Sensitizing and Protecting Lanthanide Ion Emission Using Optically Active Nanocrystals

Pawan Rastogi*[1], Javier Vela*, and Jennifer Hollingsworth*, *Center for Integrated Nanotechnologies at Los Alamos National Laboratory, [1]Columbia University Chemistry Department

BACKGROUND INFORMATION

LANTHANIDES (Ln^{3+}) AS LIGHT EMITTERS

Advantages…

- Specific electron transitions (f-block elements)
- Ultra-narrow band emitters of UV to NIR light
- Long luminescence lifetimes

Disadvantages…

- Possess specific and narrow absorption bands
- Small absorption cross sections
- Luminescence is quenched by O-H and N-H vibrations in protic solvents

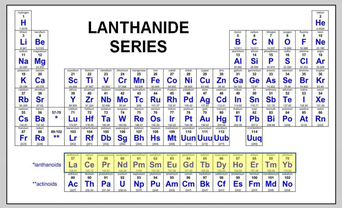
Potential Applications

- Bioimaging
- Photon Up-conversion
- Optical Amplification and Lasing

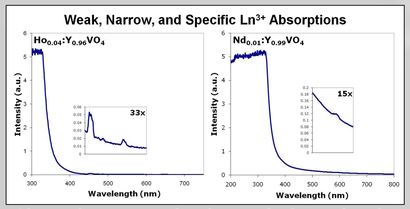
Boilot et al., *Chem. Mater.*, **2002**, *14*, 2264-2269.

TECHNICAL CHALLENGE AND OBJECTIVES

- **PROBLEM:** Ln^{3+} applications are currently limited by a lack of effective and/or versatile protection and sensitization strategies.
- **OBJECTIVE 1 :** 'Sensitize' Ln^{3+} absorption for enhanced emission and larger cross sections.
- **OBJECTIVE 2:** Provide 'protection' for the Ln^{3+} against solvent quenching and general stability.



Periodic table highlighting the lanthanide elements.



Absorption spectra showing weak absorptions by Nd^{3+} and Ho^{3+} ions relative to the intense absorption by the YVO_4 groups.

NANOCRYSTALS (NCs) AS LANTHANIDE-HOSTS

Rare Earth NCs

- Luminescence quenching can be suppressed by doping the Ln^{3+} ions into rare earth (RE) NCs (e.g. LaF_3, $LaPO_4$)
- Ln^{3+} ions can be excited by way of energy transfer (ET) from optically active host matrices (e.g. YVO_4)

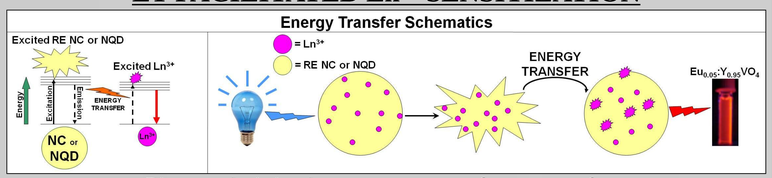
Capobianco et al., *Nano Lett.*, **2007**, *7*, 847-852.

Nanocrystal Quantum Dots (NQDs)

- Alternative optically active matrix
- Large absorption cross sections over a wide spectral range
- NQD-size tunable absorption onsets
- Efficient ET partners with other NQDs, dye molecules, and transition metals

Hollingsworth and Klimov, New York: Marcel Dekker, 2004, Ch. 1.

ET-FACILITATED Ln^{3+} SENSITIZATION



Diagrams depicting the quantum process of energy transfer.

PROPOSED METHODS

- Dope Ln^{3+} ions into YVO_4 RE NCs following an aqueous synthesis
- Assess the effectiveness of coupling NQDs with Ln^{3+}-doped YVO_4 via thin films
- Dope Ln^{3+} ions into In_2O_3 NQDs using an organic route and determine efficacy

AQUEOUS SYNTHESIS OF Ln^{3+}-DOPED YVO_4

$$Y(NO_3)_3{\cdot}4H_2O + Ln(NO_3)_3{\cdot}xH_2O + NaC_6H_5O_7 \longrightarrow \{Ln(C_6H_5O_7)_x \text{ Complexes}\}$$

