FINAL PROGRESS REPORT

1. **DOE Award Number:** DE-SC0001928

   Institution: University of Texas at Austin

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2. **Project Title:** Extracting hot carriers from photoexcited semiconductor nanocrystals

   Principal Investigator: Xiaoyang Zhu

3. **Date of the Report:** December 9th, 2014

   Period Covered: 09/01/2010 – 12/31/2012.

4. **Brief Description of Accomplishments**:

We have achieved the first direct and quantitative determination of hot electron relaxation dynamics in semiconductor QDs. We used femtosecond time-resolved two-photon photoemission spectroscopy to carry out a complete mapping in time- and energy-domains of hot electron relaxation and multi-exciton generation (MEG) dynamics in PbSe quantum dots functionalized with 1,2-ethanedithiols. We also established graphene nano-materials as viable candidates for hot carrier chromophores. We probed hot electron injection and charge recombination dynamics for graphene quantum dots (QDs, each containing 48 fused benzene rings) anchored to the TiO_2(110) surface via carboxyl linkers. We find ultrafast hot electron injection from photoexcited graphene QDs to the TiO_2 conduction band and charge recombination dynamics that depend the depth (and thus electron energy) of the initial injection.

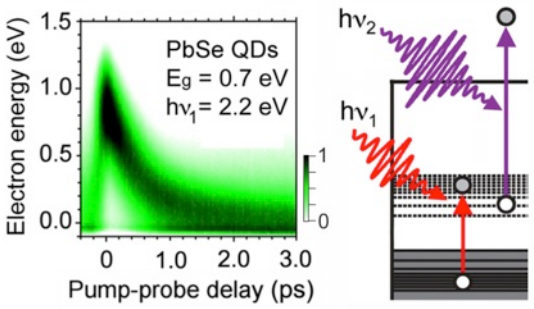

Fig. 1. Pseudo-color representation of TR-2PPE spectrum of a PbSe QD thin film with excitation photon energy $h\nu_1$ = 2.20 eV and probe photon energy $h\nu_2$ = 4.28 eV. The electron energy is referenced to the bottom of the conduction band. The right shows schematically the principle of the TR-2PPE experiment. *Nano Lett*. **2012**, *12*, 1588-1591.

The best-understood property of QDs is the size-dependent optical transition energies due to the quantization of charge carriers near the band edges. In contrast, much less is known about the nature of hot electron-hole pairs resulting from optical excitation above the bandgap. The PI has successfully applied TR-2PPE spectroscopy for a complete mapping in time- and energy-domains of hot electron relaxation and multi-exciton generation (MEG) dynamics in PbSe QDs functionalized with 1,2-ethanedithiols, as illustrated in Fig. 1. This experiment led to the discovery of a linear scaling law between the hot electron relaxation rate and its energy above the conduction band minimum. There was no evidence for carrier multiplicagtion from intra-band hot electron relaxation for excitation photon energy as high as three times the bandgap ($3E_g$). Rather, carrier multiplicagtion occurs in this system only from inter-band hot electron transitions at sufficiently high photon energies (~$4E_g$). These results suggest that photoexcitation significantly above the bandgap of PbSe QDs creates hot carriers that behave like those in the bulk semiconductor.

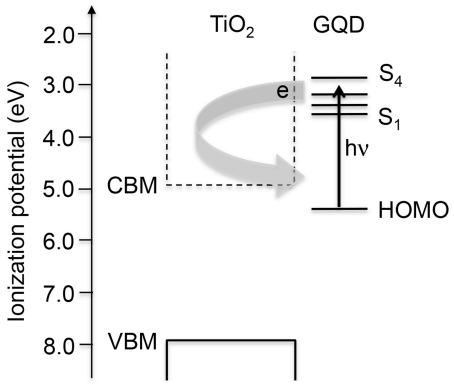

Fig. 2. Energy level diagram of the C132A molecule (GQD) on the TiO_2 surfaces. VBM: valence band maximum; CBM: conduction band minimum. See text for a discussion on the approximate position of the conduction band (dashed box). The thick arrow illustrates hot electron injection into TiO_2 conduction, cooling and localization of the electron into an electron polaron, and recombination across the interface of the electron polaron with the hole on a GQD. *ACS Nano* **2013**, *7*, 1388-1394

As an alternative to inorganic semiconductor QDs, we found that graphene based materials may be viable candidates for hot carrier chromophores. We probed hot electron injection and charge recombination dynamics for graphene quantum dots (QDs, each containing 48 fused benzene rings) anchored to the TiO_2(110) surface *via* carboxyl linkers, Fig. 2. We found ultrafast electron injection from photoexcited graphene QDs to the TiO_2 conduction band with time constant t_i < 15 fs and charge recombination dynamics characterized by a fast channel (t_{r1} = 80-130 fs) and a slow one (t_{r2} = 0.5-2 ps). The fast decay channel was attributed to the prompt recombination of the bound electron-hole pair across the interface. The slow channel depended strongly on excitation photon energy or sample temperature and could be explained by a "boomerang" mechanism, in which hot electrons were injected into bulk TiO_2, cooled down due to electron-phonon scattering, drifted back to the interface under the transient electric field, and recombined with the hole on graphene QDs. We explored feasibilities of implementing the hot carrier solar cell using graphene nano-materials.

