Abstract

The aim of this work is to exploit the unique photophysical properties of fluoroprobe molecules and semiconductor material near various sizes and shapes of metal nanostructures, their metal-probe hybrid and metal-semiconductor assembly formation and studies of their photophysical and thermodynamic behavior. For this purpose, the present Ph. D. thesis entitled **“Photophysical Properties of Molecular Probes near Nanostructured Metallic Surfaces”** has been chosen. This thesis includes the synthesis of gold and silver nanoparticles of various sizes and shapes (spherical, dogbone nanorods, multispikes nanostructures) and the formation of metal-fluoroprobe hybrid assembly using various fluorophores and their photophysical properties based on Förster resonance energy transfer and electron transfer mechanism. Moreover, size selective metal nanoparticles-semiconductor assembly and their various physical properties have been studied using microscopic (transmission electron microscopy, scanning electron microscopy) and spectroscopic (UV-visible spectroscopy, steady state and time-resolved fluorescence spectroscopy, Raman spectroscopy, energy dispersive X-ray analysis, Fourier transform infrared spectroscopy, X-ray diffraction, and selected area electron diffraction) techniques. The complete work of the thesis has been divided into seven chapters.

Chapter 1. General Introduction

This chapter describes the general introduction about the current literature related to the research work presented on plasmonic metal nanoparticles and fluorophore molecules near to the surface of the nanostructures.

Chapter 2. Experimental

This chapter presents a brief description about the chemicals and reagents used and various techniques and analytical instruments used for the characterisation for the synthesised materials and metal-fluoroprobe hybrid assemblies.

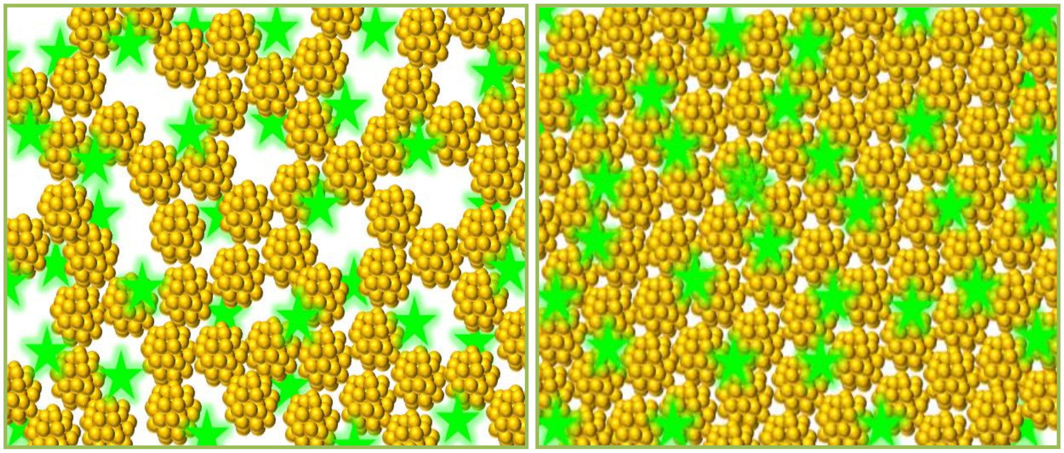
Chapter 3. Fluorescence of Molecules near Aggregated and Isolated Gold Nanoparticles

This chapter describes the fluorescence enhancement with aggregated gold nanoparticles of variable sizes under different aggregation conditions and different energy transfer processes

between the fluoroprobe and the nanoparticles and the effect of size in energy transfer process. This chapter consists of two sub-sections:

Chapter 3.1. Fluorescence Enhancement in Spontaneous and Induced Aggregated Gold Nanoparticles

