Generating Efficient and Tunable White Light Using Electronically Coupled Nanocrystal and Molecular Building Blocks



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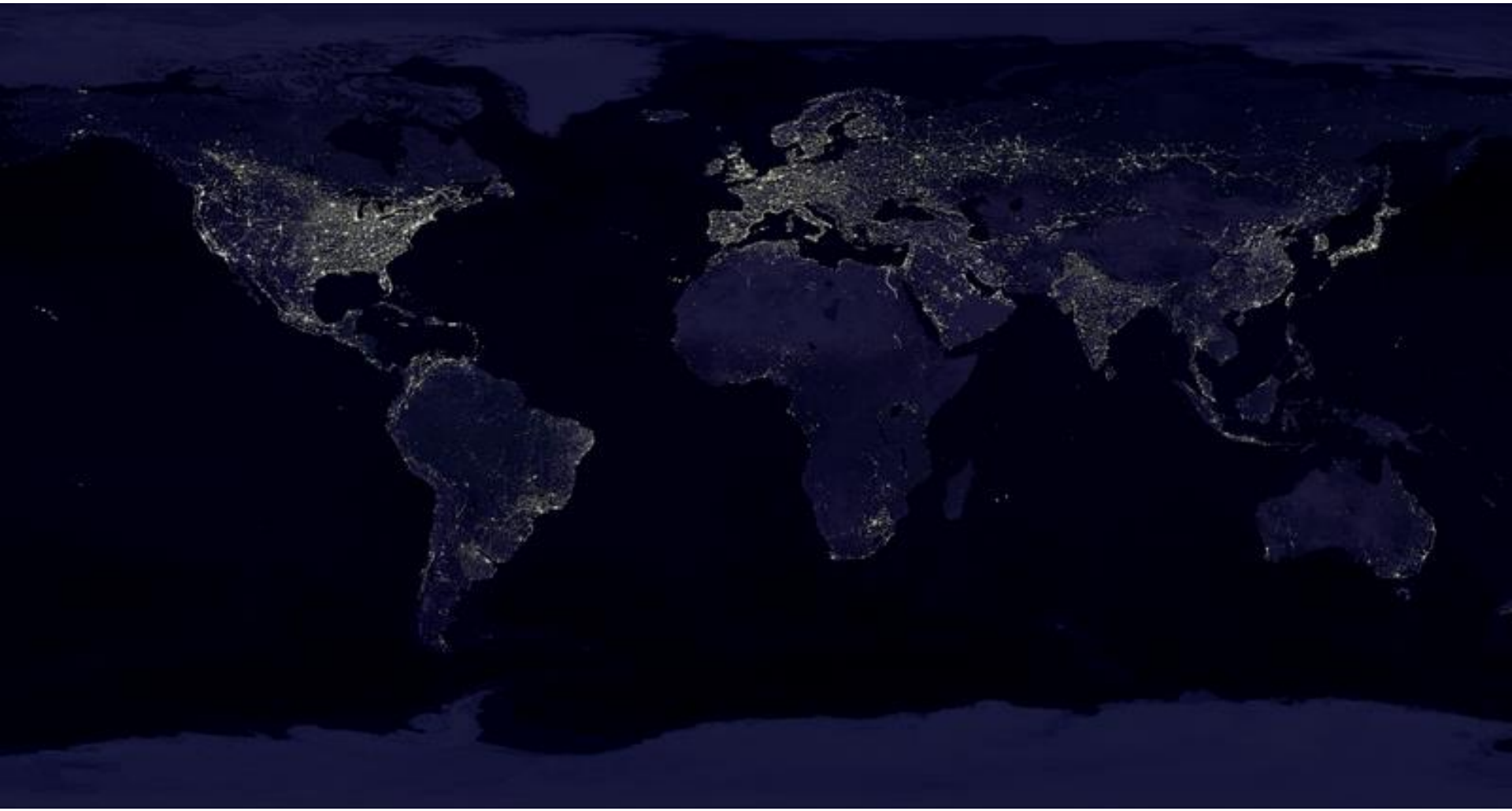
Radovanovic
RESEARCH GROUP

Pavle V. Radovanović

Department of Chemistry

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CONCORDIA CUM VERITATE

Lighting Sources

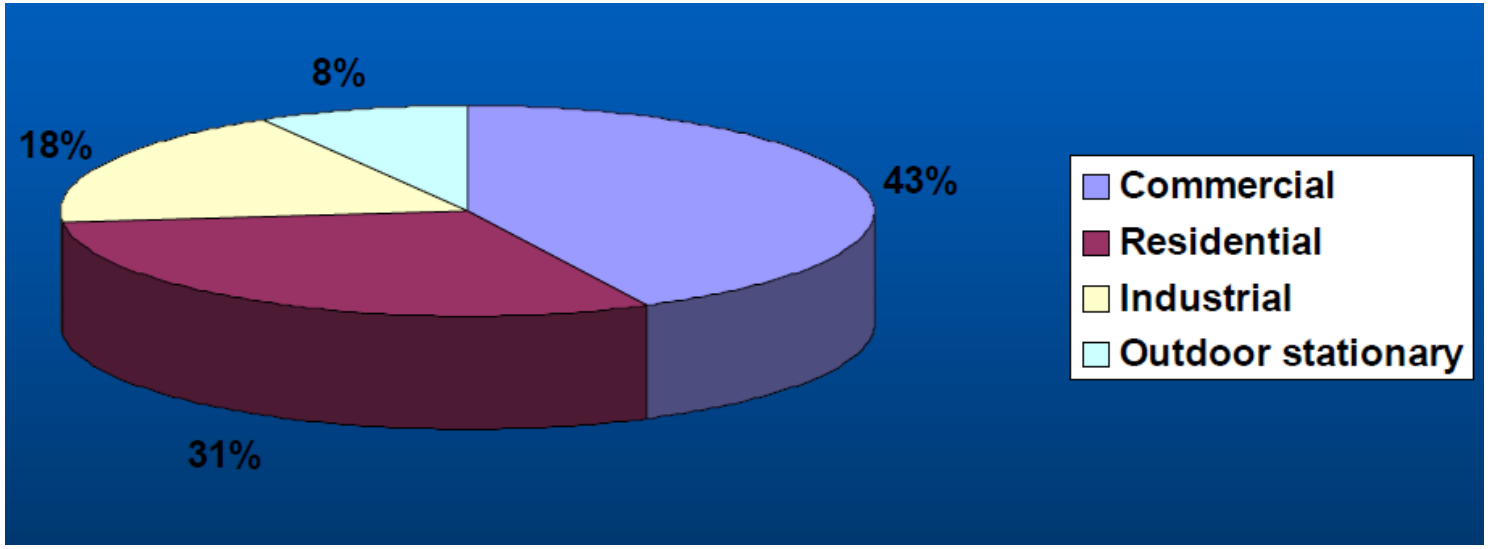


Why is Lighting Source Significant?

