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Transparent conducting films of CdSe(ZnS) core(shell) quantum dot xerogels

Lasantha Korala^a, Li Li^b, and Stephanie L Brock^a

Stephanie L Brock: sbrock@chem.wayne.edu

^aDepartment of Chemistry, Wayne State University, 5101 Cass Ave, Detroit, MI 48202, USA. Fax: (313) 577-8822; Tel: (313) 577-3102

^bDepartment of Chemical Engineering and Materials Science, Wayne State University, 5050 Anthony Wayne Drive, Detroit, MI 48202

Abstract

A method of fabricating sol-gel quantum dot (QD) films is demonstrated, and their optical, structural and electrical properties are evaluated. The CdSe(ZnS) xerogel films remain quantum confined, yet are highly conductive ($10^{-3} \text{ S} \cdot \text{cm}^{-1}$). This approach provides a pathway for the exploitation of QD gels in optoelectronic applications.

Semiconductor quantum dots (QDs) have attracted tremendous attention because of their size and shape dependent optical and electronic properties, which make them promising for use in optoelectronic device applications such as field-effect transistors (FFTs),^{1,2} photodetectors,^{3,4} light emitting diodes (LEDs)^{5,6} and solar cells.^{7,8} However, the method of QD assembly plays a major role in determining the performance of these devices, which require facile electronic communication between adjacent QDs while retaining quantum confinement. Sol-gel methods have the potential to fulfill these requirements and methods have been developed to assemble metal chalcogenide QDs into gels, xerogels and aerogels comprising three dimensional networks of QDs.^{9–11} Although the synthesis of QD gel materials is now well established, the incorporation of gel materials into device architectures has not been explored. In a recent review of nanocrystal-based gel materials, Eychmüller and coworkers have emphasized the importance of developing strategies to fabricate gel materials in film form, and have described methods of fabricating Au/Ag xerogel films along with their electrical properties (sheet resistance $\sim 2\Omega$, comparable to ITO).¹² However, there have been no published reports on the fabrication and properties of metal chalcogenide QD sol-gel films. Herein, we report, for the first time, a method to fabricate transparent CdSe(ZnS) xerogel films, and their optical, structural and charge transport properties.

Recently, we probed the kinetics of aggregation and gelation of 11-mercaptopundecanoic acid (MUA)-capped CdSe(ZnS) QDs by scattering techniques and showed that the cluster size at the gelation point has a major impact on the macroscopic properties (e.g. transparency) of the resulting gels. For CdSe(ZnS) QDs (average diameter 4.6 nm), transparent gel structures resulted at low QD particle concentration ($4 \times 10^{-7} \text{ M}$) and oxidant concentration, where aggregation follows reaction limited colloidal aggregation (RLCA) kinetics.¹³ Accordingly, these conditions were exploited to create the transparent films reported here.

Correspondence to: Stephanie L Brock, sbrock@chem.wayne.edu.

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The synthesis of transparent xerogel films of CdSe(ZnS) QDs was achieved by immersing glass substrates horizontally in pre-oxidized sols of MUA-capped CdSe(ZnS) core(shell) QDs, gelling and drying under ambient conditions. The film thickness can be varied by adjusting the height of the volume fraction of sol on top of the substrate. Scheme 1 illustrates the formation and overlapping of clusters during the gelation process to construct the gel film. Oxidation of the precursor thiolate-capped CdSe(ZnS) QDs (dispersed in methanol) by tetranitromethane (TNM) removes the thiolate ligands from the QD surface and exposes the QD surface to the oxidizing environment. Solvation of surface Zn^{2+} ions, and then further oxidation of exposed S^{2-} ions by the oxidant, links the QDs together via polysulfide bonding,¹⁴ initiating the aggregation process. During the aggregation, clusters are formed and cluster sizes increase with time due to continuous collision and sticking of QDs. At the gel point, clusters overlap and fill the volume above the substrate, resulting in a wet gel film. Drying under ambient conditions causes pore collapse and further shrinking, principally from the top-down, while preserving the interconnected network of QDs within the xerogel film.