In this sub-section, we have mentioned the synthesis of gold nanoparticles by sodium borohydride reduction using poly(N-vinyl 2-pyrrolidone) as the stabilizing agent in aqueous medium in the size regime of 1 to 5 nm. Aggregation amongst these polymer-stabilized gold nanoparticles has been accomplished by the controlled addition of hydrazine or aggregation may occur spontaneously (devoid of any chemicals) that is ubiquitous to nanoparticulate systems. The isolated gold nanoparticles and their aggregates have been characterized by UV-vis spectroscopy and transmission electron microscopic studies. It is noted that ultrasmall gold nanoparticles do not exhibit any characteristic surface plasmon band in the visible region rather a continuous absorption is seen over the entire UV-vis region. However, upon aggregation, characteristic surface plasmon band of the gold nanoparticles is observed which gradually becomes broadened without any significant change in the wavelength. Now, fluorescencein isothiocyanate (FITC), a prototype molecular probe has been employed in understanding the physical principles of aggregation phenomenon of the size-selective gold nanoparticles undergoing spontaneous and induced-aggregation under stipulated conditions. It is seen that there is enhancement of



Spontaneous **Induced**

Scheme 1. Schematic presentation of the plausible binding modes of the dye molecules to the spontaneous and induced-aggregated gold nanoparticles.

fluorescence intensity of FITC in the presence of both spontaneously and induced-aggregated gold nanoclusters as compared to free FITC. Interestingly, it is observed that the fluorescence sensitivity is able to distinguish seven different sizes of the gold nanoparticles in the aggregates and maximum enhancement of intensity arises at higher concentration with increase in size of gold particles within the aggregates. With increase in concentration of gold nanoparticle aggregates, the intensity increases, initially, reaches a maximum at a threshold concentration and then, gradually decreases in the presence of both spontaneously and induced-aggregated gold particles. However, the salient feature of physical significance is that the maximum enhancement of intensity with time has remained almost same for induced-aggregated gold while decreases exponentially with spontaneously aggregated gold particles.

Chapter 3.2. Energy Transfer Processes in Gold Nanoparticles-Probe Hybrid Systems

This sub-section explains the different energy transfer processes (FRET and NSET) between the fluoroprobe and the gold nanoparticles. Gold nanoparticles of variable sizes (1-55 nm) have been synthesized using sodium borohydride as reducing agent and poly(N-vinyl 2-pyrrolidone) (PVP) as the capping agent and/or citrate as reducing and capping agent functionalized with PVP for the stability in aqueous medium. The synthesized gold nanoparticles have been characterized by UV-vis spectroscopy and transmission electron microscopy. It is noted that ultrasmall gold for the stability in aqueous medium. The synthesized gold nanoparticles have been characterized by UV-vis spectroscopy and transmission electron microscopy. It is noted that ultrasmall gold

