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Title: Nanocrystal Quantum Dot Composite Structures: Two Examples

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Nanocrystal Quantum Dot Composite Structures: Two Examples

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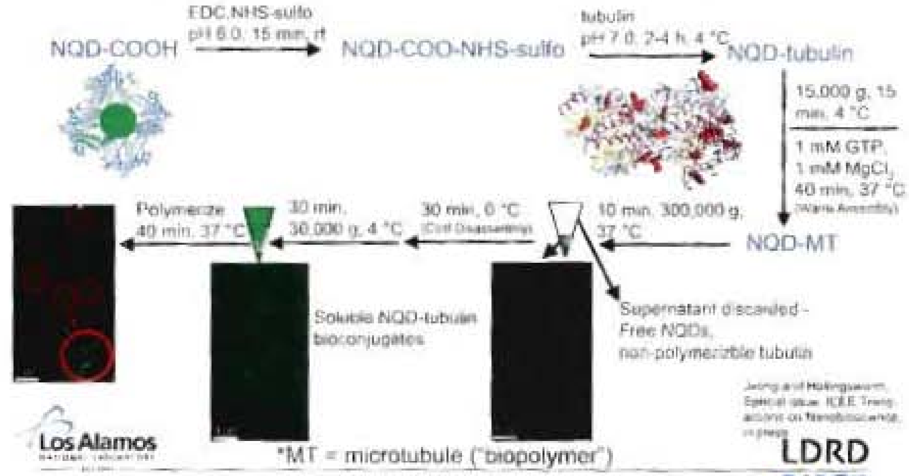
Polymerization of NQD-Tubulin Bioconjugates: Our Approach

- Two-step crosslinking procedure: Warm assembly/cold disassembly



Jeong and Hollingsworth, Special issue, IEEE Transactions on Nanobioscience, in press

*MT = microtubule ("biopolymer")

"Complete" Polymerization Not Initially Achieved

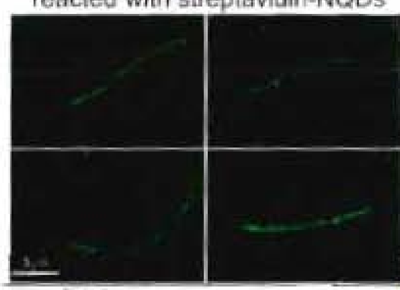
- Identical polymerization conditions yield different results

NQD-tubulin polymerized

Vs.

Dye-tubulin polymerized

Biotin-tubulin polymerized then reacted with streptavidin-NQDs



*1 mg/mL, 20% glycerol, 37 °C, 25 - 40 min

Time-Dependent Polymerization

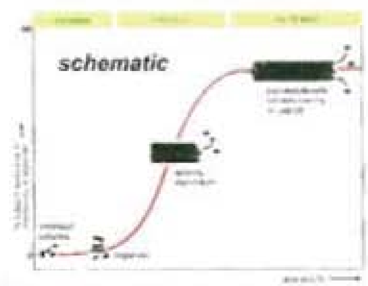
- Longer MTs formed with longer incubation times

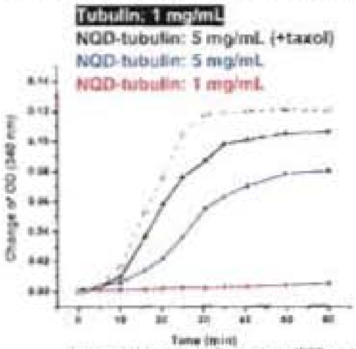
Fully formed MTs after 2 h

Aster formation (MT arrays) prompted by taxol addition at 60 m

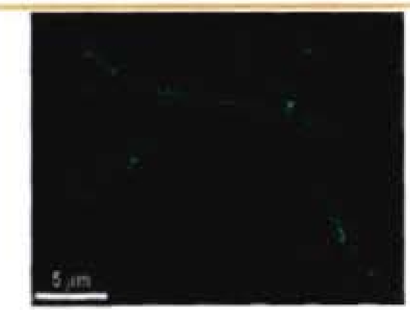
Polymerization Kinetics

- Tubulin polymerization monitored by measuring solution turbidity at 340 nm
- NQD coupling increases the critical tubulin concentration required for polymerization





