Synthesis and Characterization of Silica-Lead Sulfide Core Shell Nanospheres For Applications in Optoelectronic Devices

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Abstract

Nanoscale miniaturization of chalcogenides semiconductors, such as lead sulfide (galena), can generate interesting quantum confinement effects in the field of optoelectronic applications. At this work, a process in order to obtain SiO₂ nanospheres coated with Galena, as the denominated core-shell system, is developed, this process it is based in Stöber's method, where only the magnetic stirring was replaced by an ultrasonic bath, to achieve well rounded, and highly stable silica nanoparticles with diameters average of 70 nm. The PbS shell cover presents a thickness of 10 nm around.

Nanostructures chemical composition, morphology and optical properties were determined by Transmission Electron Microscopy and UV-Vis spectroscopy, respectively. As a result, the nano shells correspond to cubic PbS, presenting some interplanar distances of 2.95 Å and 3.41 Å; this nano shell also shown a toward blue optical spectrum shift and a remarkable increase in its band gap, 3.75 eV, was obtained, compared with the PbS bulk value. The chemical composition it is studied by energy scattering spectroscopy, and X-ray photoelectron spectroscopy analyzes.

Introduction

Heavy metals sulfides, like PbS are semiconductor materials used in different electronic devices as thermal detectors [1], photoresistors [2] and thin films solar cells [3]. Due to their size scales, from nano metric to macroscopic, it is possible to observe changes in their physicochemical properties. Some semiconductors nanoparticles are comparable in size to their excitons, that lead to significantly affects in theirs optical, electronic, luminescent and material oxidation-reduction properties [4, 5]. This way, we have found new applications by reducing their size. For instance, there are reports that PbS nanoparticles have interesting nonlinear optical properties, with applications in gates and as optical signal processors [6]. Some semiconductor nanoparticles are synthesized by techniques such as solvothermal synthesis [7], sonochemistry [8, 9] sol-gel [10, 11], colloidal microemulsion [12] and chemical precipitation of aqueous solutions [13]. The sonochemical synthesis technique is used in order to obtain very small particles, due to acoustic cavitation [8, 9]. Also, with the intention of building concentric multilayer semiconductor nanoparticles core shell type [14].

The relevance of Core-Shell nanoparticles has increased exponentially in the last 20 years since these nanostructures have allowed the exploration of a new range of applications that link the chemistry of materials and other areas such as electronics [15], biomedicine [16] and optics [12]. The potential applications of these nanostructures in electronics are particularly interesting, like enhancing photoluminescence and the manufacture of photonic crystals [17–20]. To achieve a colloidal dispersion containing monodisperse spheres on a nanometric scale was used the Stöber process, this process consists in the preparation of controllable and uniform size silica particles through hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in a water/alcohol solution and using ammonium hydroxide as the catalyst system [21]. In the case of complexing agents, triethanolamine was combined with citric acid, that is commonly found and easily biodegraded, to improve the adhesion and deposit

control of the compound. Then, both solutions are mixed and, using the sonochemical method, the silica nanospheres are covered with PbS, and finally the core-shell nanometric structures are formed. Through the results obtained in the characterizations made to the samples, the success of the synthesis of nanoparticles with the desired size, morphology and composition was achieved. The above confirms the validity of the new formulation used, with which it is possible to considerably reduce the reaction times without affecting the stability of the final product.

Experimental

At first, monodisperse silica nanoparticles were produced by the sol-gel process, through a modified Stöber's method. To reduce the reaction time, the sonochemical technique was used, submerging the solution in an ultrasonic bath instead of the traditional magnetic stirring. The following compounds are used: Tetraethyl Orthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$) (TEOS, 1 ml) as a precursor of silica, deionized water (1 ml) and ethanol ($\text{C}_2\text{H}_5\text{OH}$, 27 ml) as solvent liquids, and ammonium hydroxide (NH_4OH , 1 ml) as a catalyst. TEOS and deionized water were mixed into a clear 50 ml plastic vial later it was deposited into a flask and was shaken for 15 seconds, observing a transparent mixture. Subsequently were added ammonium hydroxide and alcohol and were applied 5 minutes of ultrasonic vibrations in a Cole-Parmer 8891 Ultrasonic Cleaner to form a homogeneous whitish solution.

