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Development of Luminescent Nanoparticles for Various Applications

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I INTRODUCTION

Nanoparticles of luminescent materials (nanophosphors) emit light when excited with suitable energy. Such luminescent nanoparticles offer great potential for superior light emitting devices, displays, energy harvesting applications, security ink, fluorescence tracking and targeted drug delivery in biological systems and many others. The development of nanophosphor for a particular application including lighting and display require different window of excitation energy and specific emission energy. For example, solid state lighting with LED requires suitable nanophosphor excitable by blue/UV LED to produce white light; for Plasma Display Panel (PDP) they should be excitable by vacuum ultraviolet (VUV) light and emit in three primary colours Red/Green/Blue, for efficient solar spectrum conversion nanophosphor must absorb solar UV and IR radiation and convert into visible light for efficient photovoltaics. Moreover, fluorescence emission from nanoparticles can be enhanced through plasmonic coupling for better device efficiency.

Synthesis of luminescent nanoparticles of various inorganic host materials and doping with appropriate light emitting atoms to devise nanophosphor for various applications has been done using chemical methods such as co precipitation, sol gel, auto combustion and controlled solid state diffusion. Phase characterization has been done by x-ray diffraction, morphology and particle size examined by transmission electron microscopy. Photoluminescence properties have been studied with Edinburgh Instruments combined steady state and time resolved luminescence spectrometer (FLSP920) and confocal fluorescence microscope (WITec Instruments). Phosphors/ nanophosphors developed for particular applications and their properties are described below.

II NANOPHOSPHOURS APPLICATIONS

(a) Phosphors for Plasma Display Panel (PDP)-Phosphors for PDP applications have to be excitable by vacuum ultraviolet (VUV) light and emit in three primary colours red, green and blue (RGB) so that all the hues can be reproduced in PDP TV pictures. We have developed three phosphors for PDP application which are $Y_4Al_2O_9$: Eu^{3+} (YAM:Eu^{3+}), for red, YBO_3: Tb^{3+} for green and $BaMgAl_{10}O_{17}$: Eu^{2+} (BAM) for blue. The phosphors were synthesized by high temperature solid state reaction method in an ambient atmosphere suitable for the valence state of the rare earth activator ion. Emission spectra and photographs of developed RGB phosphors under VUV excitation is shown in Fig.1(a). Degradation of phosphors due to thermal treatment during panel baking process and operation under VUV irradiation is major challenge in PDP industry. We successfully arrested degradation of PDP phosphors by coating individual phosphor grains with nanometer thick silica layer as shown in the inset TEM imag23e.

(b) Phosphors for Solid state lighting-Production of white light from monochrome LED light is mostly realized by coating a blue LED chip with blue to yellow down conversion phosphor so that part of blue LED light is absorbed by phosphor that emits yellow light and part of blue light is transmitted so that white light is generated by intermixing of blue and yellow - two complimentary colours (Fig.1b). Nanophosphor can reduce light scattering and improve the light output by 50%. Commercial white LEDs presently available in market uses coating of yellow emitting YAG: Ce (Ce^{3+} doped $Y_3Al_5O_{12}$) phosphor on blue LED chips (450 –480 nm) and produce heavily blue tinged white, deficient of red part of the visible spectrum. Example of a rare earth ion doped alkaline earth aluminates $SrAl_2O_4$: Pr^{3+} with broad excitation band ranging from 430 – 490 nm covering the emission wavelength of all commercial blue LEDs and PL emission spectra showing broad emission in yellow orange spectral region is shown in Fig.1.

(c) Phosphors for solar spectrum conversion for efficient energy harvesting by solar cells-A very important emerging application of nanophosphor is solar spectrum conversion for enhancing solar cell efficiency. Effective absorption of silicon solar cells is limited in the range of 550- 1100 nm ($h\nu \sim E_g - 2E_g$) and Dye sensitized solar cells (DSSC) absorb mostly in the visible region. Thus most of the terrestrial solar energy (~ 300 - 2400nm) in the UV and IR remains unutilized by solar cells. Suitable nanophosphor layer, when integrated with solar cells, can convert solar UV and IR radiation in the visible range which can be utilized by solar cells for photo carrier generation. Mostly individual down conversion (UV to visible) and/or upconversion (IR to visible) nanophosphors that can be used on the front or rear surface of solar cell respectively are discussed that require a bifacial solar cell. A novel solution is to employ a dual excitation phosphor that can be simultaneously excited by both UV and IR solar radiation and emit in the visible region with high luminescence yield. Towards this goal, we have developed a dual excitation, dual emission phosphor YVO_4:Eu^{3+},Er^{3+},Yb^{3+} and the emission spectra and photograph under UV and IR light is shown in Fig.1.

