

PREPARATION OF PbS/SiO₂ NANOCOMPOSITES FROM SILICA GELS CONTAINING COVALENTLY INCORPORATED LEAD THIOLATE PRECURSORS

JOSHUA T. MOORE, TIFFANY P. MARSH, AND ELVIN WOODRUFF

Tennessee State University, Department of Chemistry, Nashville, TN 37209 (JTM, TPM)
Magnify Inc., Nashville, TN, 37216 (EW)

ABSTRACT—Precursor gels containing covalently incorporated lead thiolate complexes have been prepared using the bifunctional linker molecule, 3-mercaptopropyltrimethoxysilane along with typical sol-gel processing techniques. Formation of PbS/SiO₂ nanocomposite materials with average particle sizes of 7.97 nm have been prepared by the controlled thermal decomposition of the precursor gels in a N₂ atmosphere. Precursor gels and nanocomposite materials have been characterized using powder X-ray diffraction and transmission electron microscopy. These results demonstrate a facile and convenient method for the production of practical quantities of nanocrystals of PbS embedded in a ceramic host matrix.

The synthesis, characterization, and properties of nanoscale materials has been an area of considerable research interest in many diverse areas of scientific endeavor due to their unique optoelectronic, magnetic, and catalytic properties (Stucky, 1991). In particular, semiconductor nanostructures have received a great deal of attention due to their size-tunable optical properties, quantum confinement effects, and applicability in a wide range of technologies (Henglein, 1989; Steigerwald and Brus, 1990; Alivasatos, 1996).

Preparation of semiconductor/ceramic nanocomposites (materials consisting of nanoparticles [diameters \leq 100 nm] dispersed throughout a ceramic host matrix) is an attractive option for the preparation of practical and easily processed quantities of semiconductor nanocrystals. Ceramic SiO₂ matrices are ideal host materials for semiconductor nanocrystals because SiO₂ is a well characterized material that is known to passivate semiconductor nanocrystal surfaces. However, with the exception of I–VII and select II–VI materials, semiconductor nanocrystals cannot withstand the harsh oxidizing environment found in the high temperature melts associated with traditional ceramic processing. The sol-gel method is an attractive and practical alternative to traditional ceramic preparative methods. The sol-gel reaction provides a low-temperature, solution-phase route for the preparation of various ceramics and metal oxides thus providing an environment suitable for the incorporation or growth of semiconductor nanocrystals. The preparation, characterization and properties of semiconductor/ceramic nanocomposites have recently been reviewed (Moore, 2008).

Lead sulfide is a narrow band-gap, IV–VI semiconductor that absorbs strongly in the infrared region of the electromagnetic spectrum. This property grants PbS a myriad of potential applications in IR sensing and detection technologies. The small band gap energy of 0.41 eV for PbS gives it a large Bohr exciton diameter leading to pronounced quantum confinement effects with nanoparticle diameters of up to \sim 18 nm.

Some of the most prevalent preparative methods for the synthesis of PbS nanocrystals and nanocomposites involve either precipitation from aqueous solution or the reaction of either lead(II) acetate or lead(II) oxide with bis(trimethylsilyl) sulfide in diphenyl ether or other coordinating solvents (Murray et al., 2001; Lobo et al., 2005). These syntheses yield nanocrystalline PbS colloids with average diameters of 3.1–7.6 nm in solution but require subsequent reactions to functionalize the nanocrystal surface in order to incorporate the PbS nanocrystals into a ceramic host matrix. PbS/SiO₂ nanocomposites have been prepared previously by Espiau de Lamaestre et al. (2004, 2005) using a sequential ion implantation and annealing technique. Yao et al. (2000) have prepared silica aerogels doped with PbS nanocrystals by impregnating a preformed silica aerogel with an aqueous solution of PbS colloids, followed by annealing forming nanocomposites with nanocrystal diameters of \sim 15 nm. Another method for the preparation of PbS/glass nanocomposites illustrated by Romano and Alves (2006) involves the use of lead dithiocarbamates, *e.g.* Pb(S₂CNR₂)₂, as single-source molecular precursors, first demonstrated by Trindade et al. (1997) for the preparation of PbS nanocrystals from similar lead dithiocarbamates. Solution impregnation of the precursor molecule into a sample of porous vycor glass followed by pyrolysis at 250°C for 12 h affords PbS/glass nanocomposites with nanocrystal diameters of 10–20 nm. Krauter et al. (1994) have reported the preparation of bulk samples of PbS via the thermal decomposition of lead bis(butylthiolate) precursors such as Pb(SBu¹)₂. However, to the best of our knowledge, lead thiolates have not been used as single-source molecular precursors for the preparation of PbS nanocrystals or PbS/SiO₂ nanocomposites.

