

Synthesis, Assembly, and Optical and Transport Studies of Magnetic Nanostructures

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Profs. Horia Metiu, Steven Buratto, Geoffrey Strouse and David Awschalom

University of California, Santa Barbara

Introduction

Throughout the past several years synthetic techniques for preparing intrinsic, monodisperse semiconductor quantum dots with high optical quality and a high degree of crystallinity have been developed. [1,2] Building on the success of this work we have developed new synthetic procedures for preparing doped quantum dots, particularly magnetically-doped quantum dots, and pursued the self-assembly of quantum dots into two and three-dimensional superlattice structures with novel photophysical phenomena. In addition, the push toward smaller structures has motivated our development new characterization techniques with nanoscale spatial resolution and high sensitivity based on recent developments in the field of near-field scanning optical microscopy (NSOM). [3-6] We have utilized NSOM techniques to map the luminescence, photoconductivity, and energy transport in a variety of quantum-confined and self-assembled which have yielded images with unprecedented spatial resolution and striking detail resulting in important new insights into the nanoscale structure of these materials. We have supplemented our experimental program with state-of-the-art theoretical techniques which provide important insight into the interpretation of our NSOM images.

While the full details of our research can be found in the papers published acknowledging support of this grant, this overview highlights four specific parts of our research:

1. The development of synthetic techniques for preparing electrically doped and/or magnetically doped II-VI quantum dots with controlled surface functionality suitable for incorporation into layered superlattice structures via ionic interactions.
2. The photo-activation of the luminescence of self-assembled of quantum dot monolayers, and the development and application of NSOM and near-field spectroscopy methods for directly probing the nanoscale energy migration in quantum dot monolayers
3. Probing quantum optics of single CdSe quantum dots.
4. The development of reliable theoretical methods for describing near-field excitation of quantum dot structures, including accurate descriptions of the polarization fields.

1. Synthesis of chemically-doped quantum dots.

We have developed a modified version of the lyotropic synthesis using hexadecylamine and a single source precursor to nucleate the nanocrystals in the growth medium.[1,2,7] This method has allowed us to control dopant atoms in our nanocrystals by incorporating these atoms in the precursor molecule. We have successfully produced Cu-doped CdSe nanocrystals by this method.

2. Nanoscale Photophysics of Self-Assembled Quantum Dot Monolayers.

Monolayers of CdSe nanocrystals are assembled at the air-water interface using a Langmuir film balance. The film is transferred to a clean glass cover slip by the Schaeffer lift-off method and results in large domains of close-packed quantum dots. In these assemblies we have observed that the luminescence from CdSe quantum dot monolayers can be strongly influenced by the interaction of water molecules adsorbed on the surface. [8] Light-induced alterations in the surface states following adsorption of water, results in quasi-reversible luminescence changes in the quantum dot. The excitonic quantum yield (QY) increases by a factor of 10 during the first 200 s of illumination in air (post vacuum) and then steadily decreases to a level 6 times that of the vacuum reference after 5000 s. The exciton emission exhibits an exponential blue shift of nearly 16 nm (60 meV) over 1 hr. of illumination. Our model suggests that water molecules adsorbed on the surface of the quantum dot act to passivate surface traps, which results in increased luminescence, similar to an effect well known for bulk CdSe surfaces. In addition, adsorbed water molecules act to oxidize the surface of the quantum dot, which results in the blue shift of the exciton emission and eventually introduces new surface defects that lower the luminescence QY. It is the competition between these two processes that is responsible for the complex kinetics of the luminescence QY.

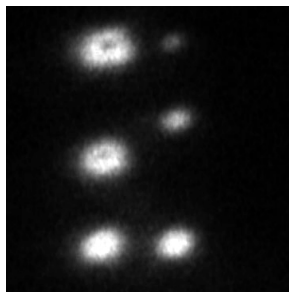


Figure 1. NSOM photopatterning of a CdSe monolayer. The $3\ \mu\text{m} \times 3\ \mu\text{m}$ image shows bright spots (ccw from the upper right) are from exposures of 1s, 10s, 30s, 60s, 100s and 200s, respectively.

