Published in Colloids and Surfaces A: Physicochemical and Engineering Aspects
Volume 232, Issues 2-3, 23 January 2004, Pages 119-127
http://dx.doi.org/10.1016/j.colsurfa.2003.10.021

Synthesis of CdS-Ag_2S Core - Shell / Composite Nanoparticles using AOT/n-heptane/water Microemulsions

G. Hota,[1] Shikha Jain[2] and Kartic C. Khilar[1*]

[1] Department of Chemical Engineering, Indian Institute of Technology, Bombay, Powai,
Mumbai 400076, India.

[2] Department of Chemical Engineering, H.B.T.I., Kanpur, India.

* To whom correspondence should be addressed.

E-mail: kartic@che.iitb.ac.in

Contact No. 91-22-25767230

Fax No. 91-22-25726895

Abstract:

An attempt has been made to synthesize CdS-Ag_2S core-shell and composite nanoparticles using AOT/n-heptane/water microemulsion technique. We have systematically studied the different microemulsion mixing methods to prepare core and shell nanoparticles. Four methods have been used. Whilst all methods produced nanoparticles and nanocomposites, only two i.e. the post-core and partial microemulsion methods have shown promise for core and shell formation and enhanced stability and sphericity of the nanoparticles. These core and shell nanoparticles and nanocomposites have been characterized using TEM, EDAX, photoluminescence and UV-VIS spectrophotometer techniques. Results and possible mechanism of formation of nanoparticles via all four methods have been discussed.

Key words: Core-Shell; Nanoparticles; Nanocomposites; W/O Microemulsions;
CdS-Ag_2S

1. Introduction

Nanoparticles, particles in nanometer size range are attracting increasing attention with the emergence of nanotechnology. Nanoparticles display fascinating electronic and optical properties arising out of their small dimensions and they may be easily synthesized from a wide range of materials. Nanophase and nanostructure materials as a component of nanotechnology have attracted a great deal of attention of today's research. Arising out of its ultra-fine sizes, high surface areas, useful interfacial defects and interface dominated character, nanoparticulate materials are used as key components in many areas such as electronics and optical devices [1-4], pharmaceuticals [5], paints [6], coatings [7,8], superconductors [9], semiconductors [10-12] and catalysis [13,14].

Different metals [15-17], metal sulfides [18-22], oxides [23], ceramics, composites [24-28] and core-shell [29-32] (coated) nanoparticles having crystalline, amorphous and polycrystalline phases with unique and improved mechanical, chemical, magnetic [33], electronics and optical properties, have been synthesized in last few decades using different preparation techniques. Microemulsion technique offers good promises for preparing some of these nanoparticles, at room temperature and pressure [15,18,23,27].

Microemulsion technique provides a micro-heterogeneous medium for generation of nanoparticles [34,35]. This technique involves precipitation reaction with in the aqueous core of reverse micelles. Two water-soluble compounds that will react to form a precipitate are dissolved separately into two microemulsions of specific composition. The resulting microemulsions are then mixed together; causing precipitation reaction to occur within the aqueous core of reverse micelles to form the nanoparticles.

The formation of nanoparticles in such system is controlled by the reactant distribution in the nanodroplets and by the dynamics of inter-micellar exchange [15]. The surfactant-stabilized micro-cavities provide a cage-like effect that limits the particles nucleation, growth and agglomeration, in a complex manner.

Several research groups have conducted studies on the preparation of CdS and Ag_2S nanoparticles and have investigated the quantum size effect [3,18,20]. Foglia et al. [19] have reported the sol-gel synthesis of CdS nanoparticles with different surface capping organic molecules. In this paper the CdS particles obtained were either in the form of nanoparticles or nanoclusters having the size range of 8-20 nm.

The mechanism of formation of CdS ultra-fine particles in w/o microemulsion by the chemical reaction between $Cd(NO_3)_2$ and Na_2S have been studied [17,18]. The authors have reported the effect of reactant concentrations and water content on the particle diameter. Nanosize Ag_2S semiconductor particles have been synthesized in reverse micelles [22]. The size and polydispersity of Ag_2S nanoparticles is controlled by the size of water droplets. Standard techniques such as TEM, XRD, have been used to characterize the nanoparticles, primarily for their size, shape and contents.

Recently, attempts have been made to prepare core-shell nanoparticles and nanocomposites of both organic and inorganic materials [36-40]. Core-shell nanoparticles are essentially defined as the particles containing a core and a shell and have dimensions in the nanometer range. Core-shell nanoparticles often exhibit improved physical and chemical properties over their single-component counterparts, and hence are potentially useful in a broad range of applications. The controlled synthesis of novel, uniformly coated stable nanoparticles have for many years remained as a technical challenge.

Qi et al. [38] have synthesized CdS - coated ZnS (ZnS@CdS) nanoparticles using AOT/heptane/water microemulsions. They have characterized the core and shell nanoparticles using optical absorption and photoluminescence spectroscopy. They have observed that the absorption spectrum of ZnS@CdS is similar to that of CdS@ZnS. They did not observe any significant luminescence activation. Han et al. [36] have conducted the nonlinear absorption studies of coated CdS@Ag_2S nanoparticles, prepared by inverse microemulsion technique. The authors have reported that the existence of a long absorption tail covering the entire visible spectra region is due to the formation of Ag_2S shell on the surface of CdS core nanoparticles. Recently titania-coated silica, and silica-coated iron oxide nanoparticles have been synthesized in water-in-oil microemulsion [39,40].

The mechanism of core and shell nanoparticles formation is not well understood. It is not even clear how core and shell nanoparticles can be convincingly documented and adaquately characterized. None of the studies done so far is clearly successful in measuring the shell thickness. It is not certain that some of TEM micrographs showing good contrast to discern core from the shell can be used for other materials or for that matter, at lower size level. Overall, the research on the formation and characterization of core and shell nanoparticles is in its infancy and focused studies are called for, to develop further on the formation method as well as on the characterization technique.

In our study, we have used four different microemulsion addition methods in an attempt to produce core and shell nanoparticles. CdS-Ag_2S nanoparticles were used as core and shell. Two methods are used, which strongly indicate the formation of core and shell nanoparticles whilst the other two indicate the formation of composite nanoparticles. Nanoparticles are produced at different conditions. Results are discussed and interpreted to gain insights into mechanism of formation.

