ULTRAFAST SPECTROSCOPY OF CHEMICALLY SYNTHESIZED SEMICONDUCTOR NANOPARTICLES

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Engineerable Optical Properties: CdSe Nanodots

size: 2.3 nm
λ = 470 nm

size: 5.5 nm
λ = 620 nm

*Murray, C.B.; Norris, D.J.; M. Bawendi, M.G. J. Am. Chem. Soc. 1993, 115, 8706
Some potential applications

- Biological tags for imaging (Alivisatos et al)
- Electroluminescence from monolayers of CdSe NCs in organic devices (Coe et al, Nature 2002)
- Optically pumped CdSe NC’s lasers (Eisler et al, APL 2002)
- Microring lasing (Malko et al, APL 2002)
- Solar Energy research
- Quantum computing and information
Chemical Synthesis of QDs

- Inexpensive preparation, produces large quantities
- Chemical flexibility: II-VI, III-V, IV-VI elements (CdSe, CdS, CdTe, PbS, InP, PbSe, …)
- Control of Size: Monodisperse (size distribution ≤ 5%)
- Control of shape: Dots, Rods, Tetrapods, Rice grains, Cubes, etc…
- High luminescence quantum yield up to 80%
- Functionalizeable surfaces for various applications
- Doping, immobilization in polymer matrices
- Self assembly in 2D and 3D-superlattices with controlled inter-particle spacing.
Control of Size: Monodisperse (size distribution ≤ 4%)
Chemical Synthesis: Control of Shape and Lattice structure

Hexagonal lattice (Wurzite)

Cubic lattice (Zinc blende)

Hexagons

Tetrapods

Cubes

Tetrahedra

Nucleation in ZB & growth in W

Nucleation in ZB & growth in W

Nucleation & growth in W form

Nucleation in ZB & growth in W
Control of Shape: Dots, nanorods, tetrapods, etc...

CdSe Nanorods

PbSe Nanocubes
Control of lattice structure
Hybrid ZB-W CdSe nanorods

Li & Wang, Nanoletters (2003)
Chemical synthesis of CdSe Nanoparticles

**Factors which affect the shape of the nanocrystals:**

1. Temperature
2. Type of surfactant, and its concentration
3. Monomer concentrations

**Se powder is dissolved in TOP injected rapidly to a hot solution of CdO dissolved in surfactant or a mixture of surfactant such as TOPO, HPA, TDPA or ODPA at 300 C**

**After size selective precipitation, the obtained particles dissolved in Hexane**

**Thermodynamic control:**

Zinc blende is the most stable form at lower temperature, Wurtzite is more stable in high temperature

**Kinetic control:**

Some polar facets are more stable in the presence of polar surfactant

Murray, C. B.; Norris, D. J., Bawendi, M.G., JACS 1993;
Xiaogang, P.; Manna, L.; Weidong Yang, Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P.,
Optical Properties

EFFECTS OF QUANTUM CONFINEMENT:
- Tunability of band gap
- Discretization of energy levels
- Enhanced oscillator strengths

Tonti et al, NanoLetters (submitted)
Emitted vs Scattered Light

- Pristine sample (1-T)
- Pristine sample (emitted light)
- Sample with NQ (emitted light)
- Solvent scattering
No changes in ns decay times over this power range!

Son et al, PRL 2004
Summary

• Continuum due to absorption
• Continuum not due to ionization, or barrier (due to ligands) for electron escape too high.
• Intraband relaxation too fast (< 1ps) to allow for other channels
• Electron acceptors: Quenching of luminescence occurs at band edge states.
• High power excitation does not change lifetimes in nsec range. However, total yield of luminescence levels off.
• Dot dependence of luminescence yield for high powers suggests an Auger ionization channel.
• Luminescence quantum yield does not follow lifetime changes, i.e. sub-ensemble of dots that fluoresce.
The band edge structure

The eight-fold degeneracy of the lowest excited state \((1S_e, 1S_{3/2})\) in spherical dots, lifted by:
1- The particle shape
2- The crystal field of the hexagonal lattice
3- electron-hole exchange interaction

Electron: \(s=1/2\) (\(m_s=\pm1/2\))
Hole: \(F=L+J\)
Excitons: \(N=F+s\) (\(N_m=\pm2, \pm1, 0\))
\(|N, N_m>\)

One colour Pump-Probe transient absorption measurements

$\lambda_{\text{pump}} = 595 \text{ nm}, 570 \text{ nm}$ (far red edge of the first absorption band)

Dot radius $\sim 2 \text{ nm}$

$\Delta t = 50 \text{ fsec}$ (55 meV spectral width)
- Signal mainly due to bleaching
- 210 cm\(^{-1}\) (165 fs) oscillation: LO mode of CdSe
  (Mittleman et al, PRB (1994))
- Oscillations due to Impulsive Raman scattering and/or Excited state absorption contributions
- Damping time of coherences \(\leq 1\) ps
- Anisotropy decays in \(< 1\) oscillation and stabilises at finite level
Summary

• Damping of oscillations due to multimode character of LO phonon (uncertainty $\Delta \omega$ introduces different frequencies)

• Damping of anisotropy due to changes in e.s. wavefunction in $< 1$ oscillation. At higher energy state mixing more dramatic, i.e. bigger loss of anisotropy. Thus interstate relaxation at band edge is very fast ($< 160$ fs). Implies that vibrational coherences are in the e.s.
Multiexcitonic effects

• In bulk, if $\rho_{\text{excitons}} > 1$ exciton/excitonic volume $\rightarrow$ metallic e-h plasma and reduced Coulomb interaction (e.g. SC-to-metal phase transition in Si, Johnson et al, PRL 2003)

• In QD’s high confinement and several excitons are squeezed.

• Multiparticle interaction due to wf overlap

• Auger relaxation processes (Klimov et al, Zunger et al)
Multiexciton formation

uncorr. electron and hole

coumb interaction

exciton $|x\rangle$
biexciton $|xx\rangle$
formation
Ground State Biexciton

Single exciton

Excited biexciton

Charged biexciton

Triexciton

Charged triexciton

Tetraexciton

• High power excitation: >1 exciton/dot
• High time resolution: Auger processes shorten the lifetime of Multiexcitons

→ Power dependence studies
→ Ultrafast time resolved photoluminescence
\(\tau \leq 20 \text{ ps}\)

\(\tau \leq 5 \text{ ps}\)

\(\tau \leq 10 \text{ ps}\)

\(\tau \leq 10 \text{ ps}\)

Wang et al, PRL 2003
Experimental set-up: Broad Band Femtosecond Photoluminescence up-conversion set-up

Wavelength range: 480 to 730 nm

Time resolution: ~ 70 fs
Time-resolved luminescence of CdSe NDs of 3 nm diameter
Power dependence of Photoluminescence at $t = 1$ ps
Typically: 1-15 e-h pairs/dot
Spectral decomposition

Neutral Biexciton

12-50 psec

Single exciton

~25 nsec

Charged biexciton

5 psec

Triexciton

3-5 psec

Bonati et al, PR B (submitted)
Summary

- Observation of:
  - neutral Biexcitons: $\Delta E \approx 25 \text{ meV}$, $\tau \sim a^3$
  - Charged biexciton: $\Delta E \approx 130 \text{ meV}$, $\tau \sim a^3$
  - Neutral triexciton: $\Delta E \approx 70-150 \text{ meV}$ for decreasing $a$
  - Exciton and trion: Almost overlapping

- Lifetimes and energies in agreement with Zunger and co-workers PRL 2003, PR B 2001
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