Herein we report the synthesis of silica gel precursors containing covalently bound lead thiolate precursors and the subsequent formation of PbS/SiO₂ nanocomposites with average nanocrystal diameters of approximately 8 nm *via*

pyrolysis of the *in situ* generated lead thiolate single-source precursors.

MATERIALS AND METHODS

Reactions were performed under ambient conditions in oven-dried glassware unless otherwise noted. The chemical reagents tetramethylorthosilicate (TMOS) and 3-mercaptopropyltrimethoxysilane (HS(CH₂)₃Si(OMe)₃) were purchased from Acros Organics. Lead acetate trihydrate (Pb(O₂CCH₃)₂·3H₂O, Pb(OAc)₂), and 2-methoxyethanol were purchased from Fisher Scientific. All other solvents were of reagent grade and were used as received from Fisher Scientific. Lead thiolate containing precursor gels were prepared using conventional sol-gel processing techniques (Brinker and Scherer, 1990).

Thermal treatments of the precursor silica gels and xerogels were carried out in a Lindberg Blue programmable tube furnace. Samples were ground to fine powders and were transferred to a glazed alumina combustion boat which was then inserted into a vycor glass reaction tube equipped with a thermocouple situated directly above the boat. Gas flow rate through the quartz reaction tube was approximately 150 mL/min.

Nanocomposite materials were examined and imaged using a Phillips CM10 transmission electron microscope operating at 100 kV equipped with an AMT 2 mega-pixel camera. Samples for TEM were prepared by putting one drop of a nanocomposite/acetone suspension onto a 3 mm diameter copper grid covered with lacey carbon film as a substrate and allowing the solvent to evaporate. Particle-size distributions were obtained by manual measurement of particle diameters from bright-field TEM micrographs.

Powder X-ray diffraction (XRD) data was obtained using a Shimadzu XRD-6000 automated powder diffractometer with a Cu target, a Ni-monochromator, and a solid state detector. For particle-size determinations, XRD scans were corrected for background scattering and were stripped of the K_{α2} portion of the diffracted intensity using the XRD-6000 software package provided by Shimadzu. Observed peaks were fitted with a profile function to extract the full-width-at-half-maximum (FWHM) values. Average crystallite size, *L*, was calculated from Scherrer's equation, $L_{hkl} = K\lambda/b\cos\theta$, assuming that peak broadening arises from size effects only (where *b* is the FWHM of the peak measured in radians on the 2θ scale, λ is the wavelength of X-rays used, θ is the Bragg angle for the measured *hkl* peak, and *K* is a constant equal to 0.90 for *L* taken as the volume-averaged crystallite dimension perpendicular to the *hkl* diffraction plane) (Klug and Alexander, 1974).

Preparation of PbS/SiO₂ Nanocomposites—PbS/SiO₂ nanocomposites were prepared with a nominal 25:1 SiO₂:PbS molar ratio. A beaker was charged with 5.0 mL (5.15 g, 33.8 mmol) of TMOS, 0.287 mL (0.301 g, 1.53 mmol) of HS(CH₂)₃Si(OMe)₃, 1.0 mL (55.5 mmol) of water, and 0.200 mL of 0.296 M NH_{3(aq)}. This turbid solution was made clear upon the addition of 5 mL of methanol. This solution was allowed to pre-hydrolyze for 1 h. During this period, a solution of 0.583 g (1.54 mmol) of Pb(OAc)₂·3H₂O in 5 mL of 2-methoxyethanol was prepared. After 1 h, the Pb(OAc)₂ solution was added to the TMOS/HS(CH₂)₃Si(OMe)₃ solution/sol in one portion yielding a yellow solution. A clear yellow gel was obtained after standing for 12 h. The gel was fractured, harvested, and washed with three 25 mL portions of reagent grade acetone to remove excess organic compounds.

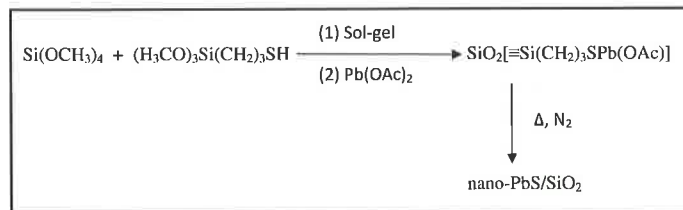
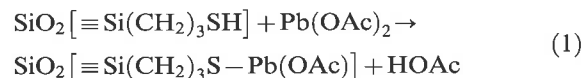


FIG. 1. Synthesis of PbS/silica xerogel nanocomposites.

The gel was dried at 125°C for 30 min affording a dry, pale yellow lead thiolate doped silica gel precursor. Pyrolysis of the precursor gel at 300°C for 30 min in an N₂ atmosphere yields a uniformly brown-black PbS/SiO₂ xerogel nanocomposite.

