

7. SUMMARY

Although a wide range of synthetic methodologies are now available for the synthesis of semiconductor NPs; however there is still a major problem associated with the reproducible preparation of robust materials of the kind that will be needed for technological applications. The unique properties of these materials, especially the possibilities for band gap tailoring and tuned luminescence, can lead to their potential use in many future technologies. The various generic methods have advantages as well as certain disadvantages too, that are needed to be pinpointed through detailed and comparative investigations. Among many chemical synthetic methods, the colloidal methods, as a top-down approach to nanotechnology, are of immense advantage because of low temperatures and trouble-free compatibility with coatings onto other soft substrates. An understanding of the surface chemistry of the semiconductor NPs (i.e., the nature of capping agents) is equally important. Colloidal methods, though the first way to prepare nanodispersed materials, still have problems with particle instability and precise size control. With endeavor to improve this perspective, the present work is an effort for diligent study on colloidal synthesis of semiconductor NPs. Five cationic surfactants (CTAB, TTAB, DTAB, CPyC, CTAC) and three anionic surfactants (SDS, SDBS, SL) have been chosen to assess their capabilities in synthesis of stable NPs. The main emphasis in this work has been on two important aspects: First, to compare the role of surfactant structure on various aspects of a specified semiconductor NPs and second, the selectivity of surfactant-semiconductor interactions by comparing the role of a particular surfactant on different semiconductor NPs.

The NPs have been synthesized by simple mixing the aqueous surfactants solution containing the metal acetates and Na_2S . Although various characterization techniques have been used to establish the role of surfactants in stabilization of ZnS NPs, the major information has been derived from two simplest techniques i.e. UV-vis spectroscopy and PL emission spectroscopy. The preliminary results of concentration dependence have revealed that the average sizes of NPs are independent of $[\text{ZnS}]$ and surfactant concentration. Therefore, a fixed surfactant concentration of 3 mM has been used to compare the role of various surfactants. Formation of highly stable, spherical ZnS NPs in the size range of 3–40 nm has been evident from TEM images in all the surfactants except DTAB. A well defined surfactant dependent

absorption shoulder in 292-310 nm regions is characteristic for ZnS NPs. The optical band gap and particle size calculated by applying quantum mechanical model to UV-vis spectra of as prepared NPs have revealed the strong dependence of these two parameters on surfactant structure. The particle size increases with decrease in hydrocarbon chain length in cationic surfactants whereas; the anionic surfactants with similar chain length have stabilized the ZnS NPs at comparatively smaller sizes. The smallest size of ZnS NPs obtained in SDBS followed by CPyC, CTAC and CTAB has inferred that either the large head group with aromatic ring or the longer hydrocarbon chain are essentially effective in stabilizing the ZnS NPs at smaller sizes. A new modification, correlating the particle size distributions with slope of the linear region (M_{ES}) between absorption edge and absorption shoulder of UV-spectra has also been worked out for the ZnS NPs. A high M_{ES} value has been proven as an index for the narrow size distributions and low M_{ES} for broad size distributions. On the basis of M_{ES} values, the significantly different size distributions of ZnS NPs for CTAB/CTAC/CPyC, TTAB/DTAB and SDS/SDBS surfactant pairs has justified the reliability of slope method.

The changes in absorption spectra as a function of time have been proven as an indicative of growth kinetics and aggregation of the ZnS NPs. In four cationic surfactants, the slight red shift in small wavelength region of absorption shoulder without any apparent change in spectra or band edge position indicates certain structural transitions from metastable to stable ZnS without much affecting the average particle size. In DTAB, the continuous reduction of absorption spectra without any noticeable shift in the band edge position also indicates the immediate growth and precipitation of NPs after nucleation. The successive red shifts in spectra with time have justified the Ostwald ripening phenomenon responsible for the growth of the NPs in anionic surfactants. The changing spectral features after 20 h ripening and 3 h UV-irradiation reveal an increase in size due to Ostwald ripening alongwith some changes in the crystal lattice of ZnS NPs, which in turn leads to certain structural transitions in the adsorbed surfactant over the surface of NPs.

