Characterization of nano-sized CdS–Ag₂S core-shell nanoparticles using XPS technique

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Abstract

This paper reports the use of X-ray photoelectron spectroscopy (XPS) method for the characterization of surface composition of core and shell nanoparticles. The core and shell nanoparticles were synthesized using sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/n-heptane/water microemulsion technique. The post-core and partial microemulsion methods have shown promise for core and shell formation and enhanced stability and sphericity of the semiconductor nanoparticles. In addition to above technique, the core-shell nanoparticles have also been characterized using SEM-elemental detection X-ray analysis (EDAX) and results are discussed. The XPS studies of CdS, Ag₂S, and CdS–Ag₂S nanoparticles prepared by post-core/partial microemulsion methods were carried out and results are compared with physical mixing of CdS and Ag₂S nanoparticles. The Ag/Cd atomic ratio is found to be 5 and 10 as determined by XPS methods for nanoparticles prepared by using post-core and partial microemulsion methods, respectively. These results show the formation of core and shell nanoparticles.

Keywords: Core-shell; Nanoparticles; w/o Microemulsion; XPS; CdS–Ag₂S; AOT

1. Introduction

Nanophase and nanostructured materials as a component of nanotechnology have attracted a great deal of attention of today’s research [1]. The synthesis of inorganic nanocrystals and nanoparticles in a controllable fashion has been the goal of much active research over the past decade [2,3]. Semiconductor nanocrystals and nanoparticles have been studied extensively as their properties are dependent on size, morphology, and surface composition [4–10].

The synthesis and characterization of core and shell nanoparticles is an important research area at the frontier of advanced material chemistry [11,12]. These core and shell composite material can increase the luminescence quantum yield due to improved passivation of the surface and tend to be more physically robust than the “bare” organically passivated clusters [13,14]. Recent research interest arises from the diverse attributes of core and shell nanoparticles as model building blocks towards functional materials, including (1) monodispersity; (2) core and shell processability; (3) solubility; (4) stability and tenability; (5) capability of self assembly; and (6) functional activities in involving optical, electronic, magnetic, catalytic and chemical/biological phenomenon. Examples of core and shell structures include CdS–ZnS [15], Au–SiO₂ [16], Ag–SiO₂ [17], CdS–SiO₂ [18], CdS–HgS [19], CdSe–CdS [20], SiO₂–TiO₂ [21], Fe₂O₃–SiO₂ [22], and CdS–Ag₂S [23]. From these examples, we can note that these are potentially useful in a broad range of application. The controlled synthesis of novel uniformly coated stable nanoparticles, however, for many years has remained as a technical challenge.

The CdS–Ag₂S coated nanoparticles were synthesized by Han et al. [23], by inverse microemulsion technique and were characterized by means of elemental detection X-ray analysis (EDAX) and TEM technique. The TEM micrographs of these particles do not clearly show the core and shell structure because of the nanometer size and similarity in core and shell materials. Therefore, a better characterization technique is needed for characterizing these kinds of core and shell nanoparticles. In general, it is not clear how core and shell nanoparticles can be clearly documented and adequately characterized. It is not certain that some of TEM micrographs showing good contrast to discern core from 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 better formation methods as well as better characterization techniques.

X-ray photoelectron spectroscopy (XPS) is a surface analytical technique with a sampling depth of 2–5 nm [24] and it is well suited for interrogation of the surface composition of the colloidal particles [25]. Recently it has been used for surface characterization of gold nanoparticles [26]. In a perfectly coated “core-shell” particle the core material would be completely buried under a uniform layer of the shell material. If the thickness of the shell were in between 3 and 6 Å, XPS and X-ray excited Auger spectroscopy techniques whose sensitivities lie in this range may be reasonably used to demonstrate the layering of shell materials [25,27,28].

In this study, we have used two different methods, post-core and partial microemulsion methods to prepare CdS–Ag2S core and shell nanoparticles. We report a detailed X-ray photoelectron spectroscopy study of these core and shell nanoparticles. These results are compared with SEM-elemental detection analysis as well. In this paper, we have discussed the various features of Cd 3d, Ag 3d and S 2p core levels, which provide an understanding of the elemental surface composition and formation of core-shell morphology of prepared CdS–Ag2S nanoparticles.