• Lighting of homes, offices and public buildings accounts for more than 20 percent of the global electricity consumption, or ca. 3400 TWh

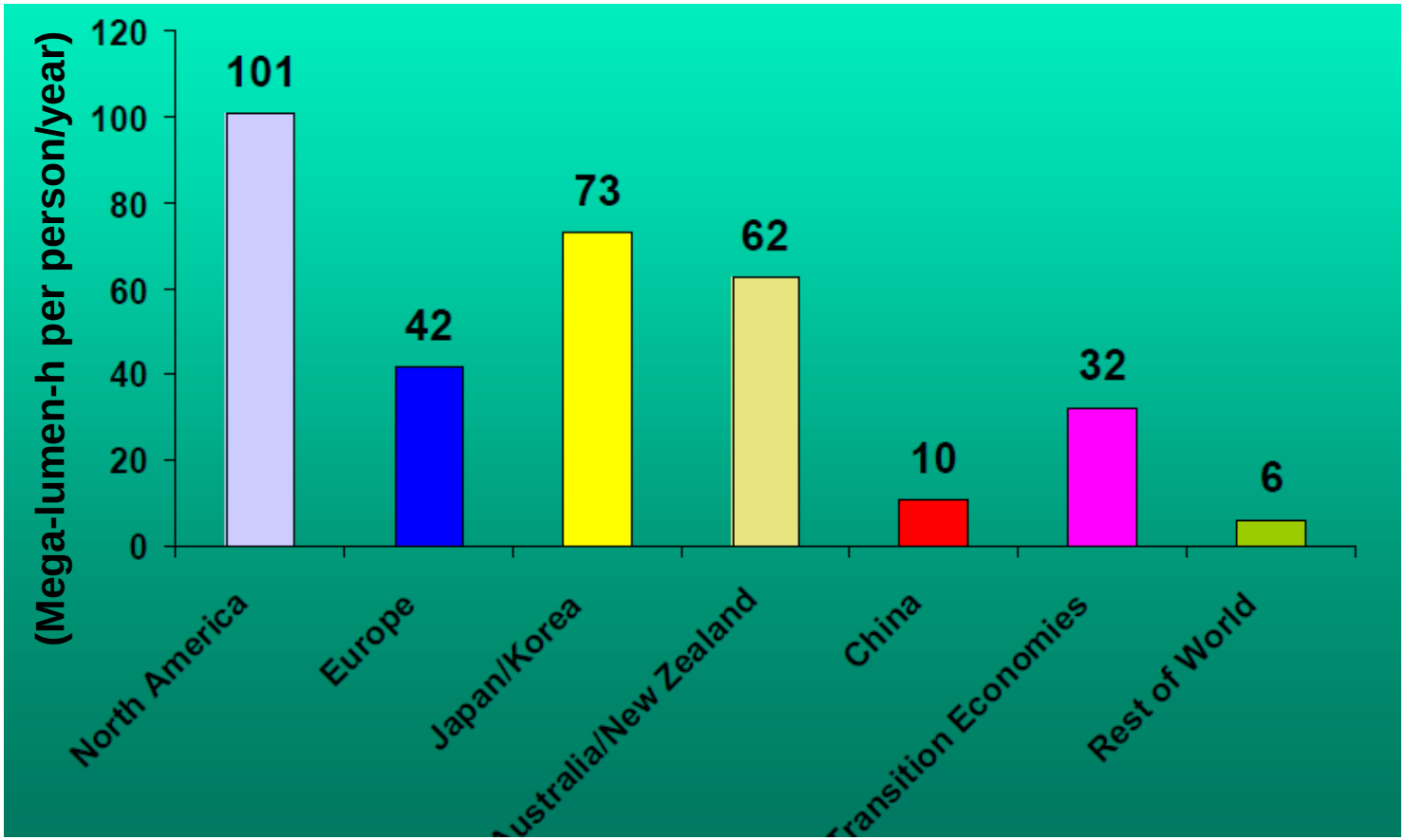
• 15-17% greater than nuclear or hydro power

• ca. 1900 $MtCO_2$ emission



Hawken P. "*Natural Capitalism: Creating the Next Industrial Evolution*" Little, Brown & Co.: Boston, 1999.

Average Electric Light Consumption



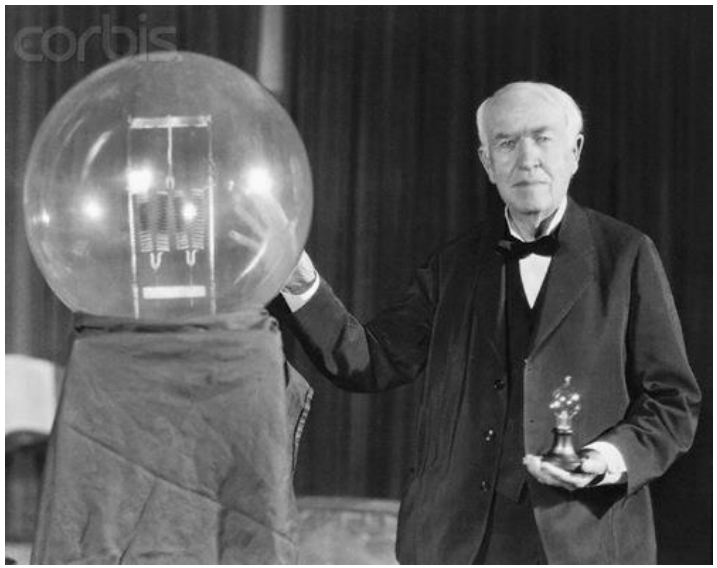
- A measure of human progress and development (expected to increase with economic development of emerging markets)

Incandescent Light Bulbs

• Traditional incandescent light bulbs have only ca. 5% efficiency

• They are expected to be phased out worldwide in the next 2-4 years, and replaced with more energy efficient devices.

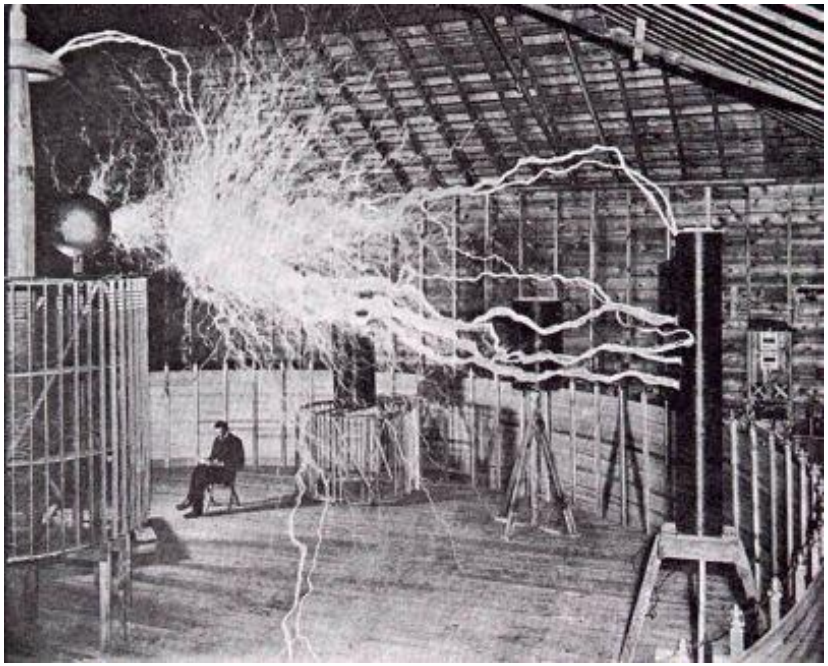
• Ban on 100 and 75 lumens/Watt incandescent bulbs started in 2014; 60 and 40 lumens/Watt bulbs followed