5. Publications Acknowledging DOE support during this funding period

- L. Miaja-Avila, J. Tritsch, A. Wolcott, W.-L. Chan, C. A. Nelson, X.-Y. Zhu, "Direct mapping of hot electron relaxation and multiexciton generation dynamics in PbSe quantum dots," *Nano Lett.* **2012**, *12*, 1588-1591.
- C. A. Nelson, X.-Y. Zhu, "Reversible electronic traps in PbS quantum dot solids induced by an order-disorder phase transition in capping molecules," *J. Am. Chem. Soc.* **2012**, *134*, 7792-7795.

- K. J. Williams, C. A. Nelson, X. Yan, L. Li, X.-Y. Zhu, "Photo-induced hot electron transfer from graphene quantum dots to TiO_2," *ACS Nano* **2013**, *7*, 1388-1394.

6. People working on the project

Kenrick J. Williams (100%), Cory Nelson (100%), Luis Miaja-Avila (50%, the other 50% from internal support at UT-Austin)

7. Current and pending support

Current

National Science Foundation, Zhu (PI) 06/01/12-05/31/15
"Exceeding the limit in solar energy conversion with exciton fission", $461,000
The project is aimed at understanding exciton fission and energy transfer in organic semiconductors.

National Science Foundation, Zhu (PI); Liu (co-PIs) 08/01/12-07/31/15
"Dynamic Self-Assembly of Glycolipids for Unveiling Complex Glycan-Protein Interactions", ($300,000)
The project is aimed at developing fluidic glycan microarrays for large scale screening in glycomics.

Sandia National Lab – subcontract, Zhu (PI) 08/01/13-12/31/14
"Collaborative research on the Auger mechanism in semiconductor light-emitting diodes" $150,000
The project is aimed at understanding the Auger mechanism for the Droop phenomena in QW based white light LEDs. There is **no overlap** with the current proposal.

Department of Energy, Zhu (PI) 09/01/13-04/30/15
"Extracting hot carriers from photoexcited semiconductor nanocrystals" $352,759.
The project is aimed at understanding the charge separation mechanism in nanomaterial based photovoltaic.

Department of Energy, Zhu (PI); Frisbie (co-PI, UMN) 09/01/13-12/31/15
"Spectroscopy of charge carriers and traps in field-doped single crystal organic semiconductors" $470,103.
The project is aimed at obtaining direct spectroscopic signatures of charge carrier trapping in organic electronic materials and devices. There is **no overlap** with the current proposal.

Samsung Global Research Initiative, Zhu (PI) 11/01/13-10/31/14
"Probing Hot Electron Dynamics by Femtosecond Time-resolved Nonlinear Optical Spectroscopies**".** $100,000/yr

The project aims to develop and apply nonlinear optical spectroscopies to characterize hot electron dynamics in 2D nanomaterials. There is **no overlap** with the current proposal.

Air Force Office of Scientific Research, Nuckolls (PI); Zhu is 1 of 3 co-PIs. 09/01/13-08/31/16
"Artificial Atoms, Molecules, and Solids: Multiple Functions and Emergent Properties"
$1,300,000.
The project explores the synthesis and emergent physical properties of new electronic materials from the assembly of super-atoms.

Pending:
National Science Foundation, Hone (PI); 11/01/14-08/31/19
(Zhu is an IRG leader and one of 14 co-PIs)
"Columbia University MRSEC (Materials Research Science and Engineering Center)"
$16,819,346
The proposal consists of two independent research thrusts, designated IRG1 and IRG2. IRG1 will study the properties of van der Waals heterostructures while IRG2 will explore the design and synthesis of new electronic materials from the assembly of super-atoms (atomically precise nano-clusters).

Department of Energy, co-PIs: Zhu & Nuckolls 01/01/15-12/31/17
"Building a Toolbox of Singlet Fission Molecules for Solar Energy Conversion" $913,620.
The proposal aims to develop new strategies for the synthesis of molecular materials with high singlet fission yields.

Department of Energy, Zhu (PI) 05/01/15-04/30/18
"Charge carrier dynamics in hybrid organic-inorganic semiconductors" $689,820.
This is a renewal of DE-SC0001928.

8. Unexpended fund

none.