2. Experimental

2.1. Materials

The surfactant, dioctyl sulfosuccinate sodium salt (aerosol OT, or AOT) was purchased from Sigma with 99% purity. Silver nitrate (AR) and cadmium nitrate (LR) were purchased from S.D. Fine Chemicals, India. Ammonium sulfide [(NH4)2S, 25%] was purchased from SISCO, India. Heptane was purchased from DISCO, India and was used after refluxing over sodium wire for 2 h to remove moistures. Double distilled water was used throughout the experiments.

2.2. Sample preparation

Aqueous solution of cadmium nitrate (0.1 M), silver nitrate (0.1 M) and ammonium sulfide (0.2 M) were freshly prepared. Neat and clean previously dried 15 ml centrifuge 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.

2.3. Preparation of core-shell nanoparticles

AOT capped CdS and Ag2S nanoparticles were prepared using w/o microemulsion as reported by Hota et al. [29]. In an attempt to prepare core-shell/composite nanoparticles, we have used two mixing methods using w/o microemulsions. These methods are as follows.

a. Post-core method: In this method, a microemulsion, \( \mu \text{E} \) of AgNO3 solution was added to the \( \mu \text{E} \) 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 (NH4)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 AgNO3 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. Physical mixing method: In this method, two individual microemulsion, containing CdS and Ag2S nanoparticles have been mixed physically for the reference point of view.

The nanoparticles of CdS, Ag2S, and core-shell CdS–Ag2S prepared by post-core/partial microemulsion methods were separated from microemulsions by addition of acetone followed by ultracentrifugation and washed three to four times with double distilled water and then ethyl alcohol in order to remove the surfactants. The nanoparticles were dried using the vacuum desiccator and used for XPS studies.

2.4. X-ray photoelectron spectroscopy

XPS measurements were performed on a V.G. Microtech Unit ESCA 3000 Spectrometer with twin anode, Al Kα (1486.6 eV) and Mg Kα (1256.6 eV). The vacuum in the analyzing chamber was <1 × 10\(^{-7}\) Torr. Multichannel detectors were used to detect the photoelectron and a spherical sector analyzer was used to detect the photoelectron’s energy. The X-ray flux used was 200 W. The spectrometer was calibrated by determining the binding energy values of Au7/2 (84.0 eV) Ag 3d5/2 (368.8 eV) and Cu 2p 3/2 (932.4 eV) using spectroscopically pure metals obtained from Johnson-Matthey, London. The binding energy values (measured to an accuracy of 0.2 eV) are good agreement with the literature values. The XPS spectra were acquired at 50 eV pass energy, 5 mm slit width and take off angle (angle between electron emission direction and surface plane) of 55°. Due to a large number of channeltrons the detection limit has been increased. The instrumental resolution under these conditions is 1.6 eV full width at half maximum (FWHM) for the Au 4f7/2 level. The sample material was mounted in a thin layer film on sample holder and used for recording the XPS spectra. All spectra were recorded with similar spectrometric parameters.

The general scan and C 1s, O 1s, S 2p, Cd 3d and Ag 3d core levels were recorded with referring un-monochromatized Al Kα (1486.6 eV) radiation at 50 eV pass energy and take off angle (55°). The peak shift due to charging was corrected using the C 1s level at 285 eV as an internal standard.

The XPS peaks assumed to have Gaussian line shape and were resolved into individual components after proper subtraction of baseline using Shirley background subtraction method with the help of software supplied by V.G. Microtech.