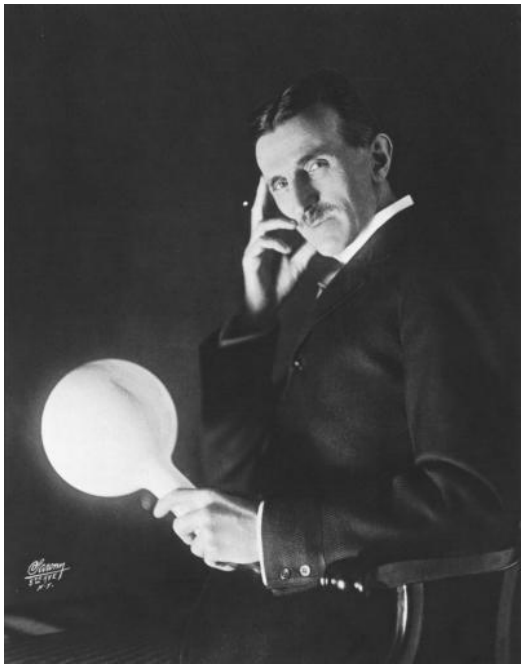




Fluorescent and Induction Lamps

- It is based on electrical discharge or magnetic induction
- Both contain mercury; have bulky design; high CCT and low CRI.
- Induction lamp has the longest life of any light source 85,000-100,000 hours; efficient and no flickering; robust and durable-good for large area illumination; radio interference is a major issue; still expensive and under-commercialized





Light Emitting Diodes (LEDs)



Oleg V. Losev
(1903-1942)

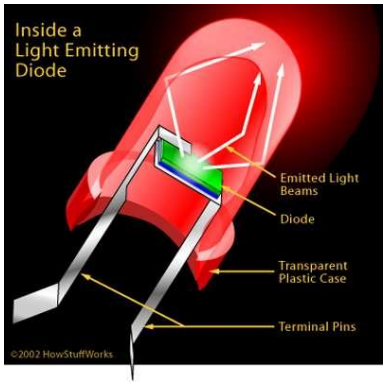
CII. *Luminous Carborundum Detector and Detection Effect and Oscillations with Crystals.* *By* O. V. Lossev *.

[Plates XVII.–XX.]

Abstract.

In this paper are described further observations on the phenomenon of the luminescence produced at the contact of a carborundum detector in connexion with a view on luminescence as a consequence of the process in the contact which is very similar to cold electronic discharge.

Losev, O. V. *Phil. Mag.* **1928**, *6*, 1024-1044



• LEDs have a number of advantages over conventional illumination sources: lower power consumption (up to 90 % less energy than traditional incandescent bulbs), extended lifetime (useful lifetime of up to 50,000 hours), smaller size, improved durability and reliability.

So why are we not using LEDs more as a lighting source?

Current Design of White LEDs

• Combining LEDs with blue, green and red outputs in a final device to give an illusion of white light.

• Coating UV or blue LEDs (usually based on III-V semiconductors – GaN, GaInN or AlN) with phosphors emitting complementary colors

• Coating UV or blue LEDs with doped phosphors, such as Ce:YAG (a yellow emitter) giving off quasi-white light upon illumination.

• Organic LEDs (OLEDs): generally cheap and easily processable, but may involve complex synthetic procedure, and are less efficient and less stable than inorganic-based LEDs.

•Barriers to LED adoption: design complexity, cost and quality of white light

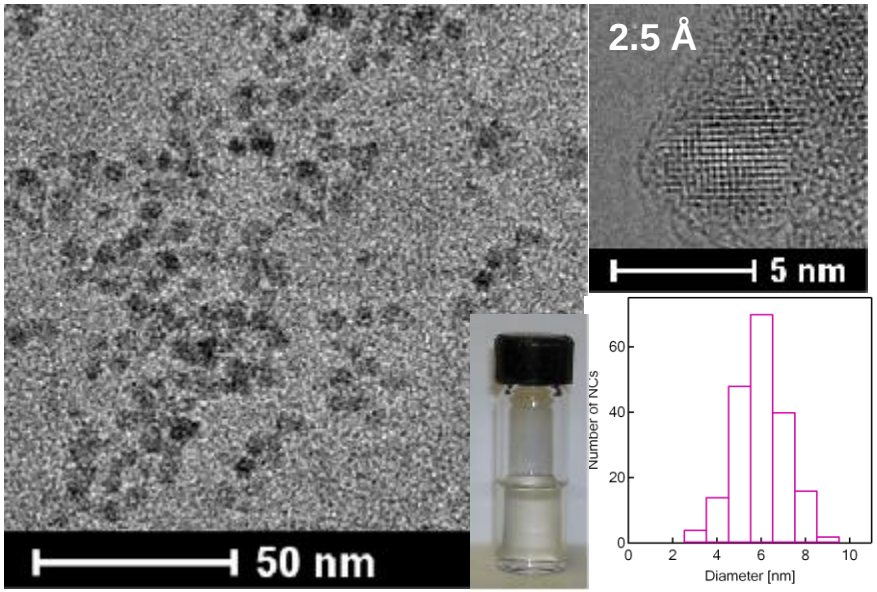
Transparent Conducting Oxides

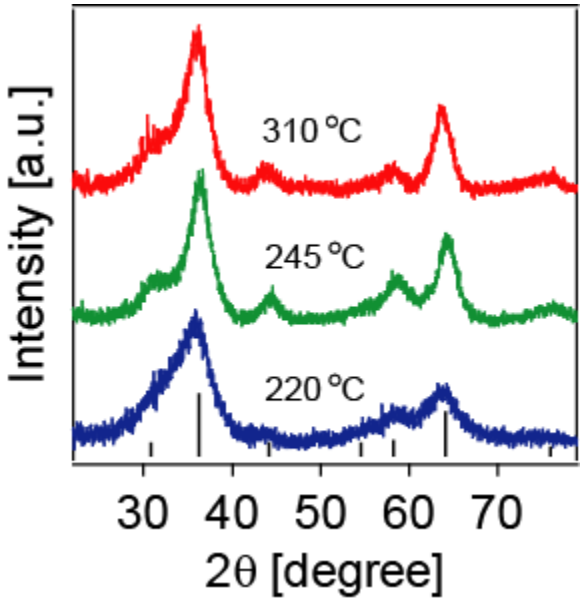
- **Combine transparency and conductivity (key functionalities that do not naturally stand together)**
- **Ga_2O_3 is wide band gap semiconductor (up to 4.8 eV)**
- **High charge carrier density and mobility (oxygen vacancy is the major donor which causes the n-type conductivity)**

$$O_O^x \rightarrow V_O^{\bullet\bullet} + \frac{1}{2}O_2 + 2e^-$$

Size-Determined Stabilization of γ-Ga_2O_3

- **Gallium oxide is stabilized in metastable phase below critical size (ca. 6 nm)**

