

# Stability promoted close-packed quantum dot- $\text{AlPO}_4$ glass films with tunable and bimodal luminescence



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## ABSTRACT

Broadly tunable and multi-emission PbS quantum dot (QD)-solid systems have drawn great attention to the applications of telecommunication, microelectronics and solar cells. Here, we propose a simple and practical method for creation of QD-systems in porous  $\text{AlPO}_4$  glass film matrix. Tunable and bimodal luminescent films in near infrared are achieved by a layer by layer assembly method with PbS QDs of different sizes. Atomic force microscopy and scanning electron microscopy reveal the successful deposition and homogeneous surface morphology of QD- $\text{AlPO}_4$  glass films. Furthermore, as a result of adsorption and confinement from pores of  $\text{AlPO}_4$  substrate, the photostability of QD- $\text{AlPO}_4$  glass films is dramatically improved. The red-shift of QD photoluminescence spectra after depositing onto the matrix and the energy transfer between QDs of different sizes indicate the formation of close-packed QD solid systems. This work extends the research in QD close-packed systems and has important implications for the applications of blended QDs in broadly tunable optical devices and telecommunication.

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## 1. Introduction

In recent years, the prospect in optics and electronics makes semiconductor quantum dots (QDs) promising roles in application of optical amplifiers [1,2], absorbers [3], fluorescence [4–6] and photoelectronic devices [7,8]. In most of these occasions close-packed QDs with some individual features were efficiently used. For example, fluorescence resonance energy transfer (FRET) can occur in QD ensembles with a range of size distribution. Because of the particle size dispersion, radiationless mechanism occurs between QDs of different sizes, which results in FRET that can be used in various applications [9,10]. Among various researches focusing on FRET of QDs, the most common and simplest method to create close-packed quantum dots is spin-coating [11,12]. It provides good homogeneity and free parameter controllability. Benefit from broadband absorption and multicolored emission of QDs based on layer-by-layer deposition strategy, concentrated interests on solar cells and LEDs [13,14] increasing extremely. Especially in near infrared, due to the large bandgap and strong quantum size effect, the lead chalcogenide QDs possess a number of unique properties [15]. These

QDs, such as PbS QDs, were considered a promising material for new solar cells. However, a main limitation for their utilization is the weak environmental and photostability. Due to high ratio of surface area to volume, the promoted high trap state densities make damage to QD crystal structure and recombination of charge carriers, which eventually result in detriment to device performance. That's why it's important to investigate QD aging and design new QD close package systems. Ihly et al. [16] had investigated the stability of naked solid state PbS QD films, a blue shift as much as 169 nm after 30 days storage in open air was found and smaller blue shift can be obtained if QDs were stored in Ar atmosphere. Litvin et al. [17] tried to embed PbS QDs into a macroporous matrix, but the fluorescence still showed a blue shift as much as 300 nm after 90 day storage at room temperature in air environment. To improve the photostability of solid state PbS QD films, mesoporous  $\text{AlPO}_4$  glass materials [18] with huge surface area and pore diameters of 2–10 nm offer new solutions.

Here we reported multilayer QDs decorated  $\text{AlPO}_4$  glass films fabricated by a layer-by-layer assembly method. Tunable and bimodal luminescent films in near infrared were achieved and the photostability of QD- $\text{AlPO}_4$  glass films was dramatically promoted. Energy transfer between QDs of different sizes was observed, which indicated the formation of close-packed QD solid systems. Blended PbS QDs of different sizes embedded in sol-gel films are very promising as broadband light

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sources and optical devices for various applications in the near infrared region, including optical communication and nonlinear optics.

## 2. Materials and methods

Sodium sulfide nonahydrate ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , 98%), A-monothioglycerol (TGL, 97%), 2,3-dimercapto-1-propanol (DTG, 98%), triethylamine (TEA, 99%) and aluminum L-lactate (98%) were purchased from Sigma-Aldrich. Phosphoric acid ( $\text{H}_3\text{PO}_4$ ), ammonia, isopropanol, ethanol and lead acetate (PbAc) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as purchased.