3. Results and discussion

The formations of nanoparticles via two addition techniques are as shown below.
Post-core method

\[ \mu E(\text{CdS, excess S}^2) + \mu E(\text{AgNO}_3) \to \mu E(\text{CdS} - \text{Ag}_2\text{S}, \text{Ag}_2\text{S}) + \text{NH}_4\text{NO}_3 \]

Partial microemulsion method

\[ \mu E(\text{CdS, excess S}^2) + \text{aq.}(\text{AgNO}_3) \to \mu E(\text{CdS} - \text{Ag}_2\text{S}, \text{Ag}_2\text{S}) + \text{NH}_4\text{NO}_3 \]

The UV–vis spectra obtained from the addition techniques to obtain core-shell/nanocomposite are indeed, difficult to interpret as reported earlier by Hota et al. [29]. It should be mentioned here that the nanoparticles are formed due to intermicellar exchange. This intermicellar exchange being random in nature, four different types of particles formation might take place such as CdS, Ag$_2$S, and CdS–Ag$_2$S core-shell/composite nanoparticles. The absorption spectra of samples containing these particles may turn out to be a complex combination. Nevertheless, we believe that in the mixing methods used, the formation of core-shell nanoparticles will be dominant while the single core CdS and Ag$_2$S nanoparticles will be comparatively less. To the best of authors’ knowledge there is no technique available for the quantitative analysis of these mixtures of nanocomposites.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental composition (atomic%)</th>
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<tbody>
<tr>
<td>Post-core CdS–Ag$_2$S</td>
<td>Ag: 80, Cd: 20</td>
</tr>
<tr>
<td>Partial emulsion CdS–Ag$_2$S</td>
<td>Ag: 88, Cd: 12</td>
</tr>
<tr>
<td>Physical mixture (50:50) CdS and Ag$_2$S</td>
<td>Ag: 52, Cd: 48</td>
</tr>
</tbody>
</table>

#### 3.1. SEM-EDAX analysis

The elemental composition of CdS–Ag$_2$S nanoparticles is also determined using SEM energy dispersive analytical X-ray spectroscopy by performing the spot measurements on nanoparticles powder. The major peaks we found due to presence of Cd and Ag along with sulfur and negligible amount of carbon and oxygen. The elemental ratios of Ag to Cd in the CdS–Ag$_2$S core and shell nanoparticles were obtained using EDAX data. The Table 1 summarizes the results of elemental composition EDAX analysis of the nanoparticles prepared by post-core/partial microemulsion methods.

We observe from Table 1 that the percentage compositions of Ag and Cd vary with in the range of 80–90 and 10–20%, respectively, for post-core/partial microemulsion method. This result clearly shows that the materials in the outer portion of the

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**Fig. 1.** XPS spectra of CdS and Ag$_2$S nanoparticles (a) Cd 3d; (b) S 2p; (c) Ag 3d; and (d) S 2p core level.
nanoparticles primarily compose of Ag. This observation is also evidenced by Tougaard analysis in the post-core method.

### 3.2. XPS analysis

XPS is very sensitive to the chemical composition and environment of the elements in a material. In XPS spectra, each element will give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies. The presence of peaks at particular energies therefore indicates the presence of a specific element in the sample under study—furthermore, the intensity of the peaks is related to the concentration of the element within the sampled region. Thus, the technique provides a quantitative analysis of the surface composition. Arising out of the fact that the chemical surrounding slightly influences the inner energy levels of the atoms, it is possible to distinguish the signals originating from the atoms in different chemical surrounding like those located at the surface or the volume phase of the particles. It was used to evaluate the chemical composition of CdS, Ag2S and CdS–Ag2S nano-materials.

The survey scans were carried out to search for the presence of particular elements in the sample showed the presence of C 1s, O 1s, S 2p, Cd 3d and Ag 3d core levels. The C 1s core levels was resolved into two components at binding energies, CI = 285 eV and CII = 287.8 eV and are assigned to the hydro-