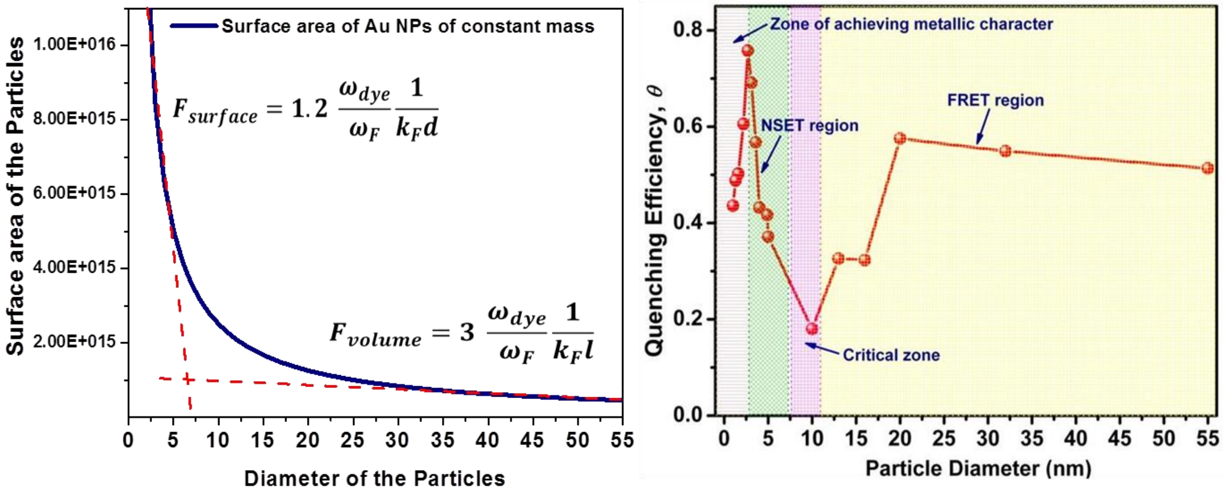
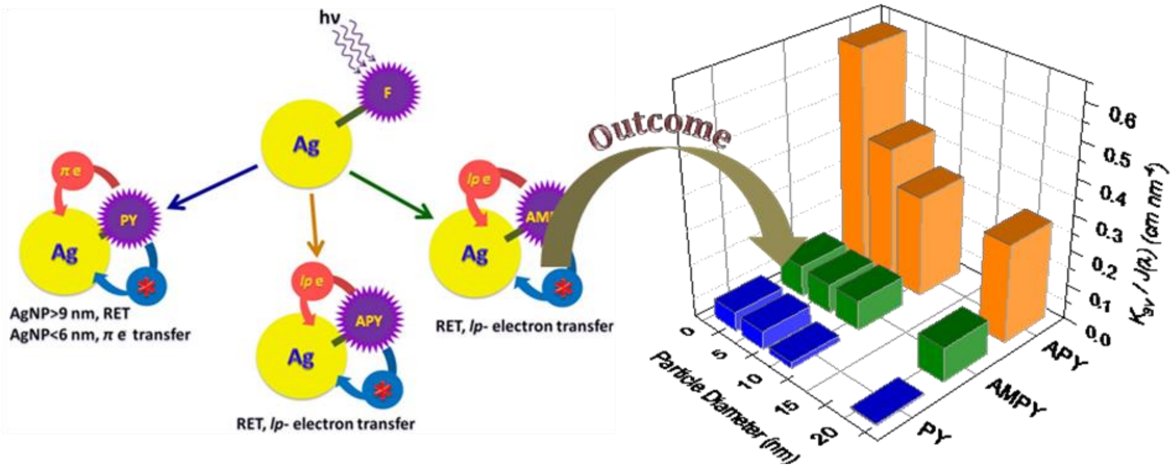


Figure 1. (left) Surface area and (right) quenching efficiency of the gold nanoparticles as a function of particle diameter.

nanoparticles (<5 nm) do not exhibit any characteristic surface plasmon band in the visible region rather a continuous absorption is seen over the entire UV-vis region while larger gold nanoparticles (>5 nm) exhibits prominent surface plasmon band at around 520 nm wavelength region. Then, highly intense fluorescent dye molecule containing high quantum yield, fluorescencein isothiocyanate (FITC) have been employed as molecular probe in understanding the physical principles of surface behavior of gold nanoparticles and their variable sizes in fluorescence quenching and the excited state fluorescence lifetime of the dye molecules at neutral condition. It is seen that quenching efficiency increases with increasing amount of gold nanoparticles and the dipole-surface energy transfer is more prominent than dipole-dipole energy transfer. It is also observed that the increasing of fluorescence quenching and the decreasing of the excited state fluorescence lifetime of the FITC molecules with decreasing the size of the particles up to a critical dimension/size and then again reverse order is followed with further decreasing the size. These phenomena could be explained by NSET and FRET mechanism. In addition, it has also been found from both experimental evidence and theoretical calculation of the critical point at which the coverage of the two distance dependence process exactly occur in the particular size regime.

Chapter 4. Relative Contributions of Electron and Energy Transfer in Nanoparticle-Induced Fluorescence Quenching

Metallic nanostructures are known to drastically modify the spontaneous emission of molecular probes placed in their vicinity. The main critical parameters that modify the spontaneous rate of emission of organic fluoroprobes near metallic nanostructures are the location of the fluoroprobe around the particle, its separation from themetal surface, and the molecular dipole orientation with respectto the particle surface. Depending on its relative position and orientation with respect to the nanostructures, the fluoroprobe may experience an enhanced or suppressed electric field, leading to a higher or lower excitation rate, respectively, in comparison to a fluoroprobe in free space. The fluorescence of molecules in direct contact with the metal is completely quenched. In this work, pyrene and its amine derivatives haveelegantly been employed as fluorescent probes, and four sets of different sizes of citrate capped silver nanoparticles have, judiciously, been selected to study the interactions in metal−fluoroprobe hybrid assemblies. Because fluorescence spectroscopy is a very sensitive technique, strong correlation is observed between the observed fluorescence intensity and the photophysical properties of the metal−fluoroprobe hybrid assemblies. It is observed that fluorophore-bound silver nanoparticles provide a convenient way to examine the mechanistic details of various deactivation pathways of photoexcited fluoroprobes, such as, electron and energy transfer to the bound nanoparticles, and eventually, paves a substantial avenue in realizing the relative electron and energy transfer contributions in nanoparticle-induced fluorescence quenching.



