Chapter 7

Overall Conclusion and Future Scope of the Work

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7.1. Overall Conclusion

Four chapters of the thesis, i. e., chapter 3, 4, 5 and 6 describing the research work, mainly, focused on the photophysical properties of various molecular probes and semiconductor fluoroprobes placed in the vicinity of isotropic and anisotropic nanostructures of different noble metals particles of variable sizes and studied the photophysical properties of the metal-probe assemblies.

In chapter 3.1, fluorescence spectroscopy has been employed in realizing the physicochemical insights of aggregation phenomena and differentiation of spontaneous and induced aggregation processes in size-selective gold nanoclusters. It is seen that there is enhancement of fluorescence intensity of FITC in the presence of both spontaneous and induced-aggregated gold nanoclusters and able to distinguish seven different sizes of the gold nanoparticle aggregates. Moreover, the maximum enhancement of intensity with time has remained same for induced-aggregated gold while decreases exponentially with spontaneously aggregated gold particles. This reflects the increased detection efficiency with enhancement of the molecular fluorescence by amplifying/tailoring the electromagnetic radiation field of the neighboring fluorophores near metal nanoparticles.

In chapter 3.2. it has been shown that the quenching efficiency is very sensitive in smaller particle size regime. Moreover, the quenching efficiency does not change regularly rather increases or decreases with increasing the size of the particles. With increasing the size of the particles, the surface area decreases and hence, NSET decreases and FRET become significant. It is also observed that the quenching efficiency of the Au NPs increases with increase in the size of the particles up to a critical dimension/size and again, sharply decreases. Therefore, this offers an experimental evidence of the critical point at which the coverage of the two distance dependence process exactly occur in the particular size regime.

In chapter 4, it is observed that pyrene and its amine derivatives-bound silver nanostructures provide a convenient way to examine the relative contributions of electron and energy transfer in the quenching processes. A new parameter, ‘differential quenching' have been introduced in realization of individual electron and energy transfer in nanoparticle-induced fluorescence quenching. Besides, the consequence of physical interaction of nanoparticle-fluoroprobe assemblies provides strong evidence for the donation of both σ and π electrons to the small metallic particulates.

Chapter 5.1 exhibits an experimental verification of the effect of aspect ratio of gold dogbones on the fluorescence quenching of molecular probe. It is seen that, upon binding of the probe molecules onto the gold dogbones, fluorescence quenching bears an exponential relationship with increase in aspect ratio of the nanorods. Moreover, the rod with lower aspect ratio are more efficient quencher of molecular fluoroscence than higher aspect ratio rods and this is due to higher surface-to-volume ratio of the smaller nanorods.

Chapter 5.2 demonstrates the fluorescence quenching of molecular probes near the anisotropic nanostructures that does not scale linearly with the surface area; excess surface energy in specific region of the non-spherical particles play a deterministic role in governing the photophysical properties of the molecular probes. This observation has been supported by melting the branched nanostructures transformed into spherical nanoparticles because sharp tips interact more intensely with NIR laser excitation and probe their role in the modification of the emission characteristics of the dye molecules. The modeling of the tips of the nanospikes based on basic Euclidean geometry are good agreement with the experimentally observed results that validates the applicability of the proposed model to calculate the excess surface energy arising from the intriguing anisotropicity of the materials at the nanoscale dimension.

In chapter 6.1, the binding of ZnO QDs on the surface of size-specific gold nanoparticles has been investigated to resolve the interfacial charge transfer process that alters the physicochemical properties of the nanocomposites. This demonstrates that the chemical synthesis of water-soluble ZnO-Au nanohybrids are soluble in aqueous media through simple deposition of ZnO QDs on the surface of gold nanoparticles that paves an effective and alternative strategy in comparison with the *in-situ* formation of functional semiconductor-metal hybrid assemblies. Moreover, the combination of a semiconductor photocatalyst with tailored plasmonic nanostructures enhance stability and allow to absorb additional amount of visible light in photodegradation of Evans blue as compared to pure ZnO QDs. Furthermore, the band gap of the semiconductor-plasmonic metal hybrid assemblies could be miniaturised by changing the size of the gold nanoparticles and the tuneability of the band gap has been probed in the photocatalytic decomposition of Evans' blue under visible light irradiation. Lastly, the simple and facile approach of the present strategy builds a good platform towards fabricating other semiconductor-metal nanohybrids over a wide range of material combinations with morphological anisotropy and functional diversities.

In chapter 6.2., have reported the synthetic strategy of hybrid semiconductor-plasmonic metal assemblies which resolved the *in situ* nucleation and growth of the Ag domains followed by heterogeneous nucleation and growth of the ZnO component controls their spatial arrangement to induce unique morphology. This assemblies provides a natural interface for integrating multiple functions and exhibit a substantial reduction in the band gap that may lead to the discovery of new properties and functions. Photoluminescence studies elucidates that morphological variation of the ZnO–Ag hybrid assemblies controls both the UV and visible emission that is important to tailor the properties of next-generation bio-nano devices.

7.2. Future Scope of the Work

The thesis demonstrate the interaction of organic dye molecules and ZnO semiconductor QDs as fluoroprobes in the vicinity of size and shape-dependent metal nanostructures in aggregated and isolated state and tried to elucidate the mechanism of photophysical process. Further investigation might be continued to correlate the origin of fluorescence enhancement in aggregated gold nanoparticles with experimental and theoretical techniques. The absorption/emission behavior of fluoroprobes near nanostructures and elucidation of mechanism of photophysical processes via FRET and electron transfer should be investigated from theoretical perspectives. Moreover, the gold nanorods and nanospikes should be used with the intention to increase the efficiency in biological and medicinal applications, like, photodynamic therapy and cell-specific destruction of cancerous cells.