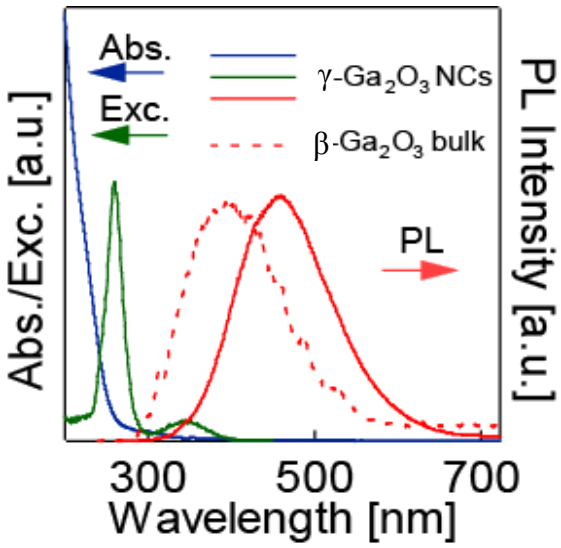


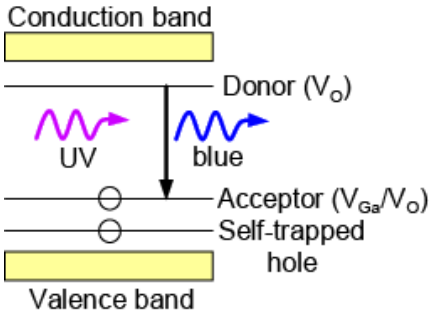


Wang, T.; Farvid, S. S.; Abulikemu, M.; Radovanovic, P. V., *J. Am. Chem. Soc.* **2010**, 132, 9250

Phase Dependence of PL Properties

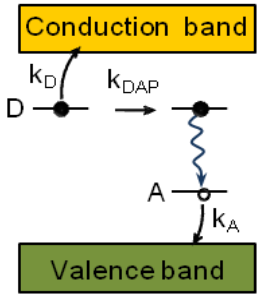
• Different native defect electronic structure leads to phase-dependence of PL properties

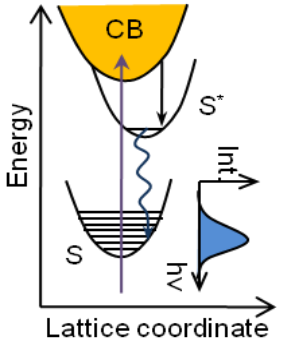




$$O_O^x \rightarrow V_O^x + \frac{1}{2}O_2 \rightarrow V_O^{\bullet} + \frac{1}{2}O_2 + e^-$$

$$(V_O, V_{Ga})' + V_O^{\bullet} + h\nu \leftrightarrow (V_O, V_{Ga})^x + V_O^x$$



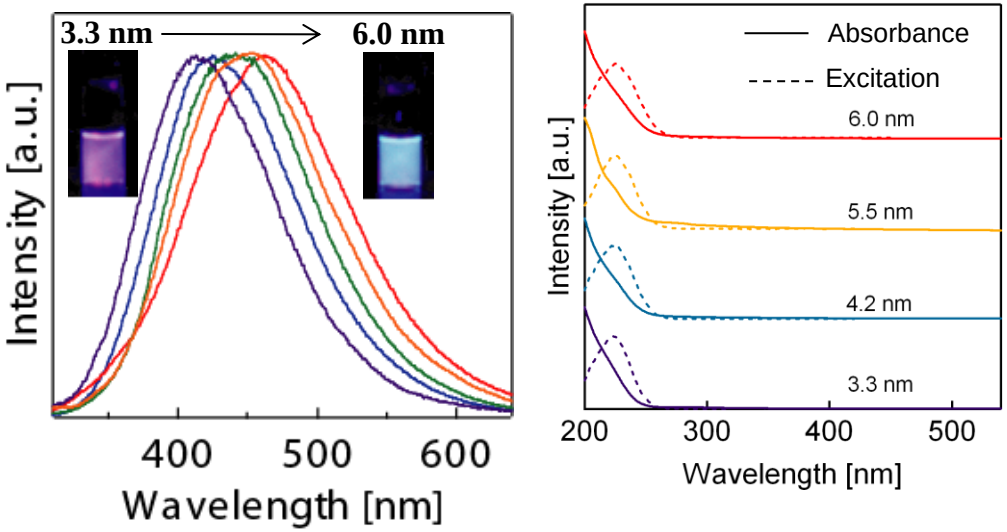


• PL broadening originates from phonon coupling and a range of defect separations

Wang, T.; Farvid, S. S.; Abulikemu, M.; Radovanovic, P. V., *J. Am. Chem. Soc.* **2010**, 132, 9250

Size Dependence of PL Properties

• Size tunability of the PL associated with Coulomb interactions of charged donors and acceptors



$$I(T) = \frac{I_0}{1 + A\exp(-\Delta E/kT)}$$

NC size [nm]	I_0 [a.u.]	A [a.u.]	ΔE [mev]
6.0 nm	32.92	1443.8	204.94
4.2 nm	35.66	3457.8	221.80
3.3 nm	38.95	8120.4	238.41