2. Experimental Section

2.1. Materials used

The surfactant, Dioctyl Sulfosuccinate Sodium Salt (Aerosol OT, or AOT) was purchased from Sigma with 99% purity. Silver nitrate of AR grade and Cadmium nitrate of LR grade were purchased from S.D. Fine (India) chemicals. $(NH_4)_2S$ (Ammonium sulfide) 25% and n-Heptane was purchased from SISCO, India. Heptane was used after refluxing over sodium wire for 2 hours to remove any moisture. Double distilled water was used throughout the experiments.

2.2. Sample preparation and characterization

Aqueous solution of cadmium nitrate (0.1M), silver nitrate (0.1M) and ammonium sulfide (0.2 M) were freshly prepared. Neat, clean and previously dried 15 ml centrifuges tubes with stopper and small glass bottles (Scam, India) were used to carryout the experimental work. Surfactant solution (stock solution) of concentration 0.1 M, was prepared by mixing appropriate amount of AOT in n-heptane as a continuous medium.

Han et al. [36] have studied the formation of w/o microemulsion at different concentrations of AOT, n-heptane and aqueous salt solution. The clear region of w/o microemulsion was determined visually by titrating the aqueous solution to Na AOT – n heptane solution. The clear turbid boundaries were established from systematic titration. The compositions chosen in this work fall in the clear region of w/o microemulsion.

2.2.1. Preparation of core nanoparticles

A microemulsion was prepared by solubilizing 0.045 ml of 0.1M $Cd(NO_3)_2$ solution in 2.5 ml of 0.1M AOT / n-heptane stock solution as reported earlier. A second microemulsion was prepared by solubilizing equal volume i.e. 0.045 ml of 0.2M aqueous $(NH_4)_2S$ in 2.5 ml of AOT stock solution. Water to surfactant molar ratio (R) in this case was maintained 10. The two microemulsions were mixed to produce a third microemulsion containing the CdS nanoparticles. Thus, these CdS nanoparticles prepared would be utilized as core nanoparticles.

2.2.2. Preparation of core-shell/composite nanoparticles

In an attempt to prepare core-shell/composite nanoparticles, we have used four different addition methods using w/o microemulsions. These methods are as follows.

a. *Post-core method*: In this method, a microemulsion, μE of $AgNO_3$ solution was added to the μE containing CdS nanoparticles, which shall act as cores. The microemulsions containing core nanoparticles of CdS also contains the S^{-2} ions since excess amount of $(NH_4)_2S$ was added while preparing the core nanoparticles.
b. *Partial microemulsion method*: This method is similar to the post-core method except the fact that the $AgNO_3$ solution was not added in the microemulsion form. It was directly added in aqueous form and in a drop wise manner followed by proper shaking.
c. *Simultaneous mixing method*: In this method, μE of $Cd(NO_3)_2$ and μE of $AgNO_3$ were added to the μE of $(NH_4)_2S$ simultaneously in a drop wise manner.

d. *Premixing method*: In this method, prior to making microemulsion, the aqueous solution $AgNO_3$ and $Cd(NO_3)_2$ were mixed. Then this mixed solution was used to make a microemulsion of salt solution. To this μE, equal volume of μE of $(NH_4)_2S$ was added.

2.2.3. Spectroscopy studies

Absorption spectra were recorded using Shimadzu UV-VIS Spectrophotometer (UV-165). The microemulsion containing nanoparticles were used directly for absorption studies. Blank microemulsion (without reactants) was used as reference in UV-VIS spectrophotometer.

Fluorescence spectra were obtained on a Perkin Elmer LS 55 Luminescence spectrometer. The excitation wavelength was 400 nm and slit width was taken as 10 nm for excitation and emission. Fluorescence measurements were obtained from the microemulsion solution containing nanoparticles using quartz cuvettes.

2.2.4. Electron microcopy studies

A Philips CM 200-HR TEM has been used to characterize the particle size. The maximum resolution of the instrument is 0.2 nm. TEM samples were prepared by placing a drop of microemulsion containing nanoparticles directly onto carbon coated copper grids. After 10 minutes, the grid was dipped in sufficient amount of n-heptane in order to remove all the surfactants and then dried for an hour under IR lamp before taking images. Particles size distribution is obtained using soft imaging analysis system.

3. Results and Discussion

The formation of CdS and Ag_2S nanoparticles in the aqueous core of w/o microemulsion follows the precipitation chemical reaction, as shown below.

$$Cd(NO_3)_2 + (NH_4)_2S \text{ ® } CdS\downarrow_{\text{(yellow)}} + NH_4NO_3$$

$$AgNO_3 + (NH_4)_2S \rightarrow Ag_2S\downarrow_{\text{(gray)}} + NH_4NO_3$$

The UV-VIS spectra of CdS, and Ag_2S nanoparticles are shown in Figure 1. Water to surfactant molar ratio R is kept constant and is equal to 10. These spectra illustrate many characteristics of CdS and Ag_2S particles formed. Spectrum 1-a shows an absorption onset at 480 nm, a characteristic shoulder peak at 410 nm. All these characteristics correspond to those of CdS nanoparticles [17]. Spectrum 1-b presents the absorption spectra of Ag_2S nanoparticles. However, unlike the CdS spectrum, it does not show a shoulder rather it shows a long absorption tail between 500 to 800 nm. These characteristics correspond to those of Ag_2S nanoparticles [22].

Figure 2 shows the TEM micrographs and particle size distributions of CdS and Ag_2S nanoparticles. We observe from the micrographs that the particles are well dispersed. We further observe that CdS nanoparticles are non-spherical in shape while Ag_2S nanoparticles are nearly spherical in shape. The particle size distribution has a wide distribution. The arithmetic average diameter is calculated to be 2.8 nm for CdS and 4.7 nm for Ag_2S particles as shown in the Fig. 2-b and 2-d. These average sizes agree reasonably well with the calculated sizes using Brus equation from the absorption data. The electron diffraction pattern of both CdS and Ag_2S nanoparticles show ring pattern. This result indicates that both CdS and Ag_2S nanoparticles formed are polycrystalline in nature.

