

One Pot Synthesis, Growth Mechanism and Optical Properties of PbS/Cu₂S Core-shell Nanoparticles

Thelma Serrano and Idalia Gómez

Abstract— The synthesis of PbS/Cu₂S core-shell nanoparticles was carried out by colloidal method using simple stabilizers such as sodium citrate and 3-mercaptopropionic acid. The characterization provided direct proof of the formation of PbS core with size of 11 nm and Cu₂S shell of 5 nm thickness, within type-I core shell arrangement.

Index Terms—About four key words or phrases in alphabetical order, separated by commas, for example, visual-servoing, tracking, biomimetic, redundancy, degrees-of-freedom

I. INTRODUCTION

THE synthesis and characterization of nanoparticles of semiconducting metal sulfide has been an intense field of research due to the interesting properties and potential applications of those compounds. [1-5] Among sulfides, lead sulfide (PbS) and copper (I) sulfide (Cu₂S) have been investigated along the time because of their optical and electronic properties, what make them suitable for photovoltaic devices. [6-7]

PbS nanoparticles are very interesting system in that their particle shapes and sizes can be varied by controlling the synthesis conditions. [8-11] The Bohr radius of PbS is large (18 nm) and its bulk band gap is small (0.41 eV), [12] therefore, it is relatively easy to prepare particles with size smaller than the Bohr radius that show strong quantum confinement effects. Their main advantage, those particles still absorb in the visible part of the spectrum. In addition, PbS and PbSe nanoparticle present the multiple exciton generation phenomena [13-14] and they can produce n excitons for each absorbed photon possessing an energy of at least n multiples of the band gap energy (E_g), where n is an integer number. [15] This phenomenon is very interesting for solar cell devices.

Cu₂S is a p-type semiconductor in which copper atom vacancies act as acceptors, [16] and it has been frequently investigated due to its attractive optical and electrical properties. [17-18] However, copper sulfide has a fairly complex crystal chemistry generally represented as Cu_xS ($2 > x > 1$), because there are numerous stable and metastable species, which have various compositions ranging between

Cu₂S (Chalcocite) and CuS (Covellite) [18-19] in which Cu₂S is not as stable in solution as the CuS [20]. It has been demonstrated that Cu₂S is a good compound for active light-absorbing component. An example is the synthesis of colloidal Cu₂S nanocrystals and its application as an active light-absorbing compound in combination with CdS nanorods in order to produce a solar cell with 1.6% power conversion efficiency and stability over a 4 month testing period. [21]

Cu₂S-PbS heterojunction has been investigated recently due to its optical and photothermal activation. A strong NIR absorption in the spectrum of the Cu₂S-PbS heteronanostructures besides the Cu₂S spectrum was found and it was attributed to the excitonic absorption of PbS nanocrystals. That fact suggest that in this type of heterostructure the photon can be absorbed by both of the two components (PbS-Cu₂S), making them a really interesting system for photovoltaic applications. [22]

An important strategy to improve the nanoparticles efficiency and stability against photo-oxidation of various types of semiconductor is their surface passivation with the growth of a second semiconductor shell, resulting in core-shell system. Scientists have studied and found several methods in order to grow core shell chalcogenide nanoparticles with an emphasis on better control of size, shape, and size distribution. [23] We propose that a material that contains PbS and Cu₂S will enhance both materials optical properties when it is arranged in the core-shell structure. The aim of this paper is to show the results on the synthesis and characterization of the PbS/Cu₂S system. To the best of our knowledge, this is the first time PbS and Cu₂S have been synthesized via a colloidal solution-phase growth method in the core-shell arrangement

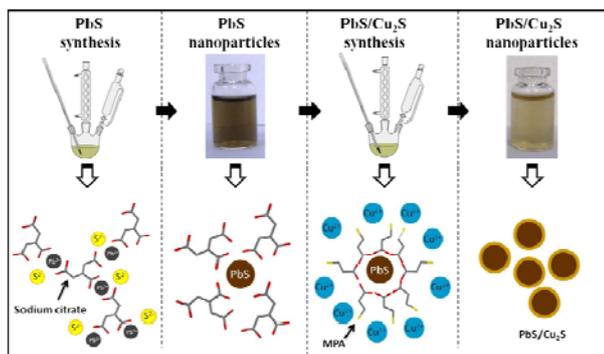
II. EXPERIMENTAL PROCEDURE:

