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# Acid-Free Sol-Gel Fabrication of Quantum-Dot Thin Films for Ultrafast Nanophotonics Research

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**Abstract:** We demonstrate a method of fabricating silica glass thin films embedded with CdSe quantum dots (QDs). Unlike the conventional sol-gel process, no acid is used to catalyze the gel-formation and hence the QDs are preserved.
**Keywords:** Quantum dots, sol-gels, glass, thin films, fluorescence spectroscopy, nanophotonics.

## 1. Introduction

Semiconductor quantum dots (QD) offer many unique optical properties because their strong quantum confinement leads to splitting of energy levels. One particular area that has attracted much interest in recent years is ultrafast nanophotonics, which studies the fast carrier or spin dynamics in highly spatially confined structures such as semiconductor QDs [1,2]. Such research often requires the QD samples be embedded in thin films with good QD-size uniformity, optical transparency, thermal tolerance, and mechanical stability. A simple, low-cost approach that meets these requirements is embedding II-VI colloidal QDs in glass thin films, and the sol-gel method is an effective technique to accomplish it [3].

We have systematically studied sol-gel fabrication of QD-embedded glass thin films, focusing primarily on using commercial II-VI colloidal QDs such as cadmium selenide (CdSe) and cadmium sulfide (CdS) QDs (manufactured by NN-Lab). These QDs have excellent size uniformity, which is crucial for our intended ultrafast nanophotonic research. One particular problem arises when the QDs are mixed in the $SiO_2$ sol – the acid (e.g., HCl) catalyst used in the standard sol-gel procedure damages the QDs and hence compromises the performance of the thin films. To address this problem, we developed an acid-free sol-gel technique, in which octadecylamine (ODA) ligands are used as a bi-functional aid in CdSe/$SiO_2$ thin-film synthesis.

## 2. Sample fabrication

Our samples were initially fabricated using the standard sol-gel recipe [3], which involves the hydrolysis and polycondensation of TEOS (Si $(OC_2H_5)_4$), carried out by dissolving TEOS in ethanol ($C_2H_5OH$) before mixing in deionized water ($H_2O$) and hydrochloric acid (HCl). The addition of the colloidal QDs (CdSe core QDs stabilized by ODA ligands) was carried out during sol formation. When the mixture shows a gel-like formation, it was spin coated on a glass substrate. The resulting samples were tested for QD emission using fluorescence spectroscopy. However, no emission was observed. We then directly coated the QDs on the glass substrate and performed the same fluorescence test. Sharp fluorescence peaks were observed at the specified wavelengths. This leads us to believe that the QDs are damaged during the sol-gel process, in particular, by the acid catalyst.

The acid catalyst is generally needed to assist the formation of $SiO_2$ gel. In our tests, without the acid catalyst, the TEOS glassy solution did not show any sign of gelation within several days. We subsequently tested base catalyst $NH_4OH$ (29% $NH_3$), but it resulted in a cloudy white solution that was unsuitable for thin-film fabrication. Meanwhile, to our surprise, significant gel formation was observed when the QDs were mixed into the glassy solution ($SiO_2$ sol) in the absence of any catalyst! Fluorescence result further showed a clear QD emission peak, indicating the QDs were successfully embedded into the glass. Since the commercial QDs we used in these tests were suspended in a toluene solution with the help of the ODA ligands, to understand which factor plays the key role in the gel formation, we added powdered QDs, ODA ligands and toluene to *separate* glassy solutions. The solution with the ODA ligands showed a gelation process consistent with the earlier one with QDs, indicating the ODA ligands can indeed assist the formation of the $SiO_2$ gel [4]. To further verify this finding, we measured the gelation time of the glassy solution with different ODA concentrations. The result shows that higher ODA concentrations result in quicker gelation (see Fig. 1(a)). This leads to a very simple technique for fabricating QD-embedded sol-gel glass, i.e. directly using the ODA ligands coming with commercial QDs to catalyze the $SiO_2$ gel formation. The ODA ligands then act as a bi-functional aid in the sol-gel process: they help suspend the QDs as well as provide basic conditions for silane hydrolysis, which accelerates the gel formation.

To convert QD-embedded sol-gel glass into thin films, we spin-coated the $SiO_2$ gel onto glass substrates and heat-treated the samples (e.g. at 500 $^oC$) immediately after spin coating. Clear, uniform films were successfully

fabricated with QD molar concentrations up to about 1.3 mM. Higher concentrations often yielded samples with significant cracking and much more fragile films. Currently, we are working on optimizing the post-coating procedure to improve the quality of the films at higher QD concentrations.

