

Concluding Remarks

This chapter summarizes the results of the investigations presented in this thesis. The scope of further studies based on the findings of the present work is also outlined.

8.1. Overview:

The work embodied in this thesis has been undertaken to explore the photophysical behavior of the quantum dots (QDs) and to understand the diffusion behavior of some fluorescent dyes in complex environments such as protein solution and ionic liquids to obtain insights into these microheterogeneous media. These studies have been carried out using fluorescence correlation spectroscopy technique.

We Chose CdTe QDs with different capping agents (Chart 1.6) and dispersed them in different solvents to understand the influence of surface related processes on the photophysics of the QDs. CdTe/ZnS core/shell QDs were also studied for the same purpose. As a study of the diffusion of organic fluorophores can effectively report the local environment of complex media such as protein solutions and room temperature ionic liquids (RTILs), we studied the diffusion behavior of the fluorescent probes in protein solution and RTILs. Apart from the FCS technique, several other instrumental techniques such as NMR and IR spectroscopy for compound characterization, TEM for determination of morphology, a cone and plate viscometer for measurements of RTIL's viscosity, UV-vis spectrophotometer, steady-state and time-resolved fluorescence techniques for spectral and kinetic information were employed for carrying out the work presented here. The findings of the present work are summarized below.

The evolution of the fluorescence properties of an aqueous solution of mercaptopropionic acid (MPA)-capped CdTe QDs under light exposure has been investigated. A faster relaxation of correlation at higher excitation power, especially at shorter correlation time in the FCS measurement, is attributed to increasing contribution of the off-state of the QDs. A decrease in the amplitude of the correlation at time zero $[G(0)]$ with increasing excitation power, despite an increasing fraction of the molecules in their off-state, is attributed to light-induced brightening of the dark QDs due to surface passivation at higher excitation power. The simultaneous occurrence of the two competing processes,

photoactivation leading to fluorescence enhancement and photodegradation resulting in quenching of the luminescence of the QDs, has been substantiated by the steady state and time-resolved emission measurements. It is suggested that surface passivation by photoadsorbed water molecules leads to photoactivation of the QDs and dissolved oxygen-induced photooxidation of the surfaces is responsible for subsequent drop of the luminescence intensity of the system.

The influence of ligand and solvent on light-induced modulation of the emission behavior of the QDs has been studied for CdTe QDs capped with hexadecylamine (HDA), mercaptopropionic acid (MPA) and 1-(1-undecanethiol)-3-methyl imidazolium bromide (SMIM) in CHCl_3 , H_2O and [bmim][PF₆] ionic liquid, respectively. Significant emission enhancement is observed only for CdTe/MPA in both aerated and de-aerated aqueous environment under light irradiation. A large decrease of the $G(0)$ value at higher excitation power in the FCS measurements is also observed only in the aqueous environment. These results unambiguously establish the critical role of the H_2O molecules in the passivation of the surface trap states of the QDs. In addition to H_2O -assisted photoactivation, photooxidation of the QDs is also shown to contribute to the light-induced modulation of their luminescence behavior.

Photostability and photoactivation of the QDs are the two important parameters which determine their applications in diverse fields. In order to study the effect of shell on the photoactivation and photostability of the CdTe QDs ZnS shell is grown over CdTe QDs. Significant improvement in the fluorescence properties is observed for CdTe/ZnS QDs compared to CdTe QDs in both CHCl_3 and aqueous environment. This indicates effective passivation of surface dangling orbitals of the CdTe QDs by the overgrowth of the ZnS shell. Photoactivation and photocorrosion in aqueous medium are observed only in CdTe/MPA QDs, but not in CdTe/ZnS(2ML)/MPA QDs. This clearly indicates that ZnS shell effectively protects the CdTe core QDs from external perturbations. FCS study further substantiates this fact as a large decrease in $G(0)$ value with increasing excitation power is observed only for CdTe/MPA QDs. This study clearly indicates that photoactivation of the QDs and decrease in the $G(0)$ value observed with increase in intensity of the exciting source are intimately related.

The diffusion behavior of three fluorescent system, electrically neutral coumarin 102 (C102), cationic rhodamine 6G (R6G), and anionic fluorescein (FL) in pH 7 phosphate buffered solutions of bovine serum albumin (BSA) protein in the absence and presence of NaCl and urea, has been investigated using FCS technique. The measured diffusion coefficients provide insight into the nature and strength of the interaction between the guest and host revealing the heterogeneity of the binding sites of the protein. The diffusion due to both free and BSA-bound molecule is observed in the case of C102-BSA system. This observation coupled with the fact that no exchange between free and bound probe is observed in the confocal volume, indicates stronger binding of C102 with BSA. On the other hand, fast exchange between the bound and free states of the molecules is observed for electrically charged hydrophilic dyes, R6G and FL, reflecting weaker binding of these dyes with BSA. The common salt and urea induced changes of the diffusion behavior allow identification of the association sites of the probes with the protein molecule.

