Lead selenide quantum dot polymer nanocomposites

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Abstract. Optical absorption and fluorescence properties of PbSe quantum dots (QDs) in an Angstrom Bond AB9093 epoxy polymer matrix to form a nanocomposite were investigated. To the authors' knowledge, this is the first reported use of AB9093 as a QD matrix material and it was shown to out-perform the more common poly(methyl methacrylate) matrix in terms of preserving the optical properties of the QD, resulting in the first reported quantum yield for PbSe QDs in a polymer matrix, 26%. The 1-s first excitonic absorption peak of the QDs in a polymer matrix red shifted 65 nm in wavelength compared to QDs in a hexane solution, while the emission peak in the polymer matrix red shifted by 38 nm. The fluorescence quantum yield dropped from 55% in hexane to 26% in the polymer matrix. A time resolved fluorescence study of the QDs showed single exponential lifetimes of 2.34 µs and 1.34 µs in toluene solution and polymer matrix respectively.

Keywords: Quantum dots, lead selenide, PbSe, nanocomposites, optical properties, fluorescence

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1. Introduction

Quantum dot (QD) and polymer nanocomposites are an increasingly important class of materials. They are being researched for use in many applications, such as luminescent solar concentrators (LSCs) [1,2], temperature and chemical sensors [3,4], biomedical imaging [5], white light emitting phosphors [6], radiation sensors [7–9], and others. Pb-salt QDs are particularly promising as luminophores for LSCs because of their wide absorption band and limited self absorption [1].

Temperature sensors can be based on both photoluminescent (PL) intensity and PL peak position, depending on the matrix and QDs used. Bueno et al. used CdTe QDs in polymer and showed a quadratic temperature dependence of PL intensity and a 0.25 $\frac{\text{nm}}{^{\circ}\text{C}}$ shift in PL peak position over the range of 25°C to 50°C [3].

Thin films of CdSe QDs in poly(methyl methacrylate) (PMMA) have been used to detect benzene, toluene, and xylenes in the environment for remediation. A 15 ppm detection threshold was demonstrated for xylenes using QD PL intensity [4].

QD nanocomposites are also useful for biomedical imaging. Wei et al. fabricated CdSe/ZnS QD nanocomposite PMMA fibers with good bio-compatibility for use as a cell growth scaffold towards PL-based imaging [5].

The lighting and entertainment industries have also been investigating nanocomposites for white light emitting or tunable phosphors. When CdSe QD nanocomposites are used as a coating for LEDs, the LEDs are able to more faithfully approximate an ideal or natural light source [6].

Numerous groups are investigating nanocomposites for radiation sensors including X-ray, neutron, gamma, and charged particle detection [7–9]. These sensors are not limited by crystal growth like many scintillators in use today, have better room-temperature energy resolution, and exhibit low afterglow from their faster PL decay time. Pb-salt QDs have better X-ray absorption properties than the Cd-salt QDs in use today for these sensors, and could improve sensitivity.

These applications take advantage of the QD's unique tunable fluorescence and other size dependent properties. Zinc or cadmium sulfide and selenide based core/shell QDs have generally dominated research interests because of their relatively high quantum yield (QY) compared to other available QDs. However, Pb-salt QDs can be tuned across a much larger spectral region, including many wavelengths important to the communications industry, making them desirable in many applications.

Pb-salt QDs have recently been produced with high QY—60% or greater—and their optical properties in solution have been reported [10]. These QDs are interesting because of their broadband absorption, greater separation of absorption and emission spectra compared to other QDs, and their ability to emit in the visible or near-IR region.

But, for many practical applications, QDs must be incorporated into a solid matrix. QDs interact with and can be damaged by their host matrix, and finding an appropriate matrix that is optically transparent and non-interacting is challenging. Additionally, different QDs can have vastly different surface chemistries, necessitating a compatibility study of each system. For example, Gallagher et al. showed that, depending on the matrix material, as much as 77.5% of the original PL intensity could be maintained for their CdSe/ZnS QDs compared to a reference solution, while other tested matrices maintained only 4% [11].

