will describe the formation of copper colloidal solutions obtained from low temperature and low pressure hydrogenolysis (3 bars)

in organic solvent of various metal organic copper precursors. This mild chemistry method offers large choices of synthesis parameters (precursor chemistry, solvent, ligand type, temperature...) which participate to the control of the resulting NPs properties (size, capping agent nature ...) and a good control of size dispersion has been achieved (20%). We have obtained stable copper NPs from copper amidinate, copper mesytile and copper isobutyrate precursors, with the help of low levels (fraction of molar eq.) of long chain alkylamine or carboxylic acid capping agents. The resulting nano objects are characterized by transmission electron microscopy and spectroscopic UV-Vis methods. An emphasis is given on the role of the precursor chemistry in order to explain the resulting size and size distribution of the copper nanoparticles. This procedure could easily be extended to more complex bimetallic systems (like CuZn or CuAg) as an example, in the aim of an improved air stability system through the protection of the copper NPs surface from oxidation. (1) Tao, A. R.; Habas, S.; Yang, P. D. Small 2008, 4, 310. (2) (a) Wang, Y. F.; Biradar, A. V.; Wang, G.; Sharma, K. K.; Duncan, C. T.; Rangan, S.; Asefa, T. Chem.-Eur. J. 2010, 16, 10735(b) Meng, H.; Chen, Z.; Xing, G. M.; Yuan, H.; Chen, C. Y.; Zhao, F.; Zhang, C. C.; Zhao, Y. L. Toxicology Letters 2007, 175, 102(c) Luisier, A.; Utke, I.; Bret, T.; Cicoira, F.; Hauert, R.; Rhee, S. W.; Doppelt, P.; Hoffmann, P. Journal of the Electrochemical Society 2004, 151, C535

SESSION CC6: Spectroscopic Studies in Semiconductor and Metal-Hybrids I
Chair: Patanjali Kambhampati
Wednesday Morning, November 30, 2011
Room 202 (Hynes)

8:30 AM *CC6.1

Hot-Carrier Dynamics in Semiconductor Nanocrystals in Relation to Carrier Multiplication and Photoluminescence Blinking. Victor I. Klimov, Chemistry Division, Los Alamos Natl Lab, Los Alamos, New Mexico.

Due to small, "sub-excitonic" dimensions, semiconductor nanocrystals can produce novel electronic interactions that involve charges residing in intrinsic quantized states as well as species located at nanocrystal surfaces. Strong coupling between quantum-confined carriers opens new energy relaxation and recombination channels associated with various types of Auger processes. For example, the interaction of a hot conduction-band electron with valence-band charges can lead to an interesting relaxation regime in which the kinetic energy of a hot carrier is not lost as heat but is used to produce additional electron-hole pairs, a process known as carrier multiplication. Alternatively, a hot electron can escape from the particle due to direct coupling to surface species leading to nanocrystal ionization. I will discuss the interplay between various channels for energy relaxation and charge recombination in the nanocrystals, with specific focus on three topics: (1) spectroscopic aspects of carrier multiplication and photoionization; (2) hot-electron transfer in relation to nanocrystal blinking; and (3) Auger decay engineering in core/shell nanostructures. I will also discuss the implications of these studies for applications of nanocrystals in solar-energy conversion and light emission.

9:00 AM CC6.2

The Excitonics of the Surface of Semiconductors Nanocrystals: Implications for Optical Gain, Multiple Exciton Generation, and Single Dot Blinking. Patanjali Kambhampati, Chemistry, McGill University, Montreal, Quebec, Canada.

The surface of semiconductor nanocrystals is well known to be a key aspect of its function, yet it remains poorly understood. The surface of the nanocrystal is particularly important in that it is related to the creation of a photoproduct that obscures measurements of multiple exciton generation, optical gain, and single dot photoluminescence blinking. The production of surface trapped charges has seen recent interest in terms of hot carrier charging. Here, we show ultrafast pump/probe as well as simple continuous wave experiments that unravel the nature of the surface of the nanocrystal, as well as its importance in key processes such as optical gain and multiple exciton generation. These experiments show that surface can be described in terms of an activated electron transfer process to surface excitonic states. We connect this excitonic surface state to the core of the nanocrystal via real-time femtosecond measurements of the pathways by which hot excitons populate these surface excitonic states. These femtosecond measurements are consistent with the continuous wave experiments, which reveal a photo-action spectrum for hot exciton surface trapping. Once a surface trapped exciton is produced, we show its role in blocking optical gain, yielding incorrect measurements of Auger recombination processes, and creating false multiple exciton generation signals.

9:15 AM CC6.3

Thermalization Dynamics in Semiconductor Nanocrystals. Daniel C. Hannah[2], Nicholas J. Dunn[2], Sandrine Ithurria[3], Dmitri V. Talapin[3,1], Lin X. Chen[1,2], Matthew Pelton[1], George C. Schatz[2] and Richard D. Schaller[1,2]; [1]Center for Nanoscale Materials, Argonne National Lab, Lemont, Illinois; [2]Department of Chemistry, Northwestern University, Evanston, Illinois; [3]Department of Chemistry, University of Chicago, Chicago, Illinois.