Figure 1 shows UV-vis and PL spectra of the sol, and the sol-gel films deposited from different volumes of sol. The deposited CdSe(ZnS) xerogel films are quite transparent and highly luminescent when viewed under a UV lamp, as shown in the inset (bottom) of Figure 1. The wavelength of the first absorption peak of the xerogel films is blue shifted compared to that of the QD solution, but there is a slight red shift of the band gap value (20 meV, inset, Figure 1) which is extracted by plotting $(\alpha h\nu)^2$ vs $h\nu$ and extrapolating the linear part of the graph to the energy axis, as shown in the inset of Figure 1. The discrepancy can be attributed to the broadening of absorbance, smearing out the primary absorption peak. Moreover, the xerogel film shows a significant red shift (58 meV) in the PL maxima. These changes in absorption/emission properties are a good indication of the presence of an interconnected network of QDs within the xerogel film, where strong coupling of adjacent QDs results in efficient Förster resonant energy transfer.^{12,15}

Structural and composition analysis of the films was done by performing X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS). The XRD pattern of the xerogel film (Figure 2) reveals the hexagonal phase of CdSe, as is also seen in the precursor QDs. Semi-quantitative analysis of xerogel films by EDS reveals that Cd:Se:Zn:S ratios are 28.00:22.43:18.05:31.52. The excess chalcogen (sulfur) is attributed to residual MUA ligands on the QD surfaces comprising the xerogel film.

The surface morphology of the xerogel films was studied by field emission scanning electron microscopy (FESEM) (Figure 3a). The films appear dense, which is a typical characteristic of xerogels, and do not have macroscopic cracks that lead to island formation. Thickness and roughness analysis of the xerogel films by atomic force microscopy (AFM) measurements (Figure 3b) reveal that the films have micrometer scale thicknesses and comparatively high roughness values (the average thickness and roughness of the films are 1.2 μm and 120 nm (Film 1, 4 mL of sol) and 1.7 μm and 140 nm (Film 2, 5 mL of sol)).

The sheet resistance, R_S , of films deposited from 5 mL of sol was measured by the van der Pauw method. Resistances are on the order of $10^6 \Omega$ per square and conductivity, σ , is on the order of $10^{-3} \text{S}\cdot\text{cm}^{-1}$. In order to compare σ of the sol-gel films directly to the QD precursor particles we tried to measure the R_S of relatively thick trioctylphosphine oxide (TOPO)-capped films (~600 nm) fabricated on a glass substrate by drop casting. However, we were not able to get a reading from the source meter, indicative of the highly insulating nature of the TOPO-capped CdSe(ZnS) films. According to the literature, the R_S of TOPO-capped CdSe films with micron-scale thickness is on the order of $10^{22} \Omega$ per square, thus we observe a fifteen order of magnitude enhancement in conductivity by converting the QDs

into xerogel films.¹⁶ In fact, the σ of the xerogel QD films is close to that obtained from pyridine-capped CdSe thin films treated with cross-linking molecules ($\sigma \sim 10^{-2} \text{ S cm}^{-1}$).¹⁷ The high conductivity of the QD xerogel film is surprising since the particle interfaces are composed of oxidized sulfide linkages (S_n)²⁻,¹⁴ and chemical reduction in solution leads to gel dispersion.

Since the high surface roughness could be adversely affecting the conductivity of xerogel films, attempts were made to deposit thin films with low surface roughness by reducing the sol volume. Unfortunately, the decrease of sol volume resulted in macroscopic cracks on the film, and consequently, the conductivity reduced significantly.

Conclusions

Sol-gel methods were employed to fabricate micron thickness CdSe(ZnS) xerogel films with high transparency and luminescence. The films were surprisingly conductive ($\sigma = 10^{-3} \text{ S cm}^{-1}$) consistent with the existence of an electrically connected network of QDs within the xerogel film. The network enhances the transport of mobile charge carriers despite the strong potential for trapping at the oxidized interfaces and/or bond cleavage due to reduction. Currently, pre- and post-gelation strategies for spin-coated QD films are being investigated with the aim of producing high-quality thinner QD sol-gel films with enhanced conductivity.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

UV-vis spectrum and PL spectrum of CdSe(ZnS) QD sol and xerogel films deposited from 4 and 5 mL of sol (particle concentration, ca. 4×10^{-7} M). The inset (top) shows the plot of $(\alpha h\nu)^2$ vs $h\nu$ for the absorption spectra and photographs (bottom) of deposited films under normal and UV light. There is a 58 meV shift in the PL peak upon going from a sol to a xerogel film.

Figure 2.
(a) XRD pattern of a xerogel film deposited from 5 mL of sol. The line diagram corresponds to bulk CdSe (from ICSD patterns (PDF # 77–2307)).

Figure 3.

(a), (b) FESEM images, and (c), (d) AFM images of the CdSe(ZnS) xerogel films deposited from 4 mL (left) and 5 mL (right) of sol. The inset of b shows the morphology of the film under higher magnification (scale bar = 100 nm).

Scheme 1.

Schematic illustration of the fabrication of a CdSe(ZnS) xerogel film