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Understanding and Directing Energy Flow Using Semiconducting Carbon Nanotubes

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14. ABSTRACT
The purpose of this grant is to understand and learn to control energy transfer in thin films made from semiconducting carbon nanotubes. Thin films of semiconducting carbon nanotubes are a new type of mesoscale material. The properties are largely unexplored but should exhibit new phenomena that can be utilized in next generation electronics. Under the support of the AFOSR, we have made the first measurements of exciton (energy) transport in these thin films using unique ultrafast 2D technology that we have developed. The current understanding of exciton transfer in these materials has come almost entirely from these experiments, Monte-Carlo modeling, and theory developed during our AFOSR funding. We also spent significant effort developing a 2nd-generation 2D White Light spectrometer and, using DURIP funds, a 2D White Light microscope, which is a first-of-its-kind instrument. Taken together, we made foundational contributions to the science and engineering of these films and the technology to study them and other materials. Using the information gained from our studies, we created new films with 10-times faster rates, rivaling the ultrafast transfer rates known to exist along the length of individual tubes. We published, submitted, or have prepared 11 manuscripts, in which we reported on the fundamental physics of nanotube films, the materials science of film preparation and device performance, and the technological developments and applications of new 2D spectroscopies and microscopies. These developments are exciting because they indicate that nanotube films are well-suited for new use in photovoltaics, photodetectors, and other devices, as initially conceived.

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Final Report

Energy flow in semiconducting carbon nanotubes using 2D WL spectroscopy

Michael Arnold & Martin Zanni
University of Wisconsin-Madison

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2/1/2015 -1/31/2019

Abstract

The purpose of this grant is to understand and learn to control energy transfer in thin films made from semiconducting carbon nanotubes. Thin films of semiconducting carbon nanotubes are a new type of mesoscale material. The properties are largely unexplored but should exhibit new phenomena that can be utilized in next generation electronics. Under the support of the AFOSR, we have made the first measurements of exciton (energy) transport in these thin films using unique ultrafast 2D technology that we have developed. The current understanding of exciton transfer in these materials has come almost entirely from these experiments, Monte-Carlo modeling, and theory developed during our AFOSR funding. We also spent significant effort developing a 2nd-generation 2D White Light spectrometer and, using DURIP funds, a 2D White Light microscope, which is a first-of-its-kind instrument. Taken together, we made foundational contributions to the science and engineering of these films and the technology to study them and other materials. Using the information gained from our studies, we created new films with 10-times faster rates, rivaling the ultrafast transfer rates known to exist along the length of individual tubes. We published, submitted, or have in review 11 manuscripts, in which we reported on the fundamental physics of nanotube films, the materials science of film preparation and device performance, and the technological developments and applications of new 2D spectroscopies and microscopies. These developments are exciting because they indicate that nanotube films are well-suited for new use in photovoltaics, photodetectors, and other devices, as initially conceived.

Report

During our AFOSR funded project, we made foundational contributions to the science of these new semiconducting carbon nanotube films and the technology to study them and other materials. We published, submitted, or have prepared, 11 manuscripts, in which we reported on the fundamental physics of nanotube films, the materials science of film preparation and device performance, and the technological developments and applications of new 2D spectroscopies and microscopies. Our program is a broad mix of optical technology, materials science, and fascinating physics. We summarize the findings of the most important of these 11 manuscripts, here.

11. Andrew C. Jones, Nicholas M. Kearns, Miriam Bohlmann Kunz, Jessica T. Flach, Martin T. Zanni, Multidimensional spectroscopy on the microscale: development of a broadband 2D white-light pump-probe microscope, Optics Express, To be submitted (2019). This manuscript

reports on the design and technical performance of a new microscope that is capable of measuring broadband transient absorption spectra and 2D White-Light spectra with sub-micron spatial resolution. We are waiting to submit this manuscript until after the manuscript submitted to Nature Chemistry, below, is published.

10. M. J. Shea, J. Wang, M. S. Arnold, Trap-limited recombination and energy offsets at the carbon nanotube-C_{60} heterointerface, Journal of Physical Chemistry C (Under Revision). In this submission, we show that undesirable trap limited recombination is not a limiting factor in the performance of nanotube/fullerene heterojunction photovoltaic devices.

9. Andrew C. Jones, Nicholas M. Kearns, Jia-Jung Ho, Jessica T. Flach, Martin T. Zanni, Imaging the structures and energetics of singlet fission microcrystals with 2D transient absorption microscopy, Nature Chemistry, (Under Revision). This study has been taking an extraordinary amount of our time but promises to be high impact. It reports the first-ever 2D White Light Microscope. We can measure transient absorption images like other groups (a hot topic) but with broadband detection. And, we can measure 2D White Light spectra at select locations with sub-micron spatial resolution. This microscope was made possible by the development of a 100 kHz 2D Spectrometer and a DURIP grant from the AFOSR for the microscope. Our first application was to singlet fission in TIPS-pentacene in which we resolved previously unseen confirmations that impact fission.