UV-Visible spectra obtained from the addition techniques to obtain core-shell/nanocomposites are indeed, difficult to interpret. It should be mentioned here that since the particles are formed due to intermicellar exchange, and intermicellar exchange being random in nature, four different types of particle formation might take place. These are CdS, Ag_2S, CdS-Ag_2S core-shell and composite nanoparticles. The absorption spectra of the sample containing these particles may turn out to be a complex combination. Nevertheless, we believe that in the mixing methods used, either the formation of the core-shell or nanocomposite is dominant, while the formation of CdS and Ag_2S nanoparticles is comparatively much less. To the best of author's knowledge, there is, however, no technique available to distinguish these four types of particles in a quantitative manner, in the mixture.

The absorption spectra of microemulsion supposedly containing Ag_2S coated CdS, (CdS@Ag_2S) and composite nanoparticles at constant water to surfactant molar ratio (R=10), prepared by four different microemulsion mixing methods are shown in Figure 3. We observe from this figure that all the four spectra for four mixing methods do not show a shoulder at 410 nm for CdS. We further observe that all the spectra show long absorption tails in the wavelength range 500-800 nm indicating the presence of Ag_2S. The spectral characteristics of CdS nanoparticles (i.e. a shoulder at around 410 nm) were not found in these spectra. This indicates that the CdS core nanoparticles are either coated with a Ag_2S layer or forming Ag_2S/ CdS composites. The spectrum 3-a and 3-b for post-core and partial microemulsion methods shows λ_{max} at 250 nm, a higher intensity, a slight red shift in absorption maximum value and a long tail. The red shift and long absorption tail features may indicate as mentioned by Han et al. [36] that the nanoparticle size has been increased due to formation of Ag_2S shell over the CdS core nanoparticles.

Again in the post-core method, two microemulsions were added one containing CdS nanoparticles with excess amount of S^{2-} and other containing Ag^+. The $AgNO_3$ molecules enter the reverse micelles containing CdS nanoparticles by intermicellar exchange process. The exchanged $AgNO_3$ molecules in microemulsion droplets containing CdS core particles react with the excess $(NH_4)_2S$ molecules already present. Reaction, and growth may lead to the formation of a shell of Ag_2S around the core of CdS nanoparticles, denoted as ($CdS@Ag_2S$). Probability of Ag_2S single nanoparticles formation cannot be neglected due to the presence of empty micelles containing $(NH_4)_2S$ molecules.

However in case of partial microemulsion method, the aqueous solution of $AgNO_3$ was directly added into the microemulsion containing CdS core nanoparticles. The $AgNO_3$ molecules directly enter into the aqueous core of microemulsion containing CdS nanoparticles as well as empty reverse micelles containing only $(NH_4)_2S$ molecules by diffusion process. These $AgNO_3$ molecules come in contact with excess $(NH_4)_2S$ within the aqueous core to form $CdS@Ag_2S$ nanoparticles through heterogeneous nucleation and growth mechanism.

Spectrum 3-c and 3-d presents the absorption spectra of CdS-Ag_2S nanoparticles prepared by simultaneous mixing and pre-mixing method respectively. In both pre-mixing and simultaneous mixing methods, the nucleation and growth of Ag_2S and CdS nanoparticles are supposed to occur simultaneously. Hence nanocomposites are formed. This observation may indicate the formation of CdS-Ag_2S nanocomposites.

In the simultaneous mixing method, all three microemulsions i. e., μE $Cd(NO_3)_2$, μE of $AgNO_3$ and μE of $(NH_4)_2S$ were added together to initiate intermicellar exchange, reaction and growth. In this case only two combinations out of three reverse micellar exchange would yield nanoparticles. Where as in pre-mixing method, two microemulsions, one containing Cd^{2+}/Ag^{+} ions and other containing S^{2-} combine to give nanoparticles. The formation takes place by exchange, reaction and growth of Cd^{2+}/Ag^{+} ions combining with S^{2-} as a result of which nanocomposite formation is favored.

It is also observed visually a difference in the color of nanoparticles prepared by four different microemulsion mixing methods. CdS nanoparticles had light yellowish color while Ag_2S nanoparticles were of gray color. While both simultaneous and pre-mixing methods gave the same greenish yellow color. Post-core gave somewhat lighter color while it was a dark gray color in the case of partial microemulsion method.

Thus, formation of nanoparticles via four addition techniques can be concluded in the form of following equations:

Post-core Method

$$\underset{\text{(light yellow)}}{\mu E(CdS)} + \underset{\text{(colorless)}}{\mu E(AgNO_3)} \rightarrow \underset{\text{(light gray)}}{\mu E(CdS\ @\ Ag_2S,\ Ag_2S)}$$

Partial microemulsion method

$$\underset{\text{(colorless)}}{\mu E(CdS)} + \underset{\text{(colorless)}}{aq.(AgNO_3)} \rightarrow \underset{\text{(dark gray)}}{\mu E(CdS\ @\ Ag_2S,\ Ag_2S)}$$

Simultaneous Mixing

$$\underset{\text{(clourless)}}{\mu E(Cd\ NO_3)} + \underset{\text{(colorless)}}{\mu E(AgNO_3)} + \underset{\text{(colorless)}}{\mu E((NH_4)_2S)} \rightarrow \underset{\text{(greenish yellow)}}{\mu E(Cd_xAg_yS,\ CdS/Ag_2S)}$$

Pre-mixing Method

$$\underset{\text{(colorless)}}{\mu E((NH_4)_2S)} + \underset{\text{(colorless)}}{\mu E(CdNO_3 + AgNO_3)} \rightarrow \underset{\text{(greensih yellow)}}{\mu E(Cd_xAg_yS,\ CdS/Ag_2S)}$$

The band gap of semiconductor particles can be determined by fitting the absorbance data to the following equation.

$$\sigma h\nu = A\left(h\nu - E_g\right)^{1/2} \qquad (1)$$

Where σ = molar absorption coefficient, A = proportionality and $h\nu$ = photon energy.

The band gap energy of bulk CdS and Ag_2S particles are found to be 2.5 and 1.0 eV respectively [10,22].

The size of the nanoparticles can be calculated by using the relationship for band gap E_g versus particle diameter d_p, which is expressed by Brus (1984) equation [17].

$$E_g = E_g(\text{bulk}) + \frac{h^2}{2d_p^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \left(\frac{3.6e^2}{4\pi\varepsilon d_p}\right) \qquad (2)$$

Where h = Planks constants, ε = dielectric constant of semiconductor, e = charge of electron and m_e & m_h are the effective mass of electron and hole respectively.