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**Table 2**

B.E. (eV) of different core levels

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cd 3d</th>
<th>Ag 3d</th>
<th>S</th>
<th>Ag/Cd</th>
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</thead>
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<tr>
<td>CdS</td>
<td>405.4, 412.3</td>
<td>–</td>
<td>161.5, 168.8</td>
<td>–</td>
</tr>
<tr>
<td>Ag2S</td>
<td>–</td>
<td>368, 374.1</td>
<td>161.2</td>
<td>–</td>
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<tr>
<td>Post-core CdS–Ag2S</td>
<td>405.5, 412.3</td>
<td>368, 374</td>
<td>161.3, 168.9</td>
<td>5</td>
</tr>
<tr>
<td>Partial emulsion CdS–Ag2S</td>
<td>405.4, 412.3</td>
<td>368, 374.1</td>
<td>161.3, 168.9</td>
<td>∼10</td>
</tr>
<tr>
<td>Physical mixture (50:50)</td>
<td>405.4, 412.3, 368,14, 374.14</td>
<td>161.9, 168.4</td>
<td>∼1</td>
<td></td>
</tr>
</tbody>
</table>

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Fig. 2. XPS spectra of CdS–Ag2S core-shell nanoparticles (post-core method) (a) Cd 3d; (b) Ag 3d; and (c) S 2p core levels.
carbon CH$_2$ and the presence of higher binding energy with CII carbon attached to oxyfunctionalities of AOT, respectively. These CdS particles possess an inorganic crystalline CdS core surrounded by organic AOT growing in to macroscopic phase and preventing agglomeration during nanoparticle formation.

The Cd 3d, Ag 3d and S 2p core levels of nanoparticles of CdS, Ag$_2$S are shown in Fig. 1. The Cd 3d spectrum in each case has a doublet feature due to spin-orbit splitting resulting in to 3d$_{5/2}$ and 3d$_{3/2}$ peaks with spin-orbit separation 6.7 eV. The characteristic binding energy of Cd 3d$_{5/2}$ and 3d$_{3/2}$ of CdS agree with those reported in the literature [6]. Fig. 1(a) represents the XPS of CdS nanoparticles. Both peaks (Cd 3d$_{5/2}$ and Cd 3d$_{3/2}$) samples have FWHM 1.8 eV and the position of the maxima at 405.4 and 412.3 eV, respectively. The Cd 3d core level could be satisfactorily fit to single spin-orbit pair at 405 eV (Cd3d$_{5/2}$) and at 412 eV (Cd3d$_{3/2}$). These values are in good agreement with the published values for CdS nanoparticles [6]. Although the relative cross section of sulfur is small in comparison to the other elements, the sulfur peaks are sensitive to the chemical environment. The lower binding energy peak at 161.5 eV is indicative of metal sulfide while the other peak at 168.8 eV has been assigned to the more oxidized form of sulfur from AOT molecule.

Fig. 1(b) represents the XPS of Ag$_2$S nanoparticles. The peak position (Ag 3d$_{5/2}$ at 368 eV and S 2p$_{3/2}$ at 161.2 eV) corresponds to Ag$_2$S. These values are in good agreement with the reported values for Ag$_2$S nanoparticles [7]. The Ag 3d core level could be satisfactorily fit to a single spin-orbit pair of Ag 3d$_{5/2}$ at 368 eV and Ag 3d$_{3/2}$ at 374 eV as shown in Fig. 2(b). The XPS of S 2p$_{3/2}$ level is shown in the Fig. 2(c). It is clear that there are two distinct species SI and SII at in the spectrum at 161.3 and 168.9 eV.

3.3. The nanoparticles of CdS–Ag$_2$S by post-core method

The CdS–Ag$_2$S nanoparticles prepared by post-core method show the presence of C 1s, O 1s, S 2p and Cd 3d, Ag 3d core levels with no significant impurities. The FWHM of CdS and Cd$_{3d}$ is increased from 2.2 to 2.8 eV and maxima are observed at binding energy of 405.5 and 412.3 eV, respectively. Fig. 2(a) shows the result obtained by using a fit procedure. The Cd core level could be satisfactorily fit to a single spin-orbit pair of CdS nanoparticles. The Ag 3d core level could also fit to a single spin-orbit pair of Ag 3d$_{5/2}$ at 368 eV and Ag 3d$_{3/2}$ at 374 eV as shown in Fig. 2(b). The XPS of S 2p$_{3/2}$ level is shown in the Fig. 2(c). It is clear that there are two distinct species SI and SII at in the spectrum at 161.3 and 168.9 eV.