In this study, we demonstrate a suitable solid polymer matrix for incorporation of PbSe QDs and report the nanocomposite's optical properties. The results of changes in optical absorption, fluorescence spectra, and QY are reported for the nanocomposite as compared to solution. The QD fluorescence lifetime in polymer is compared with QDs in a toluene solution. A polymer nanocomposite with over 25% QY has been demonstrated.

2. Experimental

2.1. QD synthesis

The procedure for fabrication of the PbSe QDs used here is based on the method described by Evans et al. [12]. Lead(II) oxide powder ($\geq 99.9\%$; PbO), oleic acid (90% tech. grade; OA), decane (99%), and selenium pellets ($> 99.99\%$; Se) were purchased from Sigma-Aldrich. Di-i-butylphosphine (97%; DiBP) was purchased from the Strem chemical company, and n-hexane ($> 95\%$) from Fisher Scientific. Toluene was purified by passage through activated alumina in Q5 columns from Glass Contour Co.

Ahead of time, 1.0 mL of DiBP (5.7 mmol) and 0.45 g of Se shot (5.7 mmol) were combined with 4.6 mL anhydrous toluene and stirred overnight in a nitrogen filled glove box to produce 1 M DiBPSe. The mixture was gently heated to 50°C yielding a clear pale yellow solution. Pb(oleate)_2 was created by combining 0.11 g PbO (0.5 mmol) with 0.375 mL OA (1.4 mmol) and 9.425 mL decane in a 100 mL 3-neck flask. The contents were heated to 120°C for 25 minutes under N_2 flow with a condenser to yield a clear, colorless solution.

After reducing to 100°C, 0.2 mL of 1 M DiBPSe solution was injected swiftly into the flask of Pb(oleate)_2. The solution instantaneously turned from clear and colorless to dark brown, indicative of PbSe QD formation. An aliquot was removed after two minutes and immediately thermally quenched with 8 mL cold ethanol. The aliquot was centrifuged at 10,000 RPM for 10 minutes and yielded a solid, dark brown pellet and clear colorless supernatant. The supernatant was discarded and the pellet was re-dispersed in hexane.

The QDs have a core diameter of ~2.5 nm and a Pb:Se atomic ratio above the stoichiometric ratio of 1:1 because the surface is lead rich [13, 14]. The dots are capped with a protective layer of OA-derived electrically insulating ligands, about 2.5 nm long.

2.2. Matrix material candidates

QDs were incorporated into a sol-gel matrix, as described by Jasieniak et al. [15]. Both titania and zirconia QD composite sols were spun onto glass substrates, but best optical properties were not realized until after a high-temperature annealing step which damaged the QDs.

PMMA powder was dissolved in a solvent compatible with the QDs, such as toluene or chloroform, and the solutions were mixed on a stir plate and dried in an open plate mold. Even thin castings of ~65 µm in thickness took days to fully dry, and resulted in samples with high levels of optical defects.

QDs were mixed in liquid methyl methacrylate monomer and thermally cured with azobisisobutyronitrile (AIBN) or UV-cured with bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (Irgacure 819) initiators. The temperature required for thermal curing [16] was too high for these QDs, and luminescence was heavily quenched in UV cured samples. Free radicals released during curing likely also led to damage [17].

Numerous clear, two part, room temperature curing epoxies were tested, including Smooth-On brand Crystal Clear 202, EpoxySet brand EB-107LP-2, and Epo-Kwik embediment resin. These polymers were added to dried QDs, mixed on a stir plate or in a sonic bath, and cured as directed by the product documentation. One part was mixed with the QDs first, then the second was added. Both mixing orders were tried, i.e. part A added first, and part B added first. These resins suffered from poor QD solubility and quenched luminescence or complete destruction of the QDs (indicated by the solution turning clear, resulting from a lack of QD optical absorption).

Angstrom Bond AB9093, a one-part, 100% solids UV-curing epoxy, was found to show great promise as a matrix material, and is the basis for the rest of this study.