$$E = E_g - (E_D + E_A) + E_C \pm nE_{phonon}$$

• Negligible quantum confinement effect

$$E_C = \frac{e^2}{4\pi\varepsilon r}$$ Coulomb interaction term

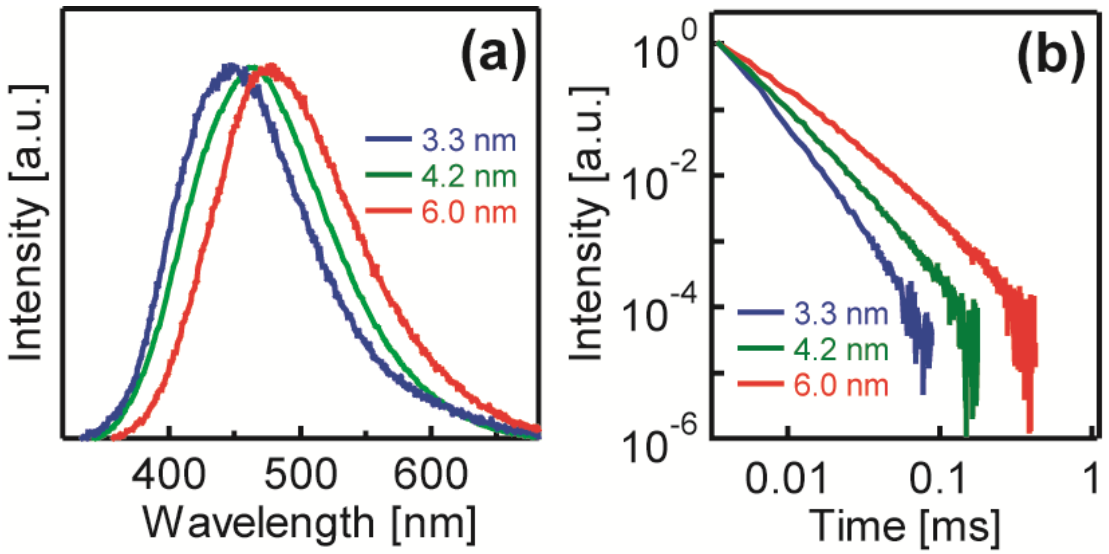
J. Am. Chem. Soc. **2010**, 132, 9250

J. Phys. Chem. C **2011** *115*, 18473

Time-Dependent Spectroscopic Studies

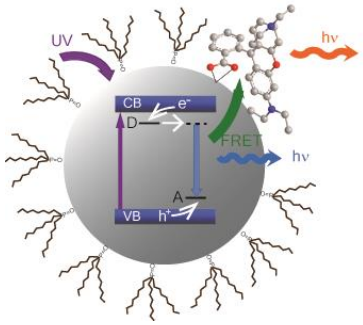
- Blue emission persists for several milliseconds and is size dependent
- Electron transfer from D to A is rate determining step
- Non-exponential decay rate (not due to the transition probability)

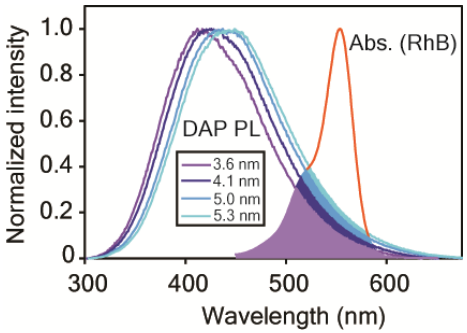
2 ms delay

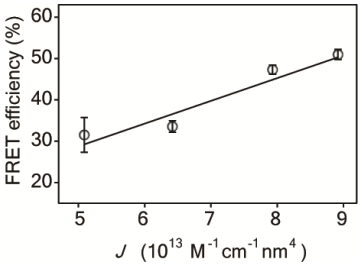


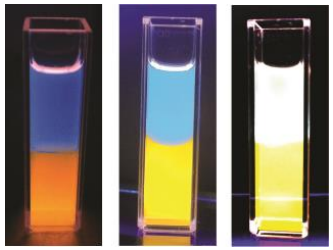
Tunable White Light Generation

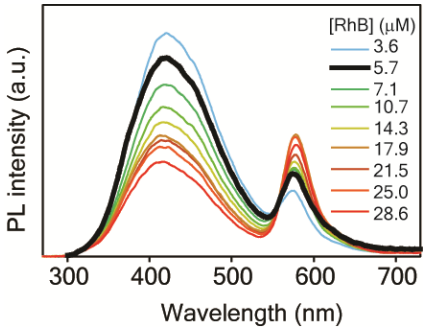
• Ga_2O_3 nanocrystal DAP blue emission is sufficiently broad and tunable in the exactly right region to require only addition of a narrow orange spectral band

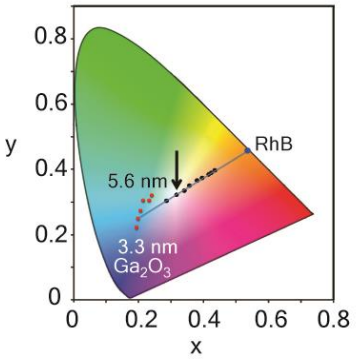


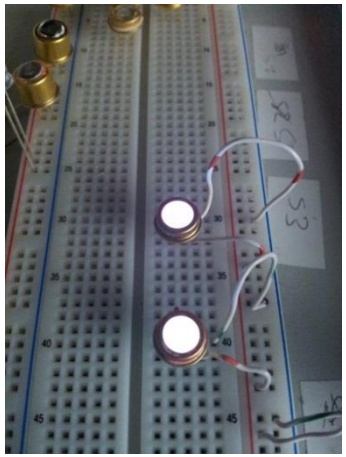












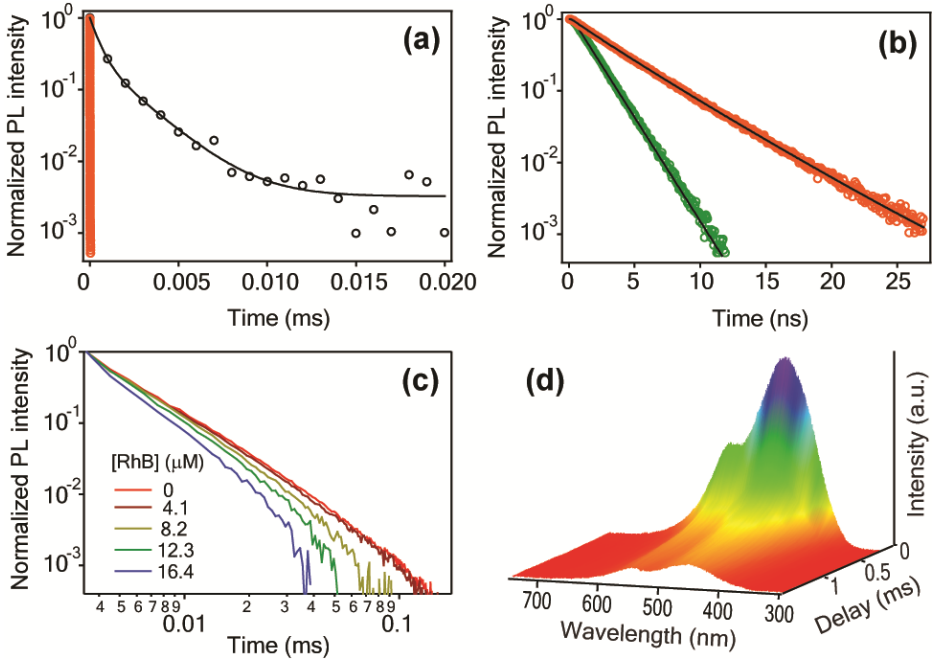
Wang, T.; Radovanovic, P. V. *U.S. Patent Appln.* **2015**, No. 20150108406

