Chapter 8

Summary and outlook

The present thesis is an attempt to carry out an exposition of the radiation and photochemical investigation of three microheterogeneous systems i.e. microemulsions, room temperature ionic liquids, and cyclodextrins, which are entirely different from each other with respect to their structure, nature of heterogeneity, composition and fluidic aspects. It is of fundamental interest as well as quite intriguing to probe the primary processes (such as electron solvation, electron transfer, free radical reactions etc.) in these media taking into account of their dissimilarities from the homogeneous systems. Subsequently, the influence of the inherent compartmentalized structural organization of these media on the morphology and the photoluminescent properties of the QDs were explored. The summary of the important findings of the work described in chapters 3, 4, 5, 6, and 7 and their outlook have been consecutively presented here.

In chapter 3, an attempt was made to comprehend the solvated electron properties in a cationic surfactant based quaternary w/o microemulsion (i.e. CTAB/H$_2$O/n-butanol/cyclohexane). It was observed that almost half of the dry electrons get solvated in the interface, while rest could escape the interface to be hydrated in the water core. Thus, the interface of the microemulsion actually impedes the solvation process and the signature of which is visible even up to few microseconds. The electrons are more stabilized in the interface as compared to that in the water core. The physical nature of the
interface becomes comprehensible with the observation of effect of $W_0$ on the lifetime of the electrons solvated at the interface. At higher $W_0$, solvated electrons at the interface become more mobile to interact amongst themselves and also gather higher probability to escape to water core and interact with hydrated electrons in addition to the other species if present. The presence of counter ions in microemulsions has not been seriously considered in earlier studies on radiation chemical as well as dynamical studies. The formation of counter ion radical i.e. $\text{Br}_2^-$ could be observed and characterized. Consequently, a two phase reaction between inorganic radicals produced in the aqueous core and a molecule that is completely insoluble in water has also been demonstrated. The spinoff of this particular part is a significant improvement in the well established kinetic protocol for free radical scavenging and antioxidant activity assay, which can now be applicable to molecules soluble in solvents with wide polarity assortment.

In chapter 4, CTAB based w/o microemulsions were employed as a template for the synthesis of CdSe QDs by normal chemical and radiation chemical route. It was observed that the dimensions of water pool in CTAB microemulsions have poor correlation with the size of the QDs. However, photoluminescent properties of the nanoparticles were found to vary with the $W_0$ values of the CTAB microemulsions. And, it was attributed to the probable variation in the shape of the nanoparticles. The nanoparticles exhibited excitation wavelength dependent PL spectra and the ratio of BG-PL and the TS-PL could be tuned by varying the precursor concentrations and the $W_0$ values. On the contrary, the PL properties displayed by CdSe nanoparticles synthesized in CTAB based microemulsions via electron beam irradiation technique were predominantly originated
from the trap states. A comparative study was conducted to investigate the fundamental role of the structural dynamics, interfacial fluidities and the chemical nature of the water pool of cationic (CTAB) and the anionic (AOT) surfactant based microemulsions in governing the morphology and various photophysical properties of QDs. Interestingly, profound and contrasting results were observed, for example, the average PL lifetime values and the quantum yields of the QDs grown in case of CTAB microemulsions were found to be at least 3 times lower as compared to that in AOT microemulsions. These results emphasize the necessity of judicial selection of the host matrix (or the template) in the synthesis of QDs. Furthermore, the inherent property of electron beam to dump large amount of energy in a small time scale leads to the formation of unsatisfied vacancies on the surface of the QDs. However, an attempt has been made to tap this feature in conjunction with the controlled induction of the surface/trap states to manipulate the band gap and the surface composition of the QDs. Evidently, the PL lifetime values could be increased from ~18 ns to as high as ~74 ns (in case of AOT microemulsions). This interesting aspect can contribute to the better understanding of the role of trapping sites on the dynamics of charge recombination processes, which eventually governs the efficiency of solar cell devices. By optimizing various experimental parameters, stable bluish-white light emitting ultrasmall CdSe QDs were obtained and the band gap of the QDs was engineered to achieve tunable broadband light emission extending from 450 to 750 nm. Such characteristics are essentially desirable for WLED applications. The methodology of combining the advantageous properties of electron beam irradiation technique with the templated synthesis of microemulsion method is relatively new for
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semiconductor nanomaterial synthesis and renders unique conditions to achieve a much finer control over the composition, morphology and size of the QDs.