2.3. Incorporation of QDs into a polymer matrix

Angstrom Bond AB9093 was used as a matrix and purchased from Fiber Optic Center, Inc. A U-shaped piece of Teflon was sandwiched between two 1 mm thick glass slides to construct an open-top cup, as shown in figure 1(a). The glass becomes part of the sample, while the Teflon can be removed and reused after curing.

The QDs are dried under N_2 flow to remove the hexane before the AB9093 is added. The vial is then sealed and sonicated to mix. At a low enough concentration, below about 100 μM (estimated concentration from the absorption spectrum), all QDs mixed homogeneously with a few minutes of sonicating without visibly clumping or sticking to the glass mixing vial. Higher loadings are possible, but the dots are not as easily or uniformly dispersed.

This mixture was then poured into the mold, degassed in a vacuum chamber, and cured under constant 368 nm UV illumination. Since the QDs absorb in the UV region, long curing times were required as the concentration of QDs was increased, up to an hour for the highest tested concentrations and thicknesses, compared to seconds for clear samples. All fabrication was done under a N_2 atmosphere, except for a brief period before and after degassing.

Philips Master Actinic 457 mm fluorescent bulbs were used as a UV source (specified 15 W electrical) and were measured to have a wide emission peak at 368 nm, along with many other higher wavelength peaks. One bulb on each side of the sample was used. Sample edges were polished on a Buehler polishing machine to P4000 grit after removing the Teflon and grinding away excess glass. Using the methodology of Dai et al. [13], the molar concentration of QDs in the tested samples was calculated to be about 60 μM.

There was a concern that sonication might damage the QDs. However, there was no change in either the absorption or steady-state fluorescence spectra measured before and after sonicating a sample of QDs in hexane for 10 minutes. Attempts were made to perform TEM, SEM, and EDS analysis of the cured nanocomposites using a JEOL 1230 TEM and a FEI Quanta 650 SEM, respectively. But, difficulties in sample preparation due to the low hardness of the polymer and the low concentration of QDs resulted in no useful TEM data. However, there were no large clusters of QDs visible in either the SEM or EDS data, indicating a homogeneous mix with little or no aggregation of QDs.

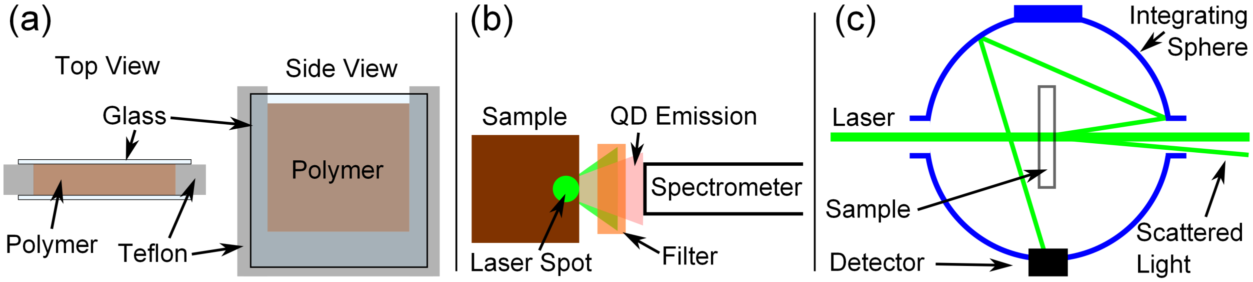

Figure 1: Various diagrams of the experimental setup. (a) Nanocomposite UV-curing mold. (b) QD nanocomposite emission measurement with laser directed near the edge. (c) Scattering measurement in an integrating sphere: light scattered at an angle $> 3°$ is collected by the sphere.

Samples were also prepared without QDs with a similar thickness of AB9093 cured between two glass sheets for evaluation of the matrix material optical properties. A thin sample, 16.0 mm × 10.1 mm × 3.9 mm (1.9 mm AB9093 between two 1 mm thick glass slides), and a thick sample, 16.6 mm × 10.4 mm × 6.1 mm (4.1 mm AB9093), were fabricated. Both were ground to size with a 60 grit then 240 grit grinding pad. Commercial PMMA Plexiglas sheets sourced from McMaster Carr, 2.9 mm thick, were also used for comparison in some tests; edges were rough-polished with 240 grit paper.