A. PbS nanoparticles synthesis:

Reactants used in this work were all obtained from Aldrich with purities above 99.0%, therefore no further purification was required. All solutions were prepared using distilled water previously degassed under N₂ flow. PbS nanoparticles were prepared with a 1 mL solution of thioacetamide (CH₃CSNH₂) and of lead(II) chloride (PbCl₂) both 30 mM. Previously, 50 mL of sodium citrate (C₆H₅O₇Na₃·2H₂O) 3.0 mM were prepared and the CH₃CSNH₂ and PbCl₂ were added to the sodium citrate solution. Then the pH was varied from 6 to 9 for the different experiments. The mixtures were placed under reflux conditions for 30 min to obtain the dispersed nanoparticles.

Thelma Serrano is with Universidad Autónoma de Nuevo León, Facultad de Ciencias Químicas, Laboratorio de Materiales I, San Nicolás de los Garza, Nuevo León, México (e-mail: serrano.thelma@gmail.com)

Idalia Gómez is with Universidad Autónoma de Nuevo León, Facultad de Ciencias Químicas, Laboratorio de Materiales I, San Nicolás de los Garza, Nuevo León, México (pone: +52 81-83294000 ext. 6362, fax: +52 81-83765375e-mail: maria.gomez@uanl.edu.mx)



Scheme 1 Growth mechanism for the synthesis of PbS/Cu₂S core-shell system by the solution-phase growth method

B. PbS/Cu₂S nanoparticles synthesis:

The PbS nanoparticles previously prepared were used without any purification. 0.50 g of 3-mercaptopropionic acid (MPA, C₃H₆O₂S) were added to the reaction vessel and the pH was adjusted to 8. The mixture was reacted during 30 min under reflux conditions and it was degassed with N₂ flux. Then, a solution of copper chloride (CuCl₂·2H₂O) was added drop wise to the reaction vessel, with a flow rate of 0.30 mL/min. After the addition of the CuCl₂ solution, the mixture was reacted during 6 hours under reflux conditions.

C. Characterization

The synthesized material was studied with different techniques. The size and dispersion of the particles were determined by ultraviolet-visible (UV-Vis), photoluminescence (PL), Dynamic Light Scattering (DSL) method and X-ray diffraction (XRD) with copper radiation ($\lambda = 0.15418$ nm). UV-vis absorption spectra were obtained using a Perkin Elmer UV-vis Lambda 12 spectrophotometer. Fluorescence experiments were performed using a Perkin Elmer PL LS-55 spectrofluorimeter using a wavelength of excitation of 330 nm. All optical measurements were performed at room temperature under ambient conditions. Samples were precipitated with i-propanol-acetone for XRD characterization. The XRD patterns were obtained from a Siemens D5000 Cu K α ($\lambda = 1.5418\text{\AA}$) diffractometer from 5 to 90° 2 θ with a 0.05° 2 θ step and 2 s per step. DSL analyses were performed with a Zetatrac NPA 152 from Microtrac. SEM images were obtained using a FE-SEM JEOL 6701 and HRTEM analysis was performed using a FEI Titan 80-300 microscope.

III. RESULTS AND DISCUSSION

X-ray diffraction spectrum of PbS processed by colloidal method at pH=8 (not showed in the document) consist of a broad peak at 24.3° of 2 θ , which is composed for two overlapped signals, the peak was fitted in order to determine the contribution and position of each signal. Signals centered at 23.8° and 31.2°, were found (see the insert figure on the plot) and they correspond to the 111 and 200 reflections. In addition, reflection at 43.3°, 49.7° and 54.4° are present and they correspond to the 220, 311 and 222 reflections, respectively. The pattern was compared to the galena diffraction pattern (JCPDS File No.5-0592) and it corresponds to the expected face-centered cubic structure of rock salt system, with cell parameter of 5.95 Å. The size of the crystal was calculated applying Sherrer's equation [25],

the mean value of the size of the crystal computed with this equation was 7 nm.