Owing to the high hydrolytic stability of FAP based imidazolium ILs, an assortment of characterization and qualitative studies were performed to explore their radiation stabilities and the same has been presented in chapter 5. The insignificant variations in the physicochemical properties even at high radiation doses clearly indicated the hidden potential of FAP based imidazolium ILs to be a good solvent for various applications involving high radiation fields. The color evolution in the post-irradiated ILs attributed due to the formation of oligomeric and multiple bond order group containing radiolytic products as indicated from the mass and vibrational studies, respectively. Besides, the hydrogen gas yields of FAP ILs were found to be comparable to that of a radiolytically stable aromatic compound, benzene. The significant radiation resistance put forth by FAP ILs has been correlated well with the fractional stopping power of the FAP anion, which clearly implicates it as an effective protector/shield (among various other fluoroanion based ILs) to the cation. However, the influence of the introduction of a hydroxyl group (in the alkyl side chain of the imidazolium moiety) on the radiation resistance of the IL was found to be detrimental, as it resulted into significant changes in the properties (of the IL) such as thermal stability, conductivity and electrochemical window. The transient spectroscopic studies carried out to delineate the radiolytic sensitization effects of the hydroxyl group on the reaction mechanistic pathways clearly showed a marked difference (from the non-hydroxyl IL) in the reactivity, reaction center and the nature of the radiolytic products. Furthermore, photophysical investigations of post-irradiated FAP ILs
showed considerable changes in the orientations and the molecular rearrangements of the ionic moieties. Moreover, such studies would be helpful in gaining the microscopic insight of the radiation induced mutations in the structure-property relationships and the nature of various interactions existing in ILs. However, for the practical applications of ILs in industrial and other areas involving high radiation fields, a lot of important aspects need to be probed. These are electron solvation and scavenging mechanisms in conjunction with various relaxation processes such as radiative, non-radiative and dissociative pathways of energy dissipation.

Chapter 6 demonstrates the application of RTILs as a novel media for the synthesis of self-assembled superstructures of nanomaterials. CdSe nanoparticles were grown in neat imidazolium based IL via radiation as well as normal chemical route. In either of the synthetic methodologies, it was observed that IL played multiple roles, i.e. a solvent, stabilizing agent and a shape directing template. In case of radiation chemical synthesis, the electron beam induced nucleation and the subsequent growth process directed by the matrix of IL leads to a unique nanomorphology, i.e. islands of CdSe within the Se nanofibers. The applications of such morphology can be envisaged from its 3-D highly porous networking structure, as the nanostructures with high surface area and porosity exhibits tremendous potential in sensing and catalysis. Furthermore, the dose rate was found to influence the growth mechanism, i.e. 3-D structure was obtained in the electron beam induced case, while 1-D structures were observed in γ-ray assisted synthesis. The mechanism proposed for the obtained nanostructures may provide an intuitive protocol for the development of such complicated nanomorphologies by employing ILs as
templates. In the normal chemical synthetic route, co-existence of anisotropic 2D sheet and flower-like 3D nanostructures was evident. The fluidic aspects of the IL in conjunction with its hydrogen bond-co-π-π stacking mechanism enabled it to perform a function of a diffusion controller and an anisotropic growth director, respectively. Accordingly, a possible mechanism for the formation of self-assembled anisotropic nanostructures has been provided. The fundamental role of water in creating a perturbation/distortion in the networking structure of the IL has been demonstrated. These results reflect the potential to maneuver the morphologies of the nanomaterials by precisely controlling the presence of water in the host matrix of the IL. However, further investigations are necessary for the better understanding of the role of intrinsic microheterogeneity prevailing in the RTILs, so that these media could be used in fine tuning the morphology of the nanoparticles vis-à-vis their properties and applications.