2.4. Optical measurements

Absorption measurements were carried out with a Beckman DU-650 absorption spectrophotometer. Measurements were referenced to an identical sample without QDs via a blank reference measurement, either a clear AB9093 sample or a quartz cuvette containing appropriate solvent, and taken with 0.5 nm wavelength resolution and $\leq$1.8 nm spectral bandwidth.

Steady state fluorescence was measured with a StellarNet EPP2000CXR-SR-200 spectrometer. The sample was excited with a 532 nm wavelength doubled Nd-YAG 500 µW laser with the beam brought as close to the measured sample edge as possible to limit self absorption effects, as shown in figure 1(b). An absorbing long-pass filter was used to block the excitation wavelength. Measurements were recorded with 0.5 nm wavelength resolution. Measurements of QDs in hexane and toluene were taken in a 4 mL, 1 cm path length quartz cuvette.

Time resolved fluorescence measurements were performed with a PicoHarp 300 with an 850 nm long-pass filter and a resolution of 128 ps per channel. Lifetimes were fit using the MATLAB software package.

Light scattering was measured at select laser wavelengths (532 nm doubled Nd-YAG, 632.8 nm HeNe, and 1064 nm Nd-YAG) inside of an integrating sphere to collect the total scattered optical power, as shown in figure 1(c). The sample under test was mounted in the center of the sphere and illuminated with a laser beam through a port in the front. The laser beam exited through another port to the rear, and the surface reflections from the sample exited through the laser entry port. Given the geometry of the sphere and the size of the ports, photons scattered at an angle > 3° were collected.

To measure the QY, the sample was mounted into the center of an integrating sphere and illuminated with a 532 nm wavelength 500 μW laser through a single open port. Input laser power and light collected in the sphere were measured with separate power meters; collected light was measured with and without a long-pass filter to block the incident laser wavelength. The number of photons absorbed and emitted by the sample was then calculated. The calculated QY value was corrected for self absorption in a similar way to the method of Ahn et al. [18].

3. Results and Discussion

In initial testing, the AB9093 epoxy showed the most promise as a matrix material candidate in terms of optical quality, QD fluorescence intensity, and absorption spectral shape of the embedded QDs, and became the basis of this study. Many of the other matrix materials that are successfully reported for other QDs [19] proved to be inappropriate in this case.

From an optical standpoint, an ideal matrix material should be perfectly transmissive and non-scattering in incident and fluorescent wavelength regions. This will maximize the incident light which can be absorbed by the QDs and the fluorescent light which can be coupled out of the material.

3.1. Matrix optical absorption and scattering properties

The transmission properties of the AB9093 sample, commercial acrylic sheets, and glass (1 mm thick microscope slide) are shown as a function of wavelength in figure 2. Based on the transmission spectra of the matrix, AB9093 can be used in the visible and NIR regions.

For many devices, such as LSCs or many sensors, it is convenient or desirable for the QD fluorescence to be wave guided to an edge for detection or collection. Thus, keeping scattering within the matrix to a minimum is required. The variation of light scattering with wavelength through various clear materials is shown in figure 3. As expected, the scattering decreases with increasing wavelength, and the thicker AB9093 sample scatters slightly more. Both AB9093 samples exhibit very low scattering, < 0.01%, comparable to optically clear commercial acrylic sheets and glass.

3.2. Nanocomposite fluorescence study

The QY of the QDs changes depending on its surrounding matrix. While no appreciable change is observed when the QDs are re-dispersed in toluene from hexane, a large shift occurs when cured in AB9093. The largest change is likely a result of the QDs being damaged. Protective ligands can be lost during incorporation into the matrix, leaving the QDs exposed to oxygen, or simply creating more surface trap states and a decrease in PL lifetime. Light exposure can accelerate the damage, as the QDs are more easily oxidized in an excited state.