Robust Polymerization Only at Higher Critical Tubulin Concentration

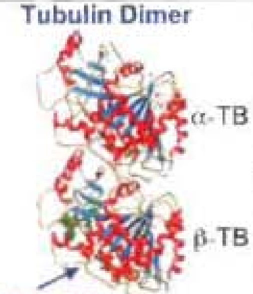


- Polymerization kinetics impacted by NQD conjugation: Critical concentration ~5 mg/mL (20% glycerol)

High NQD Concentration Deactivates Tubulin Toward Polymerization

- Reaction NQD:tubulin ratios of 1:1 and 3:1 yield polymerized ratios of 1:6; "excess" NQDs deactivate tubulin
- Conjugation through lysine residues may interfere with critical GTP binding site:
  - GTP required at β tubulin's E site
  - E site characterized by lysine residue
- NQD coverage on MTs is limited compared to molecular conjugates:
  - Rhodamine:tubulin of 1:0.4-0.9
  - Biotin:tubulin of 1:0.5-1.5
  - Size limiting factor?
- Can "dilute" NQD-MT assemblies:
  - 1:100 yields 1:87 polymerized

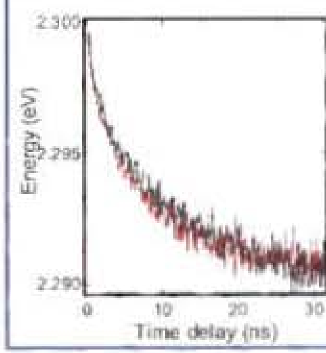
Tubulin Dimer



*GTP = Guanosine triphosphate

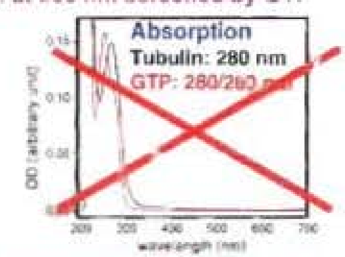
Using Energy Transfer Studies to Probe Nanoscale Structure (reorganize!)

ET Dynamics:
Free and bound QDs identical



QD coverage limited by low QD/tubulin ratio in de-polymerized sample

- Bradford assay to determine [tubulin]: abs. at 280 nm screened by GTP



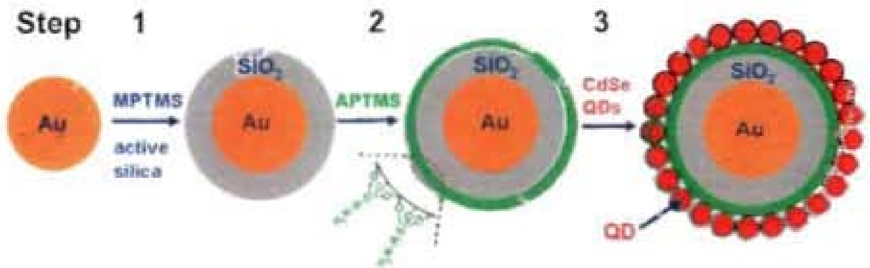
- 1S absorption to determine [QD]: *Langmuir* 2001, 17, 2861
- QD/tubulin: 1/6.4 for 1/1 in coupling rxn
- QD/tubulin: 1/6.3 for 3/1 in coupling rxn

Limit to packing density achievable by this assembly approach?