3.4. Tougaard analysis

Much effort has been devoted to the developments of new and more accurate methods in the view of high and rapidly growing technological importance of reliable information on the in-depth composition of the surface region of solids on the nanometer scale. This observation has been applied in the formulation of the new method for quantification that is based on the quantitative analysis of measured peak shape and peak intensity. This technique is sensitive on the ~1–10 nm depth scale and it is non-destructive. Due to elastic and inelastic scattering of photo-excited core electrons the ratio of the peak areas to the increase in the background signal associated with a single XPS peak depend strongly in depth composition as reported by Tougaard and co-workers [27,28].

Preliminary examination of Tougaard background analysis of Cd 3d signal indicates that the thickness of Ag$_2$S shell on CdS core is in the order of 2–3 nm as supported by TEM analysis [29]. Fig. 3 shows the XPS spectrum of (a) CdS nanoparticles and (b) core-shell CdS–Ag$_2$S (post-core method) core-shell nanoparticles.
differs from the background depends on the variations in the concentration profile with in a thin layer of materials at the surface of the CdS–Ag$_2$S nanoparticles.

The formation of Ag$_2$S shell layer on CdS core is also supported by the fact that in the Tougaard background analysis the shift in base line after Cd core level is indeed, due to the coating of Ag$_2$S over CdS species (shown in Fig. 3(b)). In this study the peak shape and peak intensity are used for quantitative analysis of core and shell nanoparticles by XPS method.

3.5. The nanoparticles of CdS–Ag$_2$S by partial microemulsion methods

The nanoparticles CdS–Ag$_2$S prepared by partial emulsion method shows the presence of C 1s, O 1s, S 2p and Cd 3d, Ag 3d core levels with no significant impurities. The peaks of Cd (Cd 3d$_{5/2}$ and Cd 3d$_{3/2}$) samples have FWHM 2.8 eV and the position of the peak maxima are observed at 405.4 and 412.3 eV, respectively, shown in Fig. 4(a). The Ag 3d core level could be satisfactorily fit to a single spin-orbit pair of Ag 3d$_{5/2}$ at 368 eV and Ag 3d$_{3/2}$ at 374 eV as shown in Fig. 4(b). The XP spectrum of S 2p$_{3/2}$ level is shown in the Fig. 4(c). In this spectrum also there are two distinct species SI (161.3 eV) and SII (168.9 eV) observed in the spectrum as in case of post-core method. The second binding energy value of 168.9 eV is a characteristic value of C–SO$_3$H group of AOT surfactant. The atomic concentration of Ag/Cd ratio is $\sim$10, where as this ratio is 5, for post-core sample, as presented in Table 2. The high Ag/Cd atomic ratio suggests that the surface of partial microemulsion sample contain Ag$_2$S molecule twice as compare to that of post-core method. This result is also supported by SEM–EDAX spot analysis.

3.6. Physical mixture of CdS and Ag$_2$S nanoparticles

The physical mixture of CdS and Ag$_2$S (1:1) was used as a reference material for quantitative analysis of composition of Cd and Ag core levels to correlate with the XPS results of samples prepared by post-core/partial microemulsion method.
4. Conclusions

The CdS–Ag$_2$S core and shell nanoparticles were synthesized by post-core and partial microemulsions addition method using AOT/n-heptane/water microemulsion system. The quantitative elemental surface composition of the core-shell nanoparticles were characterized by using X-ray photoelectron spectroscopy. The XPS data are also comparable with the SEM-elemental detection X-ray analysis. The Ag/Cd ratio as determined by the XPS spectra of core-shell nanoparticles are (≈5) and (≈10) for post-core and partial microemulsion methods, respectively. However, the Ag/Cd ratio is found to be unity (≈1) for physical mixing sample. These results indicate the formation of core-shell nanoparticles, i.e. CdS nanoparticles are coated with a layer of Ag$_2$S atoms.

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