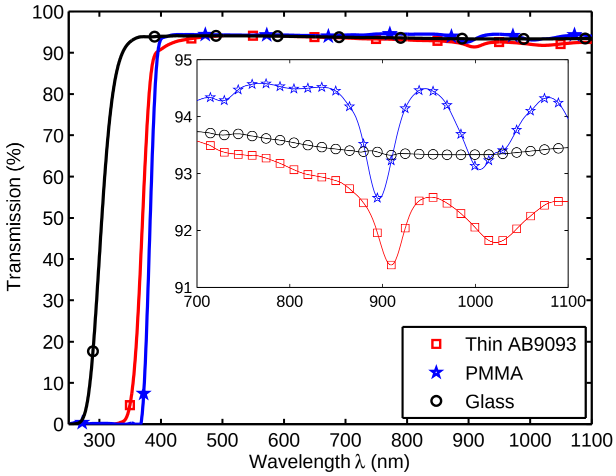

Figure 2: Optical transmission as a function of wavelength through glass-faced AB9093 epoxy, commercial PMMA, and a single 1 mm glass sheet. Inset: enlarged view of near-IR region. Markers are for visual reference, not data points.

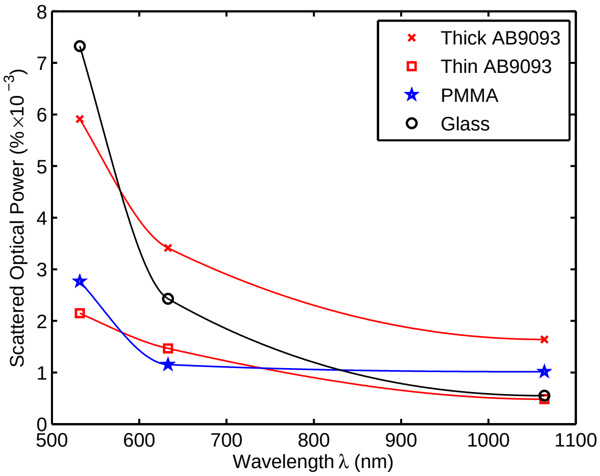

Figure 3: Optical power scattered at an angle $> 3°$ at three different wavelengths. Lines shown are piecewise polynomial interpolations as a guide for the eye.

The result is a lower PL intensity; in extreme cases the PL peak can blue-shift as the QDs become physically smaller from oxidation.

The QD fluorescence QY fell from about 55% in hexane to 26% in AB9093, a −52% fractional change. While a large loss, it is not unexpected; others report a −70% fractional change using a PMMA matrix with PbS QDs for use in cylindrical LSCs [20]; our work uses a superior matrix material to maintain a higher QY in polymer. In fact, to the authors' knowledge, 26% is the only QY reported for PbSe QDs in a polymer matrix. Smaller losses are sometimes reported, but are generally for core/shell or core/multi-shell Cd-salt QDs [2, 11]. Such a loss of QY is not ideal, but 26% QY is sufficient for many devices, including an LSC with a higher efficiency than current QD-based LSCs. It is anticipated that the QY could be increased through refinements in the synthesis and fabrication processes.

Excitons can also tunnel between QDs, increasing the chance for non-radiative decay. This effect is especially pronounced when the QDs are at a higher concentration, not uniformly dispersed in the matrix, or are coated with more conductive ligands. The emission spectra will red shift in this case as energy is lost to non-radiative processes.

As shown in figure 4, the emission of QDs in AB9093 is red shifted about 38 nm with respect to the original hexane solution, from a wavelength of 934 nm to 972 nm. An increase in surface trap states via ligand damage upon transfer to the AB9093 and curing may be playing a role in this shift.