Conclusions

- First demonstration of controlled NQD-tubulin conjugation followed by robust polymerization
- Important impact of conjugation on bioactivity (bio-polymerization) reveled
  - Implications for generalized use of NQD fluorophores to study biomolecular dynamical behavior
- Impact of NQD conjugation on biomolecular structure-function relationships must be recognized
  - Follow-on: Modify conjugation strategy to be more compatible with tubulin's structure-function

Multi-step Synthesis of Hybrid Au/SiO_2/CdSe-QD Composite Structures



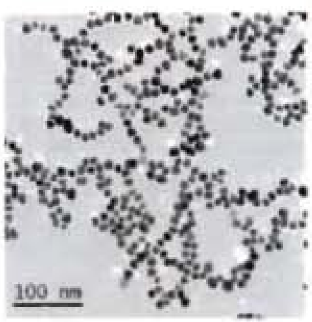
Step 1: Deposit a silica layer on the gold particle surfaces.
a) Activate Au particle surfaces using 3-mercaptotrimethoxysilane (MPTMS);
b) Deposit a thin layer of SiO_2 (4-5 nm) using active silica solution;
c) Thicker SiO_2 shell can be prepared by Stöber method (sequential growth).

Step 2: Modification of SiO_2 surface with 3-aminopropyltrimethoxysilane (APTMS).

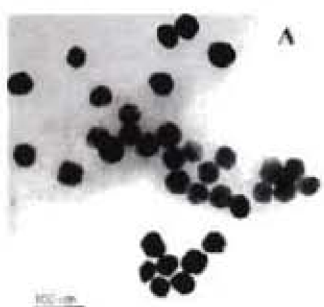
Step 3: Self-assembly of CdSe nanocrystals onto the Au/SiO_2 particle surfaces in THF or $CHCl_3$.

Synthesis of Au Nanoparticles

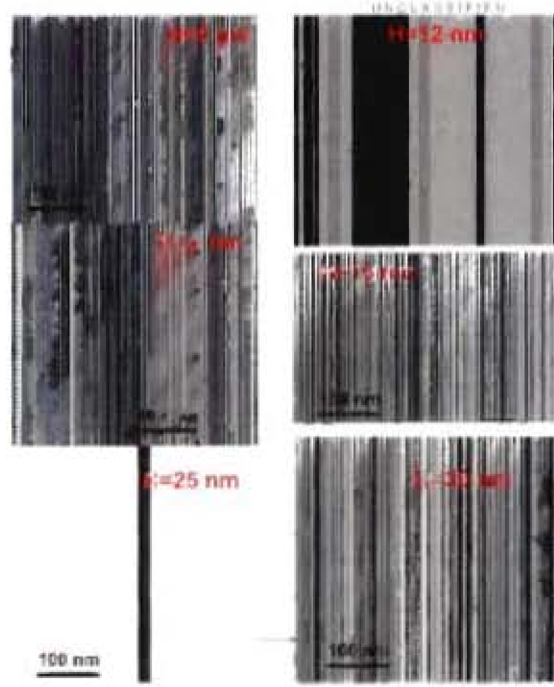
$$HAuCl_4 + Na_3Cit \xrightarrow[\Delta]{H_2O} \text{Au nanoparticles}$$



15-nm Au nanoparticles

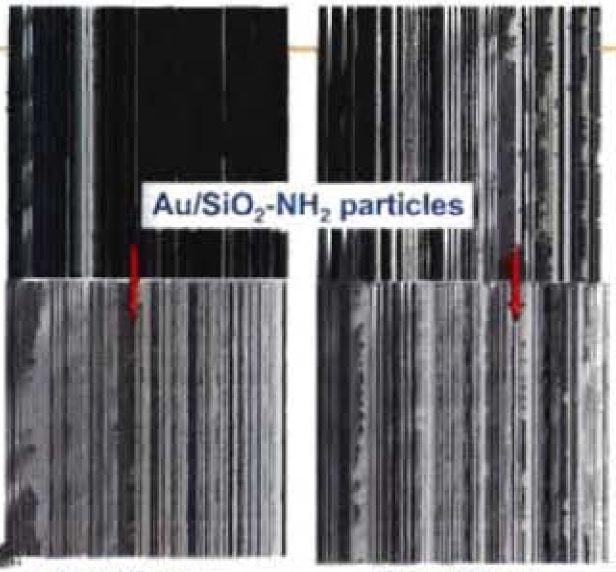


45-nm Au nanoparticles



Core/Shell Au/SiO_2 nanoparticles with various shell thickness (5 - 42 nm)