We have also used the ultrahigh resolution optical microscopy technique, near-field scanning optical microscopy (NSOM), to probe the optical and opto-electronic properties of quantum dot assemblies on a 10 - 100 nm length scale. [9] In addition, we have used NSOM to locally photopattern quantum dot monolayers on a 100 nm length scale. In

this experiment, the film is illuminated with light from a stationary NSOM tip to induce photo-activation as described earlier. The change in the fluorescence yield resulting from this exposure is then mapped using fluorescence NSOM. We find that the long-time diameter of the bright spot resulting from photo-activation is much larger than the tip diameter and is a signature of energy migration. The characteristic length of the energy migration is extracted from this data using a simple diffusion model to describe the energy transport and the kinetic model extracted from our photo-activation experiments. Our results suggest a diffusion length of the order of 100 nm for a monolayer of 4.1 nm CdSe quantum dots, or exciton migration of approximately 25 dots.

3. Quantum Optics of Single CdSe Quantum Dots.

Optical experiments involving single quantum systems have contributed significantly to the basic understanding of the interaction between light and matter. Some of these experiments include resonance fluorescence experiments which have been used to study quantum optical effects such as photon bunching and anti-bunching. [10] Experiments of this sort make use of the statistical nature, specifically the time dependent photon probability distribution $P(T)$, in which light is emitted from a source. Generally, these distributions are described using a two-time (or

second order) intensity correlation function, approximated at short times by the distribution of the separation in time between successive photons. For a single two-level system, coherent excitation results in sub-Poissonian two-photon correlation distribution, which has no classical description, and can only be described by considering quantization of the electromagnetic field. For this simplest of quantum mechanical systems, a minimum in the correlation distribution is expected for photon separation times that approach 0, an effect known as photon-antibunching. In the weak excitation regime this increases to a steady state value at a rate equivalent to the excited-state lifetime of the single two-level system.

We have used a standard two photon coincidence measurement using time-correlated single photon counting to probe the fluorescence photon correlation statistics from a single CdSe/ZnS core shell quantum dot and a cluster of several QDs as shown in the figure below. [11] The single QD data shows a minimum of coincidence counts $n(\tau)$ around a pair separation time of $\tau = 0$, and an exponential increase of $n(\tau)$ for negative and positive values of τ . This is a clear signature of non-classical photon antibunching. In contrast, the photon correlation signal of the cluster of QD's is flat. In this case many independently radiating QDs contribute to the signal.

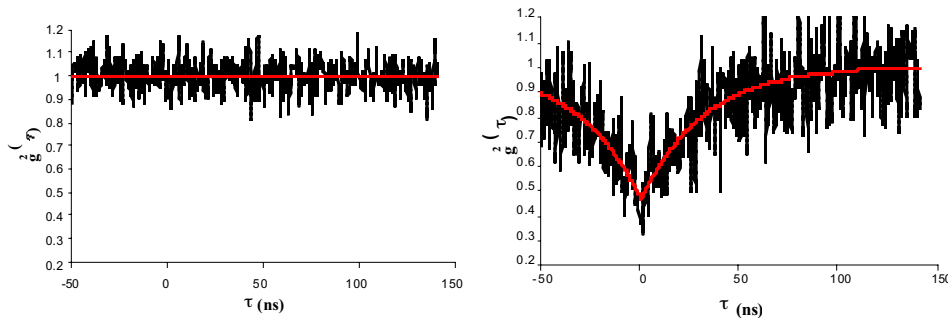


Figure 2. Photon pair distributions for CdSe quantum dots. The left trace is from a large cluster of QD's while the right trace is from a single QD. A clear antibunching dip is observed in the right trace.