Wang, T.; Chirmanov, V.; Chiu, M. H. W.; Radovanovic, P. V. *J. Am. Chem. Soc.* **2013**, *135*,14520

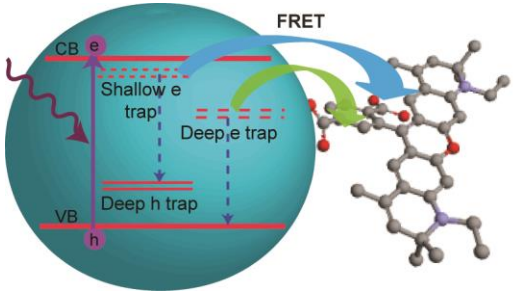
Chirmanov, V.; Stanish, P.; Layek, A.; Radovanovic, P. V. *J. Phys. Chem. C* **2015**, *119*, 5687-5696

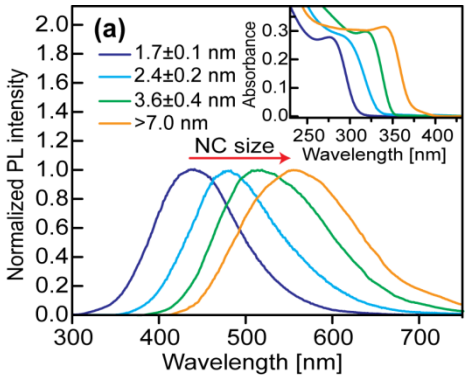
Quasi Single Chromophore

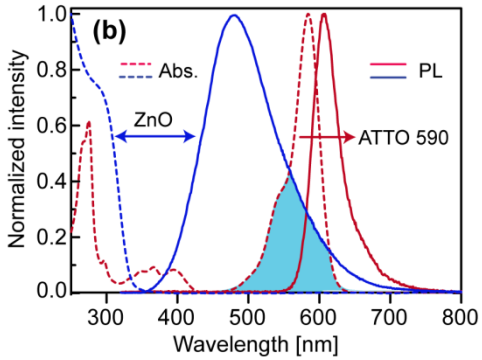
- RhB PL decays on ns timescale upon direct excitation; lifetime changes insignificantly when bound to Ga_2O_3
- RhB adopts Ga_2O_3 decay timescale after binding (when excited into Ga_2O_3 band gap)