By using Brus equation (2), calculations have been done to estimate the size of CdS nanoparticles. The parameter values used are: E_g (bulk)=2.5 eV, m_e/m_0=0.19, m_h/m_0=0.8, $\varepsilon/\varepsilon_0$=5.7. The calculated size of the CdS nanoparticles is equal to 3.2 nm. It should be mentioned here that this method only gives the approximate sizes.

The fluorescence spectra of CdS, Ag_2S and CdS@Ag_2S nanoparticles prepared in w/o microemulsion are shown in Figure 4. These spectra were obtained from the microemulsion solution containing the nanoparticles using 400 nm as excitation wavelength. Spectrum 4-a shows the fluorescence spectrum of CdS while 4-b shows the fluorescence spectrum of Ag_2S nanoparticles. We observe from these spectra that CdS nanoparticles show a high intense photoluminescence band at around 547 nm however Ag_2S nanoparticles show negligible photoluminescence band. Spectrum 4-c presents the fluorescence spectrum of Ag_2S coated CdS nanoparticles. We observe from this spectrum that the more intense photoluminescence band of CdS at 547 nm has been quenched and the spectrum is quite similar to that of Ag_2S fluorescence spectra. This result clearly suggests the formation of Ag_2S shell around the CdS core nanoparticles.

TEM micrograph and particle size distribution studies of CdS@Ag_2S core-shell nanoparticles prepared by post-core method at R=10 are shown in Figure 5-a and 5-b respectively. We observe from this TEM image that Ag_2S coated CdS nanoparticles are well defined and nearly spherical in shape. It is worth mentioning that CdS nanoparticles that were not spherical previously have gained sphericity due to formation of an extra layer over it, which is further strengthened by the fact of an increase in diameter. Core and shell structure of the nanoparticles cannot be deciphered from these micrographs however the average diameter of these particles is found to be 6.6 nm. This implies an additional layer of Ag_2S shell of 1.9 nm around the CdS core nanoparticle of size 2.8 nm.

The elemental detection analysis (EDAX) of CdS@Ag_2S nanoparticles prepared by post-core method is presented in Fig 5-c. This result indicates the presence of Cd, Ag and S elements in the core-shell nanostructures. The weight percentage of Ag to Cd as determined by EDAX is 3:1. This result also indirectly supports the formation of core-shell nanostructures.

The TEM micrograph and particle size distribution of CdS@Ag_2S core and shell nanoparticles, prepared by partial microemulsion method, are presented in Figure 6. This figure shows that the CdS@Ag_2S nanoparticles are nearly spherical in shape. The mean diameter for CdS@Ag_2S core-shell nanoparticles is found to be 5.7 nm. We believe that the increase in diameter of these CdS@Ag_2S nanoparticles may be due to the formation of Ag_2S shell of thickness ~ 1.5 nm, around CdS (~ 3.0 nm) core nanoparticles. Also, the particles were observed to be stable for months under this scheme where as the CdS particles alone settled and agglomerated within 2 hours. This may be due to core-shell formation, which enhanced the stability of the nanoparticles. This may prove to be an important characteristic in its field of application.

Figure 7 presents the TEM micrograph and histogram study of CdS-Ag_2S composite nanoparticles, prepared by using simultaneous and premixing methods. Particles are reasonably well separated and dispersed. The mean diameter of these particles is found to be 3.7 and 3.6 nm respectively, which lies in between the single CdS and Ag_2S nanoparticles size. Such intermediate size between that CdS and Ag_2S may indicate that the core and shell nanoparticles are not formed by this method. Rather it may indicate the formation of some nanocomposites (Cd_xAg_yS) [38]. We believe in this method that the nucleation and the growth of both CdS and Ag_2S nanoparticles take place simultaneously. As a result, the nanocomposite formation is favored, due to fusion / bonding of the nuclei of CdS and Ag_2S in the nanodroplets.

4. Conclusions

In this present work AOT/n-heptane/water reverse micellar system has been used to produce CdS nanoparticles. An attempt has been made to produce in-situ CdS-Ag_2S core-shell/composite nanoparticles using four different addition methods via w/o microemulsion.

The formation of CdS nanoparticles has been confirmed from its light yellow coloration and characteristics UV-VIS spectra. The CdS nanoparticles size is found to be approximately 3 nm, which is in accordance with the size calculated from absorption data and are non-spherical in shape.

The UV-VIS absorption spectra of the core-shell/composite nanoparticles prepared by all four-addition methods do not show the characteristic absorption peak of CdS. However, all the spectra show a long absorption tail in the wavelength range 500-800 nm, which is the characteristic absorption spectrum for Ag_2S. They, however, vary in their optical density and also there is a slightly variation in absorption wavelength. These results indicate that the CdS core nanoparticles are either coated with a layer of Ag_2S or are forming mixed CdS/Ag_2S nanocomposite.

The particle size distribution studies of TEM micrographs show that the post-core and the partial microemulsion method produce nanoparticles of size greater than the size of single CdS and Ag_2S nanoparticles. This result gives qualitative information of the formation of CdS-Ag_2S core-shell assemblies. This result can further be strengthened by fluorescence spectra. The high intense fluorescence peak of CdS nanoparticles has been quenched due to formation of an extra layer of Ag_2S around the CdS core nanoparticles.

While incase of other two, simultaneous and pre-mixing methods, the particle size distribution studies show the average size of the particles formed fall in between the average size of single CdS and Ag_2S nanoparticles. This result might be due to the formation of CdS-Ag_2S composite nanoparticles.

It is also observed from the TEM studies that the CdS core nanoparticles achieve the non-spherical to spherical shape and their stability is also enhanced, which is useful in the industrial applications of these nanoparticle.

Acknowledgement. We would like to thank RSIC Mumbai, for providing us the TEM facilities and IIT Bombay for giving us the research facilities and financial support. We would also like to thank Drs. Anurag Mehera, Jayesh R. Bellare and C. Manohar for many useful discussions.

