NANOSCIENCE AND NANOTECHNOLOGY: THE PATHWAY TO RURAL ELECTRIFICATION AND LOW COST LIGHTING

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Great Things from Small Things

OUTLINE

Introduction:

- **Phosphors**
- **Application**
- **Define Nanoscience and Nanotechnology**
- **Preparation**
- **Characterization**

Phosphors and LED lighting

Phosphors and solar cells

Summary and Conclusion

PHOSPHORS

Definition

- The word phosphor was invented in the early 17th century and its meaning has since remained unchanged.
- A crystalline stone (Bolognian stone) discovered by Vencitinus Casciarolo (Italian Chemist) was found to emit red light in the dark after exposure to sunlight.
- The stone found was barite ($BaSO_4$)
- Numerous light emitting stones were later discovered in Europe and were named phosphors.
- Phosphor means light-bearer - Combination of Greek words: phos – light and phoros – bearers:
- Phosphor – Chemical material that emits light when exposed to high energy particles like photons, electrons or x-rays.

PHOSPHORS

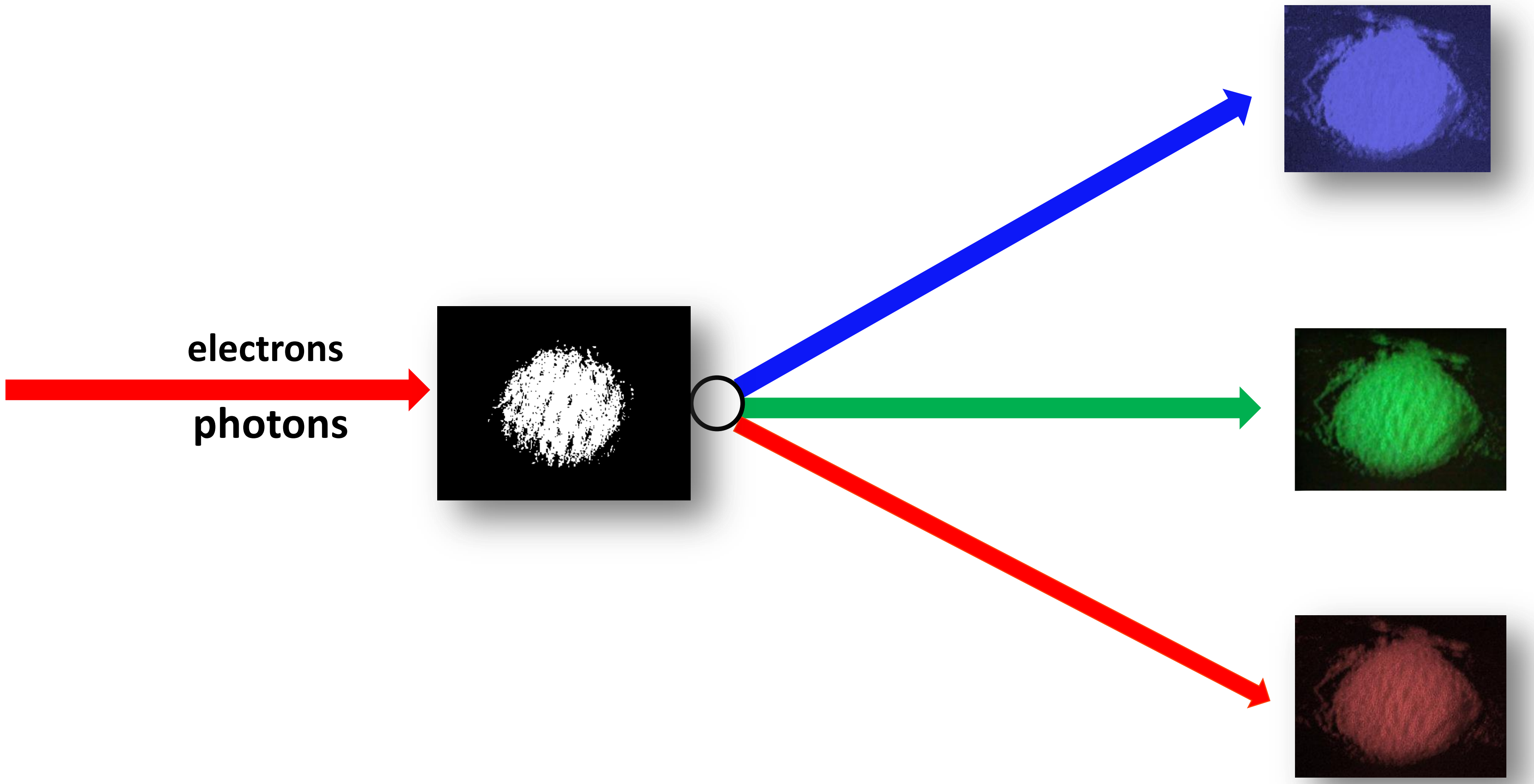
Undoped

- Zinc Oxide – ZnO
- Zinc Sulfide – ZnS
- Cadmium sulfide – CdS
- Lead Sulfide - PbS

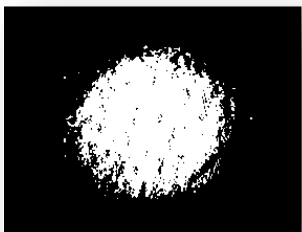
Doped

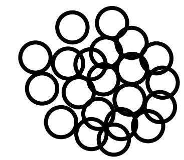
$SiO_2:Eu^{3+}$
$SiO_2:Tb^{3+}$
$SiO_2:Ce^{3+}$
$SiO_2:Tb^{3+},Eu^{3+}$
$SiO_2:Tb^{3+},Ce^{3+}$

PHYSICAL APPEARENCE



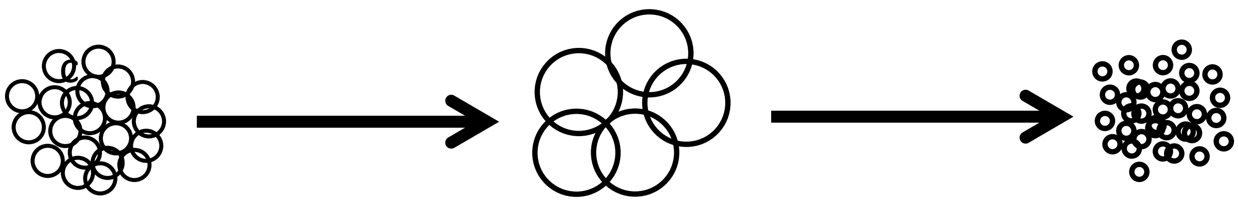
PHYSICAL APPEARENCE





PARTICLE SIZE

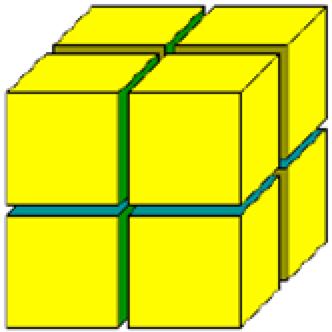
- How big are the particles?
- Can we change the sizes?
- What effects does changing the size have on the fundamental properties?



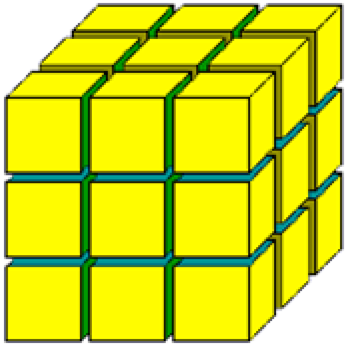
Naturally Small **Bigger** **Smaller**

PARTICLE SIZE

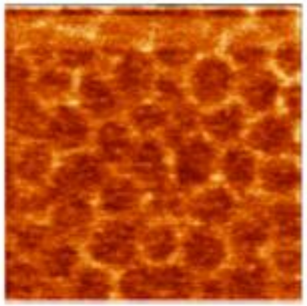
Is gold always gold?



Cutting down a cube of gold

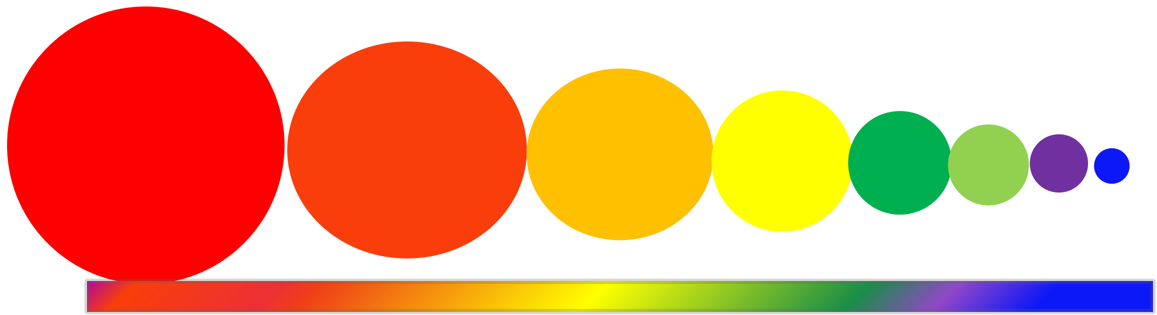


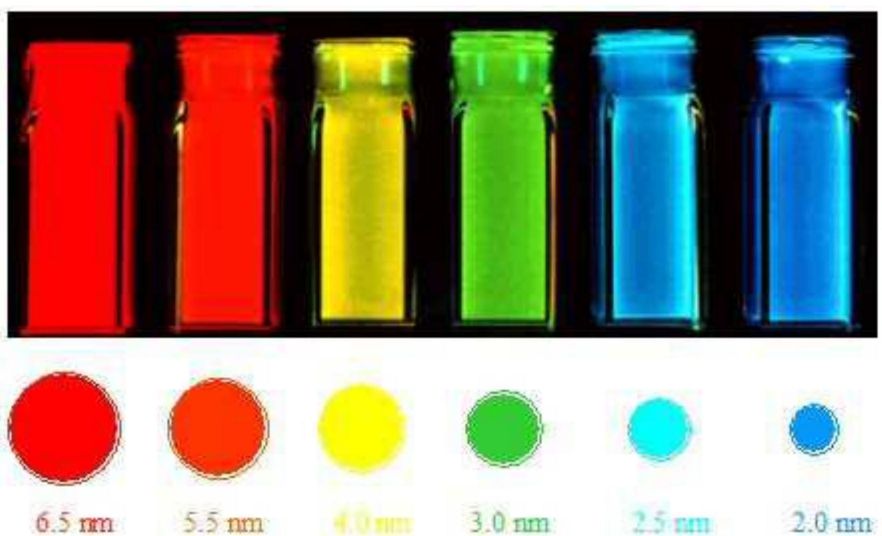
More particles on the surface : Surface to volume ratio increased



Colour changes from gold to red

PARTICLE SIZE





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PARTICLE SIZE

How small is small?

NUMERICAL PREFIXES

BIG

NUMBER	PREFIX
10	deka
100	hecto
1000	kilo
1000000	mega
1000000000	giga

SMALL

NUMBER	PREFIX
0.1 or 10^{-1}	deci
0.01 or 10^{-2}	centi
0.001 or 10^{-3}	milli
0.000001 or 10^{-6}	micro
0.000000001 or 10^{-9}	nano

PARTICLE SIZE

Nano – comes from the Greek word nanos – meaning dwarf
Nano – means extremely small
Nanoparticles – means extremely small particles

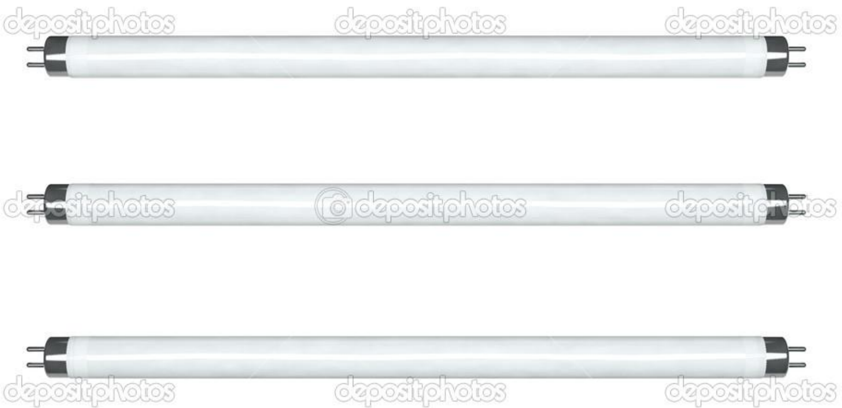
Recall : Properties of materials change when the particle sizes become extremely small

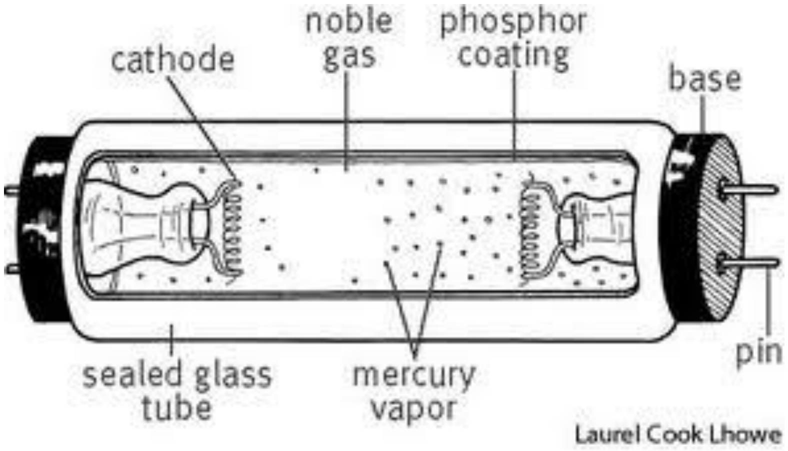
Nano + Science = **Nanoscience** = Science of nanoparticles – The study of properties of materials at the nanoscale.

Nano + Technology = **Nanotechnology** = Application of nanoscience = The science and technology of designing and manufacturing devices using nanoparticles (very small particles).