RESULTS AND DISCUSSION

Nanocrystals of PbS semiconductor dispersed throughout a silica xerogel matrix have been synthesized by pyrolysis of lead thiolate precursor gels prepared using sol-gel processing techniques, as shown (Fig. 1). The lead thiolate precursor gels are prepared by the *in situ* reaction of lead acetate with a thiol-modified silica gel. The overall process entails three steps: (1) co-hydrolysis and condensation of TMOS with the bifunctional linker molecule, (2) reaction of the sol with an alcoholic solution of lead acetate followed by gelation, and (3) pyrolysis of the precursor silica gels containing *in situ* generated lead thiolate precursor gels in a N₂ atmosphere to form PbS nanoclusters dispersed throughout a silica xerogel matrix. 3-Mercaptopropyltrimethoxysilane, structure shown (Fig. 2), was used as the bifunctional linker molecule to covalently graft lead thiolate complexes into the growing silica gel matrix. The reaction of lead acetate with the thiol moiety of the linker molecule in the growing sol generates a lead thiolate linkage through a simple acid/base reaction as shown below.



Transmission electron micrographs of the PbS/SiO₂ nanocomposites reveal PbS nanocrystals of high contrast widely dispersed throughout the amorphous silica xerogel matrix. Smaller nanocrystals do not display any definite shape and are mostly spheroidal in appearance. A representative TEM micrograph is shown (Fig. 3a). Average nanocluster diameter from bright field TEM micrographs was determined to be 7.97 ± 2.24 nm. However, very large microcrystals, diameters of 100–500 nm, can be obtained when precursor gels

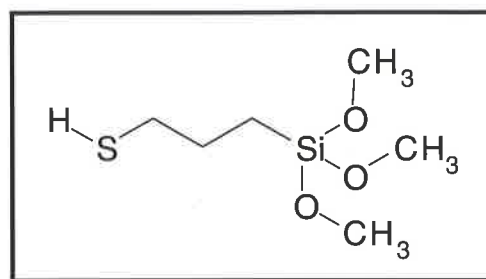


FIG. 2. Molecular structure of the bifunctional linker molecule, 3-mercaptopropyl trimethoxysilane.

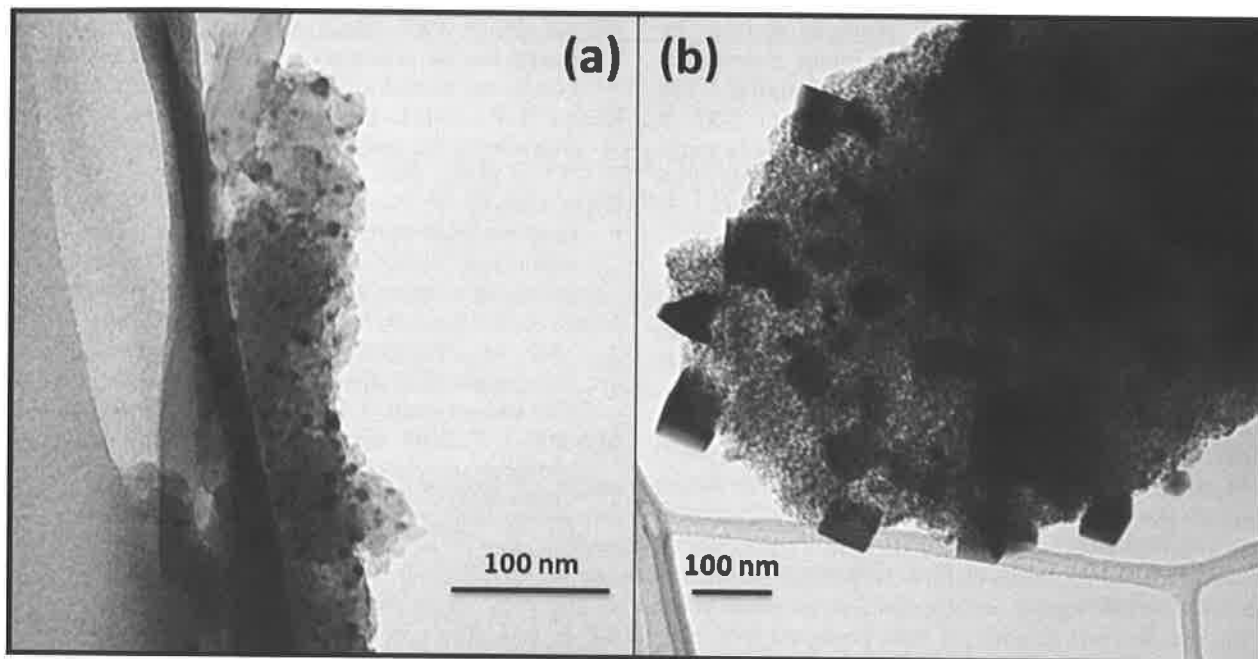


FIG. 3. TEM micrographs of (a) PbS/SiO₂ nanocomposite and (b) PbS/SiO₂ nanocomposite showing large nanocrystal sizes and cubic crystal morphology.