The XRD patterns of the powdered ZnS NPs after washing off the excess surfactant have indicated their cubic phase. The broadening of peaks in accordance with nanocrystalline nature have been justified by measuring crystallite size (6 ± 0.7 nm) using Debye-schererr formula on $\langle 100 \rangle$ peak. The identical XRD peak broadening for all ZnS samples irrespective of the surfactant structure has proved that

the different tendencies of surfactants towards NPs stabilization are significant only in aqueous solution. The SEM images of powdered ZnS NPs display nearly spherical particles in all the samples except in DTAB where SEM depicts irregular shapes. Magnified view shows single particle as an ensemble of many small primary particles. The stability of ZnS NPs, as assessed from zeta potential values, for a given surfactant concentration increases with the hydrocarbon chain length of cationic surfactants due to progressively increased hydrophobicity. Furthermore, the adsorbed cationic and anionic surfactant aggregates have generated positively and negatively charged slipping planes, respectively, over otherwise negatively charged bare NPs by forming nearly bilayer structure over the surface. The FTIR analysis has also justified the adsorption of surfactants through head group over the NPs surface.

The surfactant stabilized ZnS NPs display strong fluorescence in 350-550 nm wavelength range with maxima in the vicinity of 440 nm associated with surface defect with minor contribution from the band-edge emission. The varying surface emitting states during nucleation and growth has been assessed through time evolution studies. The exceptionally high PL enhancement with time in the presence of CPyC, SL and SDBS indicates the possible influence of pyridinium, carboxylate and benzene moieties as surfactant head group containing π -electrons, which have undergone electronic transitions when irradiated with spectrophotometer light. After 20 h of ripening in normal room conditions, the drastic PL enhancement of 342 and 263 intensity units in SL and SDBS capped NPs, respectively and similar drastic enhancement in CPyC stabilized ZnS NPs as compared to other cationic surfactants also supports the π -electrons participation in PL enhancement. The NPs stabilized with anionic surfactants display fairly good PL stability even after 75 h i.e. these surfactant have been able to maintain higher PL emission than it was before irradiation. On the other hand, the PL emission of CTAB and TTAB stabilized ZnS NPs drops even below than it was before UV-irradiation.

Similarly, the comparative accounts of the same eight surfactants have also been analyzed *w.r.t.* stabilization and different properties of CdS NPs. The TEM and DLS studies have evidenced the formation of fairly monodispersed NPs of 7–12 nm dimensions as pale yellow aqueous dispersions. The SDS and SDBS stabilized CdS NPs display unique flower like pattern in TEM images due to association of 8-10 NP during sample drying process. The UV-vis spectra of surfactant stabilized CdS NPs have an absorption onset in 470-490 nm range with a characteristic shoulder in 390-

410 nm region. The band gap values and average sizes of the CdS NPs capped with cationic surfactants of same C₁₆ chain length are nearly same with smallest value in CPyC. In concurrence with ZnS NPs, the size of CdS NPs also increases with decreasing hydrophobic chain length and least stabilized NPs in DTAB have been precipitated within half an hour of their formation. The anionic surfactants of smallest chain length (C₁₂) have stabilized NPs at comparatively smaller sizes.

The CdS NPs in all the surfactants except in TTAB and DTAB display nearly identical time evolution absorbance profiles. In TTAB, the absorbance displayed steep rise and then slow decrease after attaining small plateau of maximum absorbance due to disappearance of some nucleated particles by transforming in to the bigger ones. However, the NPs in DTAB display prominent decrease in the absorbance due to their precipitation within 20 min of their formation. The rate constant obtained by fitting the absorbance profiles to pseudo first order has increased 2.5 fold just by changing the counterion of the surfactant from Br⁻ to Cl⁻. In addition, by changing the head groups in CPyC to CTAC, SDBS to SDS and SL, the rate constants have also increased by 3.7, 2.7 and 2.5 time, respectively, which reveals that the larger head group size inhibits the process of particle formation/growth. The time evolution UV-vis spectra display beautiful isosbestic behavior at 388±5 nm for the NPs stabilized with surfactants with C₁₆ chain length due to the growth of CdS NPs of particular size range at the expense of very small particles. The decrease in the spectral absorbance recorded after 24 h along with blue shift indicates the coalescence of particles during growth. In photocorrosion process, the CdS NPs have been bleached by daylight in aqueous solution leading to the formation of CdSO₄.