APPLICATIONS

Fluorescent bulbs - Phosphor transforms ultraviolet light into visible light
Light produced depends on the composition of the phosphor





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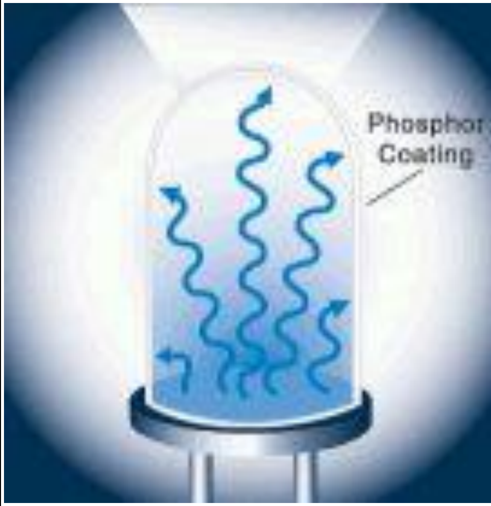
APPLICATIONS

LIGHT EMITTING DIODES (LEDs)
LEDS – Traditionally used as indicators in different devices
Phosphors are used as sources of light in LEDs



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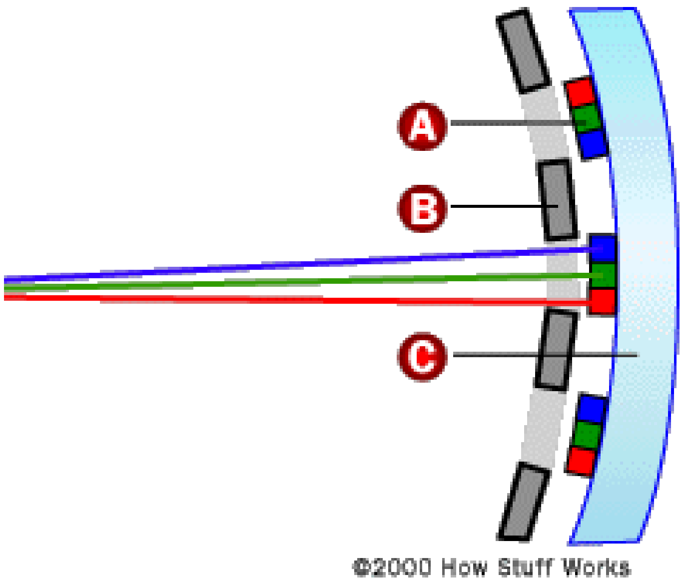
APPLICATIONS

Cathode Ray Tubes – TV and Computer Screens



Extinct – Due to high power consumption, poor picture quality, heavy weight, etc.

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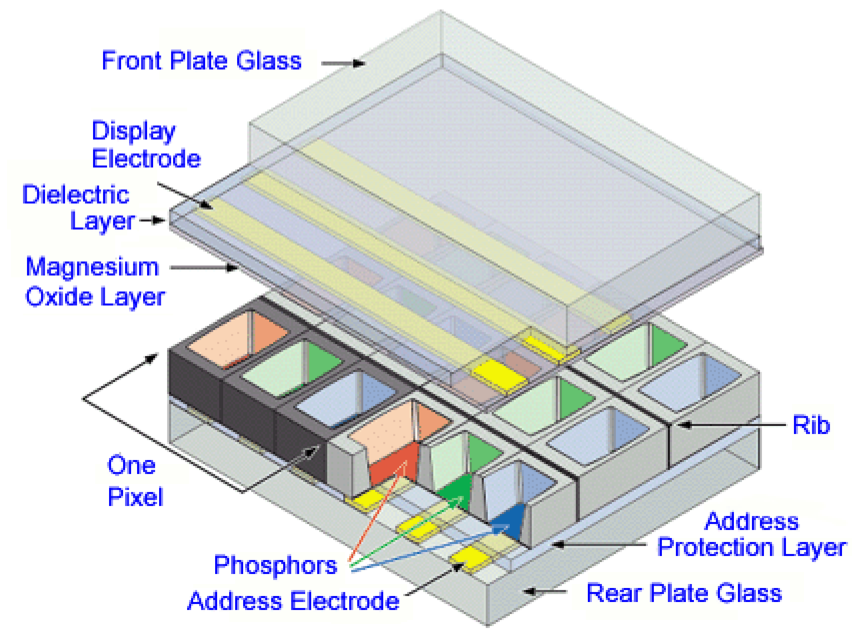
APPLICATIONS

PLASMA TV – Phosphors used as light sources in plasma TVs



cf LED – Heavier, Less bright, uses more power, liberate a lot of heat.

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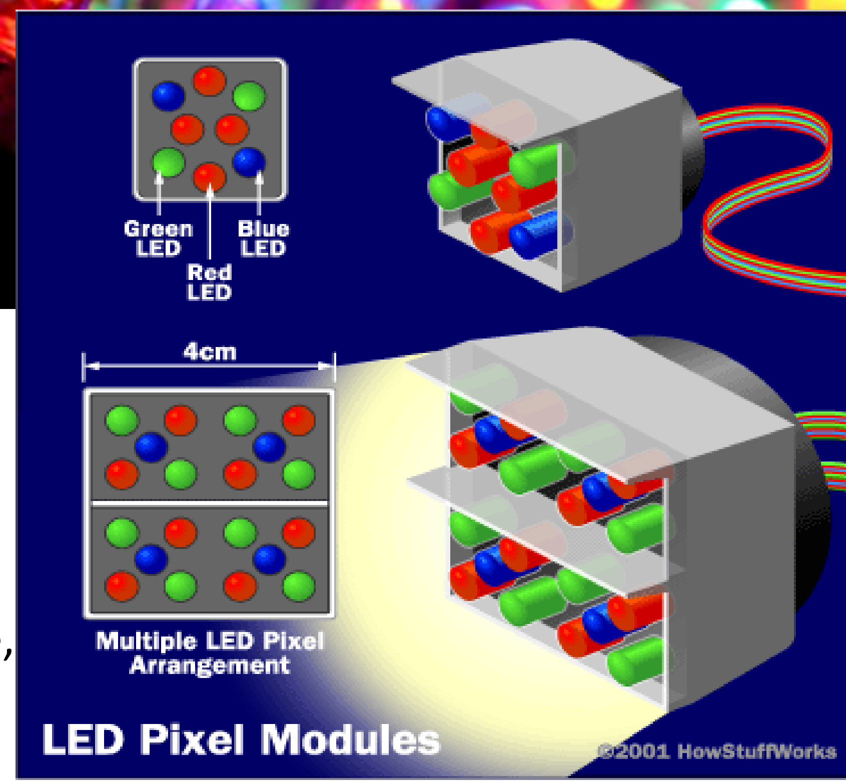
APPLICATIONS

LED TV – Phosphors used in LEDs – LEDs in TV s

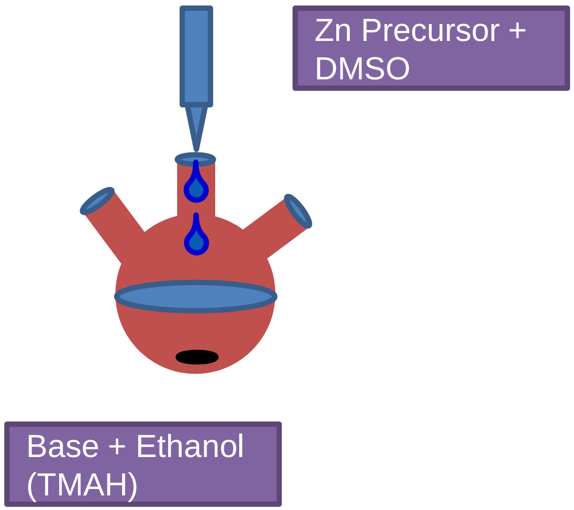


Cf Plasma – Thin, lightweight, very bright, durable,

PREPARATION OF PHOSPHORS

1. **One pot synthesis – hot solutions**

Synthesis schematic



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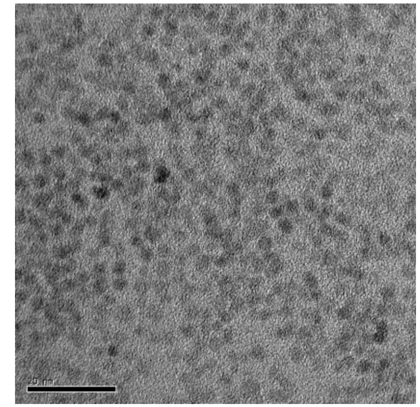
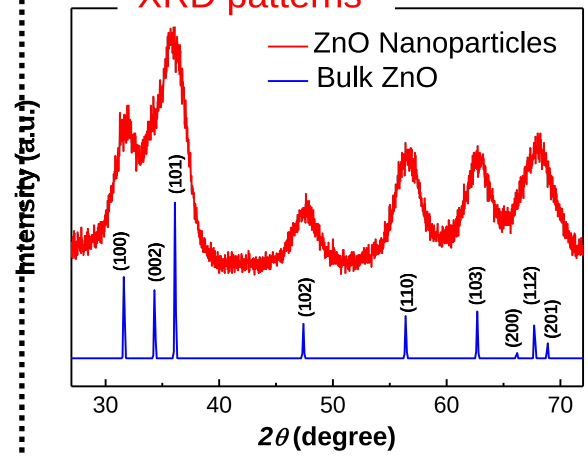
Centrifuging

Crystalline ZnO nanoparticles



Average diameter: 3 nm

XRD patterns



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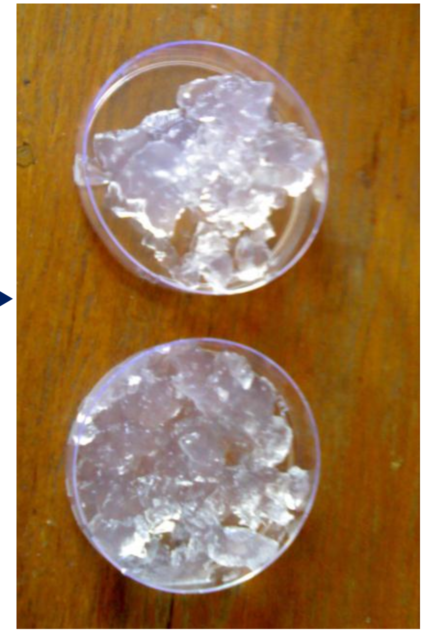
PREPARATION OF PHOSPHORS

2. SOL – GEL METHOD – SiO_2

Precursors

Cooling



Drying

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Product

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PREPARATION OF PHOSPHORS

2. COMBUSTION METHOD

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Mixing of precursors

Preheated furnace (500 – 1000^{o}C

Product

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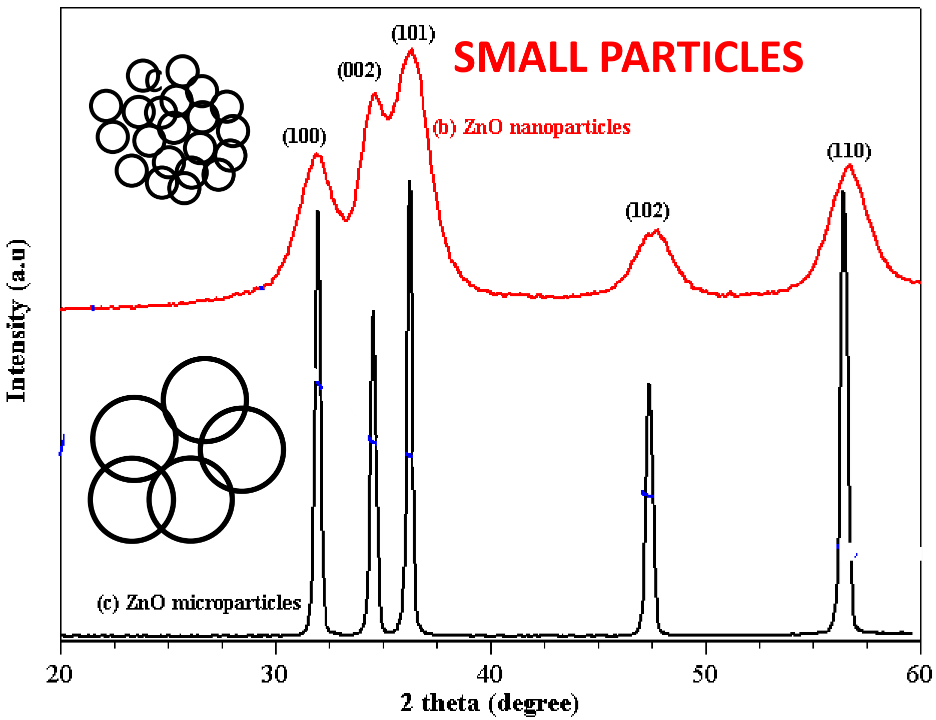
CHARACTERIZATION

STRUCTURE – ZnO nanoparticles



X-ray diffractometer

Bigger particles – Have sufficient units cell , diffraction peaks are produced at precise location of Bragg angle due to coherent scattering, all incoherent scatterings are cancelled out.

Smaller particles – Have insufficient planes, therefore incomplete cancelling of incoherent scattering results in peak broadening.

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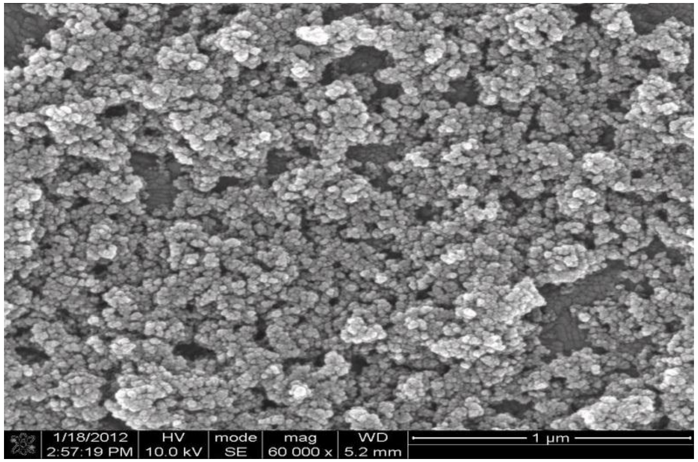
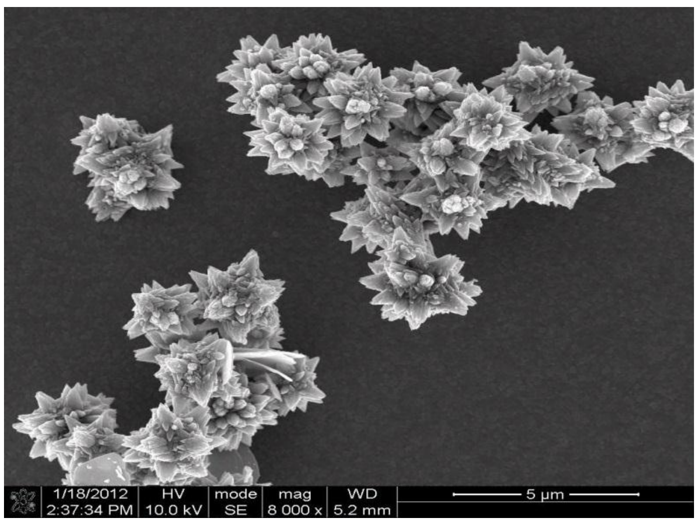
CHARACTERIZATION