The synthesized nanoparticles remain dispersed in the reaction solution, and they presented a dark-brown color. It is well known that the absorption edge is blue-shifted when the size of semiconductor nanoparticles decreases.[26] For PbS nanoparticles, it was reported that the UV-vis absorption edge shows a marked blue-shift from that of the bulk PbS crystals which is expected around 1200 nm.[19] UV-Vis spectroscopy was applied to obtain information about the size and the light interaction of the PbS nanoparticles. The UV-Vis absorption spectra of the PbS nanoparticles prepared at different pH are show the absorption of the PbS nanoparticles starting at around 800 nm and it increases with decreasing the wavelength, three salient shoulders are present around 600, 400, and 300 nm and they are attributes to exciton peaks of 1s_e-1s_h, 1s_e-1p_h, and 1p_e-1p_h transitions, respectively. [27-28] This is due to quantum confinement, because the average size of the PbS nanoparticles is smaller than the exciton Bohr radius of bulk PbS (18 nm).

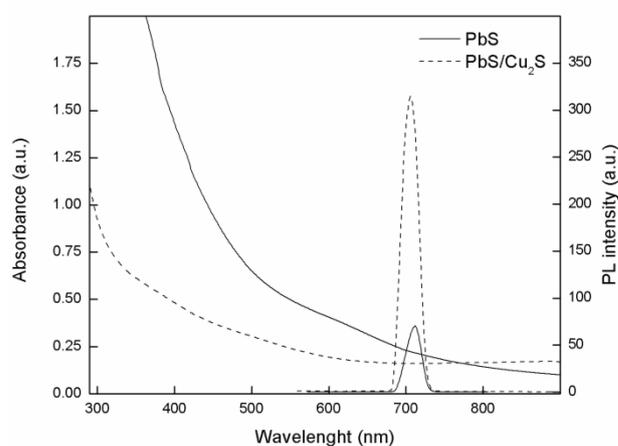


Fig.1 Absorption and PL spectra of PbS nanoparticles and PbS/Cu₂S core-shell nanoparticles

For the PbS nanocrystals prepared in solution, band gap values of 2.2, 1.8 and 1.6 eV were estimated from the UV-vis absorption for the experiments at pH 7, 8 and 9, respectively. It is clear that changing the pH of the reaction mixture, the size particle and the optical characteristics of the material are changing. it can be assumed that particles synthesized at pH=7 present stronger quantum effects, however the chemical stability of those particles is lower than the particles synthesized at pH=8 and the higher amount of defects present on the surface of the particles synthesized at pH=7, may act as exciton traps. In this case, it was decided to work at pH=8 for the synthesis of the core-shell structure. Fig. 1 shows the absorption and luminescence spectrum for PbS nanoparticles synthesized at pH=8 where the absorption spectra follows the previous description meanwhile the PL spectra present an emission peak centered around 700 nm, which correspond to the previously discussed absorption on the UV-Vis spectra for the 1s_e-1s_h exciton transition. FESEM analysis performed on PbS nanoparticles revealed the formation of spherical nanoparticles with an average size of 12 nm. DSL analysis shows a particle size distribution of the PbS synthesized centered around 40 nm obtained. It corresponds to the size of the agglomerates observed by FESEM.

After the addition of the copper solution, the sample presented a change in color and the solubility of the system decreases until the precipitation of gold-brown particles. Scheme 1 illustrates the synthesis process. MPA is an organic carboxylic acid with a thiol functional group (-SH) which may act at the same as a sulfur source, reducing agent for the Cu^{2+} ions and capping agent. Those properties make MPA an ideal candidate for the Cu_2S stabilization. The addition of MPA to the reaction mixture helps to stabilize the PbS nanoparticles by capping its surface, then the Cu^{2+} ions surround the PbS-MPA and they are reduced to the formation of Cu^+ ions. The thiol group leads to the presence of S^{2-} ions which react with the Cu^+ ions linked to the PbS surface to the formation of the Cu_2S shell. The presence of the MPA molecules onto the surface of the PbS/ Cu_2S nanoparticles helps to its chemical stabilization in solution as well as in atmospheric conditions. The synthesized nanoparticles are stable for four days in aqueous solution and one week on air. In the particles are kept under non-oxidative conditions the Cu_2S remains stable. This mechanism corresponds to the growth seed method, where the core acts as a seed where the nuclei of the shell material growth covering the surface to the formation of the shell.