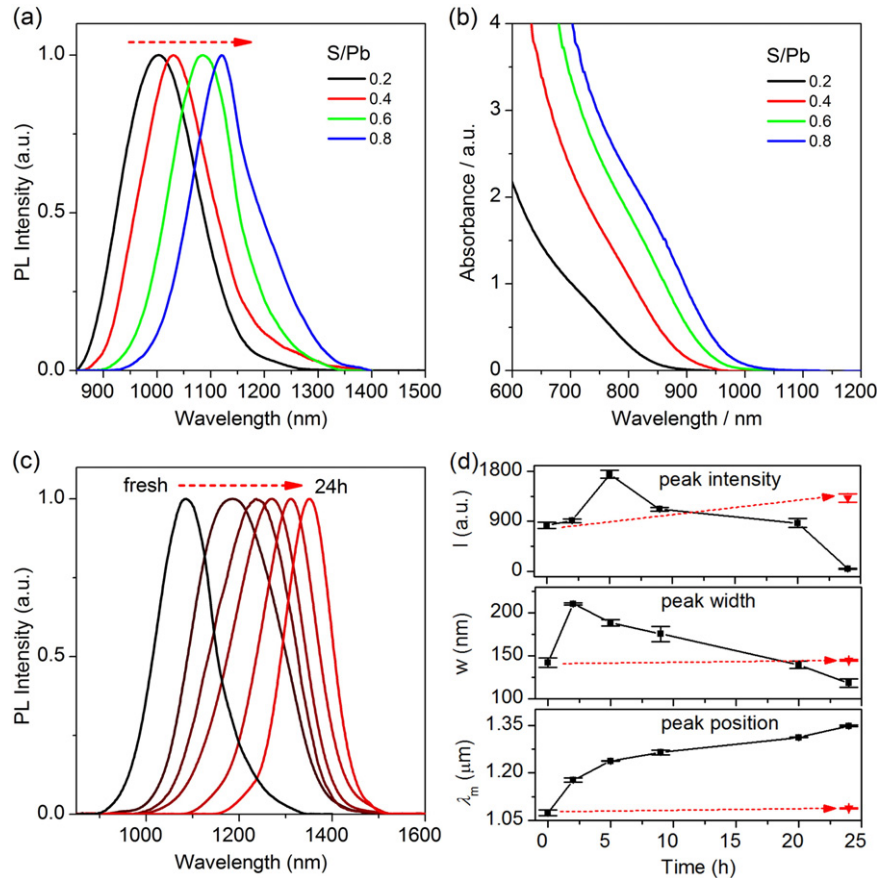
$\text{AlPO}_4$  films were fabricated via a sol-gel method. For the preparation of  $\text{AlPO}_4$  sol, 4 mmol aluminum L-lactate and 4 mmol  $\text{H}_3\text{PO}_4$  were dissolved in 10 ml deionized water and then the pH was adjusted to 2–4 by ammonia. After stirring for 2 h, the resulting  $\text{AlPO}_4$  sol was obtained. The film substrates were coverslips. All substrates were firstly dipped in a KOH solution ( $\text{KOH}:\text{H}_2\text{O}:\text{isopropanol} = 10 \text{ wt.}\%:10 \text{ wt.}\%:80 \text{ wt.}\%$ ) for 30 min. Afterwards, they're ultrasonically oscillated in isopropanol, acetone, ethanol and deionized water, respectively.  $\text{AlPO}_4$  films were deposited using the spin-coating technique with a rotational speed of 2500 rpm. After drying at 50 °C for 12 h, the gel films were calcinated at 600 °C for 4 h. Finally, transparent colorless  $\text{AlPO}_4$  glass films were obtained. PbS QDs were synthesized via an aqueous route as Bakueva's [19]. PbS QDs with different sizes were prepared using different ripening time or precursor ratios between Pb and S. The loading of QDs on the  $\text{AlPO}_4$  film was processed by spin-coating method. Typically, 50  $\mu\text{L}$  of QD dispersions was dropped on  $\text{AlPO}_4$  films with a rotational speed of 1000 rpm. After deposition, the QD- $\text{AlPO}_4$  films were dried at room temperature for 30 min.

Absorption spectra were measured on the PerkinElmer Lambda 750 UV-Vis-NIR spectrometer. Photoluminescence (PL) spectra were recorded using the FLsp920 spectrometer pumped by a semiconductor laser at 803 nm. The systematic error of PL spectrometer is given as  $\pm 0.1 \text{ nm}$  and the test step size was set as 1 nm in practice. The random errors from data collection were analyzed and determined by repetitive tests. Atomic force microscopy (AFM) was performed using a Nanoscope IIIa microscope from Digital Instruments. Scanning electron microscopy (SEM) was carried on Zeiss Auriga S40. All spectroscopic measurements above were performed at room temperature.

## 3. Results and discussion

Due to the strong quantum size effect, fluorescence of PbS QDs exhibits a super-wide tunability by modifying either particle size or surface state. The fluorescence of QDs which was synthesized via chemical route can be tuned by synthesis parameters and post-processing. Fig. 1(a, b) show PbS QDs that were prepared using different precursor ratios between Pb and S. As molar ratio of S/Pb rises, emission and absorption spectra shift to longer wavelength. The emission peak shifted from 1004 to 1120 nm when the molar ratio of S/Pb was tuned from 0.2 to 0.8. According to the theoretical calculations [20], the corresponded particle size increase from 3.0 to 3.7 nm. It is easy to understand that higher precursor ratio of S/Pb causes enhanced concentration of PbS sources. As a result, the growth of QDs is promoted. Because of quantum size effect, the bandgap energy  $E(R)$  in the QDs with the radius  $R$  is given as [20]:

$$E(R) = E_g + \frac{\hbar^2 \pi^2}{2m^* R^2} - \frac{1.8e^2}{\epsilon_2 R} + \text{polarization term},$$



**Fig. 1.** (a, b) Normalized emission spectra and absorption spectra of PbS QDs prepared at different molar ratios of S/Pb. (c) Normalized emission spectra of PbS QDs prepared with different ripening time of 2 h, 5 h, 9 h, 20 h and 24 h at 50 °C using S/Pb ratio of 0.6. (d) Peak intensities ( $I$ ), peak widths ( $w$ ) and peak positions ( $\lambda_m$ ) of spectra in panel (c) corresponding to ripening time at 50 °C. The stars refer to samples stored at 0 °C.

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