Shape and Size or Morphology – ZnO nanoparticles



Spheres

Scanning Electron Microscope



Flowers

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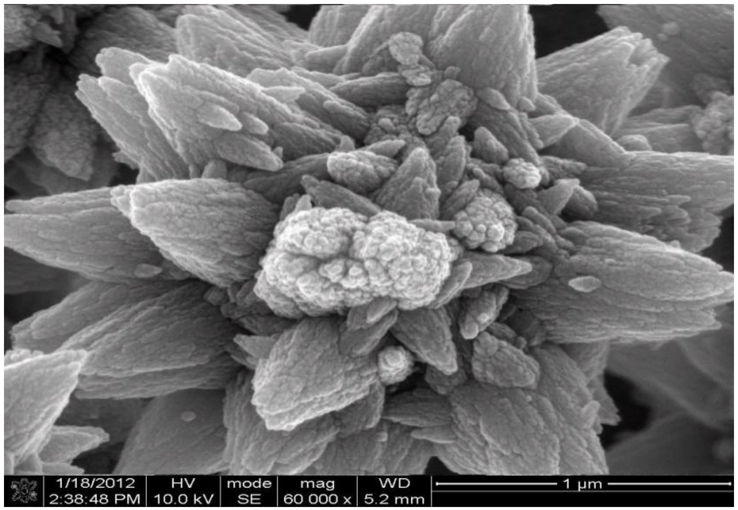
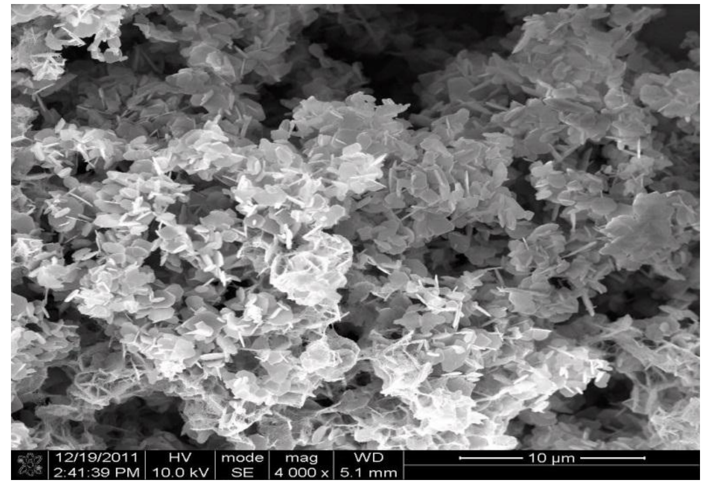
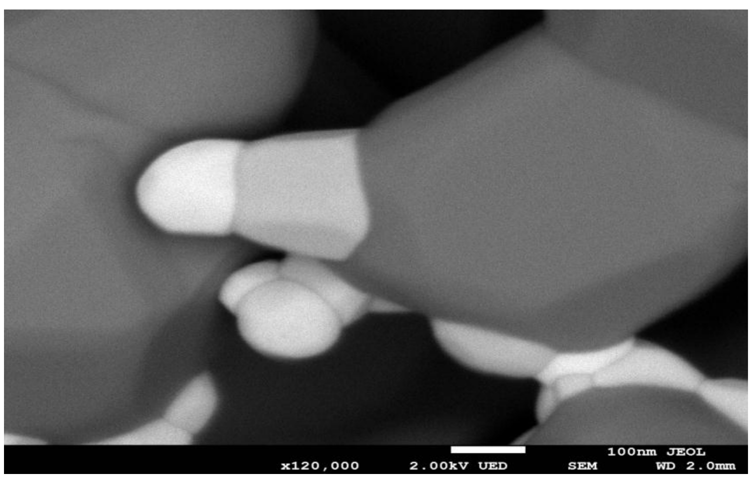
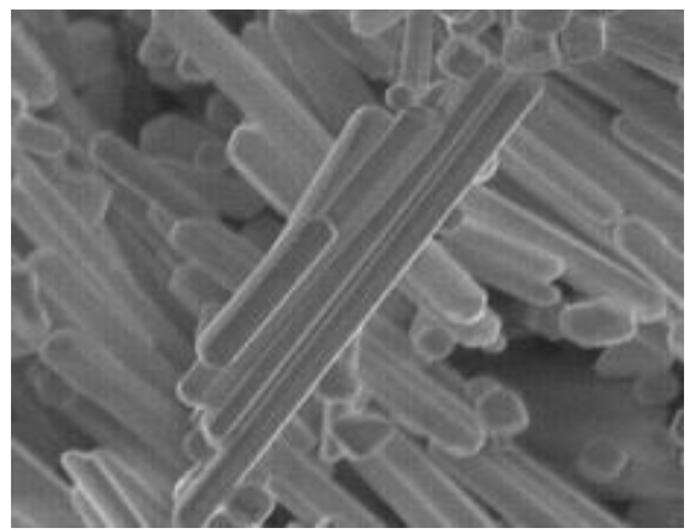
CHARACTERIZATION

Understanding what is happening at the bottom……









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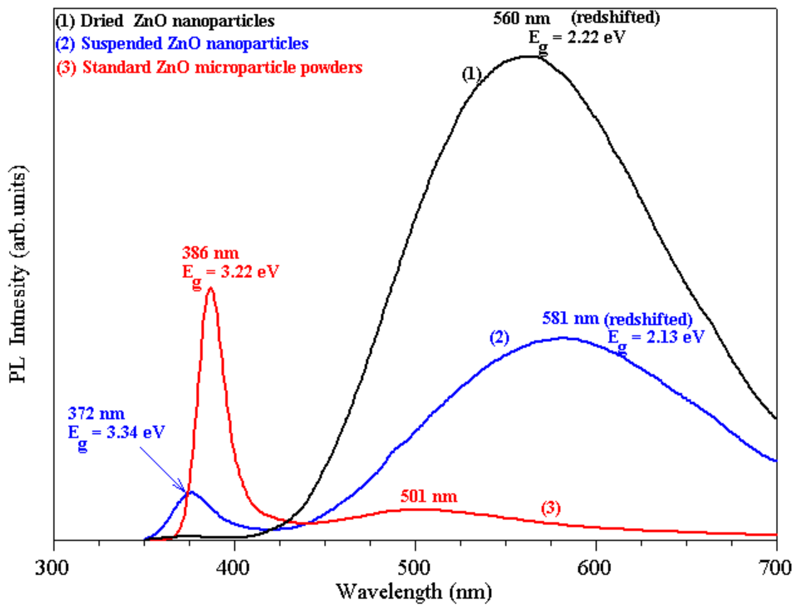
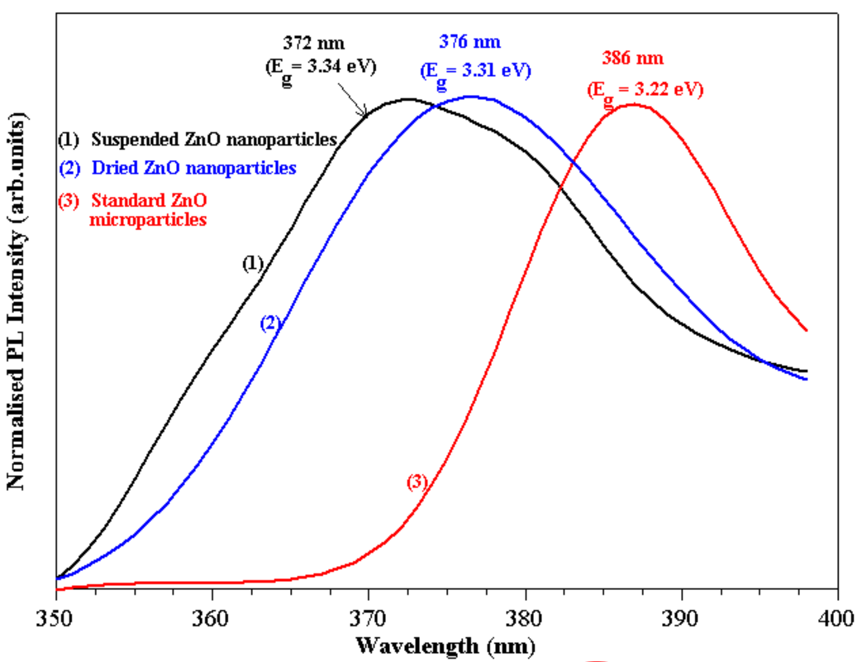
CHARACTERIZATION

LUMINESCENT PROPERTIES - ZnO

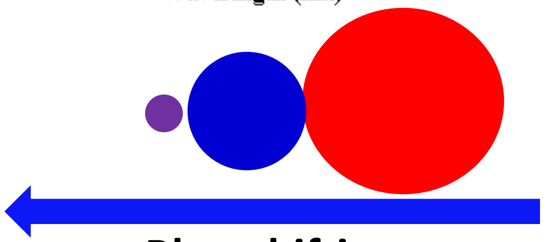
UV - Visible emission



SH**IFTING**



Nanoparticles – Green light – more defects
Big particles – UV light – less defects
Defects created deliberately to suppress UV light



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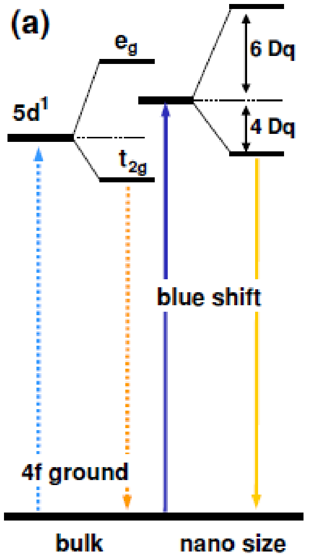
SHIFTING: BLUE/RED SHIFTING

Quantum confinement :

Quantum confinement –confinement of e/h in exciton Bohr radius.

When particle sizes become smaller, the height and energy difference between energy levels increases:

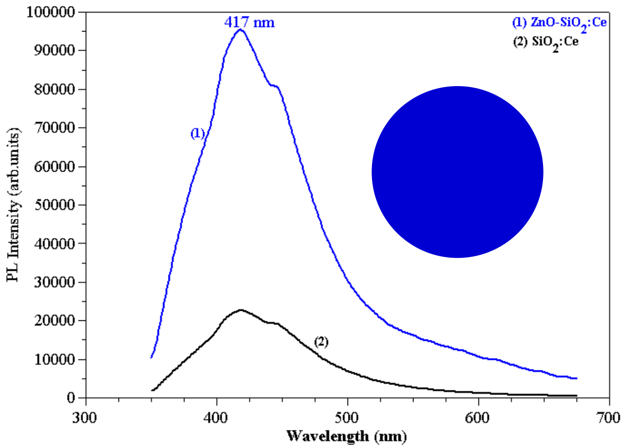
Effects:
Shifting of wavelengths, increases in energy level spacings, bandgap, peak broadening

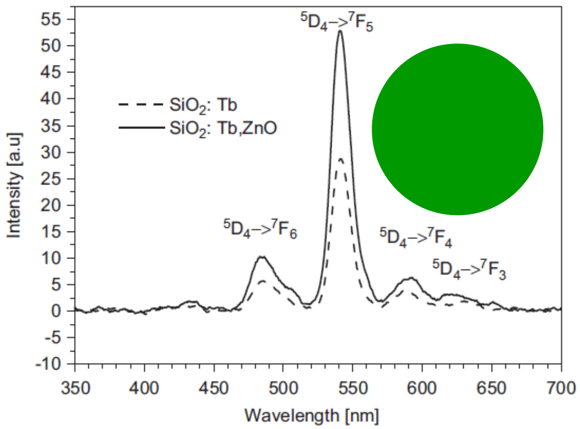


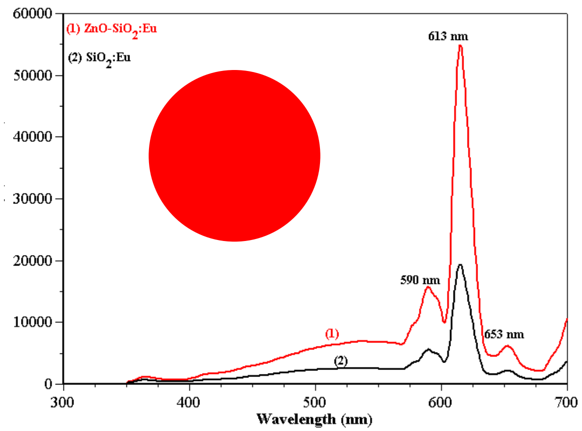
APPLICATIONS: ZnO nanoparticles

What did I do with ZnO nanoparticles?

Luminescent Properties







$SiO_2:Ce^{3+}$
ZnO- $SiO_2:Ce^{3+}$

$SiO_2:Tb^{3+}$
ZnO-$SiO_2:Tb^{3+}$

$SiO_2:Eu^{3+}$
ZnO-$SiO_2:Eu^{3+}$

ZnO nanoparticles increased blue PL intensity from Ce^{3+} by about a factor of 4

ZnO – harvests activation **energy and transfer** it non-radiatively to rare-earth dopant ions

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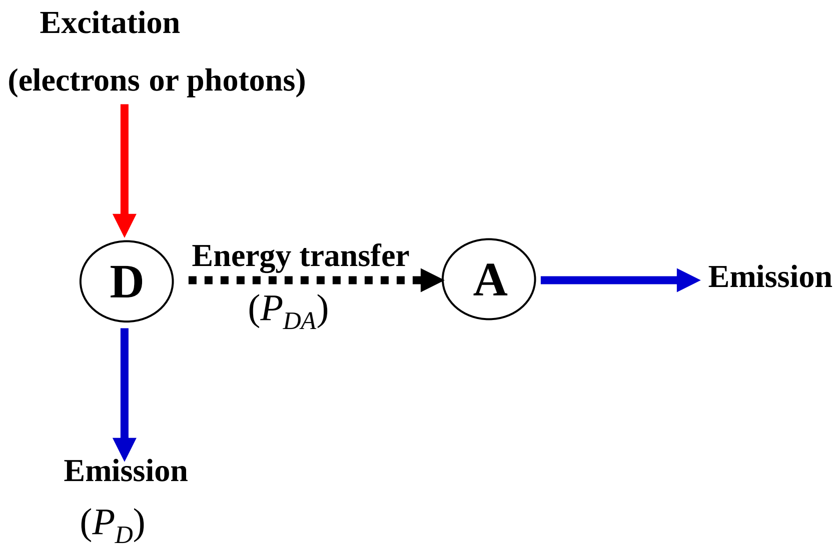
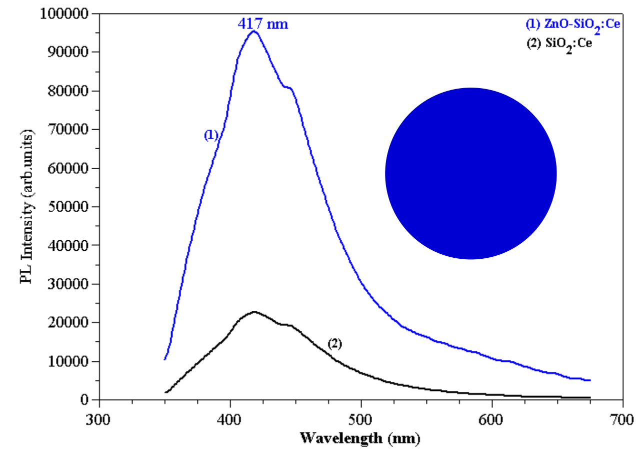
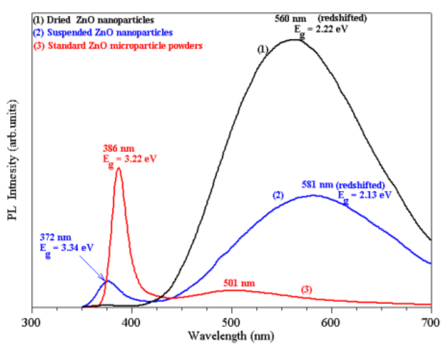
APPLICATIONS: ZnO nanoparticles

