



Stability and aging studies of lead sulfide quantum dot films: Photoabsorption, morphology, and chemical state characteristics



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H I G H L I G H T S

- The optical and morphological stability of colloidal PbS QD films deposited on glass substrates was characterized.
- Optical microscopy, TEM, NIR, XPS and XRD were used to characterize the QD films.
- Two QD deposition approaches were compared: traditional solvent deposition and supercritical fluid CO₂ deposition.
- The study examined the QD stability over a short term and a long term periods.
- The PbS QD characteristics were found to be affected by two simultaneous processes, oxidation and sintering/ripening.

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The stability of colloidal PbS quantum dot (QD) films deposited on glass substrates was studied over a short term and a long term periods, when left unprotected in air under ambient conditions. Two deposition approaches were used, traditional solvent deposition method (SDM) and supercritical fluid CO₂ deposition (SFD). To track possible changes to the QDs over time, near infrared (NIR) spectrometry, X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and optical microscopy, were employed. Evidence points towards initial oxidation-induced shrinking of the active QD volume causing a blue shift of the absorption over the first four months, and then experiencing competition from oxidation and sintering/ripening of the QDs, resulting in a red shift. The presented studies have important consequences for the long term reliability of light emitters based on PbS QDs.

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1. Introduction

Semiconductor quantum dots (QDs) have attracted great attention due to their unique optical absorption and emission properties related to the quantum confinement effect. Thin films of these QDs are emerging as an important class of materials for electronic and optoelectronic devices such as field-effect transistors [1,2], photodetectors [3–6], light-emitting diodes [7–9], metamaterials [10–12], and solar cells [13,14], making QDs promising candidates for many potential applications.

As a consequence, the optical and electrical stability of colloidal quantum dots used in these types of devices is an important issue. During the last decade, the effects of UV photo-induced oxidation on the chemical state of colloidal PbS QD films have drawn

attention [15–19]. Oxidation and heating can also have a detrimental impact upon the morphology and optical properties of PbS QD films. QD oxidation causes a blue shift of both the absorption and the emission transitions [17]. The oxidation-induced reduction in the size of the PbS “core” increases quantum confinement, causing shifts to higher energies in both the emission peak and the NIR absorption band edge. To date, most investigations of IV–VI QD stability have focused on thermally-activated oxidation of PbX (X = S, Se, Te) QD solutions or solid films, which rapidly decreases the physical and electronic size of the QDs, increasing the confined state energy separation and causing excitonic blue shifts of absorption and emission spectra [15–17]. However, the rate of aging of PbS QDs in ambient environments has not been thoroughly studied.

In this study, the stability of the PbS QD films under ambient conditions was studied, with particular attention to changes in the oxidation state of the QDs over a period of eleven months. The PbS

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QD films were fabricated by supercritical fluid CO₂ deposition (SFD) and traditional solvent deposition method (SDM). The aging of these films was investigated using UV–Vis–NIR spectrophotometry, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), powder X-ray diffraction (XRD) and optical microscopy. The impact of the PbS QD film deposition processes on QD morphological stability was also studied.

2. Experimental

2.1. Sample preparation and measurements

Oleic acid-capped PbS nanoparticles were synthesized in our laboratory using a procedure reported by Hines and Scholes [20]. The synthesized PbS QDs were dispersed in toluene. The films were formed by employing both the SFD and SDM methods. The SFD process was carried out using a 35.3 mL high-pressure stainless steel chamber. A typical supercritical fluid deposition system consists of a CO₂ source (liquid CO₂ tank), a syringe pump (ISCO model 260D) with a pump controller (ISCO Series D), high-pressure stainless steel cells, and a collection vessel. In this study, PbS QDs with size 4.7 nm and glass substrate were used.

For the glass substrates, a special apparatus designed in our laboratory [21] was used to deposit PbS QD films uniformly in the SFD method. TEM samples in copper grids were stored over long periods in polyethylene sample holders in air and at room temperature.

2.2. Instruments

Carbon-coated copper grids were purchased from Ted Pella and used to prepare samples for TEM nanoparticle imaging and size determination. To deposit nanoparticles on the copper grids, the grids were immersed in small glass container containing a nanoparticle solution. The container with solution was placed in a supercritical fluid CO₂ reaction cell which was preheated to a desired temperature. A 4 μ L droplet of diluted PbS toluene solution was dripped onto copper grid, and then dried at room temperature in air. A Phillips CM 200 LaB₆ (lanthanum hexaboride) cathode TEM operating at 200 kV was used for both low and high resolution imaging. The average size of the PbS nanoparticles was obtained from the TEM images using ImageJ software and by counting at least 300 particles.