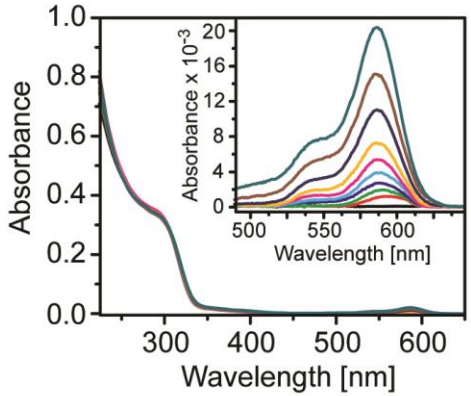


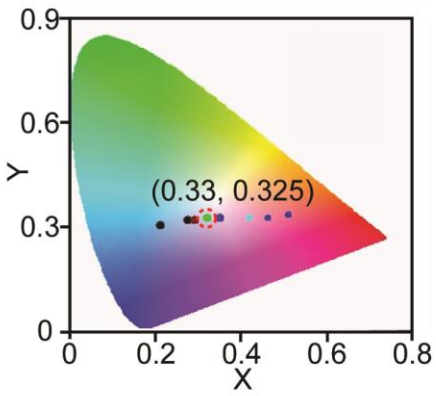
Generality: ZnO NC-Based NanoLite

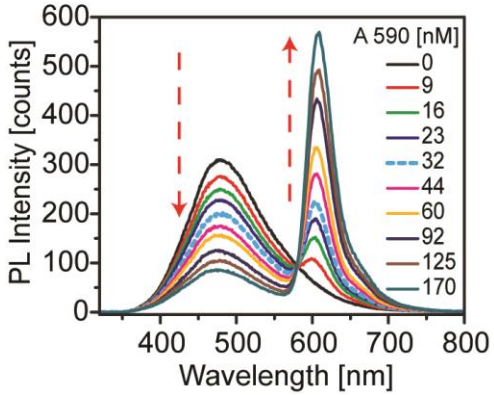


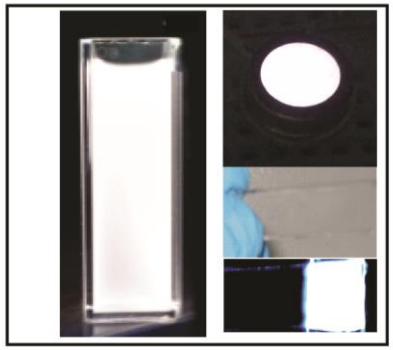








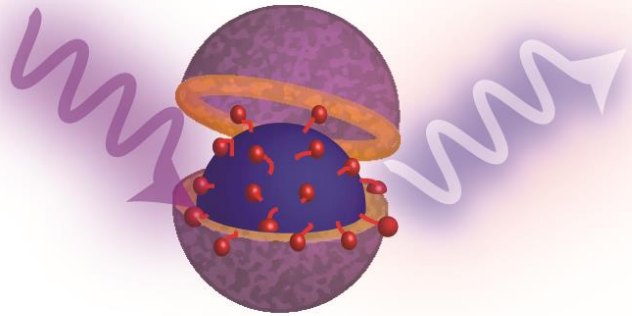


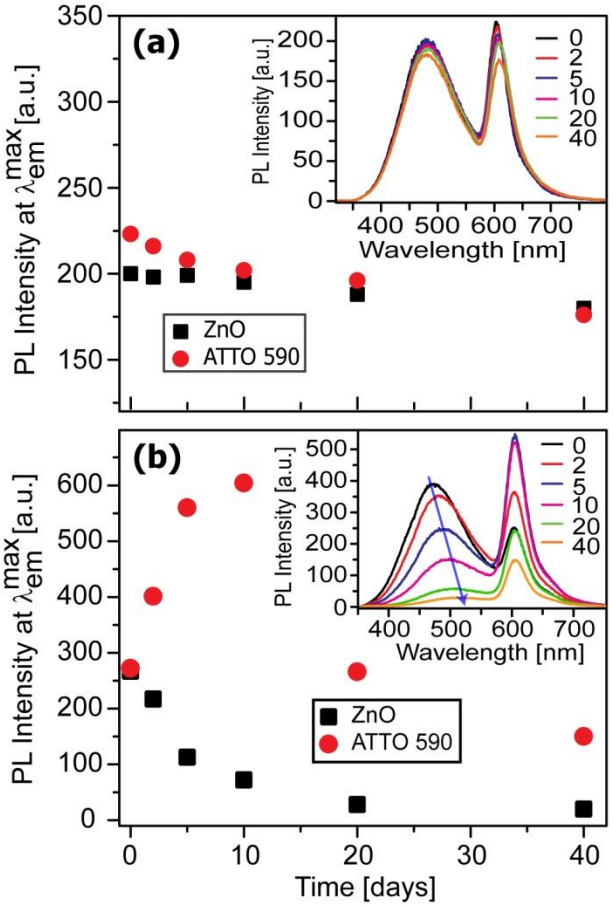


Radovanovic, P. V. *U.S. Patent Application*, **2016**, No. 20160102841

Layek et al. *Chem. Mater.*, **2015**, *27*, 1021-1030

Optimization and Stability



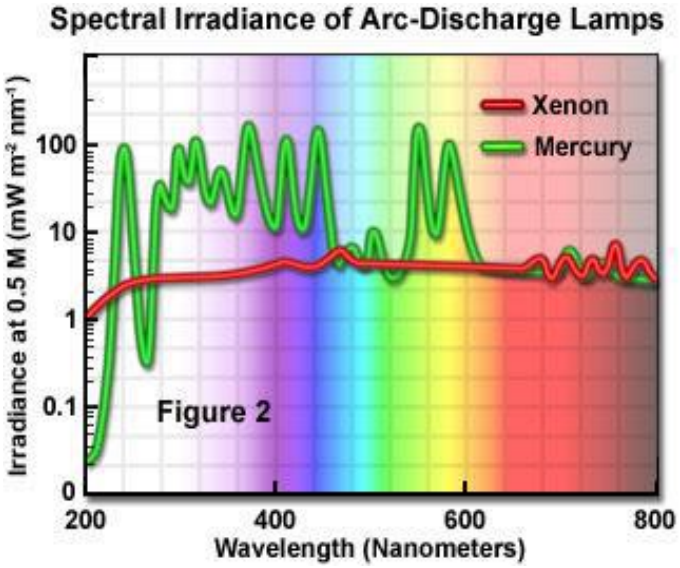


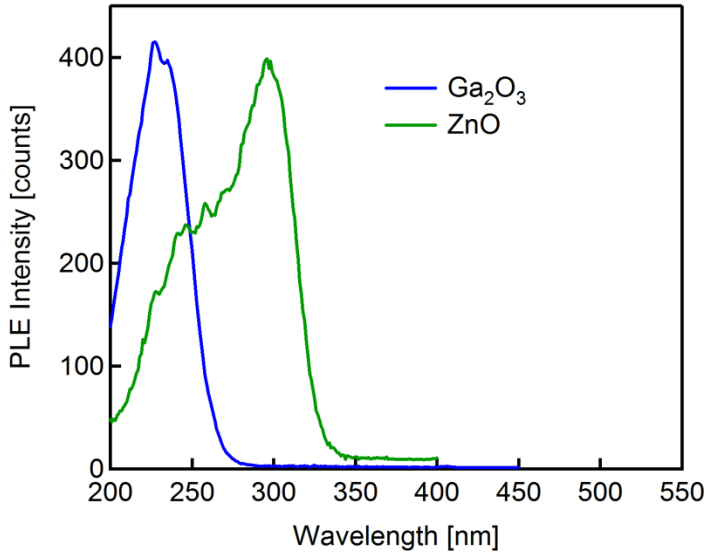
silane layer

non-protected

Radovanovic, P. V. *U.S. Patent Application*, **2016**, No. 20160102841

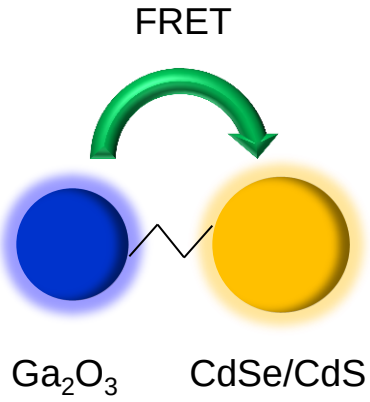
Broad UV Range Conversion

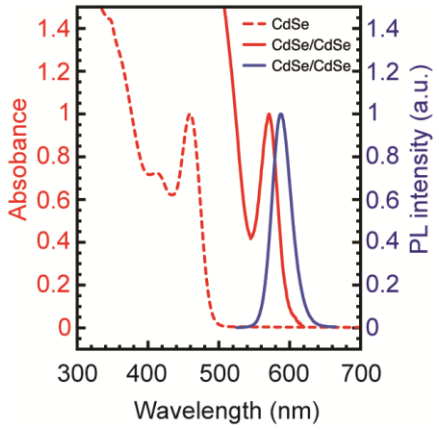


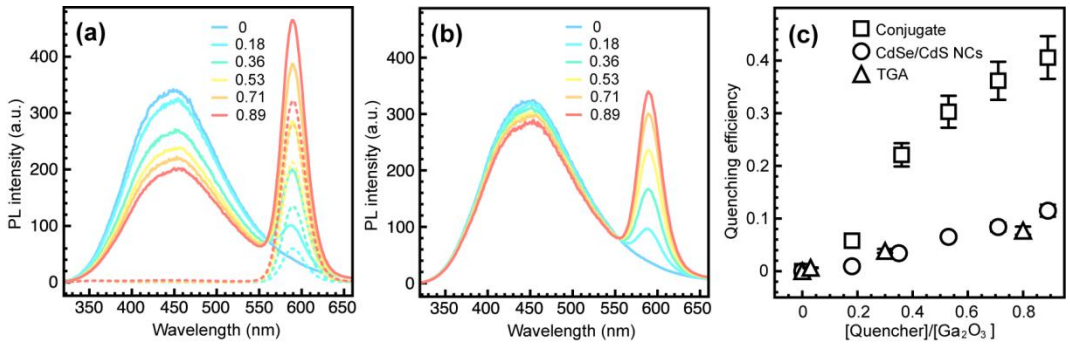


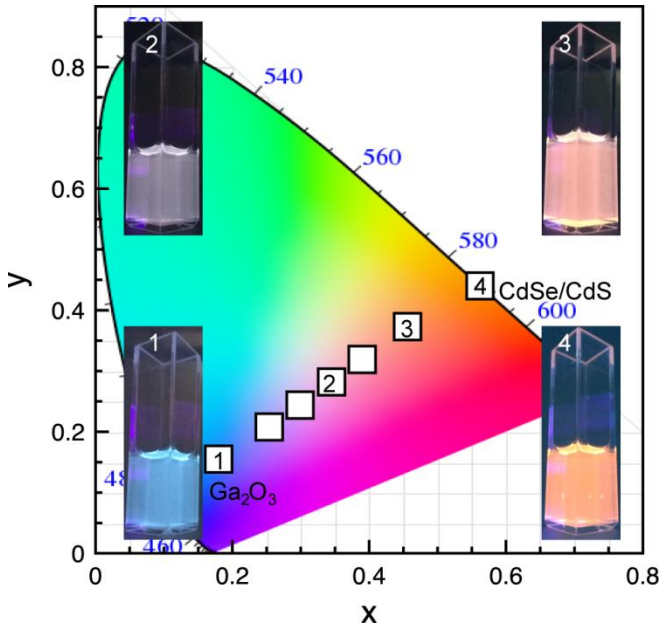
- Chromaticity, homogeneity and light characteristics independent of composition
- Different excitation for the same emission: increasing efficiency

