the best agreement between the simulated and the experimental curves. Furthermore the onset of the simulated curves is set to 350 fs, since this model describes only the dynamics after hole capture and does not take into account the fast components due to the Auger-process.

Our results support the idea that the slow relaxation process that becomes prominent when the Auger process is blocked constitutes electron relaxation via intermediate states. It should be noticed that the assumption of one discrete intermediate state between $1P_e$ and $1S_e$ is probably far too simple. However, it can be argued that a model involving multiple intermediate states or even a continuum of states will provide similar results, meaning a fast relaxation at high kinetic energies and a slower and more complex behavior at lower kinetic energies due to increasing importance of lower lying electron states. A possible mechanism of electron relaxation via intermediate states in quantum dots has been investigated theoretically.^{38,39} It has also been proposed as a possible explanation of slow relaxation processes observed in transient absorption measurements at CdSe nanocrystals with hole-trapping capping molecules.¹³

III. Conclusion. In conclusion, we have provided results showing that pump-probe two photon-photoemission spectroscopy is a valuable method to study the decay of hot electrons in a quantum dot solid. Within a CdSe quantum dot solid we find a fast Auger-like decay process that can be blocked by trapping of the hole. In this case, a slower decay process becomes prominent. Our method also allows to monitor this alternative decay path, and the results indicate that it consists of a multistep relaxation via intermediate (surface) states lying between the $1P_e$ and $1S_e$ quantum dot eigenstates.

ASSOCIATED CONTENT

S Supporting Information

TEM-picture of CdSe quantum dots; detailed information to the "backwards process"; transients for different kinetic energies at the OA and HDT capped samples for large time spans. This material is available free of charge via the Internet at http:// pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author *Tel: +31614418589.

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Author Contributions

[#]The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. P.S. and W.A. contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the BMBF (Project No.03SF0404A). We would like to thank Suzanne J. Pera and Relinde J.A. van Dijk-Moes for synthesizing and analyzing of the CdSe sample. D.V. and D.M. acknowledge the Dutch FOM (09JSP40-1) for financial support of this research.

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NOTE ADDED AFTER ASAP PUBLICATION

This Letter was published ASAP on March 22, 2013. Due to a production error, the fifth author's name was misspelled. The corrected version was published on March 25, 2013.