## 3. Sample Measurements

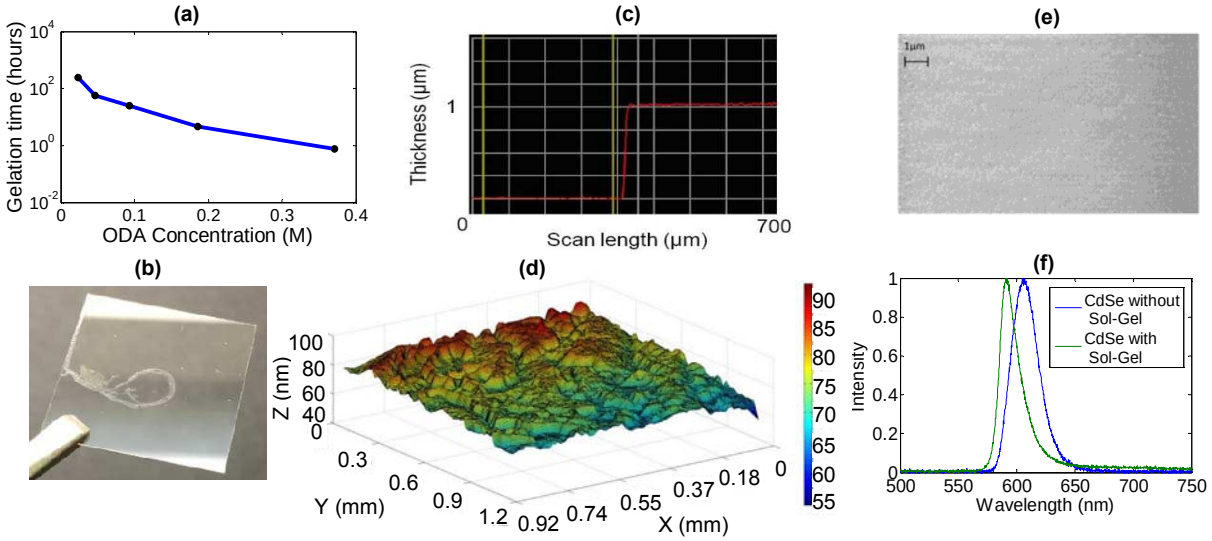


**Fig. 1**. (a) The gelation time of the glassy solution vs. ODA concentration. (b) Spin coated QD-embedded glass thin films on glass substrates. (c) Surface profilometer readings showing clear step height of ~1 $\mu$m. (d) Non-contact surface profilometry data indicate that the surface roughness falls within 100 nm peak-to-peak over an area of about 1 mm$^2$. (e) SEM image of thin film: A zoom-in view of the film shows the uniform, grainy texture of the surface. (f) Emission spectrum from a thin film sample as compared with the emission spectrum from CdSe QDs without going through the sol-gel process

A picture of our thin film sample is shown in Fig. 1(b). The thick ring-shape area around the perimeter of the coated region results from the spin coating. The clear area in the center is the uniformly coated area. A surface profilometer trace of that area shows a uniform coating about 1-$\mu$m thick (see Fig. 1(c)). The surface quality of the film is further revealed by non-contact surface profilometry measurement. A typical result is shown in Fig. 1(d). Surface roughness in general is found to fall within 100 nm peak-to-peak over an area of about 1 mm×1 mm, which indicates a very good optical quality. More insight into the quality of the film is offered by scanning electron microscopy (SEM). Fig. 1(e) shows a zoomed in view of a smooth area of the film which shows a uniform, grainy texture of the surface, as in agreement with the non-contact surface profilometry result shown in Fig. 1(d).The quality of the CdSe QDs in the thin films is characterized by fluorescence measurements. In Fig. 1(f), the emission spectrum from a thin film sample is compared with the emission spectrum from CdSe QDs without going through the sol-gel process. The similar spectral shapes of the two traces indicate that our sol-gel process did not compromise the uniformity of the QD sizes. But the spectrum from the sample has a small blue-shift relative to the unprocessed QDs (from 607 nm to 592 nm). This is likely caused by surface oxidization that occurred during the sol-gel and coating processes [5].

In conclusion, we have developed a quick, simple and low-cost technique to fabricate glass thin films embedded with commercial CdSe colloidal QDs. The ODA ligands are used as a bi-functional aid to the sol-gel process, and both the film quality and the QD characteristics prove to be satisfactory. Our method provides a simple option for developing QD–glass systems and can be of especial interest to researchers with limited facility in sol-gel chemistry.

## 4. Reference


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