8. V. Saraswat, R. M. Jacobberger, J. S. Ostrander, C. L. Hummell, A. J. Way, J. Wang, M. T. Zanni, M. S. Arnold, Invariance of water permeance through size-differentiated graphene oxide laminates, ACS Nano, 12, 7855-7865 (2018).

7. M. J. Shea, J. Wang, J. T. Flach, M. T. Zanni, M. S. Arnold, Less severe processing improves carbon nanotube photovoltaic performance. Applied Physics Letters Materials, 6, 056104 (2018). In this publication, we showed that we could improve device performance by switching from carbon nanotube films prepared by sonication to ones prepared by shear force mixing, which prepares longer and less defective nanotubes. We showed that the lifetimes get longer, from which we infer that the diffusion lengths are larger.

6. N. M. Kearns, R. D. Mehlenbacher, A. C. Jones, M. T. Zanni, Broadband 2D electronic spectrometer using white light and pulse shaping: noise and signal evaluation at 1 and 100 kHz. Optics Express 25, 7869 (2017). In this manuscript, we report our 2nd-generation 2D White Light spectrometer. Having proven that we could use continuum generation as a pump source in the Nature Communications manuscript below, we built a pulse-shaper that is specifically designed to handle the breadth of the continuum and can interface with a 100 kHz laser system. This new spectrometer measures a 2D spectrum in about 1/400th the time of the 1st-generation spectrometer. The design has now been commercialized by PhaseTech Spectroscopy, Inc.

5. J. L. Wang, M. J. Shea, J. T. Flach, T. J. McDonough, A. J. Way, M. T. Zanni, M. S. Arnold, Role of defects as exciton quenching sites in carbon nanotube photovoltaics. Journal of Physical Chemistry C 121, 8310 (2017). In this manuscript, we built a Monte Carlo model which allows for a quantitative prediction of transverse and lateral exciton diffusion within our films.

4. T. J. McDonough, L. Zhang, S. Singha Roy, N. M. Kearns, M. S. Arnold, M. T. Zanni*, T. L. Andrew, Triplet exciton dissociation and electron extraction in graphene-templated pentacene observed with ultrafast spectroscopy. Physical Chemistry Chemical Physics 19, 4809 (2017).

3. R. D. Mehlenbacher, J. Wang, N. M. Kearns, M. J. Shea, J. T. Flach, T. J. McDonough, M.-Y. Wu, M. S. Arnold, M. T. Zanni, Ultrafast exciton hopping observed in bare semiconducting carbon nanotube thin films with two-dimensional White Light spectroscopy. Journal of Physical Chem Letters 7, 2024 (2016). In this publication, we showed that we could increase the exciton transfer rate between nanotubes by using a new purification method that has no residue polymer wrapper, unlike other purification methods. Energy transfer rates improved to <60 fs, faster than we could easily measure, from 1 ps, which demonstrates that exciton transfer in our films can rival rates measured for isolated and pristine carbon nanotubes.

2. R. D. Mehlenbacher, T. J. McDonough, N. M. Kearns, M. J. Shea, Y. Joo, P. Gopalan, M. S. Arnold*, and M. T. Zanni*, Polarization-controlled two-dimensional White Light spectroscopy of semiconducting carbon nanotube thin films. Journal of Physical Chemistry C 120, 17069 (2016).

1. R. D. Mehlenbacher, T. J. McDonough, M. Grechko, M.-Y. Wu, M. S. Arnold, M. T. Zanni, Energy transfer pathways in semiconducting carbon nanotubes revealed using two-dimensional White Light spectroscopy. Nature Communications 6, 6732 (2015). This was a landmark publication for us because it demonstrated that continuum generation could be used as the pulse sequences in 2D spectroscopy. Continuum generation has been used as a probe pulse for decades, but it was not thought that continuum generation was strong enough to be used as a pump pulse, and even then, it would not make sense to do so, because pump pulses are usually narrow in bandwidth. We showed that the first assumption was wrong and that the second conclusion is overcome with 2D spectroscopy. Our efforts dramatically expand the utility of ultrafast 2D spectroscopy. We now have 10-times the bandwidth, covering the entire visible and near-IR regions of the spectrum and spanning the absorption spectra of the most materials and molecules.

Outlook

While our understanding of the energetics in these films is still incomplete and we are still learning to synthesize the most promising materials and device architectures, our experiments indicate that it should be possible to utilize the unique photophysics of nanotubes in next generation photodetectors and electronics. Experiments are now underway furthering our understanding of their photophysics and aimed at using our newfound knowledge to create films that purposefully manipulate energy flow in novel and beneficial ways, such as through films of aligned, blended, and wrinkled nanotubes with accepter materials. At the same time, we are developing the technology to measure sub-diffraction spatially resolved energy transfer. The AFOSR results obtained so far are unique for their cutting-edge spectroscopy and novel materials development, laying the scientific basis for engineering mesoscale nanotube materials into a wide range of light harvesting materials and devices.