The change in dielectric from solvent to AB9093 also plays a role, though minor. The polarization energy E_{pol} term of Brus' model for determining energy shift from bulk band gap of QDs describes the shift which occurs when QDs are moved to another matrix

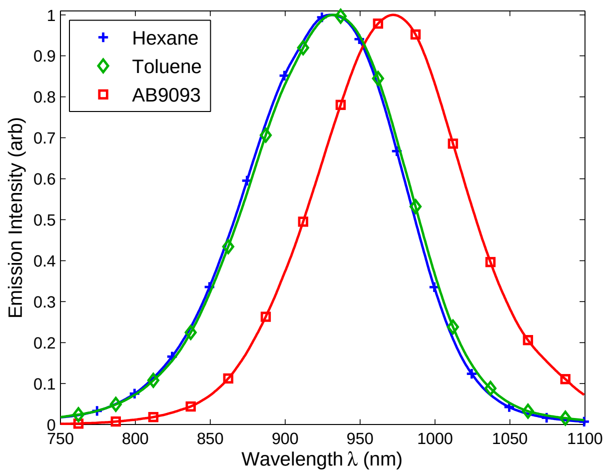

Figure 4: Emission spectra of PbSe QDs in hexane, toluene, and AB9093 epoxy. The emission peak in AB9093 shifts about 38 nm as compared to the hexane or toluene solutions. Markers are for visual reference, not data points.

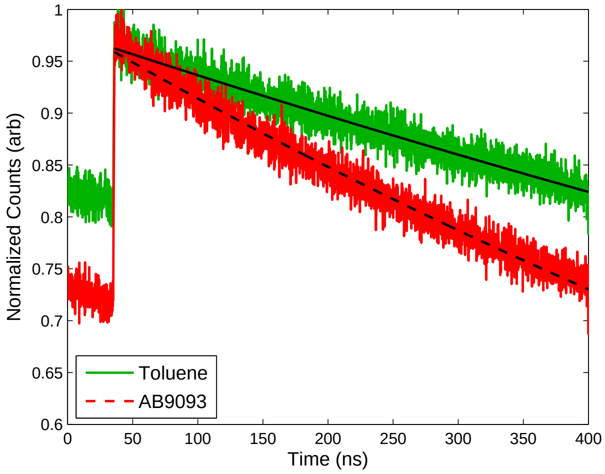

Figure 5: Time resolved photoluminescence of QDs in toluene and AB9093 epoxy with respective exponential fit lines (black).

material [21, 22]:

$$E_{\text{pol}} = \frac{e^2(\epsilon-1)}{2\pi R^2 \epsilon_2 \epsilon_0}\int_{r=0}^{R} \sin^2\left(\frac{\pi r}{R}\right)\sum_{k=1}^{1000}\frac{k+1}{(\epsilon+1)k+1}\left(\frac{r}{R}\right)^{2k}\mathrm{d}r$$

where $\epsilon = \epsilon_2/\epsilon_1$, ϵ_1 and ϵ_2 are the matrix and QD material (bulk) dielectric constants, ϵ_0 is vacuum permittivity, e is the elementary charge, and R is the radius of the QD. Assuming $R = 1.25$ nm and $\epsilon_2 = 22.9$ [23], calculating $E_{\text{pol}}(\epsilon_1 = 1.89) - E_{\text{pol}}(\epsilon_1 = 4)$ will give an approximation of the shift explained by the change in dielectric constant from hexane to AB9093 ($\epsilon_1 = 1.89$ for hexane [24] and $\epsilon_1 = 4$ for AB9093 [25]). A shift of ~8 meV is found, or about 4 nm.

Time resolved fluorescence of the QDs was investigated and the results in toluene and AB9093 are shown in figure 5. The behavior in toluene and AB9093 is single exponential with lifetimes of 2.34 μs and 1.34 μs respectively. The shortened lifetime in AB9093 as compared to toluene is indicative of the lower QY in AB9093 due to higher rates of non-radiative decay [26].

3.3. Nanocomposite optical absorption properties

Like fluorescence, the absorption of the QDs will change based on its matrix. Figure 6 shows the absorption spectra of QDs in hexane, toluene, and AB9093, as well as bulk PbSe for comparison. All curves are normalized to 75% absorption at 532 nm for ease of comparison of the 1-s peaks and to the bulk data. The bulk PbSe absorption coefficient α is calculated from the extinction coefficient κ given in the SOPRA database with $\alpha = 4\pi\kappa/\lambda$ [27].