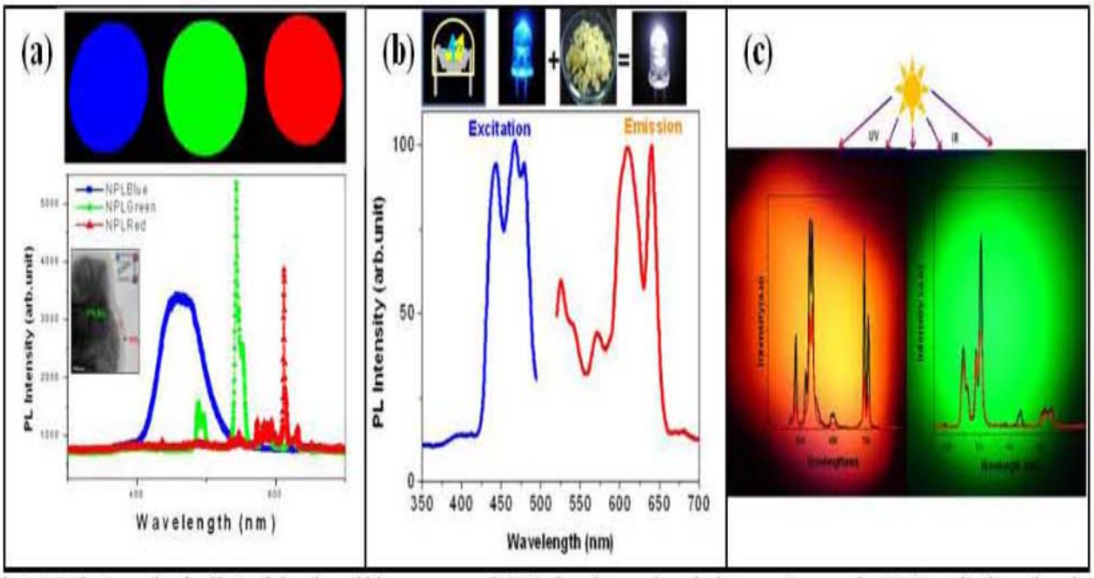

Fig1 Photograph of pellets of developed blue, green, red PDP phosphor and, emission spectrum under VUV excitation, also shown the TEM image of silica coated phosphor grain; (b) schematic of generating white light from a blue LED using a yellow emitting phosphor and excitation, emission spectra of developed SrAl2O4:Pr3+ phosphor; (c) photograph of dual excitation, dual emission phosphor YVO4:Eu3+,Er3+,Yb3+ under UV & IR excitation and emission spectra.

(d) Plasmonic enhancement of fluorescence- Metal nanoparticles (MNP) can confine and enhance the incident electromagnetic field (EM) around them due to surface Plasmon resonance (SPR) and lightening rod effect. Such plasmonic near field has the ability to enhance fluorescence from nanoparticles conjugated optimally with MNPs. We have shown that Silver nanoprisms (Ag NP) of different sizes influence fluorescence enhancement in YVO4:Eu3+ nanoparticles to various degrees. The Plasmon enhanced fluorescence process is shown schematically in Fig.2 and the TEM images of fluorescent YVO4:Eu3+ NPs (~ 5nm) and the scatter free colloidal solution; TEM images of Ag NPs and their colloidal solution showing different colours due to their respective SPR band is shown in Fig.2. The confocal images of only nanophosphor film and that of nanophosphor conjugated with Ag NPs clearly show the enhancement of fluorescence due to plasmonic near field.

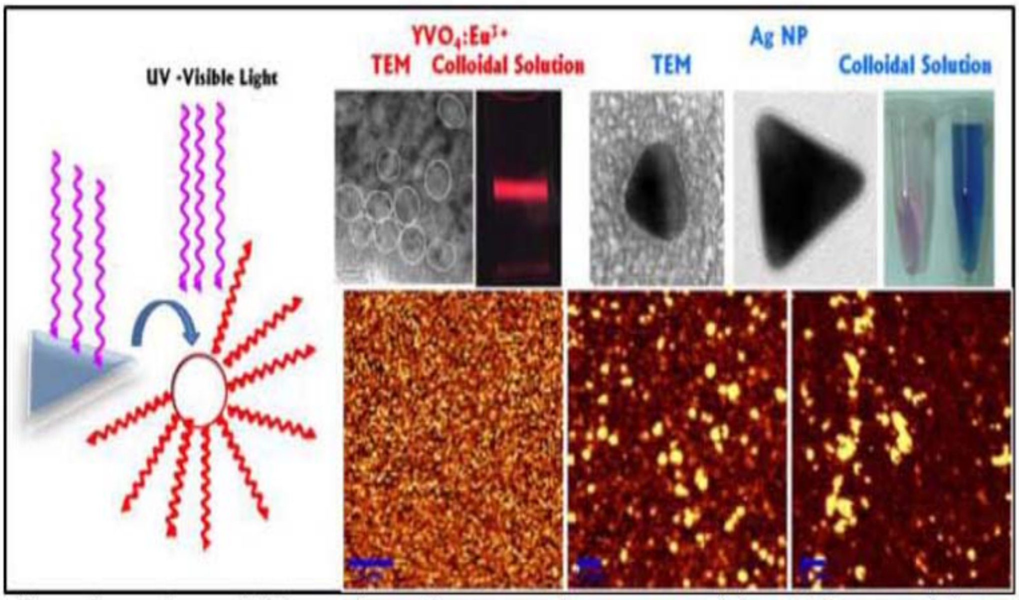

Fig.2 Schematic of how plasmonic near field can enhance fluorescence from a nanoparticle, TEM image and photograph of colloidal solution of nanophosphor YVO4:Eu3+, Silver nanoprisms of two different edge lengths and confocal fluorescence maps of (bottom: from left to right) thin film of only YVO4:Eu3+ NPs, YVO4:Eu3+ NP conjugated with smaller and larger Ag nanoprism respectively.

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