Energy Transfer in ZnO- $SiO_2:Ce^{3+}$







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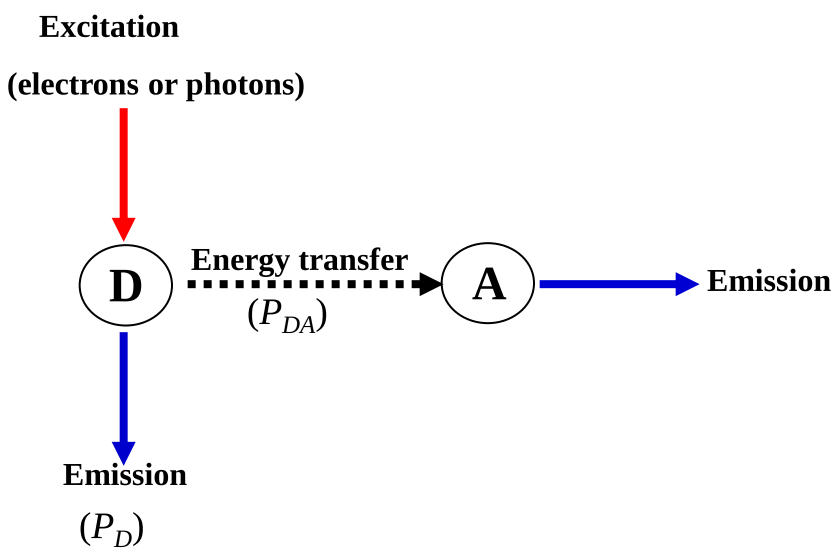
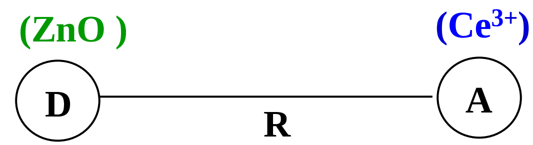
APPLICATIONS: ZnO nanoparticles

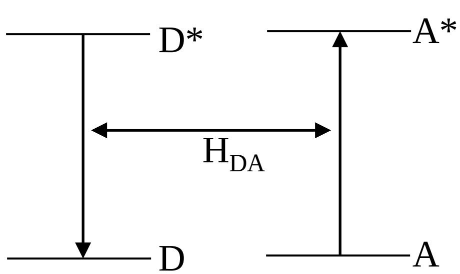




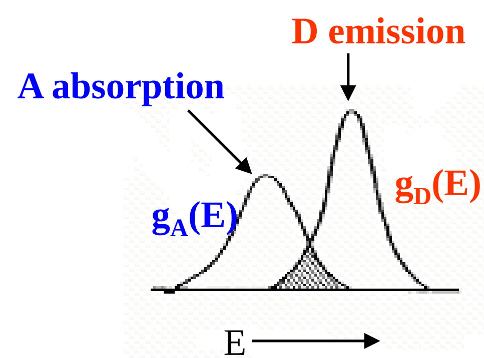
R_c = critical transfer distance for which energy transfer can occur

R < Rc = Energy transfer from D to A is faster

R > R_c = Radiative emission from D is faster



Equal energy difference



Interaction: Wavefunction/Spectral overlap

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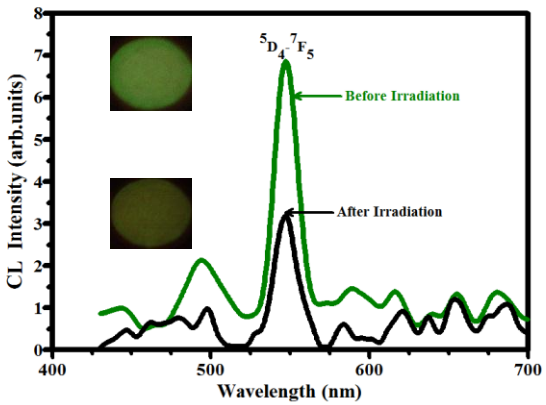
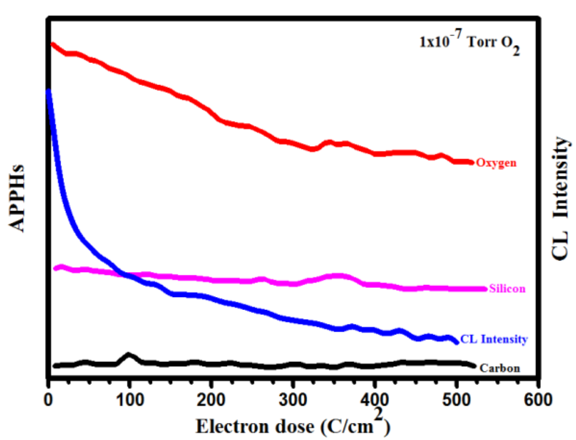
DURABILITY AND STABILITY

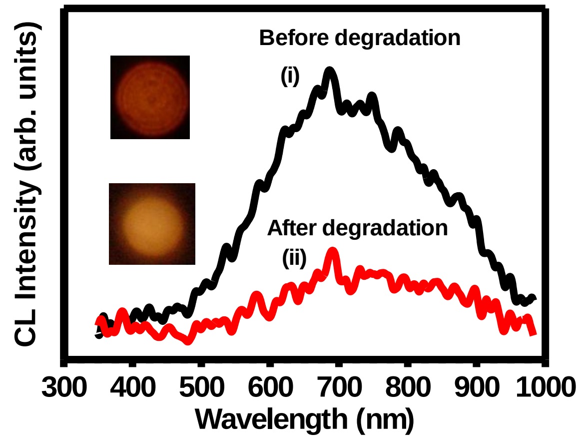
LUMINESCENCE DEGRADATION

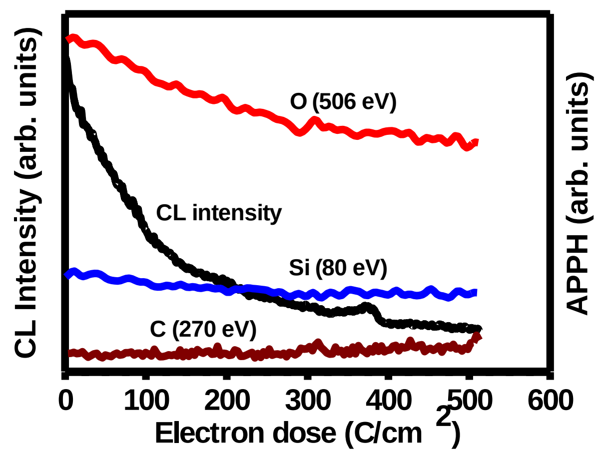
$SiO_2:Ce^{3+},Tb^{3+}$ - affected



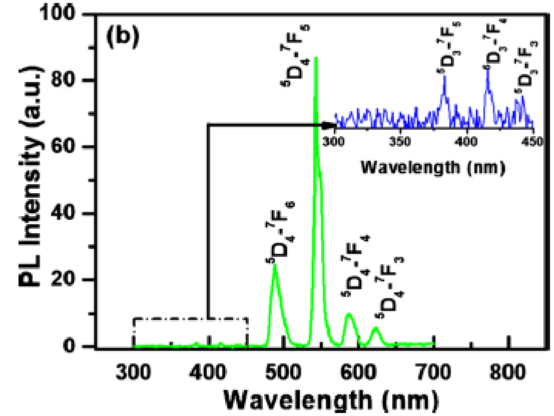


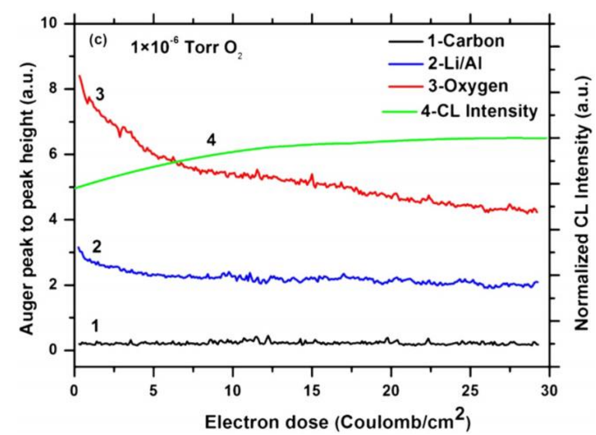
SiO_2:PbS - affected





$LiAl_5O_8:Tb^{3+}$- not affected





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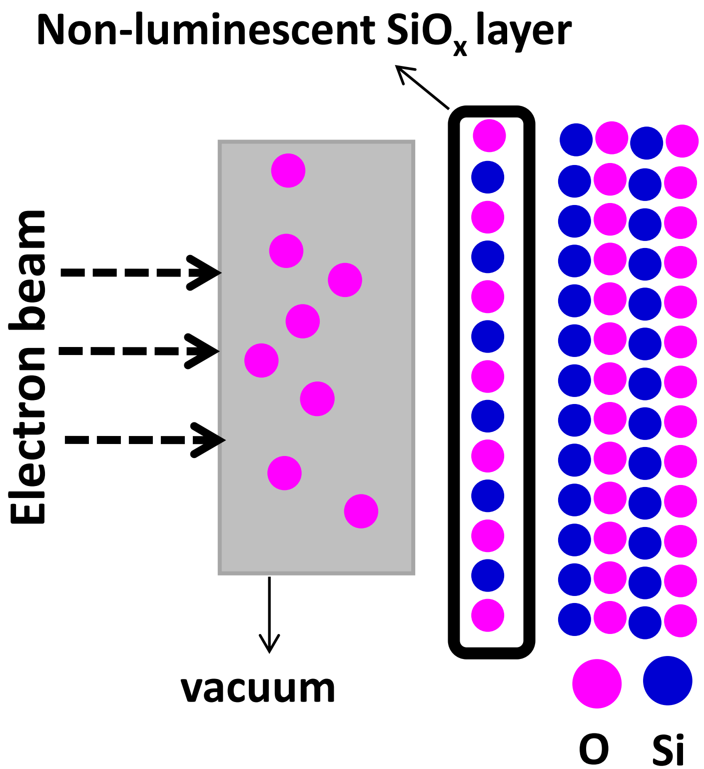
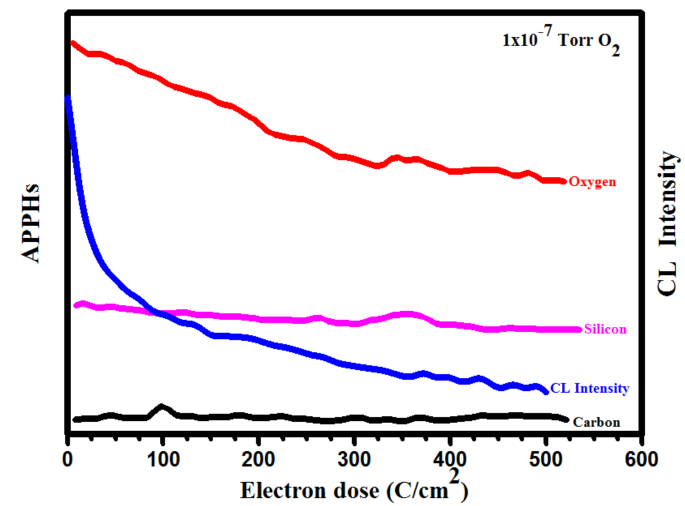
DURABILITY AND STABILITY

MECHANISMS OF LUMINESCENCE DEGRADATION

NANOPHOSPHORS – SiO_2



SURFACE CHEMICAL REACTION

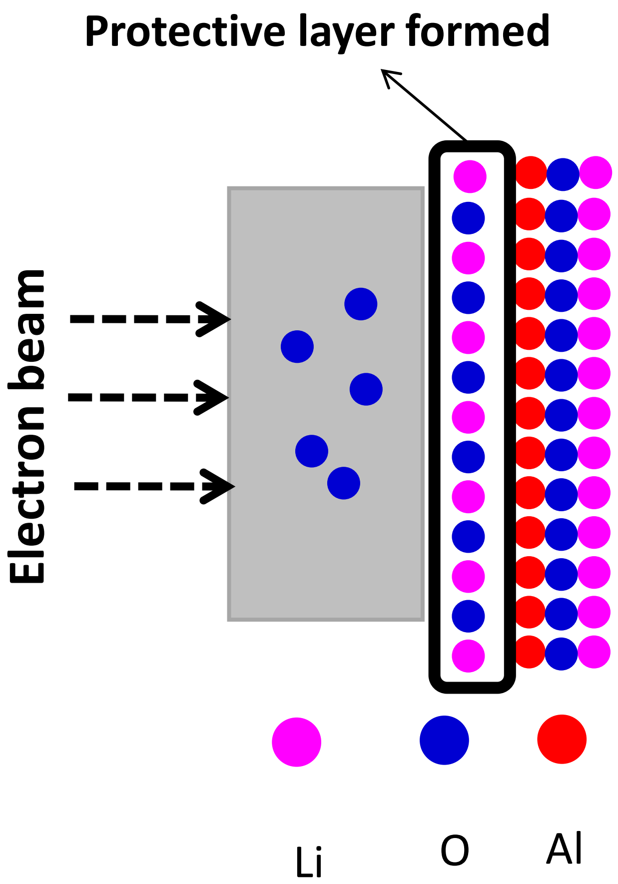


Knotek-Feiblemann ESD mechanism

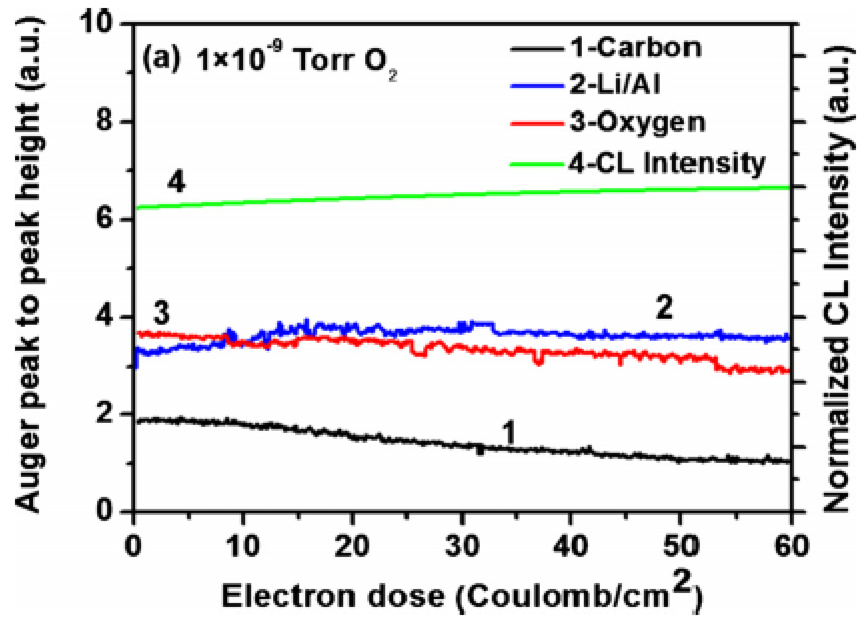
Breaking of Si – O,
subsequent desorption of O from the surface
Leaving behind the Si rich surface
Oxygen deficient SiO_x will be formed

