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Hot-electron decay in a CdSe QD solid studied by Two-Photon-Photoemission Spectroscopy.

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Investigation of the time-evolution of hot electrons in colloidal nanocrystalline quantum dots (QD) is of high fundamental interest as well as for applications of quantum dots in third-generation highly efficient thin-film photovoltaic cells. The presence of well-separated conduction electron states in quantum-dot solar cells opens the possibility to energy-selectively collect the hot and equilibrated carriers, occupying the p and s QD-orbitals, respectively. This should push the solar cell efficiency above the one-band gap limit. Decay dynamics of hot excitons in quantum dots were studied by monitoring the transient absorption[1] or terahertz-domain spectroscopy[2]. Here, we report on Two-Photon-Photoemission Spectroscopy (2-PPE) studies of $1P_e \rightarrow 1S_e$ electronic intra-band relaxation dynamics in a CdSe QD-solid that mimics the active layer in a photovoltaic cell[3]. The technique allows us to follow the (de)population dynamics of the hot $1P_e$ electron states with femtosecond time resolution. Energy donation from the 1 P_e electron to the hole followed by fast relaxation of the hole (Auger cooling) is proposed to explain the fast electron cooling with the time constant τ_{auger}. However, if the oleic acid capping is exchanged for hexanedithiol capping, fast deep hole trapping competes efficiently and block the Auger-type electron-hole energy exchange. In this case, a slower decay process, with a time constant (τ_{auger}) higher by one order of magnitude, becomes prominent. Our data indicate also existence of the alternative decay path 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 $1P_e$ (Figure 1).

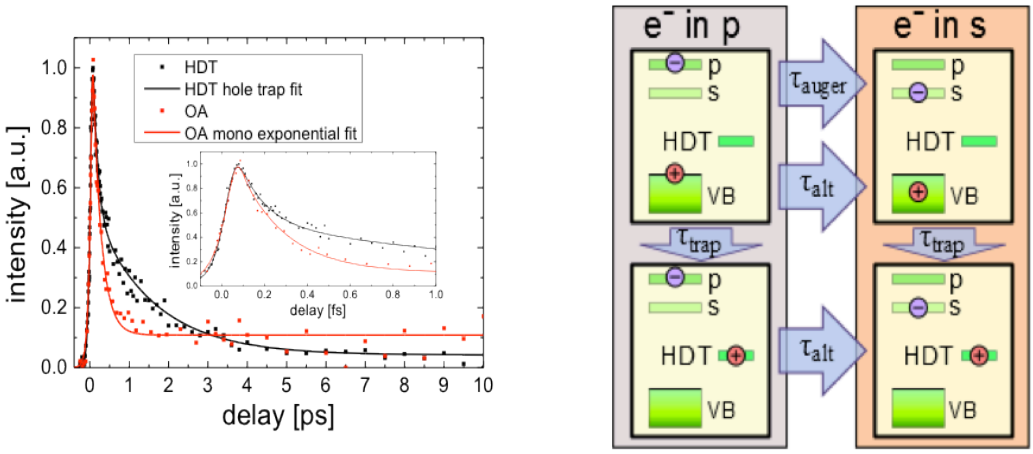

Figure 1. Decay dynamics of hot electrons in p-type QD orbitals measured with two-photon Photo-emission spectroscopy. (Left) Transient occupation of the $1P_e$ levels in oleic acid (red) and hexanedithiol capped (black) CdSe samples. Red: Fast decay of the p-electron by Auger-type energy donation to the valence hole. Black: decay in a solid of dithiol-capped quantum dots, where fast hole trapping blocks the Auger decay. (Right) 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.

1. Pandey, A. et Guyot-Sionnest P. *Science* 322, **2008**, 929-932
2. Hendry, E. et al. *Phys Rev. Lett.* 96 **2006**, 057408
3. Paper submitted to NanoLetters 2012