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)

Advantages…

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

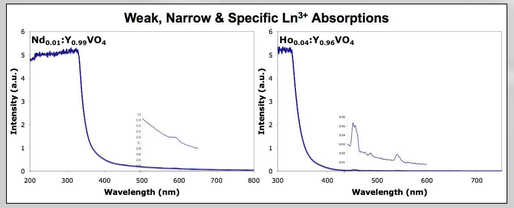
Disadvantages…

- 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.



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

RARE EARTH NANOCRYSTALS (NCs)

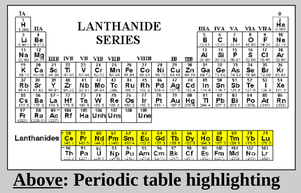
- Luminescence quenching can be suppressed by doping the Ln^{3+} ions into rare earth (RE) NCs (e.g. LaF_3, $NaYF_4$, $LaPO_4$)
- Ln^{3+} ions can be excited by way of energy transfer (ET) from optically active host matrices (e.g. YVO_4)

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

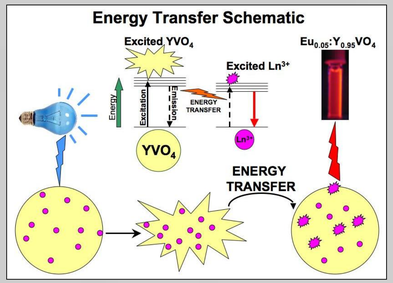
NANOCRYSTAL QUANTUM DOTS (NQDs)

- 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 metal luminescent ions

Hollingsworth and Klimov, New York: Marcel Dekker, 2004, ch. 1, pp. 2-72.



Above: Periodic table highlighting position of lanthanide elements.



Right: Diagram depicting the quantum process of energy transfer.

MAIN OBJECTIVES

- 'Sensitize' Ln^{3+} absorption for enhanced emission and larger cross sections
- Provide 'protection' for the Ln^{3+} against solvent quenching and general stability

PROPOSED METHOD

- Dope Ln^{3+} ions into YVO_4 NCs and In_2O_3 NQDs, and evaluate effectiveness
- Assess possibility of coupling NQDs with Ln^{3+}-doped NCs

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

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

Temperature = 60 °C

Formation and precipitation of white Ln-Citrate complexes

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

$$\text{Ln-Citrate Complexes} + Na_3VO_4 \longrightarrow Ln_xY_{1-x}VO_4$$

Reaction aged for 1 h

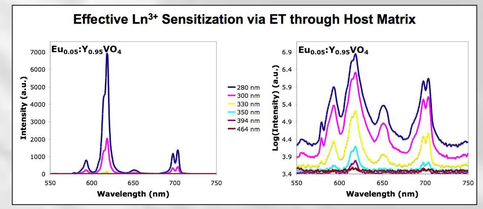
Purified via Dialysis for 3 Days (MW cut-off = 10 kDa)

Average Size: 22 nm (Dynamic Light Scattering)

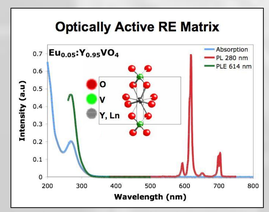
Water-Soluble and Thermally Stable

Hydrothermal Treatment in Microwave Reactor (200 °C, 200 psi, 200 W, <8 h)

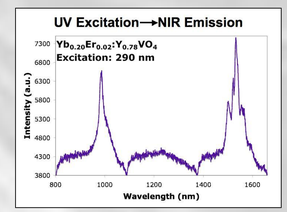
Kong et al., *Chem. Mater.*, **2006**, 18, 2726-2732.



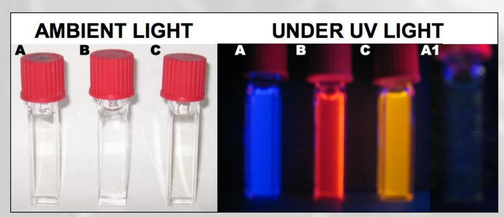
Photoluminescence (PL) spectra of $Eu_{0.05}{:}Y_{0.95}VO_4$ at varying wavelengths, showing enhanced Eu^{3+} emission when excited through the YVO_4 host matrix, supporting effective sensitization.



