

Chemical and structural characterization of PbS-SiO₂ Core-shell structures synthesized by ultrasonic wave-assisted chemical bath deposition.

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Heavy metal sulphures such as lead sulfide (PbS) are semiconductors used in electronic devices. By controlling the size, shape and chemical components of this type of materials, it's optical and electronic properties can be manipulated [1]. PbS has a small hole which is almost equal to electron mass, this leads to a large exciton with a Bohr radius of 20nm, approximately. In nanometric size, electrons and holes and, by consequence, the exciton, can be strongly confined [2]. The ability for adjusting the energy emitted by the lead's photon in a quantum system, in the region near IR of the electromagnetic spectrum makes this material desirable for the production of quantum dots, nanotransistors, solar cells, among other optoelectronic devices. The commonly used formula to synthesize PbS contains trietanolamine as complexing agent. In this work we exchange that compound for citric acid (C₆H₈O₇), which is commonly found and easily biodegraded.

Monodisperse silica microspheres were synthesized by sol-gel process, using the Stöber method [3]. By varying the concentration of the precursors, the size of the silica particles can be controlled. The following precursors were used: tetraethylorthosilicate (TEOS, Si(OC₂H₅)₄) as precursor of silica, ethanol and deionized water as solvents and ammonia hydroxide (NH₄OH) as a catalyst. The synthesis took place in a glass beaker at room temperature with magnetic stirring for 24 hours. Once the reaction is finished, the obtained microspheres were washed using centrifugation and deionized water.

For the core-shell PbS-SiO₂ structures, the monodisperse silica microspheres were used as a base for PbS nanoparticles to grow on by using ultrasound assisted chemical bath. The following precursors compounds were used: lead acetate (Pb(C₂H₃O₂)₂) 0.5M and thiourea (SC(NH₂)₂) 1M as a PbS precursors, sodium hydroxide (NaOH) to enhance OH⁻ ion release, this way controlling the reaction's pH, citric acid (C₆H₈O₇) as complexing agent and deionized water. We included the colloidal spheres solution and placed the beaker in an ultrasonic bath for sonication. The obtained samples of decorated spheres were washed with deionized water; afterwards they were dried in a conventional oven at 75°C. For comparison, a sample without silica microspheres was synthesized to obtain only PbS nanopowders.

Monodisperse silica of ~550 nm was obtained; they were analyzed by Dynamic light scattering using a Zetasizer Nano Range analyzer (Malvern). PbS was synthesized in an ultrasonic bath with an innovating, less harmful and less costly formula than conventional ones. In Figure 1, X-Ray Diffraction patterns of both samples with and without silica are presented. It is observed that for both samples PbS is obtained, and for the PbS-SiO₂ sample the presence of hydrocerussite (Pb(CO₃)₂(OH)₂) was identified. It seems that the citric acid in the presence of the microspheres promotes the formation of the hydrated lead carbonate as a secondary reaction product. X-ray photoelectron spectroscopy (XPS) of the PbS powders was carried out in Perkin Elmer PHI 5100 spectrometer and the results are displayed in Figure 2. Analysis of the high resolution spectra of C 1s, O 1s, S 2p and Pb 4f photoelectron lines shows

that PbS powders it does contain hydrocerussite and lead oxide. Pb $4f_{7/2}$ is located at 138.3 eV and it corresponds to lead in hydrocerussite [4]. Scanning electron microscopy measurements were performed on the PbS decorated silica spheres, the samples were gold coated for observations. It can be seen in Figure 3 a) the laminar crystals of hydrocerussite, which have sizes larger than 1 μm . At higher magnifications it can be observed that the silica spheres are irregularly coated and small crystals are scarcely dispersed over the sphere surface. EDS analysis showed that the surface is rich in lead, which it can indicate PbS starts to growth on this new layer [4]. It can be concluded that citric acid can be used as a complexing agent for PbS synthesis by ultrasonic wave-assisted chemical bath deposition [5].

References:

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 [5] The authors acknowledge the participation of Dr. Bárbara Bermudez Reyes from the Research Center of Aeronautic Engineering and Innovation of the University of Nuevo León (CIIA-UANL), México, for her valuable assistance with SEM characterization.