Prior measurements on single QD photoluminescence and absorption have demonstrated the existence of discrete QD resonances. However, just as the observation of discrete absorption lines in an atomic vapor cannot be taken as an evidence that the observed system consists of a single atom, these experiments, at least in principle, cannot rule out the existence of several QDs. In contrast, photon correlation measurements, such as the one reported here, provide a reliable method for deciding whether or not the observed system is a single anharmonic quantum emitter. In addition, owing to interactions with the lattice, a nanostructure that acts like an anharmonic emitter at cryogenic temperatures can be indistinguishable from a higher-dimensional system at room temperature. We have demonstrated that a CdSe quantum dot behaves as an anharmonic emitter even at room temperature and we are able to distinguish between a single emitter and a cluster of emitters.

4. Electromagnetic Theory of Near-Field Optics in Nanostructures.

We have performed numerical calculations of the electromagnetic fields produced around a sharp metal tip held above a dielectric surface and illuminated from above by visible light. [12] The electric fields produced by irradiation are calculated using a real-space Green's function technique, also known as the frequency-domain method of moments. We find that when the tip

is 5 nm above a flat dielectric surface, the field under the tip is strongly enhanced in a region having a diameter of 5 nm even though the end of the tip has lateral dimensions of the order of 10 nm. The light intensity falls off rapidly as the tip-surface distance is increased and the region where the field is enhanced becomes larger. We also show that the polarization dependence of electric field near the surface is quite complicated. Regardless of the incident polarization, the tip tends to make the induced electric field perpendicular to the substrate. Moreover, different components of the field creates the possibility of deducing the orientation of molecules adsorbed on the surface.

REFERENCES

1. Murray CB, Norris DJ, Bawendi MG, Synthesis And Characterization Of Nearly Monodisperse Cde (E = S, Se, Te) Semiconductor Nanocrystallites. *J. Am Chem Soc*, **115** 8706 (1993).
2. Murray CB, et al. Synthesis And Structural Characterization Of II-VI Semiconductor Nanocrystallites (Quantum Dots). *Z Phys D Atom Mol Cl* **26** S231 (1993).
3. Betzig E, Trautman JK, Harris TD, Weiner JS, Kostelak KL, (1991). Breaking the diffraction barrier: optical microscopy on a nanometric scale. *Science*, **251**:1468-1470.
4. Betzig E, Trautman JK (1992). Near-field optics-microscopy, spectroscopy and surface modification beyond the diffraction limit. *Science*, **257**:189-195.
5. Buratto SK (1996) Near-field scanning optical microscopy. *Curr. Opinion Solid St. Mater Sci* , **1**:485-492.
6. DeAro JA, Weston KD Buratto SK (1999) Near-field scanning optical microscopy of nanostructures. *Phase Transitions*, **68**: 27-40.
7. Green M, O'Brien P (1999). Recent advances in the preparation of semiconductors in isolated nanometric particles: new routes to quantum dots. *Chem Comm* 2235-2241.
8. Cordero SR, Carson PJ, Estabrook RA, Strouse GF, Buratto SK (2000) Photo-activated luminescence of CdSe quantum dot monolayers. *J. Phys. Chem. B* **104**:12137-12142.
9. Credo GM, Lowman GM, DeAro JA, Carson PJ, Winn DL, Buratto SK (2000) Probing nanoscale photo-oxidation in organic films using spatial hole-burning near-field scanning optical microscopy. *J. Chem. Phys.* **112**:7864-7872.
10. Plakhotnik T, Donley E, Wild U (1997) Single Molecule Spectroscopy. *Ann Rev Phys Chem* **48**:181-212.
11. Michler P, Imamoglu A, Mason MD, Carson PJ, Strouse GF, Buratto SK (2000). Quantum correlation among photons from a single quantum dot at room temperature. *Nature* **406**:968-970.
12. Larsen RE, Metiu H. (2001). Resolution and polarization in apertureless near-field microscopy. *J. Chem. Phys.* in press.