References

1. A. N. Shipway, E. Katz, and I. Willner, Chem. Phys. Chem., 1 (2000) 18.
2. E. Hao, H. Sun, Z. Zhou, J. Liu, B. Yang, J. Shen, Chem. Mater., 11 (1999) 3096.
3. A. M. Roy, G. C. De, S. Saha, J. Indian Chem. Soc., 73 (1996) 31.
4. H. S. Zhou, I. Honma, J. W. Haus, H. Sasabe, H. Komiyama, J. Lumin., 70 (1996) 21.
5. S. K. Sahoo, T. K. De, P. K. Ghosh, and A. Maitra, J. Colloid. Interface Sci., 206 (1998) 361.
6. W. P. Hsu, R. Yu, E. Matijevic, J. Colloid. Interface Sci., 156 (1993) 56.
7. L. M. Liz-Marzan, M. Giersig, P. Mulvaney, Chem. Commun., (1996) 731.
8. Q. H. Powell, G. P. Fotou, T. T. Kodas, Chem. Mater., 9 (1997) 685.
9. P. Kumar, V. Pillai, D. O. Shah, Appl. Phys. Lett., 62 (1993) 765.
10. S. Shiojiri, T. Hirai, I. Komasawa, Chem. Commun., (1998) 1439.
11. M. A. Correa-Duarte, M. Giersig, L. M. Liz-Marzan, Chem. Phys. Lett., 286 (1998) 497.
12. B. I. Lemon, R. M. Crooks, J. Am. Chem. Soc., 122 (2000) 12886.
13. T. Ung, L. M. Liz-Marzan, P. Mulvaney, J. Phys. Chem. B, 103 (1999) 6770.
14. S. Shiojiri, T. Hirai, I. Komasawa, J. Chem. Engg. Japan, 30 (1997) 137.
15. R. P. Bagwe, K. C. Khilar, Langmuir, 16 (2000) 905.
16. H. H. Ingelsten, J. C. Beziat, K. Bergkvist, A. Palmqvist, M. Skoglundh, H. Qiuhong, L. K. L. Falk, K. Holmberg, Langmuir, 18 (2002) 1811.
17. T. Hirai, H. Sato, I. Komasawa, Ind. Eng. Chem. Res., 33 (1994) 3262.
18. K. Suzuki, M. Harada, A. Shioi, J. Chem. Engg. Japan, 29 (1996) 264.
19. S. Foglia, L. Suber, M. Righini, Colloid. Surf., 177 (2001) 3.
20. H. Zhao, E. P. Douglas, B. S. Harrison, K. S. Schanze, Langmuir, 17 (2001) 8428.
21. C. Y. Wang, X. MO, Y. Zhou, Y. R. Zhu, H. T. Liu, Z. Y. Chen, J. Mater. Chem., 10 (2000) 607.
22. L. Motte, F. Billoudet, M. P. Pileni, J. Mater. Sci., 31 (1996) 38.
23. S. Hingorani, V. Pillai, P. Kumar, M. S. Multani, D. O. Shah, Mat. Res. Bull., 28 (1993) 1303.

24. A. Meldrum, R. F. Haglund, L. A. Boatner, C. W. White, Adv. Mater., 13 (2001) 1431.
25. S. Chang, L. Liu, S. A. Asher, J. Am. Chem. Soc., 116 (1994) 6739.
26. B. A. Korgel, H. G. Monbouquette, Langmuir, 16 (2000) 3588.
27. T. Li, J. Moon, A. A. Morrone, J. J. Mecholsky, D. R. Talham, J. H. Adair, Langmuir, 15 (1999) 4328.
28. H. Su, Y. Xie, P. Gao, Y. Xiong, Y. Qian, J. Mater. Chem., 11 (2001) 684.
29. J. P. Abid, H. H. Girault, P. F. Brevet, Chem. Commun., 2001, 829.
30. N. Revaprasadu, M. A. Malik, P. O'Brien, G. Wakefield, Chem. Commun., 1999, 1573.
31. G. Oldfield, T. Ung, P. Mulvaney, Adv. Mater., 12 (2000) 1519.
32. M. Giersig, T. Ung, L. M. Liz-Marzan, P. Mulvaney, Adv. Mater., 9 (1997) 570.
33. V. Pillai, P. Kumar, D. O. Shah, J. Magnet. Magnet. Mater., 116 (1992) L299.
34. M. P. Pileni, J. Phys. Chem., 97 (1993) 6961.
35. J. Eastoe, B. Warne, Current Opinion Colloid Interface Sci., 1 (1996) 800.
36. M. Y. Han, W. Huang, C. H. Chew, L. M. Gan, X. J. Zhang, W. Ji, J. Phys. Chem. B, 102 (1998) 1884.
37. D. B. Zhang, H. M. Cheng, J. M. Ma, Y. P. Wang, X. Z. Gai, J. Mater. Sci. Lett., 20 (2001) 439.
38. L. Qi, J. Ma, H. Cheng, Z. Zhao, Colloids Surf., 111 (1996) 195.
39. X. Fu, S. Qutubuddin, Colloids Surf., 179 (2001) 65.
40. S. Santra, R. Tapec, N. Theodoropoulou, J. Dobson, A. Hebard, W. Tan, Langmuir, 17 (2001) 2900.

Figure captions

Figure 1. UV-VIS Spectra of CdS and Ag_2S nanoparticles prepared in AOT/n-heptane/water microemulsions.

Figure 2. TEM micrograph and particle size distributions of CdS and Ag_2S nanoparticles.

Figure 3. UV-VIS spectra of CdS-Ag_2S core-shell and composite nanoparticles, prepared by different addition methods using w/o microemulsions.

Figure 4. Fluorescence spectra of CdS, Ag_2S, and CdS @ Ag_2S nanoparticles.

Figure 5. TEM micrograph, particle size distribution and EDAX study of CdS @ Ag_2S nanoparticles prepared by post-core addition method.

Figure 6. TEM micrograph and particle size distribution of CdS @ Ag_2S nanoparticles prepared by partial microemulsion method.

Figure 7. TEM micrographs and particles size distributions of CdS-Ag_2S composite nanoparticles prepared by simultaneous and premixing methods.