NIR absorbance spectra were obtained on a Cary 5000 Varian UV–Vis–NIR spectrophotometer using pre-deposited PbS nanoparticles on a piece of glass, scanning from 400 to 1600 nm. A Zeiss Axiotron optical microscope instrument was used to study, at low magnification, the surface morphology of the PbS QD films produced by both the SFD and SDM methods.

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D&Advance X-ray powder diffractometer with graphite monochromatized Cu K α ($\lambda = 0.15406$ nm) source. A scanning rate of 0.05° s⁻¹ was applied to record the pattern in the 2 θ range of 20–90°.

XPS was used to assess long-term changes in the overall composition and chemical state of PbS QDs deposited on glass substrates by both the SFD and SDM methods. The spectra were acquired on a Perkin–Elmer Phi 5400 system, equipped with a non-monochromatic magnesium X-ray source and a hemispherical sector photoelectron energy analyzer, with the extraction lens accepting signal from a 1.1 mm diameter area. High resolution spectra were acquired using 0.1 eV step size, a dwell time of 100 ms, 400 sweeps, 25 eV pass energy, a photon-analyzer angle of 54.7°, and a take-off angle of 45°. Data manipulation was performed using CasaXPS software [22]. Compositions were determined from the

relative peak areas of the Pb 4f, S 2s, O 1s, and C 1s transitions after weighting the areas according to published atomic sensitivity factors for a 54.7° included angle between the incident X-rays and the extracted photoelectrons [23]. High resolution spectra from these same transitions were examined to identify the different oxidation states of both lead and sulfur within each transition, and to determine their relative proportions [24]. The proportions of oxidation states were determined by fitting the peak envelopes with component peaks having mixed Gaussian/Lorentzian (G/L) character. The appropriate G/L mixture, i.e., the component peak shape, was ascertained independently for each spectrum, by heuristically determining the best statistical fit for the C 1s peak of each spectrum, i.e., the G/L mixture was varied until the peak fitting algorithm produced the lowest mathematical residual when compared to the actual C 1s data [22]. The C 1s peak was chosen for this purpose because it possessed the narrowest inherent peak width of any peak in the spectrum. Typically, a 30/70 G/L ratio provided the best fit, although some samples required different ratios. The range varied from 50/50 to 25/75, presumably because of differences in charging. The subsequent fitting of the lead and sulfur peaks were constrained by that spectrum's unique G/L mixture. This peak fitting was performed after shifting the binding energy scales of the spectra to account for charging. The binding energy scales were shifted by the value that placed the lowest energy component of the O 1s transition at 532.0 eV, after subtracting the spectral signal contributions originating in X-ray source satellite peaks, and after subtracting background signal using the Shirley algorithm (Pb 4f, O 1s) or a linear background subtraction (S 2s). The oxidation state analysis of lead was performed using the Pb 4f transition in the 138–145 eV binding energy region. The sulfur oxidation state analysis used the S 2s transition at approximately 225–232 eV [24,25].

3. Results and discussion

3.1. Absorption studies of PbS films deposited by SDM and SFD

The change in maximal wavelength of optical absorbance spectroscopy is one method for characterization of QD optical properties. It provides a direct measurement of excitonic transition in absorption spectra between ground state and excited state. It avoids complications which could occur due to surface defects and less surface passivation as with photoemission spectroscopy [26,27] which is associated with the maximal emission wavelength between the two energy levels [28]. Absorbance measurements were made periodically over eleven months from PbS QDs deposited by both SDM and SFD onto glass which remained unprotected in ambient conditions. The absorbance data are shown in Figs. 1 and 2. Over the first four months, the SFD absorbance maximum (Figs. 1a and 2) experienced a blue shift by approximately 20 nm (15 meV), from the initial absorbance maximum of 1304 nm to a value of 1284 nm. The peak shift was presumably caused by an oxidizing effect due to exposure to air, in which the oxidation of Pb and S on the outer surface of the QDs reduced the active size and thereby created a blue shift [17].

Over the same four months, the PbS QD film deposited by SDM onto glass also showed a blue shift in the absorbance maximum by 34 nm (25 meV), from an initial value of 1304 nm to a final value of 1270 nm (Figs. 1b and 2). The absorbance maximum of the films made by the SFD method shifted less than that of the SDM films, perhaps because the SDM deposited films possess a relatively larger surface area due to the uneven, porous, and “coffee ring” changes in film thickness, as shown in Fig. 6a below. This presents favorable conditions for oxidation. This spectral blue shift trend for both SDM and SFD was steady over four months (Fig. 2).

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