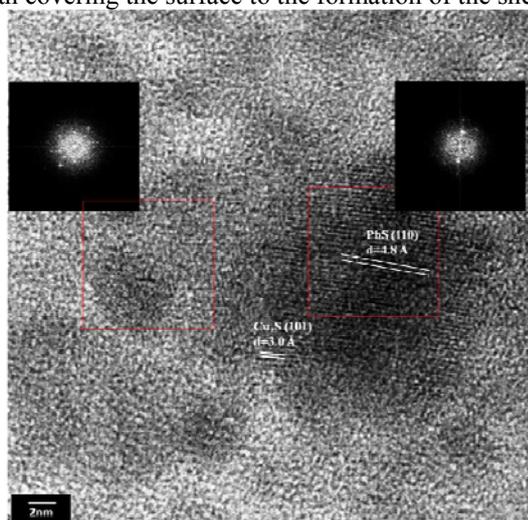


Fig.2 HRTEM image for the PbS/ Cu_2S core-shell system.

Fig. 1 shows the UV-Vis and PL spectra for PbS and PbS/ Cu_2S nanoparticles. It is observed that the main characteristics of the absorption spectra of PbS nanoparticles are present for the PbS/ Cu_2S nanoparticles, where the exciton signals still could be appreciated. The absorption wavelength for the PbS/ Cu_2S system was significantly blue shifted from the one of PbS due to the addition of the Cu_2S shell. This can be attributed to the absorption region of the Cu_2S which is regularly observed in the visible light range. This interaction provides a material with the good optical properties of the PbS nanoparticles in the visible range instead of the NIR range, what makes a good advance for the development of photovoltaic devices. In addition, the absence of peaks at NIR, characteristics of CuS formation, in the PbS/ Cu_2S spectrum indicates the formation of the Cu_2S desired material with high purity.

The band gap for the core-shell nanoparticles was calculated to be 2.1 eV, that value is larger than the $E_g(\text{bulk})$ of Cu_2S (1.21 eV) [17] and it gives an idea about the quantum confinement of the system, due to the core-shell structure. The main optical modification is observed on the PL spectra, where the intensity of the PL is dramatically

increased. This fact corresponds to the description of a type-I core-shell system where the growth of the shell reduces the surface dangling bonds, and significantly improves the fluorescence of the system. This observation is attributed to a partial leakage of the exciton into the shell material.

Finally, HRTEM, showed in Fig. 2, was employed to study the morphology of PbS/ Cu_2S . It can be seen that the nanoparticles are basically spherical shaped with a total diameter of around 20 nm. The PbS core presents a size around 11 nm, with an interplanar distance characteristic for the PbS system in the cubic face centered structure [7], this fact is in agreement with the observations discussed in the XRD analysis. The shell presents a thickness of around 5 nm, with an interplanar distance of 3.0 Å, corresponding to the (101) lattice plane of hexagonal Cu_2S [6]. This analysis confirms the presence of the material in the desired core-shell configuration.

IV. CONCLUSIONS

This work describes the synthesis of PbS/ Cu_2S core shell nanoparticles with emission on the visible range and with improved luminescence properties. The synthesis was carried out by the colloidal solution-phase growth method by using simple stabilizers such as sodium citrate and 3-mercaptopropionic acid and the core shell arrangement for particles with different crystalline structure was achieved. This is the first report related to the synthesis of PbS/ Cu_2S core/shell system, to the best of our knowledge, the data from absorption spectra, UV-vis, PL spectra, and TEM provided direct proof of the formation of PbS core with size around 11 nm and Cu_2S shell of 5 nm thickness. According to the UV-vis absorption and PL spectrum, the system presents the optical characteristics observed in a type-I core shell arrangement.

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