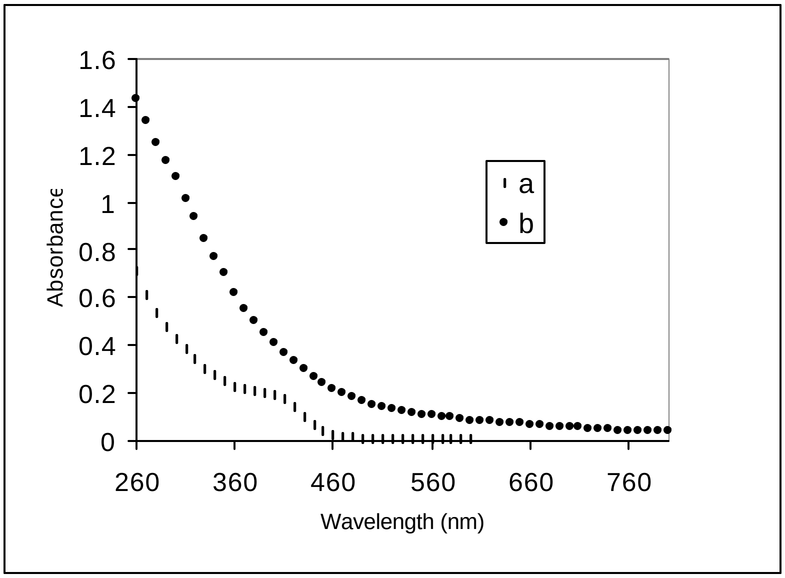

Figure 1. UV-VIS absorption spectra of (a) CdS and (b) Ag_2S nanoparticles prepared in AOT/n-heptane / water microemulsion method at R=10.

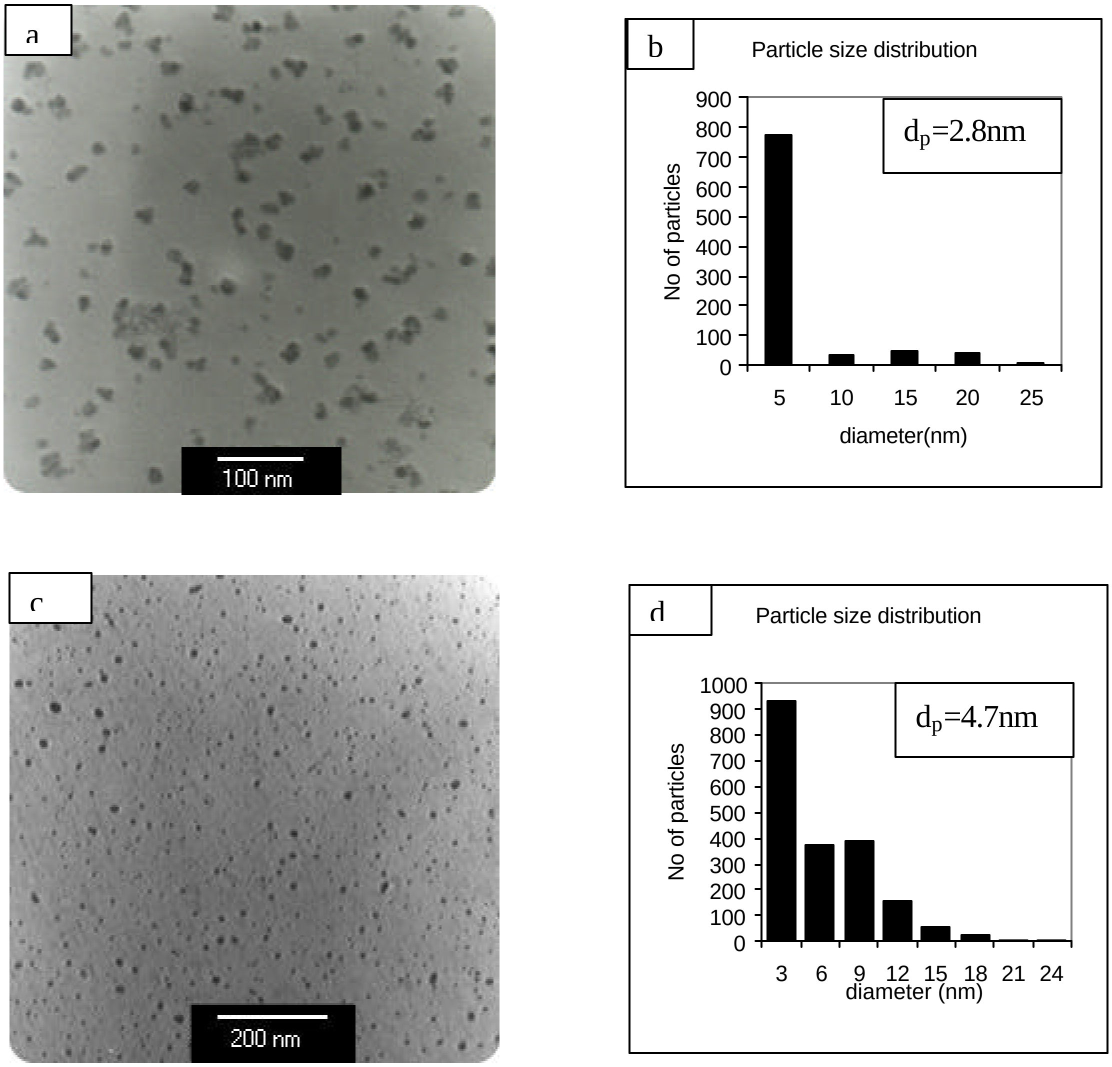

Figure 2. TEM micrographs, and particle size distributions of (a, b) CdS nanoparticles and (c, d) Ag_2S nanoparticles, prepared in w/o microemulsions at R = 10.

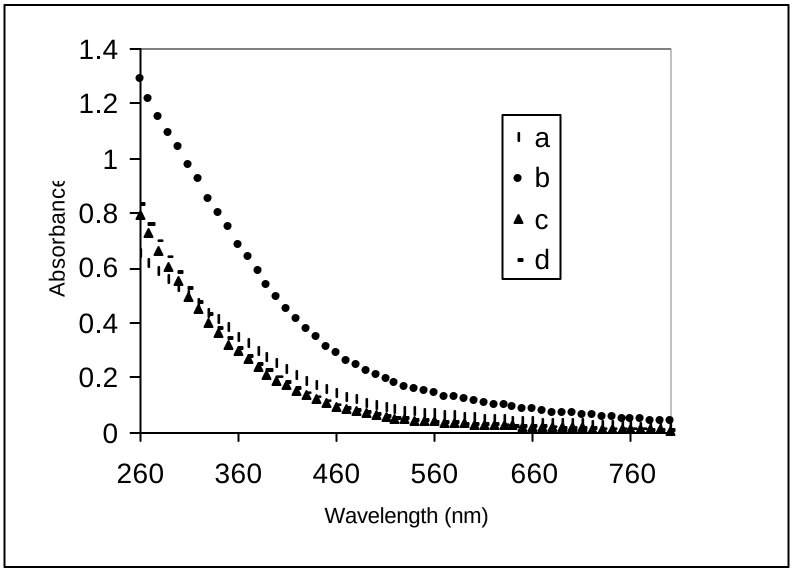

Figure 3. UV-VIS absorption spectra of CdS@Ag_2S core-shell/composite nanoparticles prepared by (a) Post-core method, (b) Partial microemulsion (c) Simultaneous mixing, and (d) Pre-mixing method.