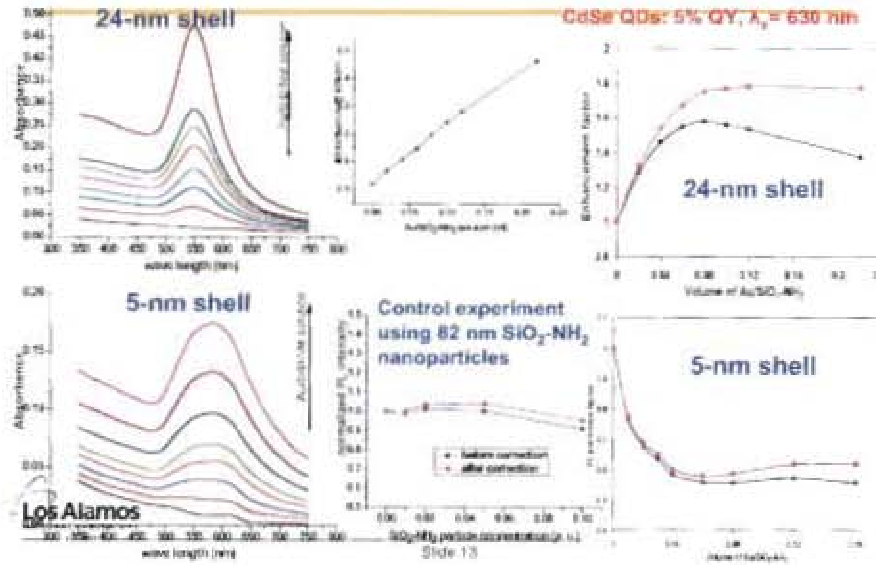
$Au/SiO_2/CdSe$-QDs Nanostructures



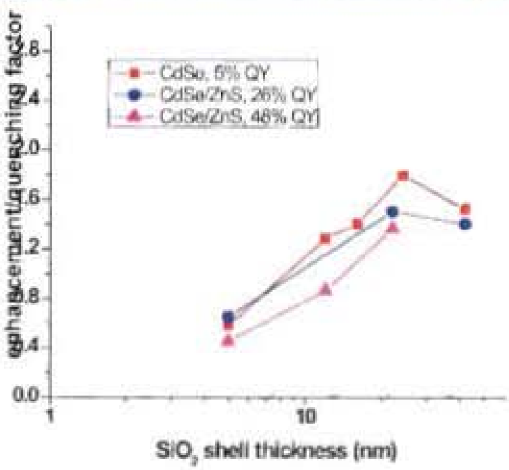
45 nm/5 nm

45 nm/24 nm

PL Enhancement/Quenching by Au Surface Plasmons



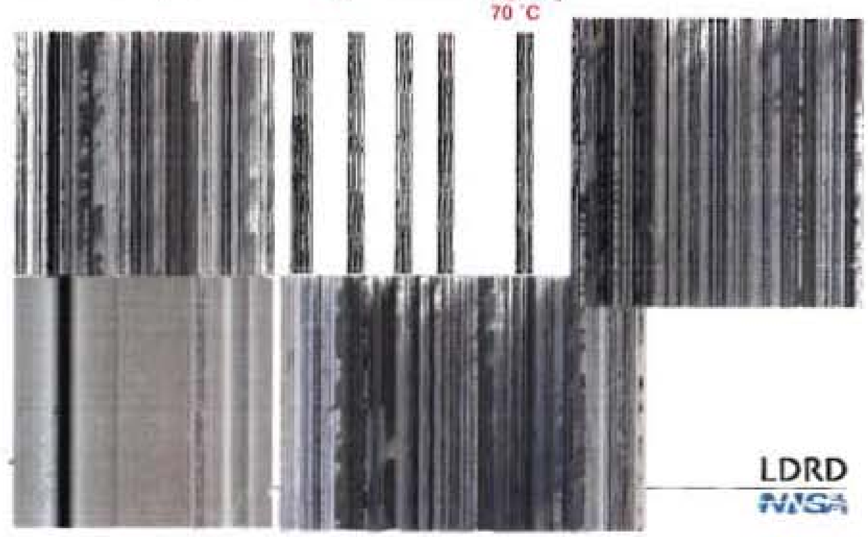
PL enhancement/quenching factors depend on metal-QD distances and QYs of the QDs