DURABILITY AND STABILITY

MECHANISMS OF LUMINESCENCE DEGRADATION



SURFACE CHEMICAL REACTION



ESSCR MECHANISM

$$Al + O_2 \longrightarrow Al_2O_3$$

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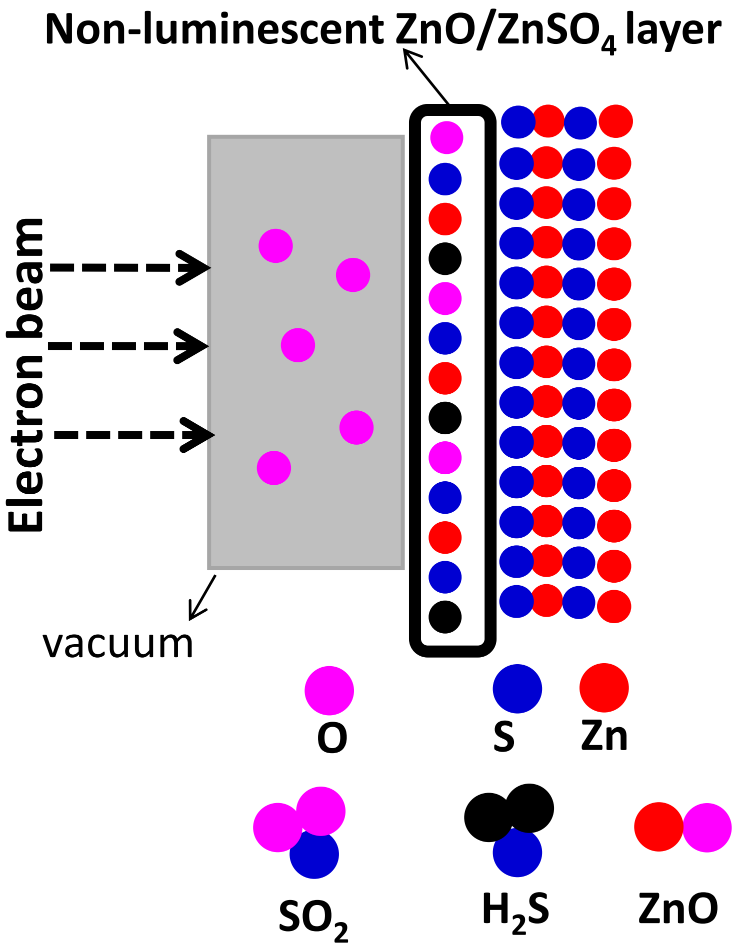
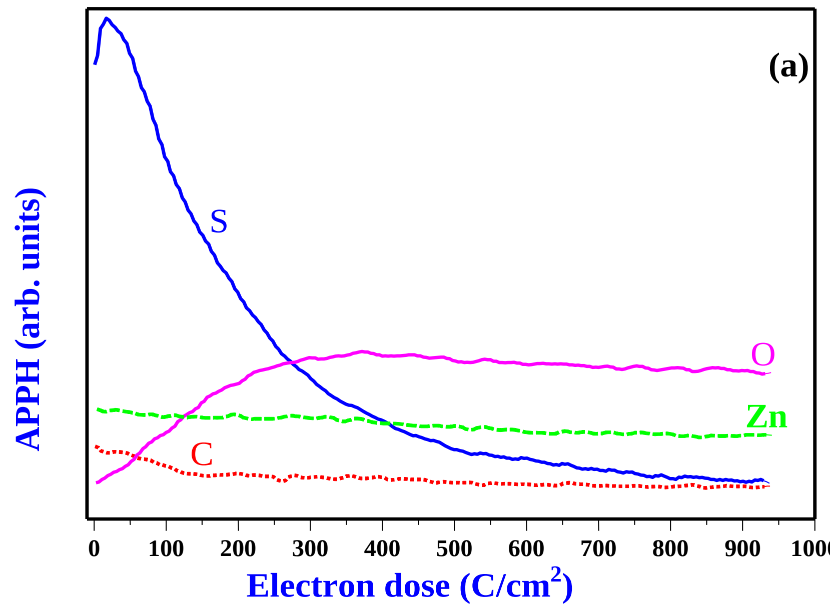
MECHANISMS OF LUMINESCENCE DEGRADATION

ZnS – traditional sulfide phosphor



SURFACE CHEMICAL REACTION



ESSCR MECHANISM – Swart/Holloway, et al.

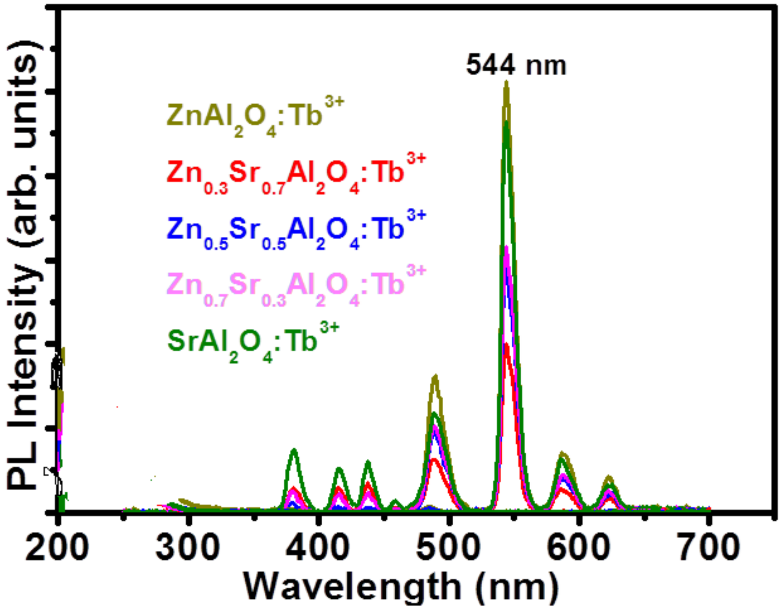
$S + O_2 \longrightarrow SO_2$

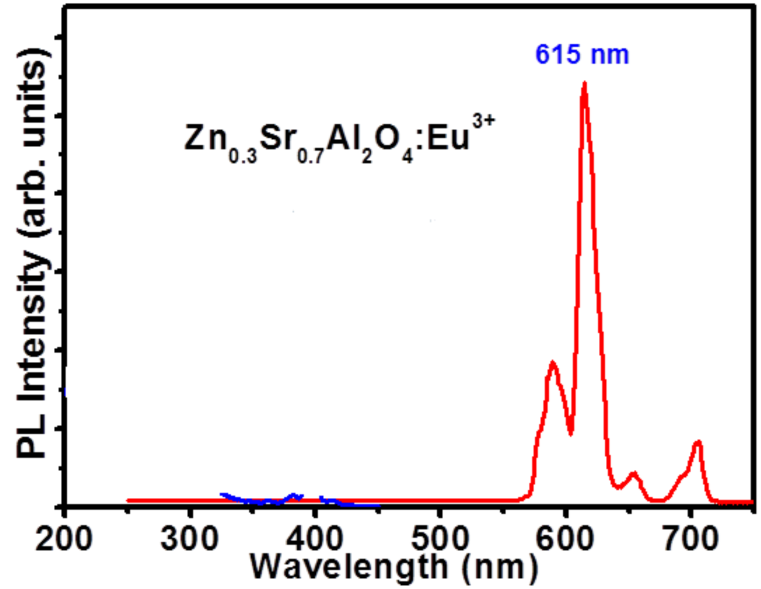
$S + H_2 \longrightarrow H_2S$

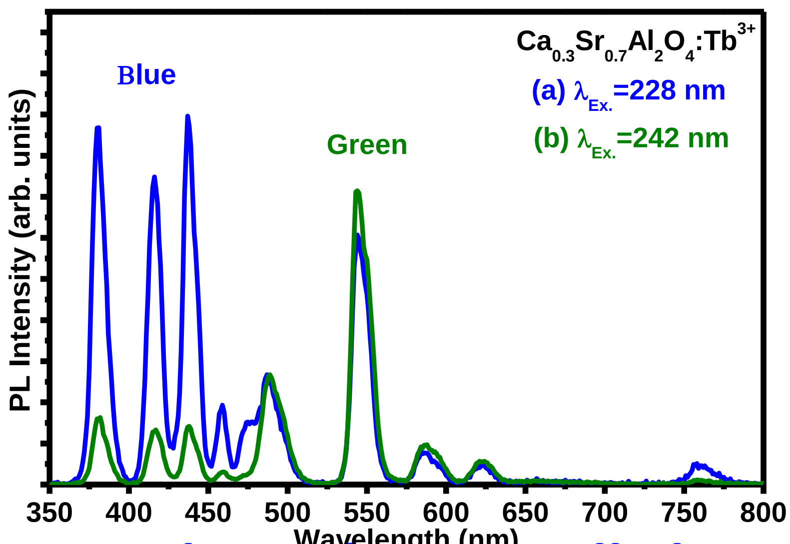
$Zn + O \longrightarrow ZnO$

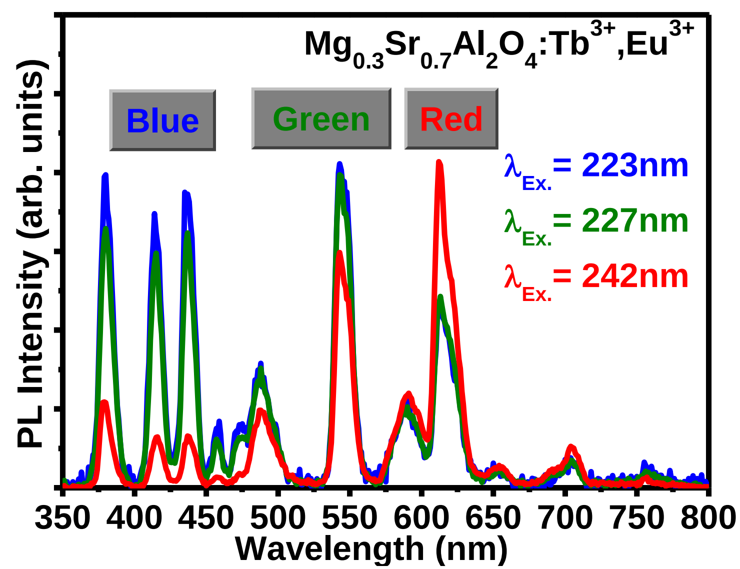
$Zn + S + O_2 \longrightarrow ZnSO_4$

WHITE PHOSPHORS FOR WHITE LED









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WHITE PHOSPHORS FOR WHITE LED

1. Mix blue +green + red colours from 3 LEDs = white LED : **EXPENSIVE**

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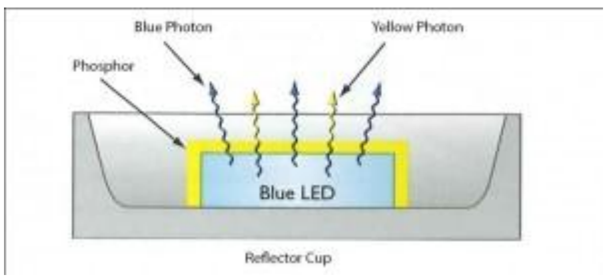
2. Mix blue LED with yellow light from phosphor coating (YAG:Ce^{3+}) : **EXPENSIVE**



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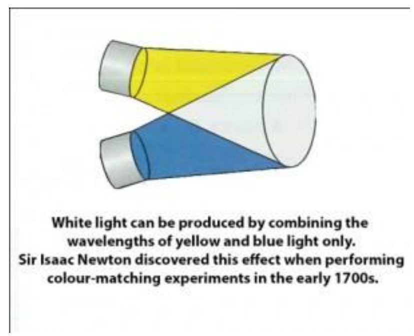


=

3. Single phosphor in a single LED =

COST- EFFECTIVE

FLUORESCENT VERSUS LED LIGHT BULBS

FLUORESCENT	LED
Short life span	Last longer than Fluorescent (10 times)
Uses mercury – emit UV radiation	No mercury/UV – Environment friendly
Gets hot and heat up a room	Cool – do not cause heat build up
Uses more energy - electricity	Less energy – 1/3 of fluorescent
Light spreads all out	Light is directional
Burn out faster (filament), with frequency of use	Durable – can be turned on and off as many times without affecting its life span.
Less efficient	30% more efficient.

PHOSPHORS AND RENEWABLE ENERGY – SOLAR ENERGY

NUCLEAR + COAL ENERGY

More 90% of electricity in South Africa comes from coal-fired power plants.

DISADVANTAGES :
Exhaustible, Global warming, Not friendly to the environment:nuclear waste / contaminate air , Expensive for ordinary citizens, Illegal connections (Izinyoka)

SOLUTION : Solar energy

ADVANTAGES

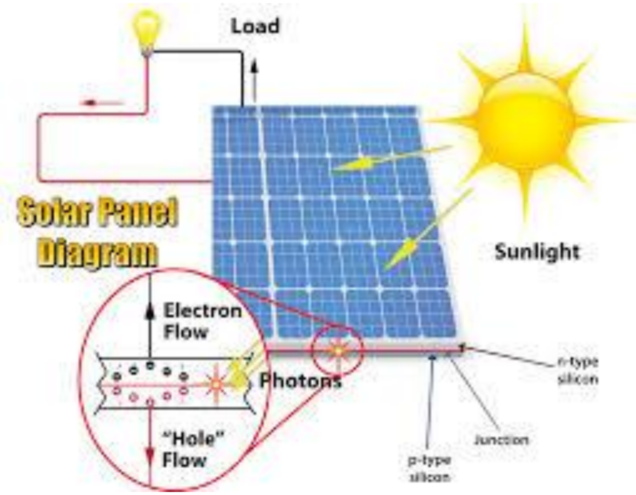
1. Inexhaustible, Readily available, Clean

Great Things from Small Things

HARVESTING SOLAR ENERGY

SOLAR CELL TECHNOLOGY

1. **Silicon solar cells**
2. Thin film solar cells
3. **Organic solar cells**



PHOSPHORS AND RENEWABLE ENERGY – SOLAR ENERGY

Why can't all houses in rural areas be electrified using solar energy?

1. **Solar Panels are expensive – though the price has gone down by almost 100% since 1977**
2. **Low efficiency (20%)– Not able to operate all appliances**
3. **Demand is low - Few companies investing in the technology – no competition.**

Great Things from Small Things

PHOSPHORS AND RENEWABLE ENERGY – SOLAR ENERGY

WHY LOW EFFICIENCY ?