Colloidal semiconductor nanocrystal (NCs) quantum dots of materials such as CdSe offer size-controlled bandgaps, intense absorption features, and substantial photoluminescence quantum yields. Such desirable light-absorbing and emitting properties, in addition to facile solution processing, make NCs attractive for solid-state lighting, photovoltaics, bio-labeling and optical amplification applications. Exciton relaxation in quantum-confined matter following photoexcitation has drawn substantial interest for both fundamental understanding and applied purposes. Intraband relaxation takes place on single-picosecond timescales while radiative recombination require tens of nanoseconds at room temperature. On the other hand, photoluminescence lifetimes becomes substantially longer with decreasing temperature owing to the material-specific exciton fine structure and, specifically, due to a lowest-energy optically passive exciton state. Here, we describe detailed studies of radiative recombination in CdSe NCs wherein we reveal signatures of NC thermalization. Specifically, measurements of spectrally and temporally-resolved photoluminescence as a function of temperature reveal signatures of phonon dissipation with clear NC size-dependence.

9:30 AM CC6.4

Ultrafast Photoinduced Intraband Absorption in PbS, PbSe and PbSe/CdSe Core/Shell Nanocrystals for near-Infrared to Mid-Infrared All-Optical Signal Processing. Bram De Geyter[1,2,3], Pieter Geiregat[1,2,3], Arjan J. Houtepen[4], Dries Van Thourhout[1,3], Laurens D. Siebbeles[4] and Zeger Hens[2,3]; [1]Photonics Research Group, INTEC, Ghent University IMEC, Gent, Belgium; [2]Physics and Chemistry of Nanostructures, Inorganic and Physical Chemistry Departement, Ghent University, Gent, Belgium; [3]Center for Nano- and Biophotonics (NB-Photonics), Ghent University, Gent, Belgium; [4]Optoelectronic Materials, Faculty of Applied Sciences, Delft University of Technology, Delft, Netherlands.

Colloidal nanocrystal quantum dots and dot-in-dots are highly tunable optical materials due to strong quantum confinement of the carriers. The quantum confinement not only raises the bandgap energy, it also relaxes intraband selection rules, making multicarrier Auger recombination ultrafast and optical dipole transitions between intraband states allowed. We present a transient absorption study which shows that photoinduced absorption below the bandgap in PbS, PbSe and PbSe/CdSe colloidal quantum dots can be attributed to intraband absorption. The power dependence agrees with a state-filling model of the bandgap excitonic states and the dynamics of the absorption decay indicate that initial state population decays through Auger recombination. The strength of the intraband transition is wavelength-independent up to (at least) 2000 nm and is about 10% of the bandgap transition strength. The broadband nature, the ultrafast dynamics and the high cross section make these material excellent candidates for all-optical high-speed signal processing on the silicon photonics platform in both the near and the mid-infrared wavelength range.

9:45 AM CC6.5

Size and Composition Dependent Carrier Multiplication Studies on PbX QDs. Jayson Stewart[1], Aaron G. Midgett[2,3], Lazaro A. Padilha[1], Danielle Smith[2], Jeffrey M. Pietryga[1], Joseph M. Luther[2], Matthew C. Beard[2], Arthur J. Nozik[2,3] and Victor I. Klimov[1]; [1]Los Alamos National Laboratory, Los Alamo, New Mexico; [2]National Renewable Energy Laboratory, Golden, Colorado; [3]Chemistry, University of Colorado, Boulder, Colorado.

MRS MATERIALS RESEARCH SOCIETY
Advancing materials. Improving the quality of life.

- **2011 MRS Fall Meeting & Exhibit**
- **November 28 - December 2, 2011**
- **Hynes Convention Center, Boston, MA**
- **Meeting Chairs:** Cammy R. Abernathy, Paul V. Braun, Masashi Kawasaki, Kathryn J. Wahl

SYMPOSIUM CC

Functional Semiconductor Nanocrystals and Metal-Hybrid Structures

November 28 - December 1, 2011

Chairs

Prashant Nagpal
Center for Advanced Solar Photophysics
Los Alamos National Laboratory
Los Alamos, NM 87545
505-665-0382

Matthew A. Pelton
Center for Nanoscale Materials
Argonne National Laboratory
Argonne, IL 60439
630-252-4598

Kurtis S. Leschkies
Energy and Environmental Solutions
Applied Materials Inc.
3225 Oakmead Village Dr.
Santa Clara, CA 95052
408-563-6816

Hedi Mattoussi
Dept. of Chemistry and Biochemistry
Florida State University
95 Chieftan Way
Tallahassee, TN 32306
850-645-8615

Patanjali Kambhampati
Dept. of Chemistry
McGill University
801 Sherbrooke St. W
Montreal, QC, H3A2K6 Canada
514-398-7228

Symposium Support
Applied Materials Inc.
Nanomaterials & Nanofabrication Labs
NanoRods, LLC
World Gold Council

Proceedings to be published in electronic-only format (see MRS Online Proceedings Library at www.mrs.org/opl) as Volume 1409E of the Materials Research Society Symposium Proceedings Series.