In chapter 7, a simple, rapid and one step method assisted by electron beam irradiation technique has been demonstrated for the synthesis as well as in situ functionalization of CdSe QDs with β-CD in aqueous solution. Through transient absorption studies, the possible mechanism for the formation of β-CD/CdSe nanoparticles was elucidated and it was inferred that β-CD do not interfere in the dynamics of radiolytic formation of CdSe nanoparticles, rather it acts as a capping or stabilizing agent. Some interesting orientation patterns of the QDs (i.e. pearl necklace shaped) were observed and attributed to the directional nature of forces of interaction between the β-CD molecules coating the QDs surface. Another important physical aspect of the present work is the tuning of optical properties of the QDs, which could be achieved by optimizing various experimental
parameters. Since, electron beam irradiation of the solutions could be carried out in the common industrial accelerator plants (generally used for sterilizing medical kits and other items); therefore this methodology could find promising applications in the large scale and cheaper production of QDs. In addition, this technique is attractive from the viewpoint of clean chemistry (no external reducing agent is involved) and ensuring reproducibility in the synthetic protocol. The employment of supramolecular assemblies such as β-CD makes this method more advantageous, as can be realized from the following points. It was observed that the β-CD molecules cap the as grown CdSe QDs by forming a non-inclusion complex. Therefore, the individual QDs self-aligns in the form of chains through the hydrogen bonding between the -OH groups of β-CD molecules chemisorbed on their surface. Apparently, it could be anticipated that the interactions between the individual nanospheres would be significantly enhanced. And, this could have considerable impact on the optoelectronic properties of such QDs, as the self-alignment can eventually boost the charge transport carrier efficiencies. Nevertheless, this could be a topic of further investigation. Furthermore, the bio-compatibility of β-CD is well proven and holds the potential in decreasing the toxicity of CdSe QDs, as has been observed from the cytotoxicity studies. Hence, the present methodology not only provide a rapid and one step approach to synthesize QDs but the employment of β-CD like supramolecular assemblies ensures fairly good colloidal stability, water dispersible, low cytotoxicity and most essential is the template free self-assembling tendency. The potential application of these β-CD/CdSe QDs in white light emitting devices has also been demonstrated.
**Future perspective**

As discussed earlier, microheterogeneity is one of the basic and versatile features of many natural systems, and plays a vital role in directing/influencing the fundamental processes such as electron, charger transfer and other free radical reactions. An in-depth understanding of these processes is pertinent for variety of societal applications. The investigations presented in the thesis may contribute toward this endeavor. For instance, the study of two phase reactions in CTAB based w/o microemulsions may significantly improve the existing protocol for free radical scavenging and antioxidant activity assay. This method now can be applicable to molecules soluble in solvents with wide polarity assortment. In radiation chemical studies of imidazolium ionic liquids, it was clearly demonstrated that even a diminutive alteration in the molecular structure of these fluids might cause marked differences in the reactivity, reaction center and the nature of the radiolytic products, which eventually lead to the significant changes in their physicochemical properties. Such findings can be of immense importance considering the potential applications of room temperature ionic liquids in high radiation fields such as space and nuclear fuel cycle.

The influence of the structure, dynamics and fluidic aspects of the microheterogeneous systems in conjunction with the inherent features of the radiation techniques was explored in directing the morphology and the photophysical properties of the CdSe nanoparticles. The mechanism behind the formation of self-assembled nanoarchitectures has been provided. Such information can be useful in synthesizing unique superstructures of other nanomaterials as well, which are important from the
fundamental point of view. Finally, the self-effacing inference here is that, attempts have been made to resolve important issues, which have been raised in the introduction of the thesis through systematic investigations. However, there is ample scope for future research in understanding the heterogeneous structural features of room temperature ionic liquids through radiation and photochemical techniques.