SiO_2 -PbS structures were synthesized in aqueous phase by using an organic compound of sulfur (thiourea), at the same time, lead acetate as precursors PbS particles were prepared by placing 2.5 ml of lead acetate ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$) 0.5M solution in a 100 ml beaker, followed by the addition of 2.5 ml of sodium hydroxide (NaOH) 2 M, 3 ml of thiourea ($\text{SC}(\text{NH}_2)_2$) 1 M, 1 ml of triethanolamine TEA ($\text{C}_6\text{H}_{15}\text{NO}_3$) 1 M, 0.5 ml of citric acid ($\text{C}_6\text{H}_8\text{O}_7$) 1 M (after 15 minutes), and then the total volume of the solution was completed to 50 ml by adding deionized water. Triethanolamine and citric acid were used as complexing agents. The solution of colloidal spheres was added to the preparation and the container was placed in the ultrasonic bath for 4 hours until the colloidal suspension acquired a cloudy and dark appearance. The entire reaction proceeded at room temperature. A sample of uncoated silica nanoparticles was separated for comparison. The obtained samples of silica nanoparticles and of the ones coated with PbS were centrifuged using a model 59A Fisher Scientific microcentrifuge during three sessions of 3 minutes at 7500 RPM, being washed with ethanol to remove remnant compounds in between sessions. The chemical composition and morphology of the nanostructures was determined by the techniques of energy dispersion spectroscopy and transmission electron microscopy respectively.

Results And Discussion

Two samples were prepared for characterization, one of the uncoated SiO_2 nanoparticles and the other coated with PbS. Both were analyzed and compared with TEM and EDS techniques. Figure 1 shows the TEM images at different magnifications of the pure silica sample. A homogeneous and spheroidal pattern in size and shape is remarkable in nanoparticles, which exhibited a narrow size distribution (~ 70

± 10 nm). 60 days after the synthesis was accomplished the TEM measures, which demonstrates the stability of the nanoparticles.

Spectroscopy studies (EDS) in Fig. 1d revealed the presence of oxygen and silicon with atomic percentages of 59.79% and 40.21% respectively, something that is consistent with the SiO_2 stoichiometry. Traces of carbon, copper and gold were also detected corresponding to the grating where the sample was deposited and are not significant. Figure 3 represents the evidence of the core-shell nanostructures where the formation of a uniform outer layer of PbS (~ 10 nm) surrounds the silica.

In this sample that had much more time of ultrasonic bath were formed some agglomerates, this can be attributed high surface energy of each particle, causing them to attract each other to form these agglomerates [22], where the coalescence of the nanoparticles is not observable, rather they seem to be embedded within what could be the protective agent and lead residues (dark areas).

In the EDS spectrum obtained, Fig. 3d, the presence of oxygen, silicon, lead and sulfur can be observed with atomic percentages of 46.75%, 36.06%, 14.94% and 2.27% respectively. In the case of lead and sulfur, they overlap in the same peak, and where it is deconvoluted, clearly appears two individual peaks of 2.34 keV (lead) and 2.46 keV (sulfur). There were also identified traces of carbon copper and gold due to the grating as explained above. The surface layer of the Core-Shell corresponds to cubic PbS (JCPDS # 01-078-1897) with interplanar distances of 2.95 Å and 3.41 Å with (2 0 0) and (1 1 1) Miller indexes, respectively (see Fig. 4).

For the analysis was used high resolution images obtained in the TEM, which were processed in the Digital Micrograph software to find the interplanar distances.

Meanwhile the XPS spectra of SiO_2 -PbS core-shell and uncoated silica nanospheres, as high-resolution XPS spectra for C 1s, O 1s, Si 2p and Pb 4f of the silica-lead sulfide system are shown in Fig. 5. The raw XPS data were corrected by shifting all peaks to the standard value of C 1s spectral component (C-C, C-H) binding energy set to 284.85 eV.