* Invited paper

SESSION CC1: Optical, Electronic, and Magnetic Functionalities Using Novel Semiconductor Nanocrystal Synthesis
Chair: Kurtis Leschkies
Monday Morning, November 28, 2011

Room 207 (Hynes)

8:30 AM *CC1.1
Silicon and Copper Selenide Nanocrystals for Biological Applications. Colin M. Hessel, Michael Rasch and Brian A. Korgel: Department of Chemical Engineering, University of Texas at Austin, Austin, Texas.

Semiconductor and metal nanocrystals have been extensively studied for use in biological applications, for both disease detection and therapy. This research, however, has focused on a relatively narrow range of materials, primarily on gold and silver nanocrystals in the case of metals and Cd-based nanocrystals in the case of semiconductors. In recent years, the nanocrystal "tool kit" has been expanding, including light-emitting silicon nanocrystals and more recently, transition metal chalcogenides like copper selenide for plasmonic heating. Here, we present recent research on the synthesis and surface functionalization of silicon nanocrystals for biological applications, including their inclusion in liposomes. We will also present our efforts on the synthesis and use of copper-deficient copper selenide nanocrystals for photothermal heating. Ligand-stabilized Cu2-xSe nanocrystals were synthesized by a colloidal hot injection method and coated with amphiphilic polymer. The nanocrystals readily disperse in water and exhibit strong near infrared (NIR) optical absorption with a high molar extinction coefficient. The NIR absorption is due to a plasmonic resonance related to the high free carrier density in the nanocrystals due to copper vacancies. When excited with 800 nm light, the Cu2-xSe nanocrystals produce significant photothermal heating with a photothermal transduction efficiency of 22%, comparable to nanorods and nanoshells of gold (Au). In vitro photothermal heating of Cu2-xSe nanocrystals in the presence of human colorectal cancer cell (HCT-116) led to cell destruction, demonstrating the viability of Cu2-xSe nanocrystals for photothermal therapy applications.

9:00 AM CC1.2
An All-Gas-Phase Approach for the Fabrication of Silicon Quantum Dot Light Emitting Devices. Rebecca Anthony[1], Kai-Yuan Cheng[2], Zachary C. Holman[1], Russel J. Holmes[2] and Uwe R. Kortshagen[1]; [1]Mechanical Engineering, University of Minnesota, Minneapolis, Minnesota; [2]Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota.

Quantum dots offer unique advantages for the manufacture of light emitting devices including their size tunable optical luminescence, and compatibility with device fabrication on low-cost, flexible substrates that may open up routes to roll-to-roll manufacturing. To date, the fabrication of light emitting devices using quantum dot luminophores exclusively has relied on colloidal chemistry for the quantum dot synthesis, surface treatment, and deposition. In this presentation we demonstrate, to our knowledge for the first time, an all-gas-phase approach for the formation of light emitting devices from silicon quantum dots. In a single gas phase reactor, silicon quantum dots are synthesized, their surfaces functionalized with organic ligands, and deposited onto glass substrates carrying a transparent conductive oxide bottom contact. Production of silicon nanocrystals is achieved through plasma decomposition of the mono-silane precursor, leading to the formation of monodisperse silicon nanocrystals. Quantum dot surfaces are functionalized with organic monolayers by injecting the vapor of various alkenes into the afterglow of the synthesis plasma. Inertial impaction of the functionalized silicon nanocrystals is used to form dense nanocrystal films. Devices are completed by metal evaporation of a top contact. The approach presented here completely avoids the use of solvents and allows the formation of electroluminescent quantum dot devices with as little as three deposition steps for the top and bottom contact layers and the silicon quantum dot layer. Primary support for this work was received from the National Science Foundation (NSF) Award Number ECCS-0925624. Partial support was also received from the NSF MRSEC Program under Award Number DMR-0819885. R.J.H. would also like to acknowledge support from 3M Company through a Non-Tenured Faculty Grant.

9:15 AM CC1.3
Pyrite Nanocrystals: Shape-Controlled Synthesis and Tunable Optical Properties via Reversible Self-Assembly. Wei Li[1], Markus Doeblinger[2], Aleksandar Vaneski[3], Andrey L. Rogach[3], Frank Jaeckel[1] and Jochen Feldmann[1]; [1]Photonics and Optoelectronics Group, Faculty of Physics and Center for Nanoscience, Ludwig-Maximilians-Universität