Temperature = 60 °C

Formation and precipitation of white $Ln(C_6H_5O_7)_x$ complexes

Ln + Y = 0.1 mmol; Ln = Eu, Nd, Ho, Tb, Yb/Er, Ce/Er

$$\{Ln(C_6H_5O_7)_x \text{ Complexes}\} + Na_3VO_4 \longrightarrow Ln_xY_{1-x}VO_4$$

Reaction aged for 1 h

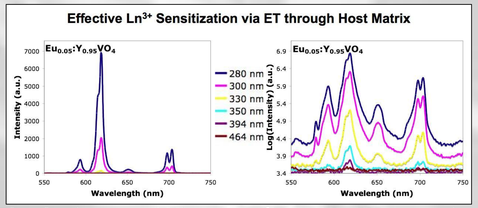
Purified via dialysis for 3 days (MW cut-off = 10 kDa)

Average Size: ~15.3 nm (Dynamic Light Scattering)

Water-soluble and thermally stable particles

Hydrothermal treatment in microwave reactor (200 °C, 200 psi, 200 W, <8 h)

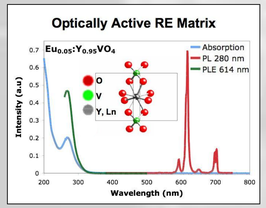
Kong et al., *Chem. Mater.*, **2006**, *18*, 2726-2732.



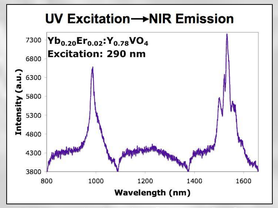
Photoluminescence (PL) spectra of $Eu_{0.05}$:$Y_{0.95}VO_4$ at varying wavelengths showing enhanced Eu^{3+} emission when excited through the YVO_4 host matrix, supporting effective sensitization.

	Absorption (nm)	Emission (nm)
YVO_4	250 to 330	
In_2O_3	300 to 330	380 to 440
CdSe	Less than 590	577 to 595
Eu	394, 464	594, 614, 660
Nd	533, 588, 808	1060
Er	520	1530

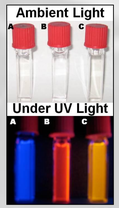
Absorption and emission wavelengths for relevant compounds and elements.



Photoluminescence excitation (PLE) spectrum confirming that the 614 nm Eu^{3+} emission arises through ET from the YVO_4 host groups.



NIR emission is observed after excitation in the UV. Both forms of light are invisible to the naked eye.



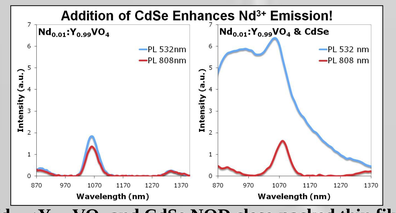
(A) Coumarin 450, (B) $Eu_{0.05}$:$Y_{0.95}VO_4$, and (C) CdSe NQDs fluorescence.

- **RESULT :** YVO_4 functions as an efficient matrix for sensitization and ET to Ln^{3+} ions.

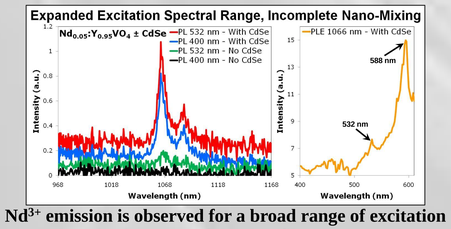
COUPLING OF Ln^{3+}-RE NCs & NQDs

- Constructed close-packed thin films composed of Nd_x:$Y_{1-x}VO_4$ NCs and CdSe NQDs by drop casting
- CdSe NQDs emit at 586 nm (a direct absorption of Nd^{3+}) and are therefore good candidates for ET
- Enhanced emission intensity using the 532 nm laser, but NOT the 808 nm laser supports communication between the particles (532 nm light can excite both the CdSe NQDs and Nd^{3+})

Brus et al., *Nature*, **2003**, *426*, 271-274.