are prepared with higher loadings of *in situ* lead thiolate precursor and thermally treated at higher and/or longer processing temperatures and times. These nanocrystals adopt a distinctly cubic nanocluster morphology as shown (Fig. 3b). This is most likely the result of coalescence growth and crystallization of larger PbS particles within the lower density areas of the ceramic matrix that may have occurred during thermal treatment. A particle-size histogram obtained from bright field TEM images for PbS/SiO₂ nanocomposites is shown (Fig. 4).

Powder XRD scans of PbS/SiO₂ nanocomposites from 20–60° in 2 θ show amorphous scattering from the ceramic gel component as well as the (111), (200), (220), (311), and (222) diffraction peaks expected for cubic PbS. A representative XRD scan of a PbS/SiO₂ nanocomposite is shown (Fig. 5). Average particle sizes of the PbS nanoclusters within the nanocomposites, determined from XRD peak widths using

Scherrer's equation, are 6.28 ± 2.62 nm. The nanocomposites prepared may contain some fraction of PbS particles having diameters significantly larger than the number-average particle sizes determined by TEM as shown (Fig. 3b). However, this fraction must be relatively small as evidenced by the average particle size determined using Scherrer's analysis. Calculation of the PbS cell constant from the *d*-spacing values extracted from the XRD data results in a value of 5.95 ± 0.1416 Å which is in good agreement with the accepted value of 5.936 Å.

CONCLUSION

The observations described herein provide convincing evidence that PbS semiconductor nanocomposites can be

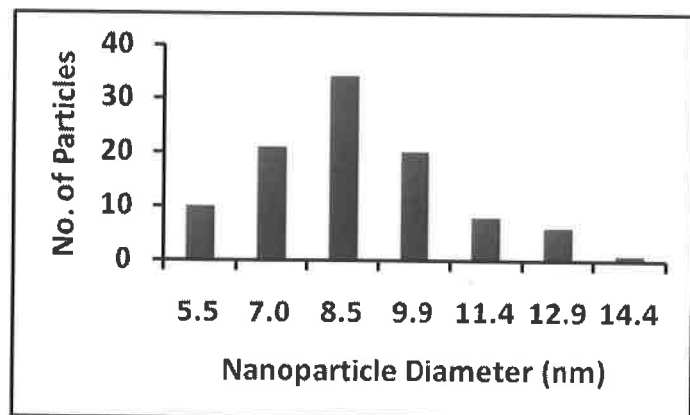


FIG. 4. Histogram of PbS nanocrystal diameters typical of the PbS/SiO₂ nanocomposites as measured from bright field TEM images.

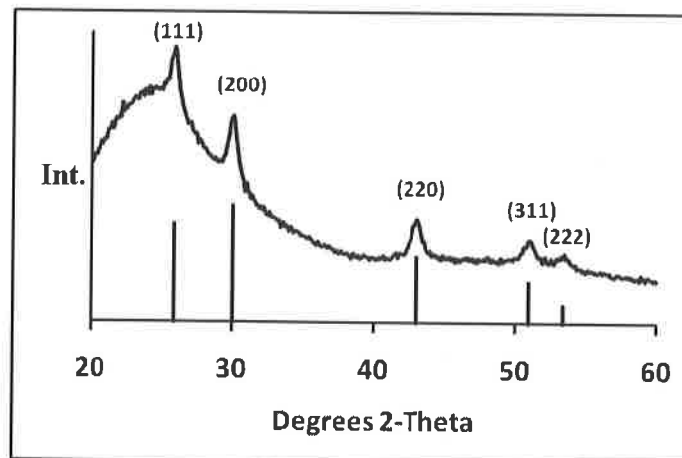


FIG. 5. Powder XRD pattern (Cu K α radiation) typical of a PbS/SiO₂ nanocomposite including the standard line pattern and peak assignments for face-centered cubic PbS. The y-axis represents diffraction intensity (arbitrary units).

conveniently prepared using a sol-gel synthesis strategy by pyrolysis of *in situ* generated lead thiolate precursors covalently incorporated into the silica gel matrix. The nanocrystals produced have average diameters of 7.97 ± 2.24 nm, are highly crystalline, and possess spherical to cubic morphology. PbS/SiO₂ nanocomposites of variable PbS content can be prepared using this synthetic strategy.

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