Scheme 2. Schematic presentation of the possible deactivation pathways in silver−fluoroprobe hybrid assemblies and the resultant differential quenching of pyrene moieties as a function of particle size of silver nanostructures.

Chapter 5. Fluorescence of Molecules near Anisotropic Gold Nanostructures

This chapter includes the anisotropic nanostructures of metallic gold and elicited the mechanism of electron and energy transfer of the emission properties of the excited fluoroprobe around the nanostructures and therefore, stability of the anisotropic materials has been examined through experimental and theoretical perspectives. This chapter is divided into two sub-sections:

Chapter 5.1. Aspect Ratio Dependence of Dogbone-Shaped Gold Nanorods

The first section describes the cetyltrimethylammonium bromide-stabilized ‘dogbone-shaped’ gold nanorods of aspect ratio varying from 1 to 6 have been synthesized by seed-mediated growth method in aqueous medium. Then, sudan red 7B, an alien molecular probe has been used as local probe to elucidate aspect ratio dependence of the nanorods on the photophysical properties of the dye molecules. It is seen that the relative intensity decreases exponentially with increasing aspect ratio and has been attributed to decrease in surface area of the nanorods. The mechanism of fluorescence quenching has been ascribed to the electron and energy transfer processes in the gold-fluorophore hybrid nanostructures.

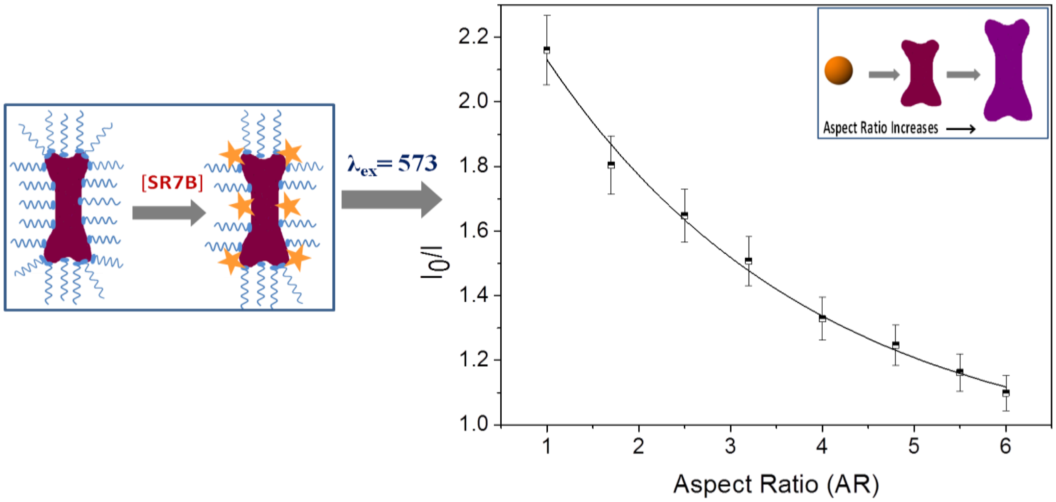
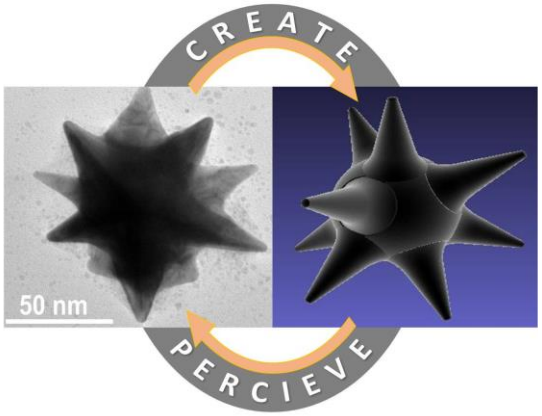


Figure 2. Profile showing the relative intensity of SR7B as a function of aspect ratio of GDNRs. Inset provides a schematic presentation showing aspect ratio gradually increases from spheres to larger dogbones.