The XRD patterns have justified the pure cubic phase of CdS NPs with average crystallite size of 2.1±0.1 nm irrespective of surfactants used in the synthesis. The decrease in zeta potential values of CPyC, SL and SDBS stabilized CdS NPs after attaining a peak value has revealed that only a definite amount of each surfactant depending up on their molecular structure is sufficient to stabilize the NPs and the excess surfactant either do not involve in stabilization or even show destabilizing effect. The colloidal CdS NPs display a broad PL emission ranging from 400 to 700 nm due to radiative recombination of charge carriers immobilized in deep-trap states of different energies. The prominent increase in PL emission of CdS NPs with time in the presence of CTAB, CPyC, TTAB, a decrease in CTAC and decrease after slight

initial increase in SL, SDS and SDBS have been attributed to continuous modification of surface emitting states depending upon the nature of surfactant-NPs interaction. The PL intensity of CdS NPs has also been increased after 20 h storage time in all the surfactants due to elimination of surface defects via dissolution reaction that lead to the formation of surface hydroxide layer. In the similar manner, 3h UV-irradiation has also led to drastic PL enhancement for the CdS NPs stabilized in all the surfactant except TTAB and SDS due to possible photodissolution similar to that observed in normal room light. The prolonged stability of CdS NPs PL emission after photoactivation has been evident from the enhanced PL emission which remains constant in all the surfactants with a little loss even after 20 h.

The comparative role of surfactants has also been investigated on the formation and stabilization of HgS NPs as dark brown suspensions in aqueous surfactant media. Spherical HgS NPs in 8-15 nm size range with a good uniformity in size and shape have been evidenced from TEM. The HgS NPs have featureless UV-vis absorption spectra with a tailing absorption onset in the range of 495-510 nm. The overall increase in baseline absorbance with increasing HgS concentration indicates continuous network of NPs at high concentration with increase in particle size. Nearly identical stabilization has been provided by four cationic surfactants viz. CTAB, CTAC, CPyC and TTAB. In time profile of the UV-vis absorption spectra, the increased baseline absorbance and successive red shifts indicate the increasing NPs size with time i.e. the growth of the NPs. The large head group moieties of CPyC and SDBS have restricted the immediate growth of the HgS NPs. The formation of HgS NPs follows pseudo first-order kinetics and significant variations in rate constant values have supported the varying tendencies of the surfactants in formation and stabilization of NPs. Unlike ZnS and CdS NPs, no significant changes have been noticed in the UV-vis spectra even after 20 h storage except a little downward shift in HgS NPs stabilized with CPyC and SDBS indicating the stability of HgS NPs towards surface corrosion. The XRD analysis has indexed the cubic or β -phase of the HgS NPs in all the surfactants. The HgS NPs do not display any PL emission peak in 400-800 nm wavelength range in any of the surfactants for different excitation wavelengths analyzed.

In conclusion, all the eight surfactants have been proven to be efficient capping agents to produce stable NPs. The stabilizing tendencies of cationic

surfactants decrease with decrease in their hydrocarbon chain length more prominently for ZnS and CdS NPs. The anionic surfactants of same hydrocarbon chain length have been found to be more efficient stabilizer towards the studied NPs than the cationic ones. However, the HgS NPs have been sufficiently stabilized even by DTAB whereas the other two (ZnS and CdS NPs) precipitated within half an hour. The stabilization tendencies of the surfactants therefore, can not be generalize and depends specifically upon the nature of surfactant-NPs interactions. The role of various surfactants in maintaining the size, shape and aggregation tendencies of the studied NPs has been limited to solution form only and the particles averages to nearly same size and shape in powder form. The PL emission properties of the semiconductor NPs have been significantly governed by the head group structure of the surfactant as well as the nature of semiconductor material. In nutshell, the presented study has explored the colloidal chemistry approach for the development of 'nano-factories' by demonstrating the ability of various surfactants in synthesis of semiconductor NPs with splendid optical and PL properties. Still certain issues need to be addressed from surfactant-NP interaction point of view, before such a synthesis approach be completely applied to develop commercial protocols.