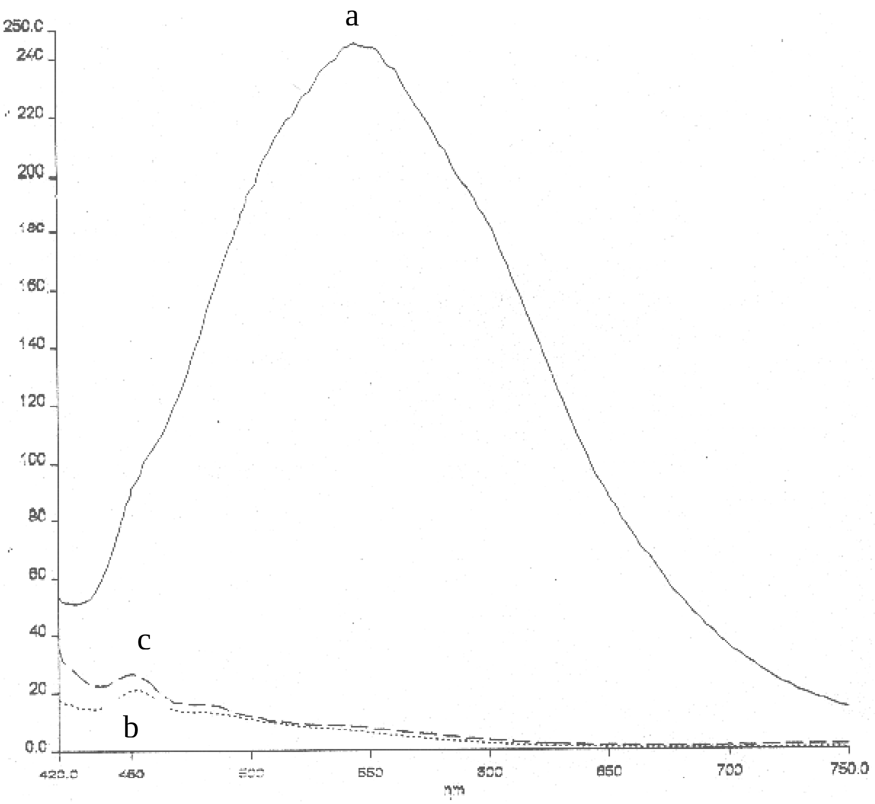

Figure 4. Fluorescence spectra of (a) CdS, (b) Ag_2S and (c) CdS @ Ag_2S nanoparticles prepared by w/o microemulsions at room temperature.

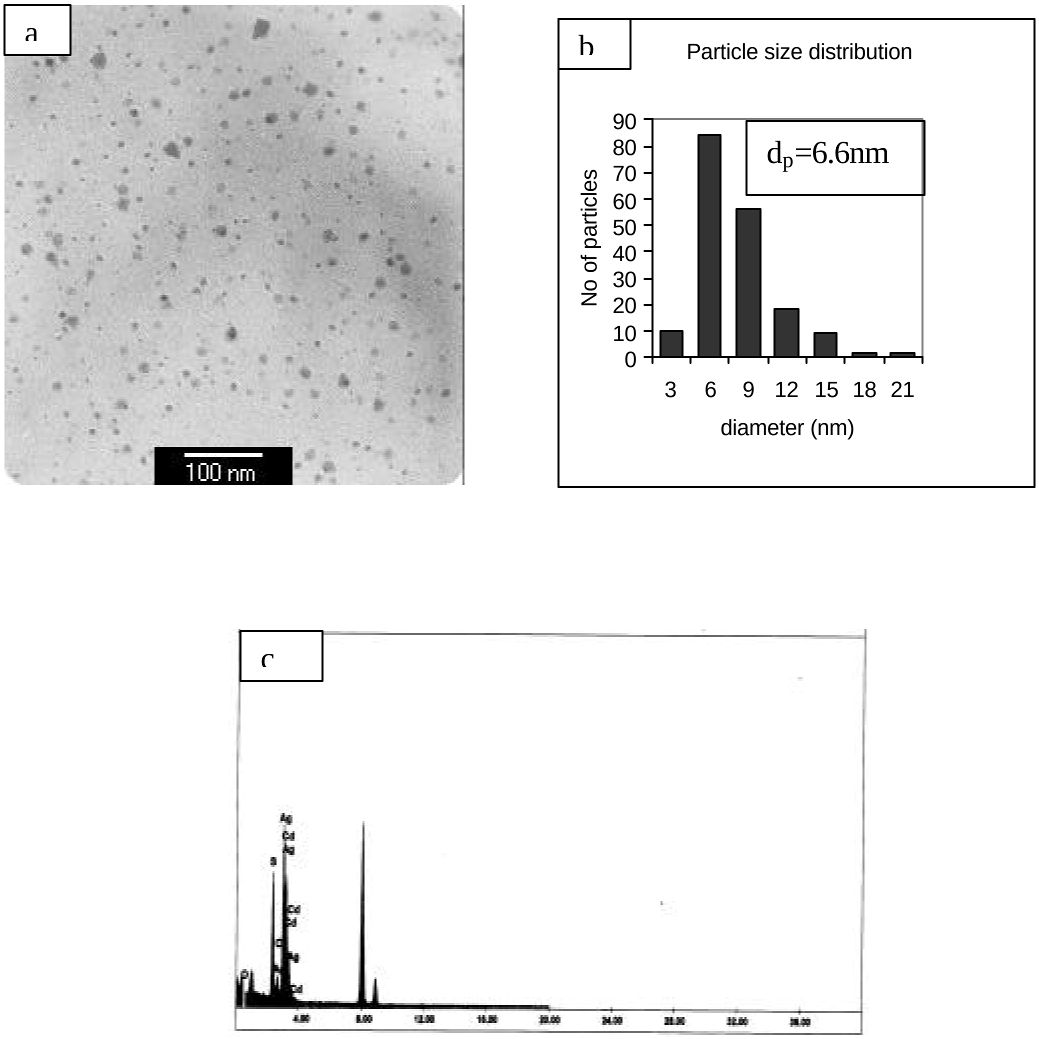

Figure 5. TEM micrograph, particle size distribution and EDAX of Ag_2S coated CdS nanoparticles prepared by post-core method using w/o microemulsions at R = 10.