Chapter 5. 2. Excess Surface Energy at the Tips of Gold Nanospikes



Physicochemical aspects of anisotropic gold nanostructures have been of considerable interest due to intrinsic shape-dependent phenomena that opens up newer perspectives from nanoscale electromagnetism to basic thermodynamics since gold has highly symmetric face-centered cubic (fcc) structure and usually tends to afford spherical geometry to reduce surface free energy. The emergence of novel properties of these anisotropic structures could be attributed to the lack of symmetry at the interface or to the confinement of electrons that does not scale linearly with size. Based on these conceptives, anisotropic gold nanospike has been chosen as typical nanostructural system that possesses different surface energy around the nanostructure in comparison to isotropic gold nanosphere to quantify the precise surface energy at the tips of these intricate nanostructures.

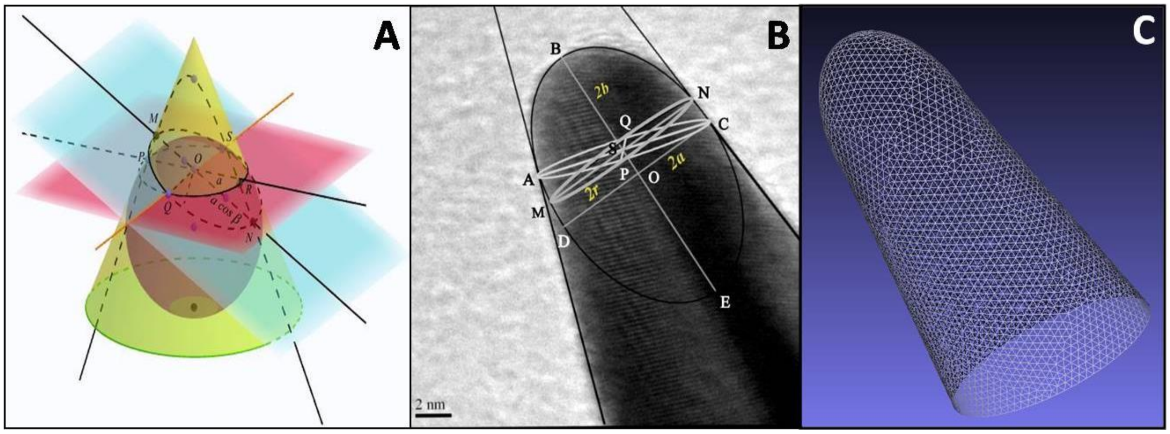


Figure 3. Three-dimensional modeling of the tip of a spike: (A) theoretical model, (B) transmission electron micrograph, and (C) three dimensional meshgrid of the rendered model of tip.