Nanocrystal Conjugate







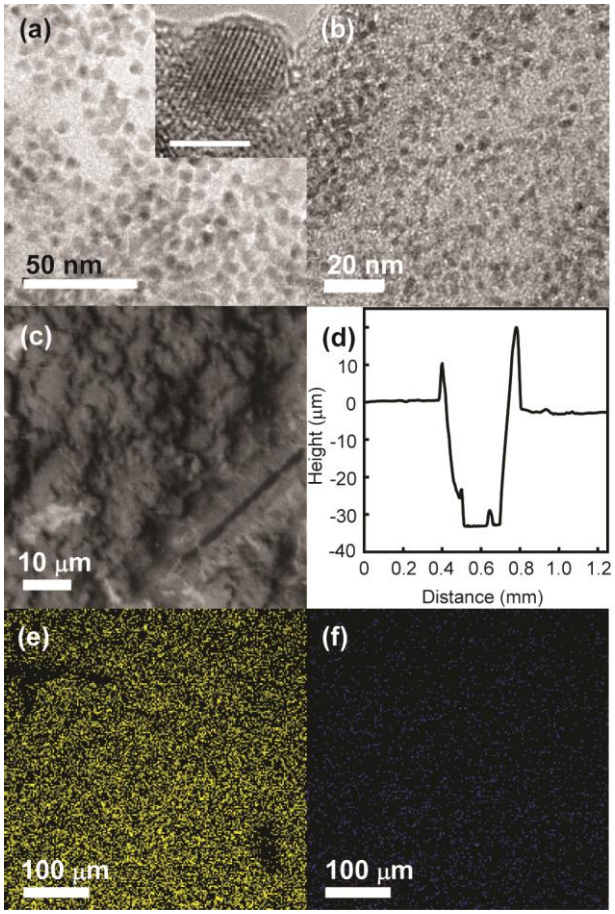


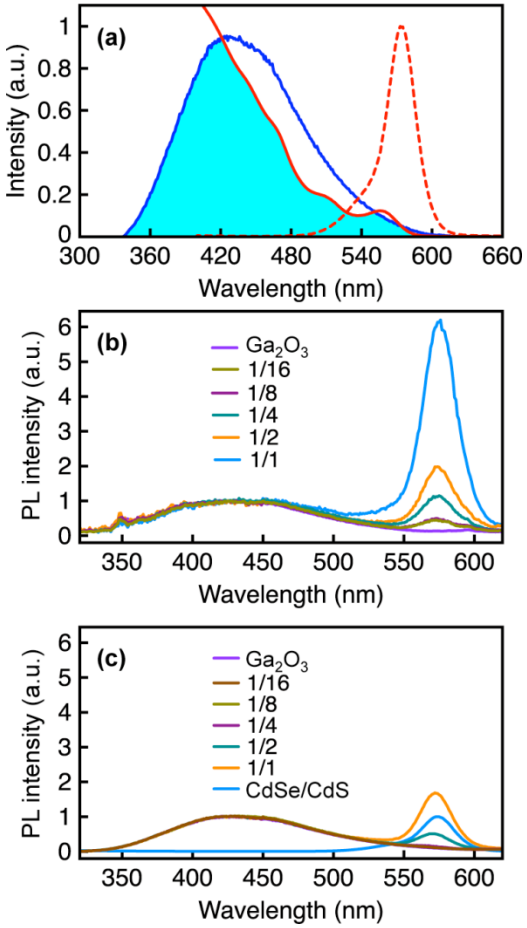
Stanish, P. C.; Radovanovic, P. V. *Nanomaterials*, **2016**, 6, 32

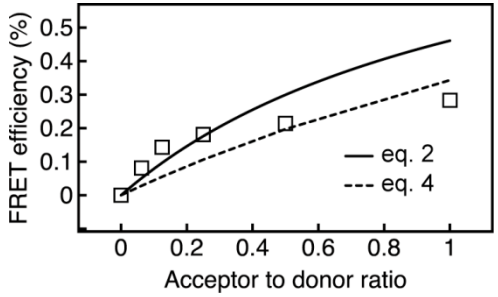
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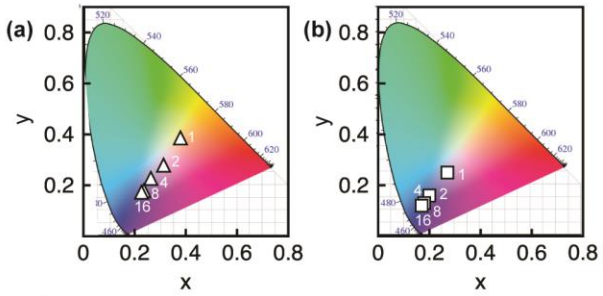
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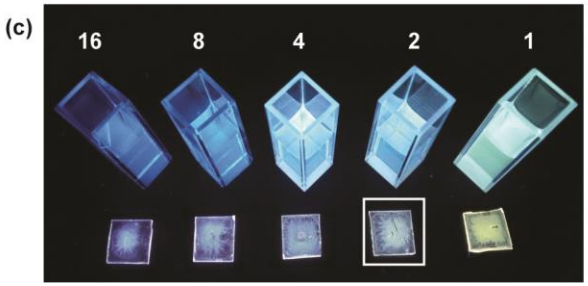
All-Inorganic White Light Emitting Phosphors











Stanish, P. C.; Radovanovic, P. V. *J. Phys. Chem. C*, **2016**, in press

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Conclusions

- **Transparent colloidal Ga_2O_3 (and other metal oxide) nanocrystals with controlled structure/defects and having strong photoluminescence have been synthesized**

- **The PL properties (steady-state and time resolved) of Ga_2O_3 NCs are size-tunable; tunability is predominantly based on Coulomb interactions**

- **Surfaces are critical for native defect formation; quantitative models have been developed**

- **New photoluminescent properties can be generated by energy transfer to rare earth dopants or molecular adsorbates**

- **Efficient and tunable white light emitting hybrid nanostructures acting as single chromophores have been achieved by rational electronic structure design (energy transfer), without the use of rare earth-based compounds**

- **Possibility of expanding functionalities and rationally tailoring the properties of complex nanostructures by materials design**

00 × 10

Acknowledgements:

Group members:

Current:

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- Manu Hegde
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- Brian Fernandes
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Collaborators:

Profs. Zoran Miskovic (University of Waterloo)

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Canada Research Chairs

Canada

Canada Foundation for Innovation

Fondation canadienne pour l'innovation

Ontario Centres of Excellence

Where Next Happens

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