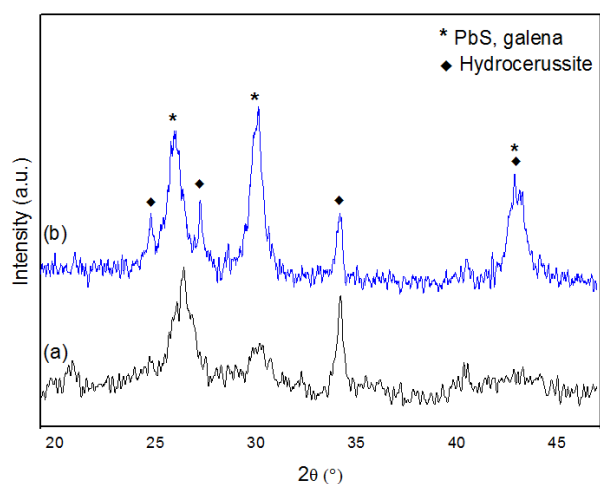


Figure 1. XRD pattern of a) PbS powder, b) PbS-SiO₂ system.

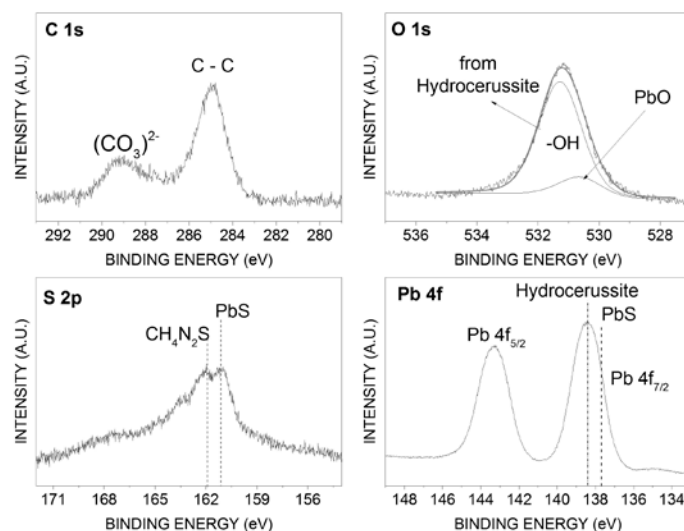


Figure 2. XPS high resolution spectra of C 1s, O 1s, S 2p and Pb 4f photoelectronic lines of PbS. [4]

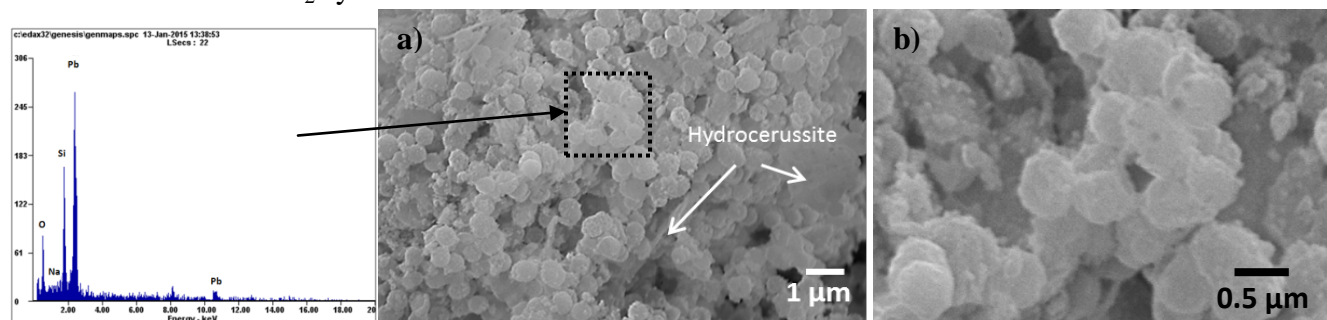


Figure 3. SEM images of the PbS-SiO₂ core-shells.