Ultrabroadband time-resolved spectroscopy in novel types of condensed matter: supplementary material

CHIH-WEI LUO,^{1,2,*} YU-TING WANG,¹ ATSUSHI YABUSHITA,¹ AND TAKAYOSHI KOBAYASHI^{1,3,4}

¹ Department of Electrophysics, National Chiao Tung University, Hsinchu 30010, Taiwan

² Taiwan Consortium of Emergent Crystalline Materials, Ministry of Science and Technology, Taipei 10601, Taiwan

³ Advanced Ultrafast Laser Research Center and Department of Engineering Science, The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan

⁴ JST, CREST, 5 Sanbancho, Chiyoda-Ku, Tokyo 102-0075, Japan

*Corresponding author: cwluo@mail.nctu.edu.tw

Published 14 January 2016

This document provides supplementary information to "Ultrabroadband time-resolved spectroscopy in novel types of condensed matter," <http://dx.doi.org/10.1364/optica.3.000082>. A detailed discussion of the relaxation mechanisms of excitonic band A in MoS₂ and the stationary absorption spectra for P3HT:PCBM devices are presented in sections 1 and 2, respectively. © 2016 Optical Society of America

<http://dx.doi.org/10.1364/optica.3.000082.s001>

1. Relaxation mechanisms of excitonic band A

The mean transition energy of excitonic band A is further calculated at every time delay, i.e., the time-dependent energy gap between excited electrons and holes, is plotted in Fig. S1. Since the photobleaching (caused by the same polarizations σ^+ for the pump and probe) and biexciton formation (caused by opposite polarizations σ^+ for pump and σ^- for probe), the results of the σ^+ and σ^- probes before 100 fs show distinct energy differences in transition A. After randomization of the polarized excitons generated by a pump pulse, the energy difference disappears. Blue shift and red shift take place when the polarizations of the pump and probe are the same and opposite, respectively. Similar energy difference (~ 13 meV at $t \sim 0$ ps in this study) is also observed on the CdSe nanocrystals with the splitting of bright-dark exciton states [1,2]. It is found that the flipping transition time scales with the energy split of bright-dark exciton states. Once the energy split increases to ~ 14 meV for the small size of nanocrystals, the flipping transition time is in the range of tens of femtoseconds. This implies that the energy difference between the K and K' valleys caused by the inhomogeneity of initially excited population in the K and K' valleys leads to the fast spin randomization time. Moreover, the exciton size (diameter ~ 1.86 nm [3]) and spin randomization time (~ 60 fs) of monolayer MoS₂ also satisfy the size dependence of spin flip rate in semiconductor nanocrystals [1,2]. The behaviors can be rephrased as follows. The time constant $\tau_{\text{spin}} \sim 60$ fs reflects the lifetime of spin polarized exciton A.

It has relevant decay time but different behaviors between the co-circular polarizations and anti-circular polarizations of the pump and probe beams. Since the hole spin states are non-degenerated at the K and K' valleys, the relaxation of hole spin is blocked by spin-valley coupling. On the contrary, spin states of electrons can be easily destroyed because the spin states of the conduction band are degenerate. Thus, the relaxation of the electron spin of excitons causes the transition from optically active excitons to dark excitons [4].

Fig. S1. Time-dependent (in log scale) mean energy of transition band A excited by 1.89 eV and σ^+ pump pulse at 78 K. The solid squares are the σ^+ probe and the open squares are the σ^- probe. Adapted from [5].

2. Stationary absorption spectra for P3HT:PCBM devices

Figure S2 shows the stationary absorption spectra for P3HT:PCBM devices with pre-annealing and post-annealing processes. The absorbance increases rapidly at photon energies greater than ~ 1.9 eV, which demonstrates that the polymer has a wide absorption band [6]. Both spectra for the pre- and post-annealed devices show a π - π^* transition of P3HT at 2.05 eV and 2.23 eV [7,8]. It is worthwhile mentioning that the significant difference between the absorption spectra of P3HT:PCBM devices with pre-annealing and post-annealing processes can be clearly observed below 2.2 eV (marked by the arrow in Fig. S2). Moreover, the absorbance of P3HT:PCBM devices with pre-annealing process is larger than that of P3HT:PCBM devices with post-annealing process, which results in the notable difference in the magnitude of transient absorption below 2.2 eV as shown in the Fig. S2.

Fig. S2. Stationary absorption spectra for P3HT:PCBM devices with post-annealing and pre-annealing processes. The black line shows laser spectrum of the light source used in this study. Adapted with permission from [9]. Copyright (2015) American Chemical Society.

References

1. C. Y. Wong, J. Kim, P. S. Nair, M. C. Nagy, and G. D. Schole, "Relaxation in the exciton fine structure of semiconductor nanocrystals," *J. Phys. Chem. C* **113**, 795–811 (2009)
2. J. Kim, C. Y. Wong, and G. D. Scholes, "Exciton fine structure and spin relaxation in semiconductor colloidal quantum dots," *Acc. Chem. Res.* **42**, 1037–1046 (2009)
3. T. Cheiwchanchamnangij, and W. R. L. Lambrecht, "Quasiparticle band structure calculation of monolayer, bilayer, and bulk MoS_2 ," *Phys. Rev. B* **85**, 205302 (2012)
4. C. Mai, A. Barrette, Y. Yu, Y. G. Semenov, K. W. Kim, L. Cao, and K. Gundogdu, "Many-body effects in valleytronics: direct measurement of valley lifetimes in single layer MoS_2 ," *Nano Lett.* **14**, 202–206 (2014)
5. Y.-T. Wang, C.-W. Luo, A. Yabushita, K.-H. Wu, T. Kobayashi, C.-H. Chen, and L.-J. Li, "Ultrafast multi-level logic gates with spin-valley coupled polarization anisotropy in monolayer MoS_2 ," *Sci. Rep.* **5**, 8289–1–8289-6 (2015)
6. C. Winder and N. S. Sariciftci, "Low Bandgap Polymers for Photon Harvesting in Bulk Heterojunction Solar Cells," *J. Mater. Chem.* **14**, 1077–1086 (2004)
7. V. Shrotriya, J. Ouyang, R. J. Tseng, G. Li, and Y. Yang, "Absorption Spectra Modification in poly(3-Hexylthiophene):methanofullerene Blend Thin Films," *Chem. Phys. Lett.* **411**, 138–143 (2005)

8. Y. Zhao, Z. Xie, Y. Qu, Y. Geng, and L. Wang, "Solvent-Vapor Treatment Induced Performance Enhancement of poly (3-Hexylthiophene): methanofullerene Bulk-Heterojunction Photovoltaic Cells," *Appl. Phys. Lett.* **90**, 043504 (2007)
9. Y.-T. Wang, M.-H. Chen, C.-T. Lin, J.-J. Fang, C.-J. Chang, C.-W. Luo, A. Yabushita, K.-H. Wu, and T. Kobayashi, "Use of Ultrafast Time-Resolved Spectroscopy to Demonstrate the Effect of Annealing on the Performance of P3HT:PCBM Solar Cells," *ACS Appl. Mater. Interfaces* **7**, 4457–4462 (2015)