PHOTON ABSORPTION

- Silicon solar cells only absorb photons from some parts of the visible light spectrum
- UV photons are not absorbed
- IR photons are also not absorbed

REFLECTION

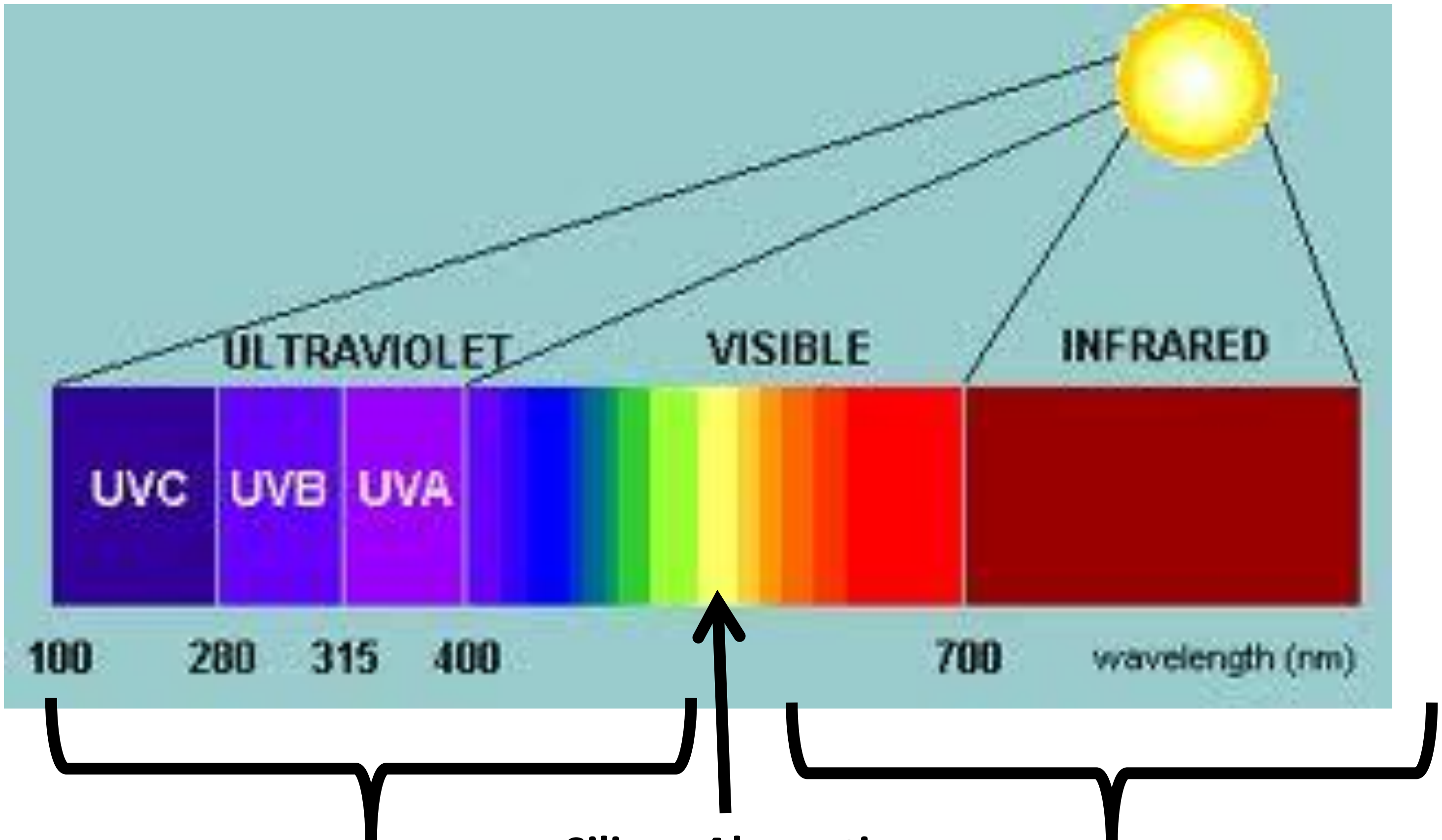
Some photons are reflected at the surface

RECOMBINATION

Some charge carriers (electron and holes) recombine instead of being collected by the electric field.

PHOSPHORS AND RENEWABLE ENERGY – SOLAR ENERGY

ABSORBED VERSUS UNABSORBED PHOTONS



Silicon Absorption

UV-Vis photons - wasted

Vis-IR photons - wasted

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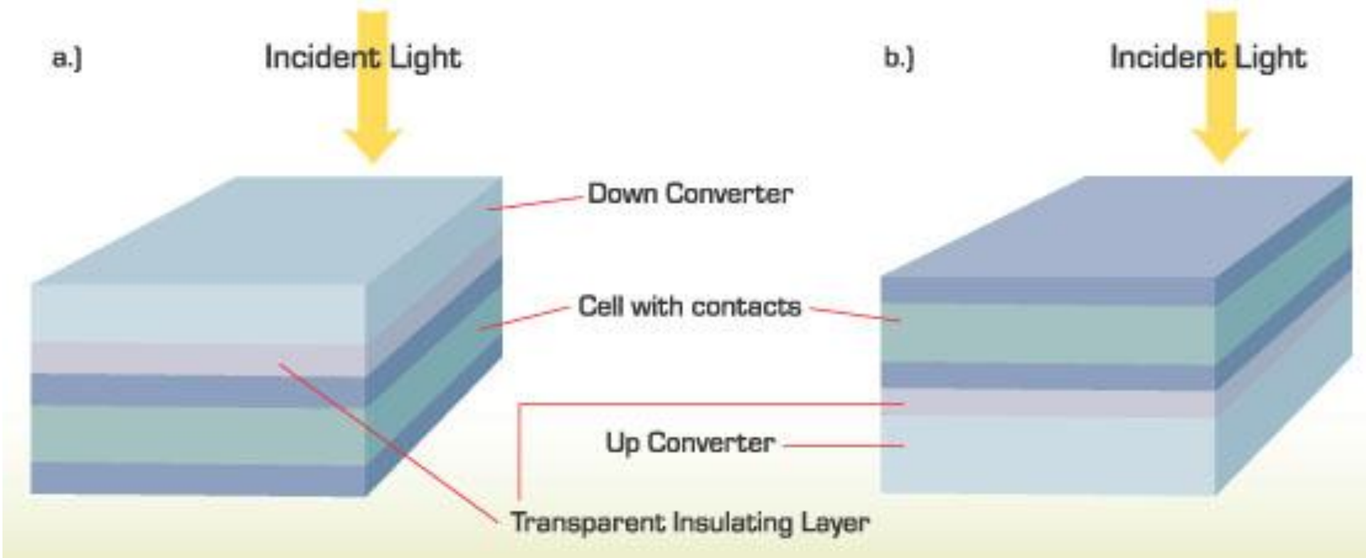
PHOSPHORS AND RENEWABLE ENERGY – SOLAR ENERGY

HOW TO IMPROVE PHOTON ABSORPTION IN Si SOLAR CELLS ?

- **DC – Shift the sunlight photons from UV to visible region**
- **UC – Shift the sunlight photons from IR to visible region**



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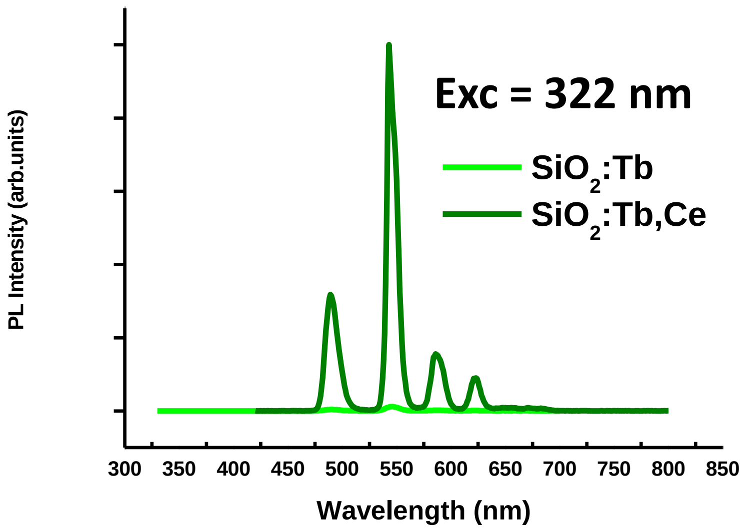
PHOSPHORS AND RENEWABLE ENERGY – SOLAR ENERGY

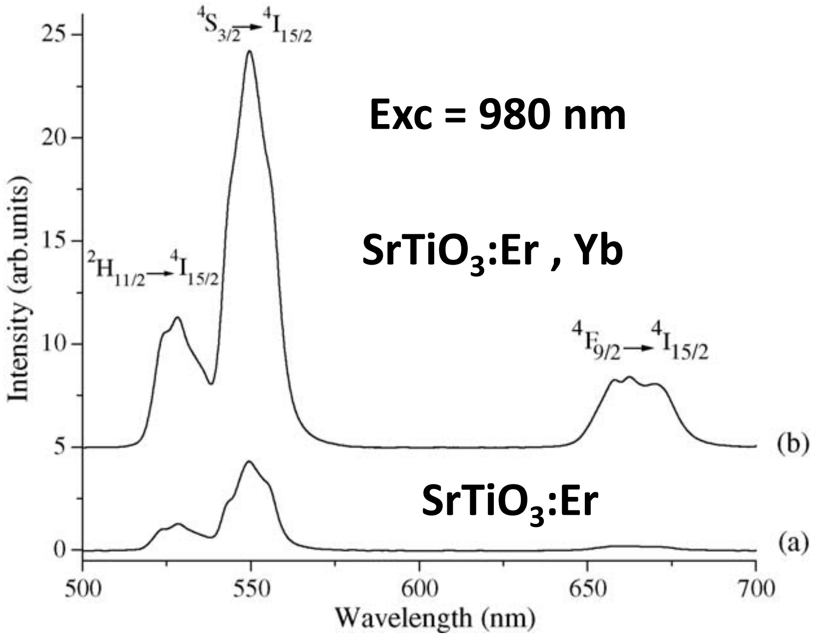
MAKING MORE PHOTONS AVAILABLE IN THE VISIBLE REGION

UV DOWN CONVERSION



Ce absorbs UV photons at 322 nm and transfer them to Tb

IR UP CONVERSION

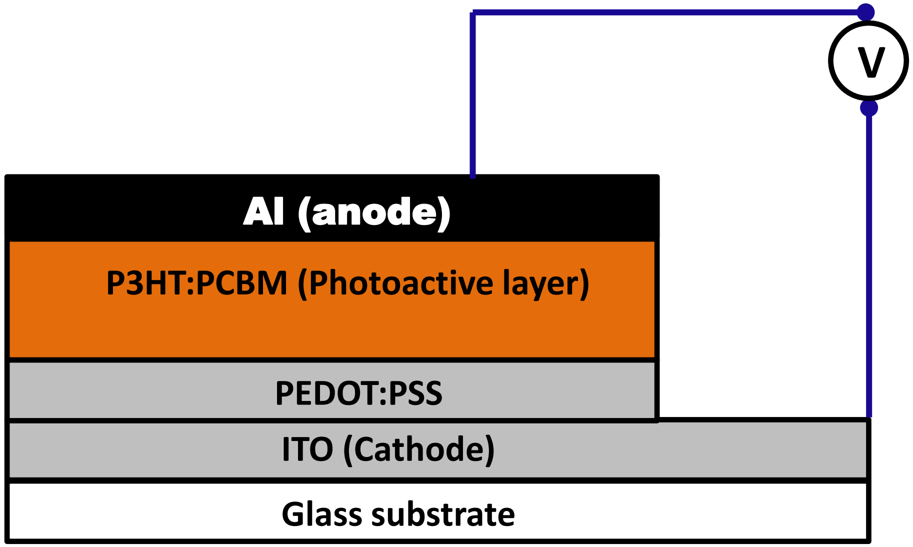


Yb absorbs IR photons at 980 nm and transfer them to Er

Great Things from Small Things

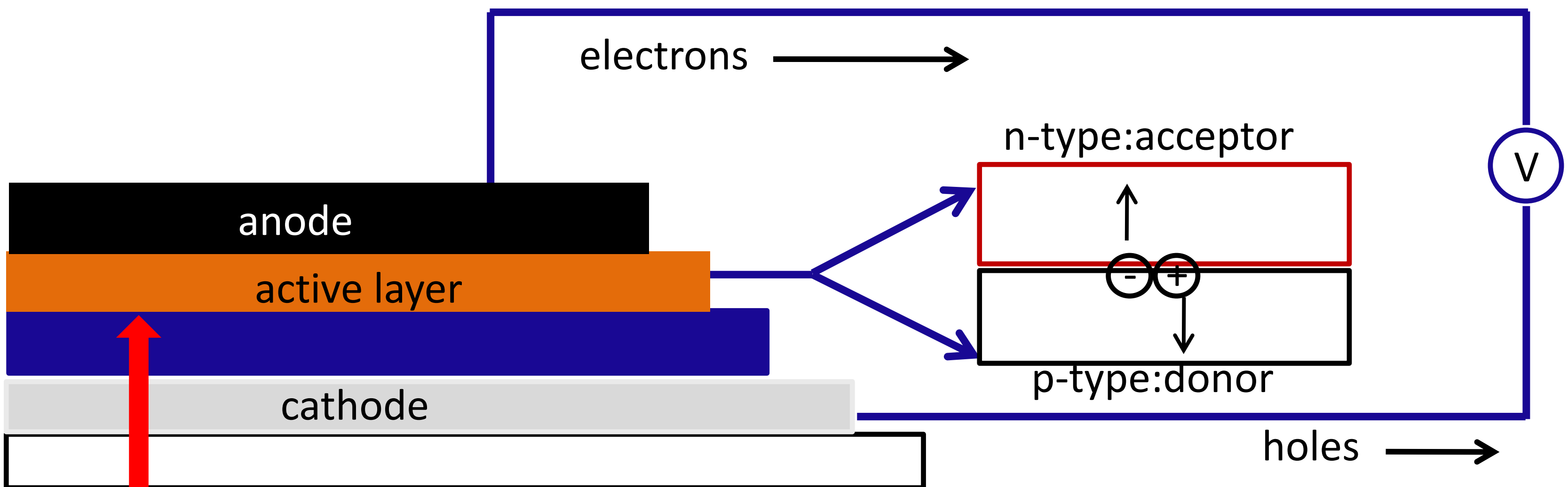
Guo et al. J. Alloy Compds, 415 (2006) 280 - 283