The microscopic structure and dynamics of the RTILs that are responsible for some of the peculiar properties of this class of solvents continue to intrigue the researchers and stimulate new investigations. In the present study we have studied the translational diffusion of some environment sensitive probe molecules in several ionic liquids using FCS technique. Biphasic diffusion dynamics observed for the probes in these media is attributed to the microheterogeneous nature of these media resulting from the segregation of the alkyl chain of the constituents. The presence of polar and nonpolar regions in these ionic liquids is further substantiated by studies on the time-resolved fluorescence decay profiles of the system, which indicate biexponential decay behavior with lifetimes typical of the probes in polar and nonpolar environment. It is shown that a combination of the fluorescence correlation and lifetime techniques can provide useful information on the nature of the micro-environment of the complex media such as the ionic liquids.

8.2. Future Scope:

We have conclusively established that passivation of the surface trap states of the QDs by photoadsorbed H₂O molecules is responsible for photoactivation of the QDs. Photoactivation dominates during the early stages of irradiation whereas, at longer irradiation times surface photooxidation (known as photocorrosion) takes over. Both photoactivation

and photocorrosion of the QDs severely restrict the utility of the QDs in various applications. We have shown that for MPA-capped core/shell CdTe/ZnS(2ML) QDs in aqueous medium remain stable even after prolonged exposure to light. However, fluorescence quantum yield (QY) of these QDs (35%), is much lower than that of CdSe/CdS (QY ~ 90%) core/shell QDs. The low fluorescence QY of the CdTe-core based type-I core/shell QDs compared to the CdSe/CdS QDs is due to the presence of trap states at the interface between core and shell. Most of the shell materials resulting type-I band alignment with the CdTe core exhibit huge lattice mismatch, which creates strain in the core/shell QDs based on CdTe core, thus generating interfacial trap states. This interfacial strain can be reduced by using an intermediate shell material sandwiched between core and outer shell. In such kind of core/shell/shell structured QDs the intermediate layer acts as a lattice adapter between core and outer shell materials having a huge lattice mismatch. A second approach is to spread the lattice strain between two mismatched materials across a large number of atoms. Core/gradient alloy-shell/shell such as CdSe/Cd_{1-x}Zn_xSe/ZnSe is a perfect example of such kind of structure where lattice strain can be spread over many atoms by gradually increasing x from 0 at the center to 1 at the surface. These core/shell/shell and core/gradient alloy shell/shell QDs has been studied for CdSe based core system. However, as such studies are yet to be undertaken on the CdTe core based system, one can explore this aspect.

Binding strength as well as the binding sites of the probe in BSA was determined following the diffusion behavior of the fluorescent probes in solutions of the protein in the absence and presence of urea and NaCl. Hydrophilic dyes R6G and FL exhibit fast exchange dynamics between the free and protein-bound probe. However, this exchange kinetics could not be determined from FCS measurements as the probe molecules exhibit similar brightness in the bound and free states. It is possible to study this fast exchange dynamics (association and dissociation constant of the probe molecule with protein) by using a dye molecule, which binds weakly with protein and whose brightness changes significantly upon binding. It will be then interesting to see how the structural changes in protein molecule affect this exchange kinetics on addition of denaturing agents such as urea. Understanding the interplay between protein structure and exchange dynamics is very important in drug delivery and for the design of the drug molecules.

Microheterogeneous nature of the RTILs is revealed from the FCS and fluorescence lifetime study. This microheterogeneity of the RTILs that arises due to the segregation of the alkyl tails into mesoscopic domains, is known to occur over a scale of few nanometers (nm) and. It will be interesting to study the diffusion of the fluorescent dyes in RTILs with increasing polarity of the side chains. The mesoscopic structure of the RTILs can be disrupted due to repulsion of the polar side chains. In addition to FCS, measurements based on other techniques such as small and wide angle X-ray scattering (SWAX), Raman scattering, neutron scattering, optical Kerr effect can also be carried out to obtain a clear picture on the structural details of RTILs. One of the major obstacles in the FCS study on RTILs is the large background scattering due to the RTILs, which interferes with the fluorescence signal of the probe molecules. However, this problem can be dealt with by using a combination of stimulated emission depletion and FCS (STED-FCS) technique. STED-FCS will significantly lower the observation volume and thus will minimize the background signal. This will also allow one to use a higher concentration of the fluorophore in the measurements. We hope that FCS-STED approach will provide more detailed insights on the microscopic structural details of the RTILs in recent future.