$Nd_{0.01}$:$Y_{0.99}VO_4$ and CdSe NQD close-packed thin film shows higher emission intensity than that of $Nd_{0.01}$:$Y_{0.99}VO_4$ alone, suggesting communication between particles.



Nd^{3+} emission is observed for a broad range of excitation wavelengths, but PLE of the thin films suggests there may not be intimate mixing at the nanoscale.

- **RESULT :** Nd^{3+} emission is enhanced and effectively has an expanded excitation window in the presence of CdSe.
- **FUTURE:** In response to inadequate mixing we hope to attempt a direct coupling via electrostatic interactions between positively charged CdSe NQDs and negatively charged Nd_x:$Y_{1-x}VO_4$ NCs.

ORGANIC SYNTHESIS OF Ln^{3+}-DOPED In_2O_3

Precursor Solution: $In(OAc)_3 + Ln(NO_3)_3{\cdot}xH_2O$

1 h dynamic vacuum for removal of water

Temperature = 120 °C, Solvent: 1-Octadecene

Ln + In = 0.1 mmol; Ln = Eu, Nd, Er

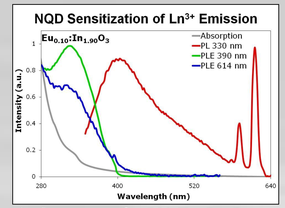
$$\text{Precursor Solution} + C_{10}H_{21}OH \longrightarrow Ln_{2x}In_{2-2x}O_3$$

Growth at 290 °C for 1 h

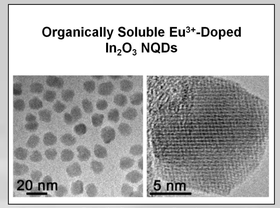
NQD particles precipitated using 3:1, Acetone:MeOH mixture

Average Size: 11.9 ± 2.2 nm

Hydrophobic and thermally stable

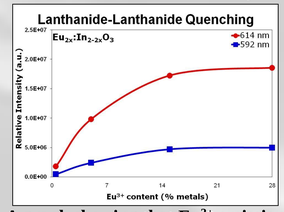


Optical spectra of a 5% Eu:In_2O_3 sample supporting that In_2O_3 is an alternative optically active NQD matrix.

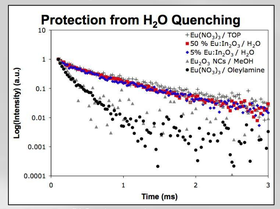


Low and High Resolution TEM Images of 5% Eu:In_2O_3.

Vela and Rastogi et al., *J. Phys. Chem. C*, **2008**, *112*, In press.



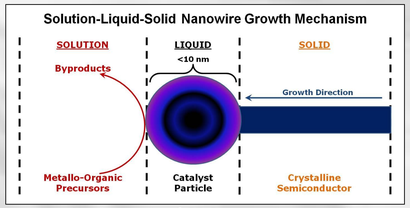
A graph showing that Eu^{3+} emission intensities begin to plateau at higher Eu^{3+} ion doping concentrations.



Eu:In_2O_3 lifetimes in water-saturated hexanes solution show better lifetimes than Eu_2O_3 NCs.

- **RESULT:** In_2O_3 serves as both a sensitizer and protector towards Ln^{3+} ion emission.
- **FUTURE:** To further sensitize Ln^{3+} ions with In_2O_3 matrices, we plan to synthesize In_2O_3 nanowires (with larger absorption cross sections) and dope them with Ln^{3+} ions.

SOLUTION-LIQUID- SOLID (SLS) GROWTH



A schematic of SLS nanowire growth.

- Heat is applied to melt catalyst nanoparticles
- Molten catalyst particles solubilize precursors and become saturated
- Precursors begin to precipitate out of molten catalyst resulting in unidirectional nanowire growth

Buhro et al., *Inorg. Chem.*, **2006**, *45*, 7511-7521.

SUMMARY OF CONCLUSIONS

- **CONCLUSION 1:** Significant sensitization and enhancement of Ln^{3+} ion emission via ET from the optically active host matrices (YVO_4, In_2O_3).
- **CONCLUSION 2:**Considerable protection against common solvent quenching demonstrated for new In_2O_3 Ln^{3+}-NQD system.

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