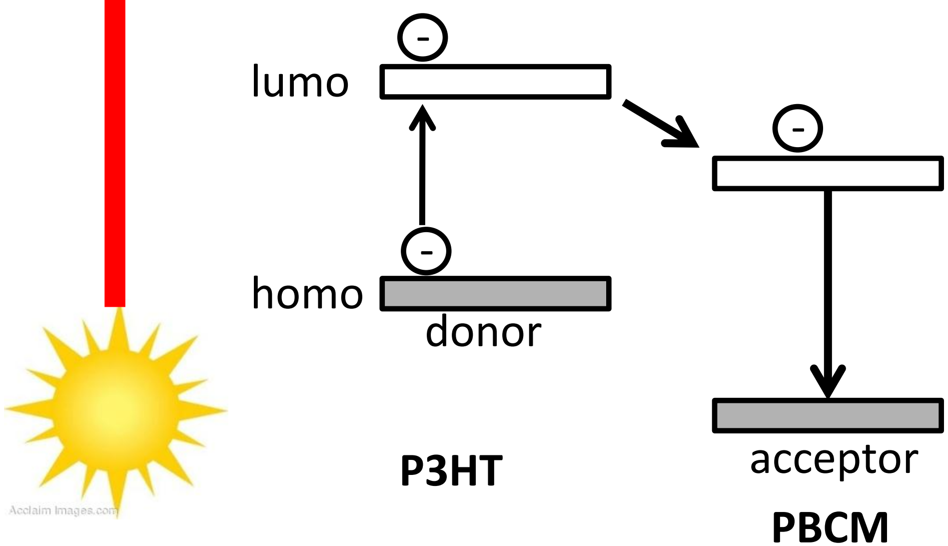
2. OGRANIC SOLAR CELLS



PHOSPHORS AND RENEWABLE ENERGY – SOLAR ENERGY

2. OGRANIC SOLAR CELL: HOW DOES IT WORK?



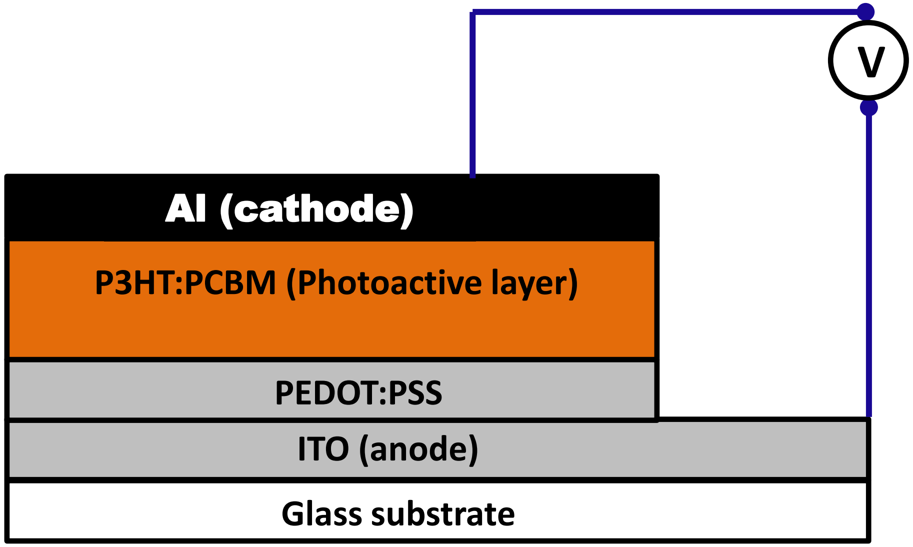


- light absorption
- creation of excitons
- exciton dissociation
- charge transport
- charge collection

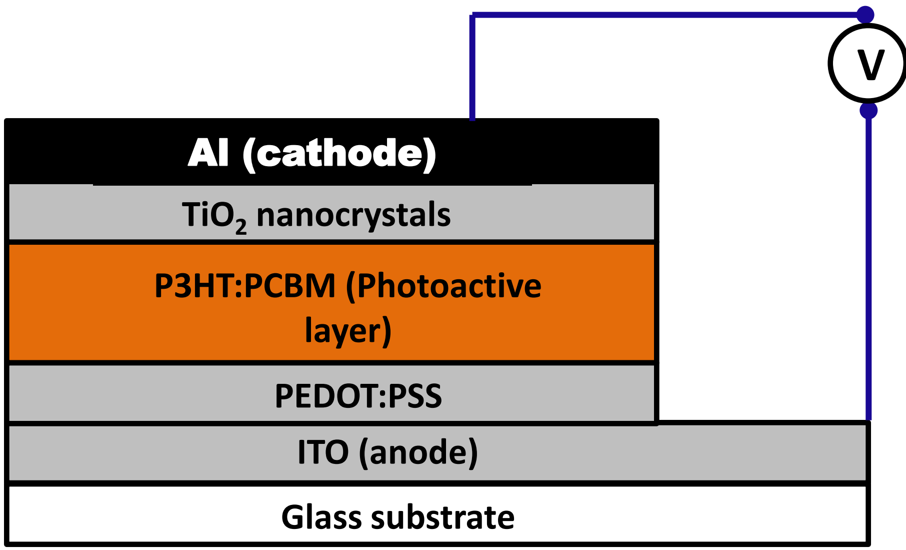
2. OGRANIC SOLAR CELLS

CHALLENGES

- Low power conversion efficiency (less than 10% cf 30% PV Si)
- Operation and storage in air – degradation of the active layer by oxygen and water
- Al atoms may diffuse into the active layer and act as recombination centres
- Holes may diffuse to the cathode -unwanted process
- Electron may diffuse to the anode – unwanted process



PHOSPHORS AND RENEWABLE ENERGY – SOLAR ENERGY



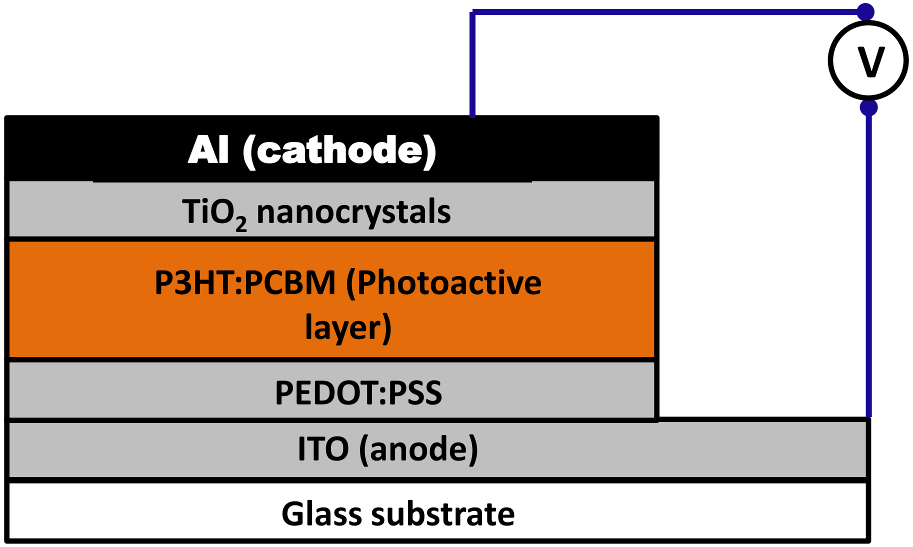
Concepts to improve PCE:

- Insert a metal oxide layer between the anode and the active layer to block holes, transport electrons
- TiO_2 nanocrystals – reduced degradation and increased the lifetimes, loss of PCE after 6 days
- Concern : Low electron mobility

(**Lee et al. Adv Mater. 19 2007 2445**)

PHOSPHORS AND RENEWABLE ENERGY – SOLAR ENERGY

ORGANIC SOLAR CELLS



Concept for improvement:

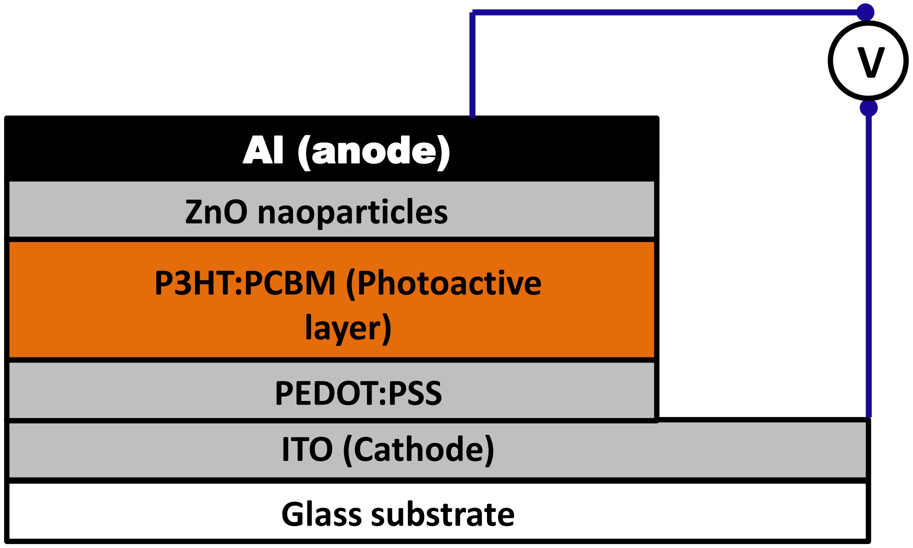
ZnO nanoparticles:

• Has higher electron mobility than TiO_2 **(6.6×10^{-2} $V^{-1}s^{-1}$ v/s 1.7×10^{-4} $V^{-1}s^{-1}$)**
• Strongly absorbs photons in the near UV which may cause photo-oxidation and degradation
• ZnO - reduced degradation and increased the lifetimes, loss of PCE after 168 days of exposure to air (**Qian et al. J. Mater. Chem. 21 (2011) 3814-3817**)

Great Things from Small Things

ORGANIC SOLAR CELLS: OUR CONCEPTS FOR IMPROVEMENT

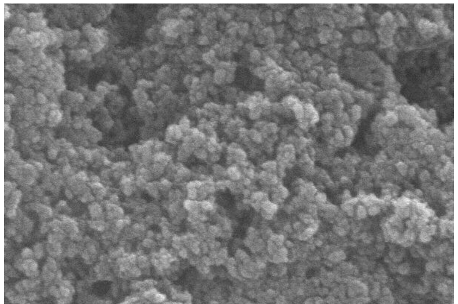
- Particle morphology (nanoparticles, nanoflowers, nanorods, nanoflakes)
- Altered device geometry – normal and inverted structure
- Thermal treatment: Annealing procedure, i.e. anneal before or after depositing top electrode

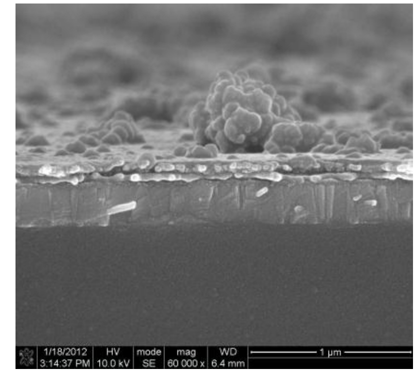


PHOSPHORS AND RENEWABLE ENERGY – SOLAR ENERGY

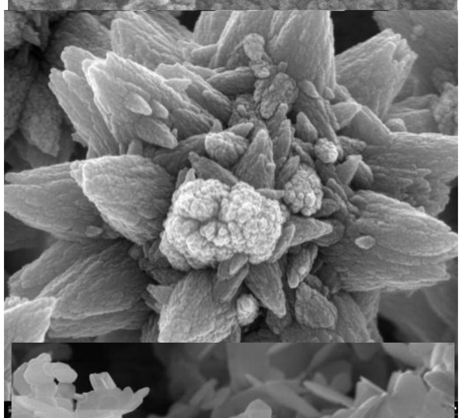
ZnO nanoparticles

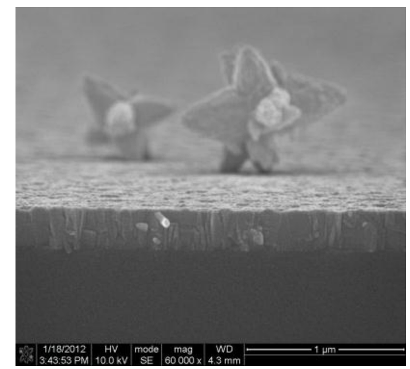
Organic Solar Cell devices



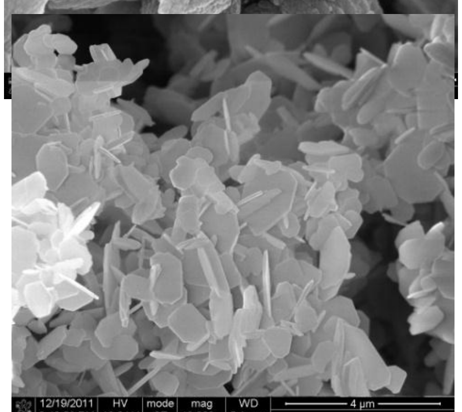


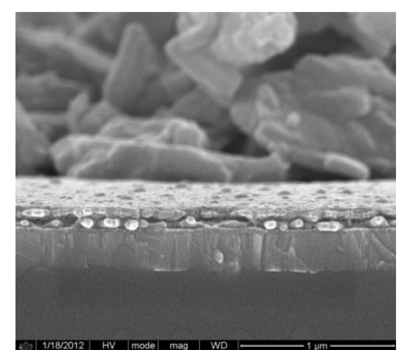
nanospheres





nanoflowers

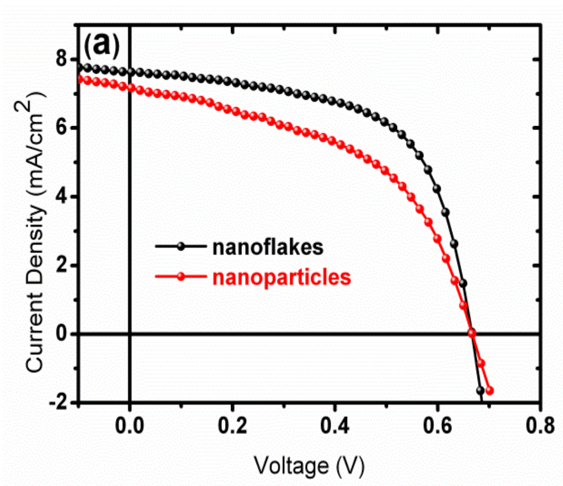


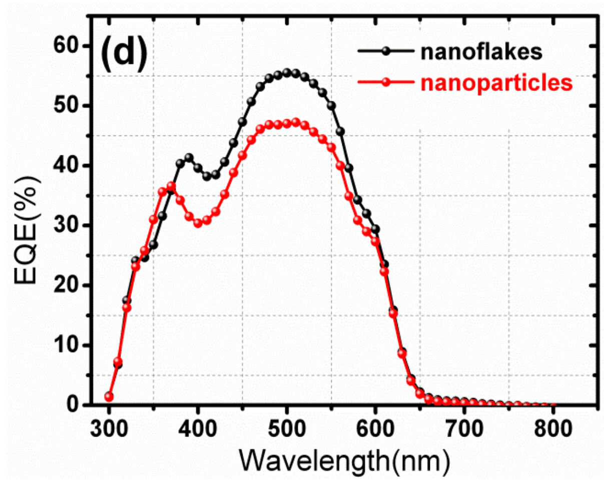


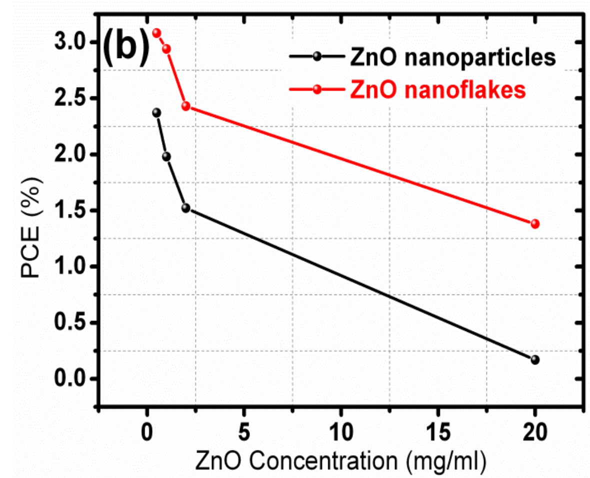
nanoflakes

PHOSPHORS AND RENEWABLE ENERGY – SOLAR ENERGY

ORGANIC SOLAR CELLS : PARTICLE MORPHOLOGY







Concentration (mg/mL)	ZnO nanoparticles J_{sc} (mA/cm²)	V_{oc} (V)	FF (%)	PCE (%)	ZnO nanoflakes J_{sc} (mA/cm²)	V_{oc} (V)	FF (%)	PCE (%)
0.5	7.18	0.67	49.5	**2.37**	7.63	0.67	60.6	**3.08**
1	6.67	0.65	45.8	1.98	7.45	0.67	59.2	2.94
2	6.38	0.67	35.7	1.52	6.94	0.66	52.8	2.43
20	0.74	0.64	36.3	0.17	6.01	0.61	37.8	1.38

Nanoflakes made a relatively superior contact with the photo-active layer and the top electrode compared to the nanoparticles.