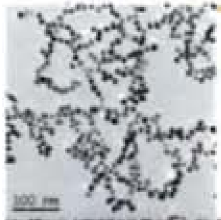
Au core size : 45 nm

$Ag/SiO_2/CdSe$-QDs Nanostructures

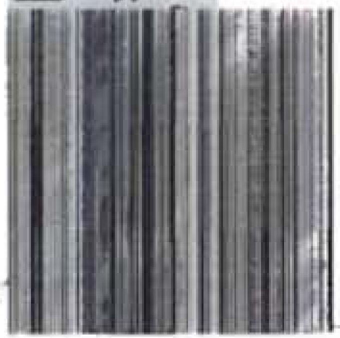
$AgClO_4 + Na_3Cit + NaBH_4 \xrightarrow[RT]{H_2O}$ Ag seeds $\xrightarrow[AgClO_4,\ 70\ ^\circ C]{\text{Ascobic Acid}}$ Ag particles



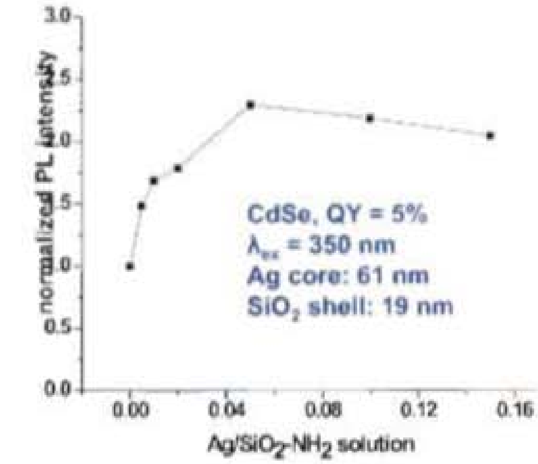
Au/Ag/SiO$_2$/CdSe-QDs Nanostructures



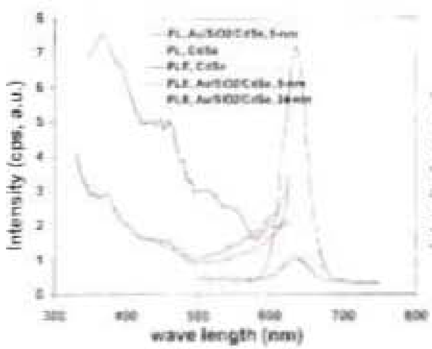
Au seeds + $AgClO_4$ + Ascorbic Acid $\xrightarrow[70\ ^\circ C]{H_2O}$ Au/Ag nanoparticles

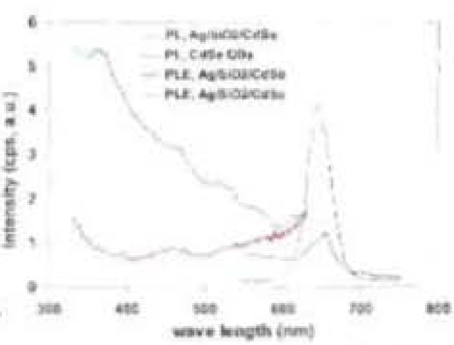


PL enhancement by Ag/SiO$_2$-NH$_2$ nanoparticles



PL and PLE spectra of Au (Ag)/SiO$_2$/CdSe nanoparticles





Conclusions

- Hybrid Au/SiO$_2$/CdSe, Ag/SiO$_2$/CdSe, and Au/Ag/SiO$_2$/CdSe superstructures were synthesized successfully.
- The dielectric SiO$_2$ spacer thickness can be controlled.
- The interactions (quenching or enhancement) between the QDs and the metal cores can be tuned by varying the SiO$_2$ spacer thickness.