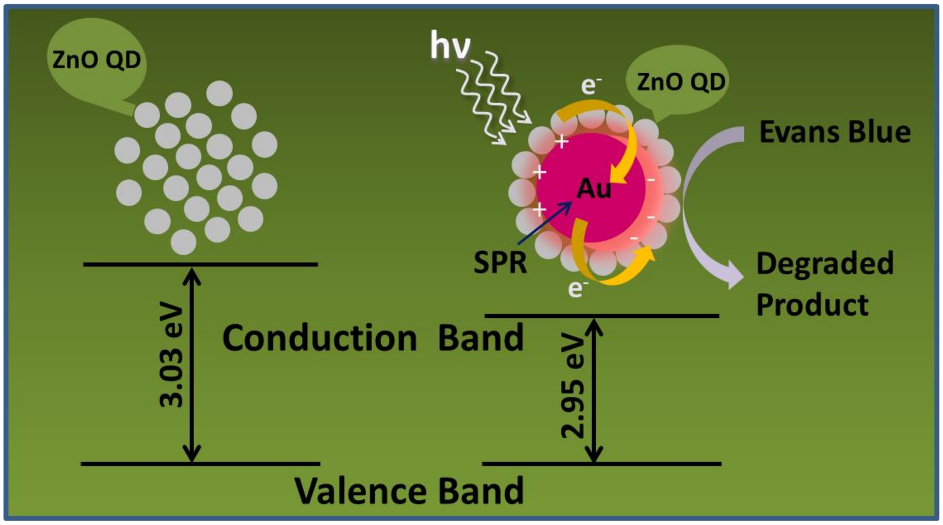
Cetyltrimethylammoniumbromide-stabilized gold nanospheres and nanospikes have been synthesized in aqueous medium under ambient condition. Since fluorescence spectroscopy is a very sensitive technique, fluorescent dye, alizarin red has been employed as a local probe to elucidate the detailed spectral characteristics of the metal-probe hybrid assemblies. The influence of morphological anisotropy of these nanostructures has been, further, emphasized by following the temporal changes in the emission characteristics during the photoinduced conversion of gold nanospikes to nanospheres under NIR laser irradiation. Experimental realization of excess surface energy at the tips of the nanospikes has been calculated from theoretical perspectives.

Chapter 6. Semiconductor Fluoroprobes near Metal Nanostructures

In this chapter, metal-semiconductor assembled nanostructures containing different noble metals and zinc oxide semiconductor composites and their photophysical properties have been studied. This chapter includes two sub-sections: firstly, the zinc oxide-gold composites and secondly, zinc oxide- silver composites.

Chapter 6.1. Manipulating Electron Transfer in ZnO-Au Nanohybrids

Hybrid semiconductor–plasmonic metal nanocomposites (NCs) tailoring of zinc oxide–gold (ZnO–Au) have been synthesized by direct addition of an aliquot of ZnO quantum dots (QDs) to aqueous dispersions of gold nanoparticles (NPs) of five different sizes. Gold nanoparticles of variable sizes have been prepared by Frens' citrate reduction procedure and ZnO QDs by alkaline hydrolysis of zinc acetate dihydrate in methanol. The optical properties of ZnO–Au NCs have been explored by absorption, photoluminescence, and Raman spectroscopy; the intrinsic changes in the optical characteristics of the individual components reflect strong interfacial interaction between ZnO and Au nanostructures. The binding of ZnO QDs to the colloidal gold particles has, further, been elucidated by Fourier transform infrared spectroscopy and cyclic voltammetry measurements. The morphology and crystallinity of the ZnO-Au NCs have been characterized by transmission electron microscopy, high resolution transmission electron microscopy, selected area electron diffraction and X-ray diffraction techniques. Absorption spectral studies have revealed that ZnO QDs attached on the size-specific Au NPs elicites the tuneability of band gap in semiconductor–metalnanocomposites. The catalytic activities of the as-prepared ZnO–Au NCs consisting of gold nanoparticles of variable sizes have been probed by employing photochemical decomposition of Evans blue under visible light irradiation as the model reaction. Finally, the trends in the alteration of different interaction parameters in structuring semiconductor–metal nanohybrids with the band gap have been correlated.



Scheme 3. Schematic presentation of the band gap modulation in ZnO–Au nanohybrid assemblies containing Au NPs and the photocatalytic degradation of Evans blue at the ZnO-Au nanocomposites surfaces.

Chapter 6. 2. Tunable Ultraviolet Photoluminescence of Hierarchical ZnO–Ag Assemblies

Zinc oxide (ZnO) is a unique material that exhibits semiconducting, piezoelectric, and pyroelectricmultiple properties. The nanostructures could have novel applications in optoelectronics, sensors, transducers, and biomedical science because it is bio-safe. Synthesis of complex ZnO architectures with well-controlled morphology and understanding of their growth mechanisms are desirable for both fundamental study of crystal growth and materials optimization for device applications. The preparation of noble metal-semiconductor hybrid nanocrystals with controlled morphologies has received intensive interests in recent years. The morphology of the assemblies becomes more and more complex by increasing the concentration of silver precursor. In this work, we demonstrate a rational approach for the bottom-up assembly into hierarchical ZnO–Ag superstructures possessingintrinsic asymmetry with multiple interesting morphologies. Morphological variation of hierarchical assemblies could be envisaged by tuning the composition of their precursors using water/*o*-xylene as the solvent medium under alkaline hydrolytic condition. The salient feature of materials significance is that a small variation on experimental conditions makes a large difference in the morphology and properties