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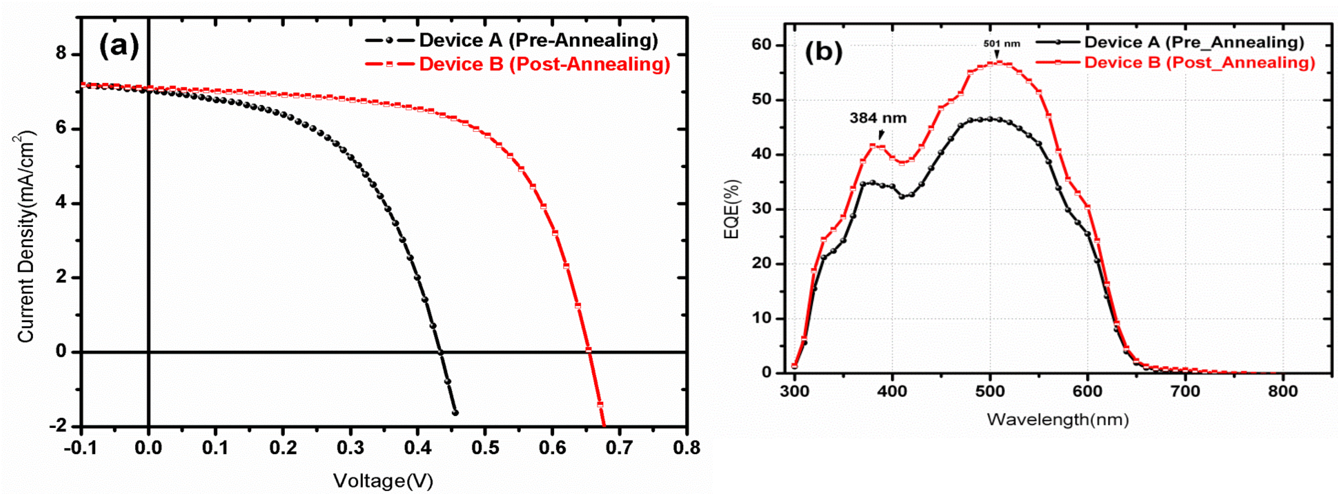
PHOSPHORS AND RENEWABLE ENERGY – SOLAR ENERGY

ORGANIC SOLAR CELLS : THERMAL TREATMENT



Thermal treatment Modifies the interface:

Rough interface necessary for light harvest and collection of photongenerated carries

Enhance crystallization of polymers

Device A				Device B			
J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
7.027.18	0.433	51.69	**1.57**	7.10	0.654	63.07	**2.93**

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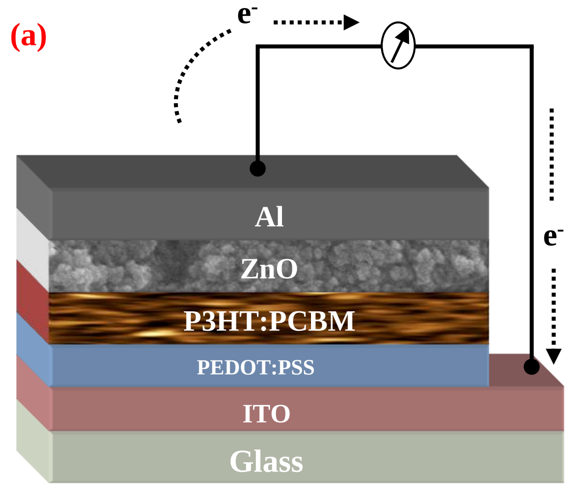
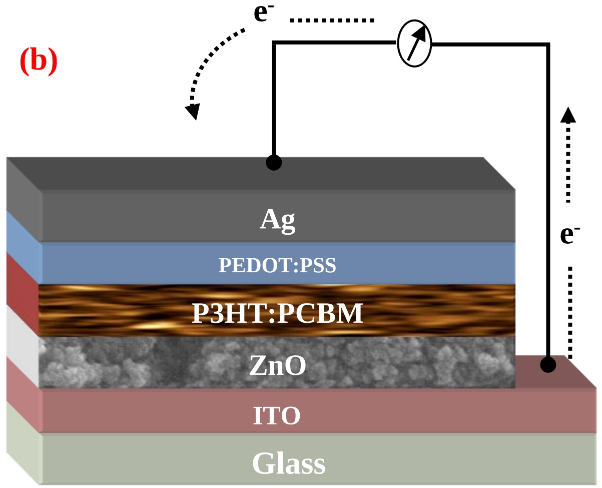
PHOSPHORS AND RENEWABLE ENERGY – SOLAR ENERGY

ORGANIC SOLAR CELLS: INVERTED DEVICES





Inverted Device	ZnO Layer	J_{sc}(mA/cm^2)	V_{oc}(V)	FF(%)	PCE(%)
(1) Inverted	Nanoparticles	8.331	0.5848	46.45	**2.26**
(2) Uninverted	Nanoparticles	7.18	0.67	49.50	**2.37**

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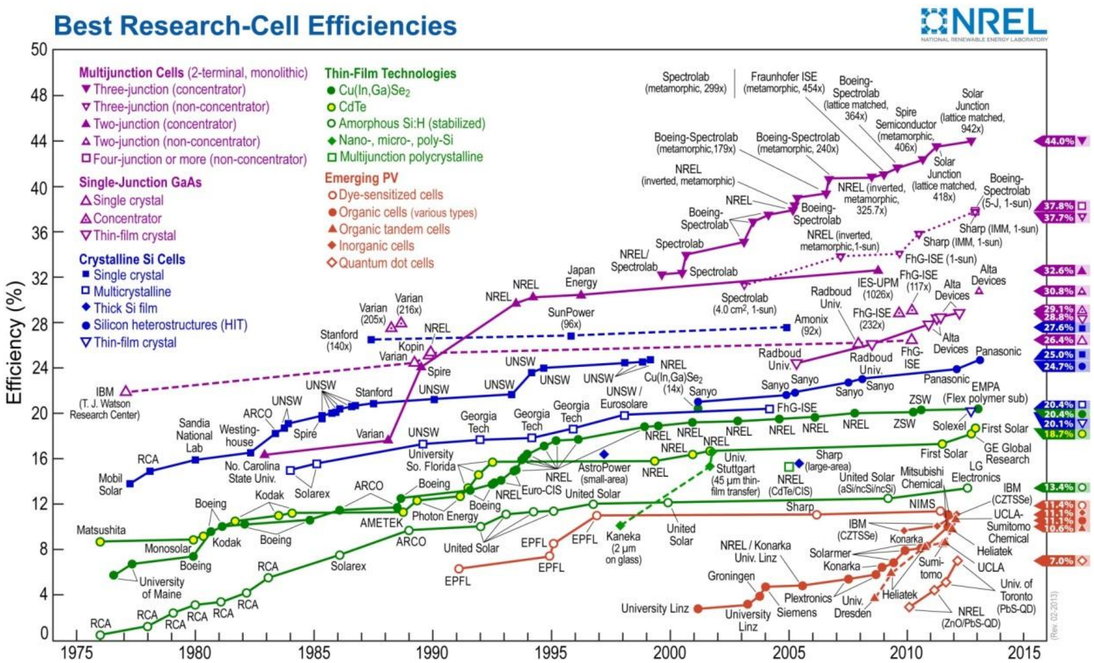
PHOSPHORS AND RENEWABLE ENERGY – SOLAR ENERGY



BEST SOLAR CELL EFFICIENCIES

SILICON SOLAR CELLS

1975 – 2013 = 35 % (after 40 yrs)

ORGANIC SOLAR CELLS

2000 – 2013 = 13% (after 13 yrs)

ORGANIC SOLAR CELLS – UFS

2010 – 2013 = 3.9% (after 3 yrs)

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PHOSPHORS AND RENEWABLE ENERGY – SOLAR ENERGY

NANOSCIENCE AND NANOTECHNOLOGY AND THE PRICE OF ELECTRICITY

- **Nanoscience research is dramatically increasing the PCE of solar cells: conventional and new generation -**
- **Nanotechnology: Is offering easy and less complicated ways to fabricate new generations of solar cell devices**

- **Improved efficiency and ease of production will eventually reduce the cost of solar cells and hence the price of electricity.**

- **Solar cells with improved efficiency will bring and end to over dependence on nuclear energy, fossil-fuels and oil.**
- **Solar cells with improved efficiency , will reduce the cost of solar panels making them affordable to people in rural areas.**
- **I therefore expect dramatic increase in solar energy driven rural electrification in the near future.**

SUMMARY

We have synthesized nanoparticles with different morphology (shapes and sizes)

We have demonstrated that luminescence intensity of phosphors can be increased considerably by energy transfer from encapsulated nanoparticles to luminescent centres

We have demonstrated that by selecting a suitable host we can produce phosphors that are chemically stable , with "non-degradable "luminescence intensity.
We have produced single host phosphors that emit white light.

Our phosphors can be used in the following applications:

1. Different kinds of light emitting devices, including light emitting diodes and bulbs.
2. Both conventional and organic solar cells to improve their power conversion efficiencies.

POTENTIAL SOCIO-ECONOMIC BENEFITS OF OUR PHOSPHORS ARE:

- Low cost lighting
- Rural electrification in the long run
- Reduction in the cost of electricity

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CONCLUSION

Is nanoscience/nanotechnology the gateway to low cost lighting and rural electrification ?

Where does your imagination take you?

ANSWER : WHATCH THIS SPACE?

ACKNOWLEDGEMENTS

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Prof. Hendrik Swart

Prof. Thembela Hillie

Prof. Paul Holloway
University of Florida

Great Things from Small Things

ACKNOWLEDGEMENTS

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1. **ALL MY COLLEAGUES IN THE PHYSICS DEPT.**

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3. Dr JJ Dolo
4. Dr GH Mhlongo
5. Dr HAA Seed Ahmed
6. Dr PD Nsimama

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FINANCIAL SUPPORT

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Penn
UNIVERSITY of PENNSYLVANIA

UF | UNIVERSITY of FLORIDA

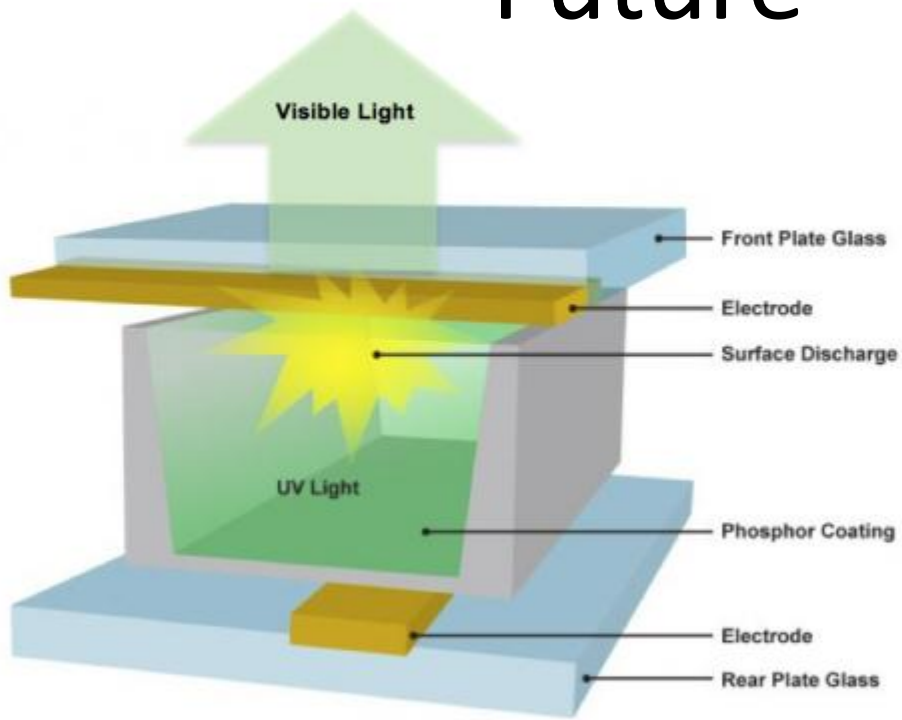
FUTURE PLANS

Develop nanomaterials for photodynamic therapy (treatment of cancer and skin diseases)

Train and develop a critical mass of nanoscientists in UFS and South Africa

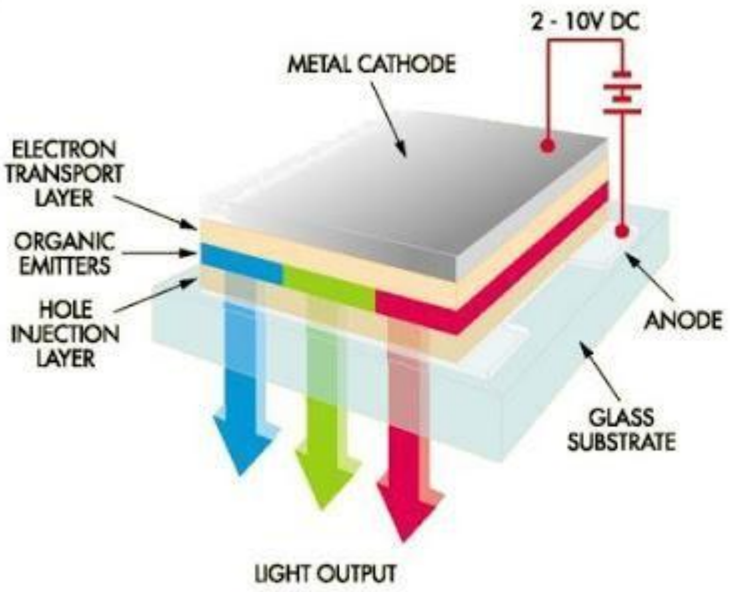
Establish a centre of excellence that develops smart nanomaterials for solid state lighting and renewable energy.

Future



OLED TVs

Plasma displays



Future

Future

Glow in the dark pathways/roads