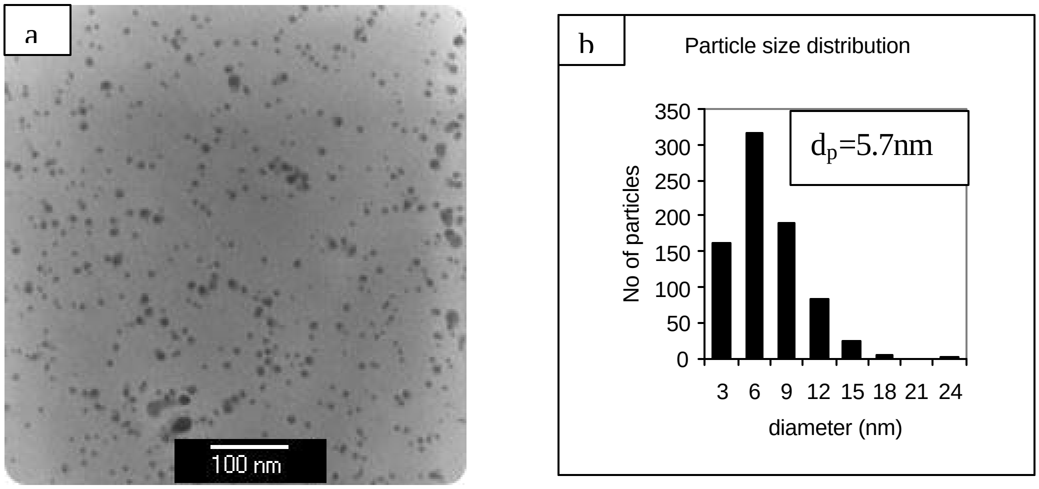

Figure 6. (a) TEM micrograph and (b) Particle size distribution of CdS @ Ag_2S prepared by partial microemulsion method at R = 10.

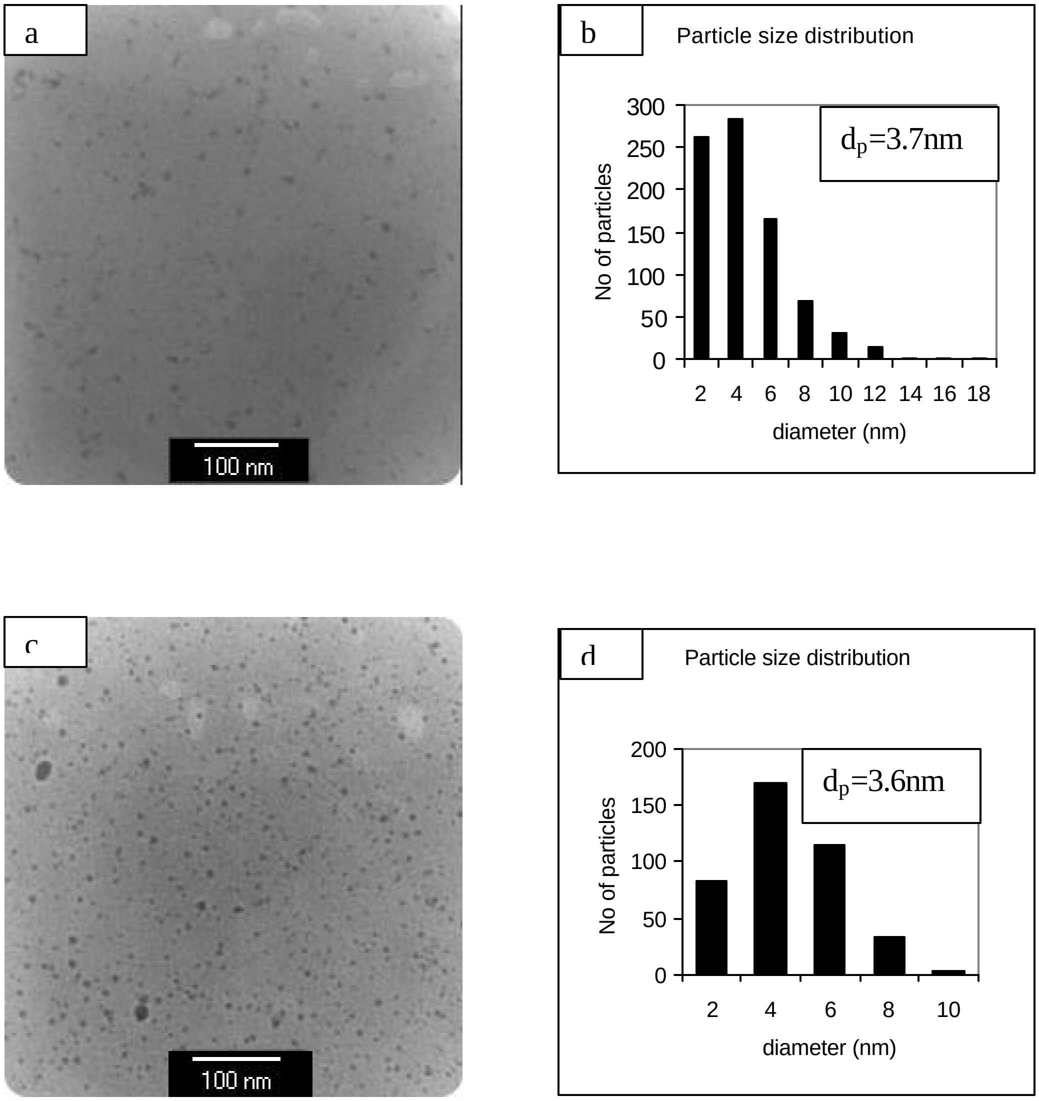

Figure 7. TEM micrographs and particle size distributions of CdS-Ag_2S composite nanoparticles prepared by (a, b) Simultaneous mixing and (c, d) by Pre-mixing method.