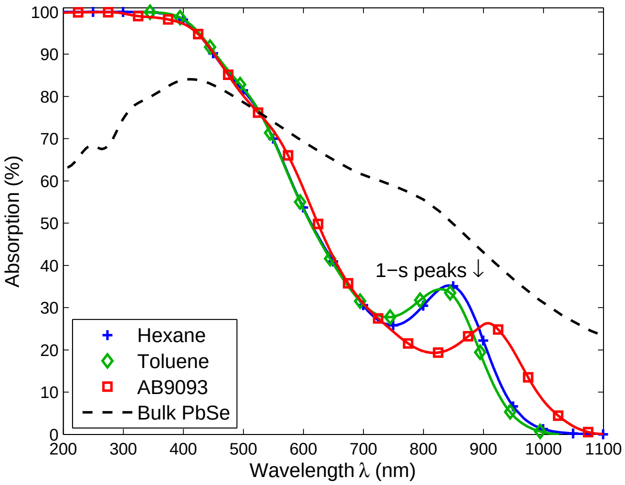

Figure 6: Absorption spectra of QDs in hexane, toluene, and AB9093 epoxy. The 1-s absorption peak of the QDs in AB9093 red shifts 65 nm compared to hexane. The calculated spectrum of bulk PbSe is provided for comparison. Markers are for visual reference, not data points.

A 14 nm blue shift of the 1-s peak occurs when moving from a hexane to toluene solution, likely partly a result of the change in dielectric constant of the solvents. Also, note the lack of the characteristic QD 1-s peak in the bulk material.

The absorption 1-s peak red shifts about 65 nm from 842.5 nm to 907.5 nm from hexane to AB9093, shifting 27 nm more than the fluorescence peak shown in figure 4. This represents a shift in the band gap E_g from 1.47 eV to 1.37 eV, compared to a bulk E_g of 0.27 eV. This is further evidence that the QDs are well dispersed, as they do not approach bulk behavior through aggregation. Note that CdSe/ZnS core/shell QDs in various epoxy, urethane, and PMMA matrices exhibit very little change in 1-s absorption peak upon incorporation [11].

Although the absorption spectra is rarely used directly in sensors, the increased overlap between absorption and fluorescence spectra would artificially red shift the average emission of the device because some lower wavelength emission would be self absorbed by other QDs in the nanocomposite. In spite of the fact that the QD absorption spectrum is widened in AB9093 compared to hexane or toluene, as shown in figure 6, there is almost no change in the total integrated absorption because of the decrease in 1-s peak intensity when in an AB9093 matrix.

4. Conclusion

PbSe QDs were incorporated into a number of matrix materials; AB9093 epoxy was found to be the most promising, outperforming the commonly used PMMA. The optical properties of the AB9093 were examined and found to have extremely low scattering, comparable to commercial PMMA or glass, high transmittance in the visible region, and low absorbance in the QD emission spectral range.

The effect of the polymer matrix on the QY, optical absorption, and PL spectra of the QDs was investigated and the results were compared to QDs in hexane and toluene solutions. The QY dropped to about half of the original value, but likely represents the highest QY for Pb-salt QDs in polymer. Both the absorption and emission spectra red shifted, 65 nm and 38 nm, respectively. Time resolved fluorescence measurements demonstrated a long-lifetime single exponential decay in toluene and AB9093, 2.34 µs and 1.34 µs respectively; the shorter lifetime in AB9093 is indicative of higher rates of non-radiative decay and lower QY.

PbSe QD nanocomposites are capable of absorbing and emitting over an extremely wide spectral region. This makes them very desirable in applications such as LSCs for their wide absorption band, X-ray detection for their greater X-ray absorption, and fiber optic communications for their ability to absorb and emit in many of the important transmission wavelength windows.

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