Figure 5a shows the typical results of XPS spectra for silica nanospheres before (A) and after coating with lead sulfide shell (B). The peaks at bond energy (BE) of 103 eV, 285 eV and 532 eV correspond to the Si 2p, C 1s, and O 1s spectra, respectively, which exist in both samples. It is observed that after the silica nanoparticles are coated with PbS, news doublet peaks with binding energies of 21, 138, 413 and 645 eV appeared, which could be assigned to the Pb 5d₃, 4 f₇, 4 d₅ and 4 p₃ orbitals respectively.

The deconvoluted C 1s spectrum shows peaks at 284.03 eV, 284.85 eV (reference peak) and 285.75 eV, corresponding to C-C, C-H and C-N bonds, respectively. Which could be explained due to used precursors. Furthermore, the O 1s spectrum was also deconvoluted into three peaks which were assigned to O = C (529.40 eV), C (530.65 eV), and SiO_2 (532.2 eV) bonds. The peak of Si 2p is at 103.1 eV, which agrees with Si 2p in SiO_2 .

The Pb 4f_{7/2} and Pb 4f_{5/2} peaks are observed at 138.7 and 143.7 eV, respectively, presenting a shift respect to the expected values for Pb bound with sulfur. This XPS size shift can be explained, by growth of surface to volume atoms relation and correspondingly relative increase of dangling bonds on the surface while particles' size decreases, providing a nonlinear growth of XPS energy shift to higher values [23]. These results illustrate that the nanoparticles have a SiO₂ core and a lead sulfide surface layer. According to the results of EDS, TEM and XPS, we can affirm that the PbS is bonded to the surface of SiO₂ nanoparticles.

Figure 6 presents the optical absorption of SiO₂-PbS Core-Shell nanospheres suspended in ethanol at the wavelengths range of 250 nm to 800 nm which shows a low and constant absorption in visible region, resulting this material with desirable features for use in window layers in solar cells [24]. The inset in Fig. 6 exhibits the Tauc diagram used to determine the bandgap of nanoparticles. The obtained band gap is about 3.75 eV, which is higher than the PbS bulk band-gap value, due to quantum confinement effect in the nanocrystalline PbS shell, which thickness is approximately 10 nm as was referred previously [9], [25]. The increased effective band gap causes that nanocrystalline PbS structures to be a more suitable window material in solar cell applications.

Conclusions

Silica nanospheres with PbS well-formed shells were successfully synthesized adding citric acid as a second complexing agent to a typical formulation with triethanolamine. Obtaining monodisperse silica nanoparticles was achieved and simplified through the modified Stöber's method in which ultrasonic bath is used instead of magnetic stirring. Both routes are remarkable for low cost and simplicity to prepare a chalcogenide core-shell with perspectives in photonic crystals, solar cells, electronics and biomedical sensors.

Declarations

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Conflicts of interest/Competing interests

No potential conflict of interest was reported by the author(s).

Availability of data and material

The data that support the findings of this study are available from the corresponding author, [A. K. Romero-Jaime], upon reasonable request.

Code availability

Not applicable.

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Figures

Figure 1

a), b) y c) TEM images of the SiO₂ nanoparticles. d) EDS graph of the sample

Figure 2

Size distribution histogram obtained from TEM images of SiO₂ nanoparticles

Figure 3

a), b) y c) TEM images of the SiO₂ nanoparticles coated with PbS. d) EDS graph of the sample

Figure 4

a), b) HRTEM images of SiO₂ nanoparticles coated with PbS. b), d) Diffraction patterns of a) y c)

Figure 5

XPS spectra of silica-lead sulfide nanoparticles (a): typical survey of silica-lead sulfide core shell (A) and uncoated silica nanospheres (B), high-resolution XPS spectra for C1s (b), O1s (c), Si 2p (d) and Pb 4f (e)

Figure 6

The optical absorption of SiO₂-PbS Core-Shell spheres suspended in ethanol at wavelengths of 250 nm to 800 nm. The inset presents the diagram used to determine the band-gap of nano-composite