A 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.



Before and after UV excitation (~310 nm) photos of aqueous solutions of (A) Coumarin 450, (B) $Eu_{0.05}{:}Y_{0.95}VO_4$, (C) CdSe NQDs, (A1) After 12 h continuous excitation of Coumarin 450 [Photobleaching].

Excitation and Emission Wavelengths of Relevant Compounds & Elements		
	Excitation Wavelengths (nm)	Emission Wavelengths (nm)
YVO_4	250 to 330	
In_2O_3	300 to 330	380 to 440
CdSe	Less than 570	577 to 595
Eu	394, 464	594, 614, 660
Nd	533, 588, 808	1060
Er	520	1530

Acknowledgements: I would like to thank Dr. Jennifer Hollingsworth, Dr. Javier Vela Becerra, the Post-Docs at Dr. Hollingsworth's Lab, LANL, and the SULI Program for making this research possible and for providing a stimulating, yet fun, summer internship.

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

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

Dynamic Vacuum for Removal of Water

Temperature = 120 °C, 1 h, Solvent: 1-Octadecene

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

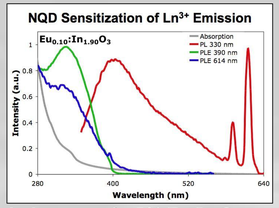
$$\text{Precursor Solution} + C_{10}H_{21}OH \longrightarrow Ln_{2x}In_{2-2x}O_3$$

Particles Precipitated Using 3:1, Acetone:MeOH Mixture

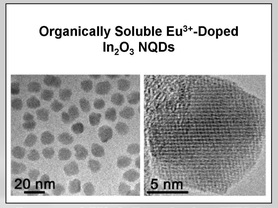
Temperature = 290 °C, 1 h

Average Size: 11.9 ± 2.2 nm

Organic Soluble and Thermally Stable

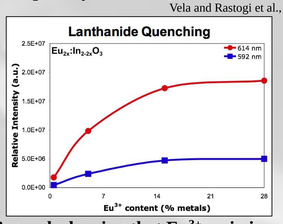


Optical spectra of a 5% Eu:In_2O_3 sample supporting that In_2O_3 is an alternative optically active NQD matrix.

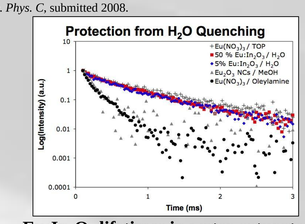


Low and High Resolution TEM Images of 5% Eu:In_2O_3

Vela and Rastogi et al., *J. Chem. Phys. C*, submitted 2008.



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



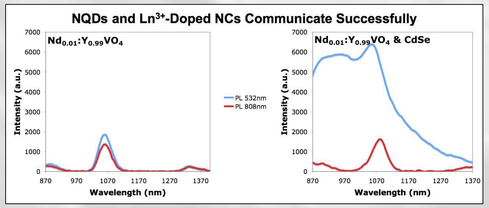
Eu:In_2O_3 lifetimes in water-saturated hexanes solution show better lifetimes than Eu_2O_3 NCs.

CONCLUSIONS

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

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

- Close-packed thin film composed of $Nd_{0.01}{:}Y_{0.99}VO_4$ NCs and CdSe cores
- CdSe cores emit at 586 nm (a direct absorption of Nd^{3+})
- 532 nm can excite both the CdSe cores and Nd^{3+}
- Successful communication would show enhanced emission intensity using the 532 nm laser, but NOT the 808 nm laser



$Nd_{0.01}{:}Y_{0.99}VO_4$ and CdSe NQD close-packed thin film shows higher emission intensity than that of $Nd_{0.01}{:}Y_{0.99}VO_4$ alone, giving promise to our future hope of chemically coupling NQDs and Ln^{3+}-doped NCs.