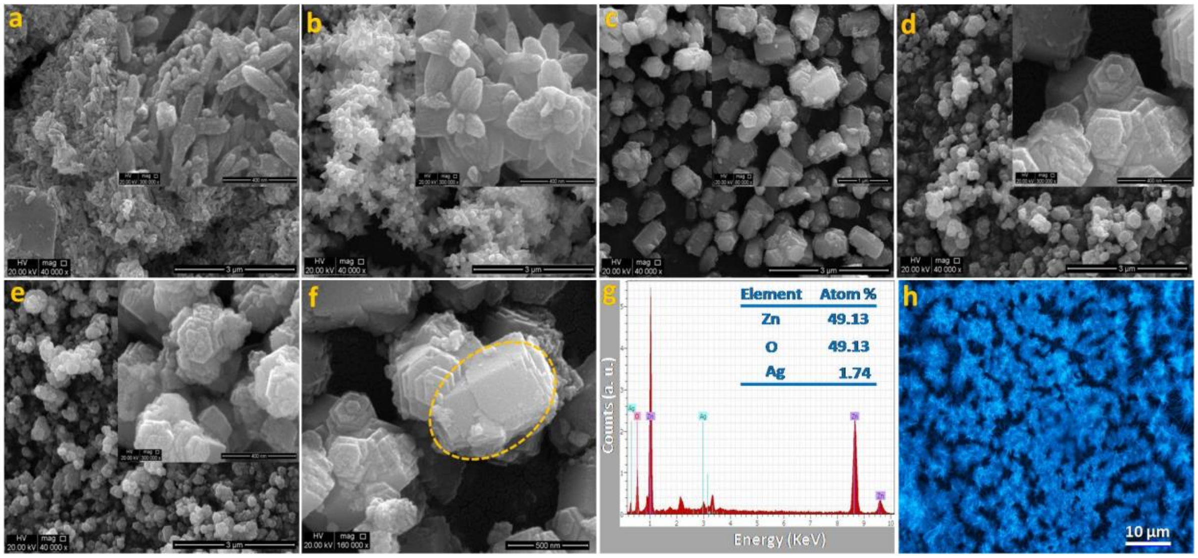


Figure 4. (a-e) Scanning electron microscopic images of silver-doped ZnO superstructures with ZnO: Ag = 1.0 : 0.010, 1.0 : 0.013, 1.0 : 0.020, 1.0 : 0.040 and 1.0 : 0.100 respectively; (f) high resolution SEM image, (g) fluorescence microscopic image and (h) energy dispersive X-ray spectrum of set E.

of ZnO–Ag hybrid assemblies. The assemblies so obtained have been characterized by transmission electron microscopy, high resolution transmission electron microscopy, energy dispersive X-ray analysis, Fourier transform infrared spectroscopy, X-ray diffraction technique, Raman spectroscopy, fluorescence microscopy and scanning electron microscopic images. The evolution of the hybrid assemblies has been followed by time-dependent diffuse reflectance spectroscopy, Fourier transform infrared spectroscopy and X-ray diffraction technique, Raman spectroscopy and a plausible mechanism of evolution of the assembles has been formulated. The photoluminescence properties of the ensuing assemblies reveal that the UV-luminescence of the semiconductor-plasmonic metal assemblies could be tuned as governed by the composition and morphology of the assemblies.

Chapter 7. Overall Conclusion and Future Scope of the Work

This chapter summarizes the overall conclusion, including, the chapters 3, 4, 5, and 6 mentioned above. This research work mainly focuses on the photophysical properties of various organic and inorganic fluoroprobes placed in the vicinity of isotropic and anisotropic nanostructures of different noble metals of variable sizes. Possible applications of the metal-fluoroprobe hybrid assemblies and future scope in this research arena have been elucidated.