Self-Assembly of CdSe and CdSe/CdS Nanoplatelets to Form Highly Porous Fluorescent Aerogels

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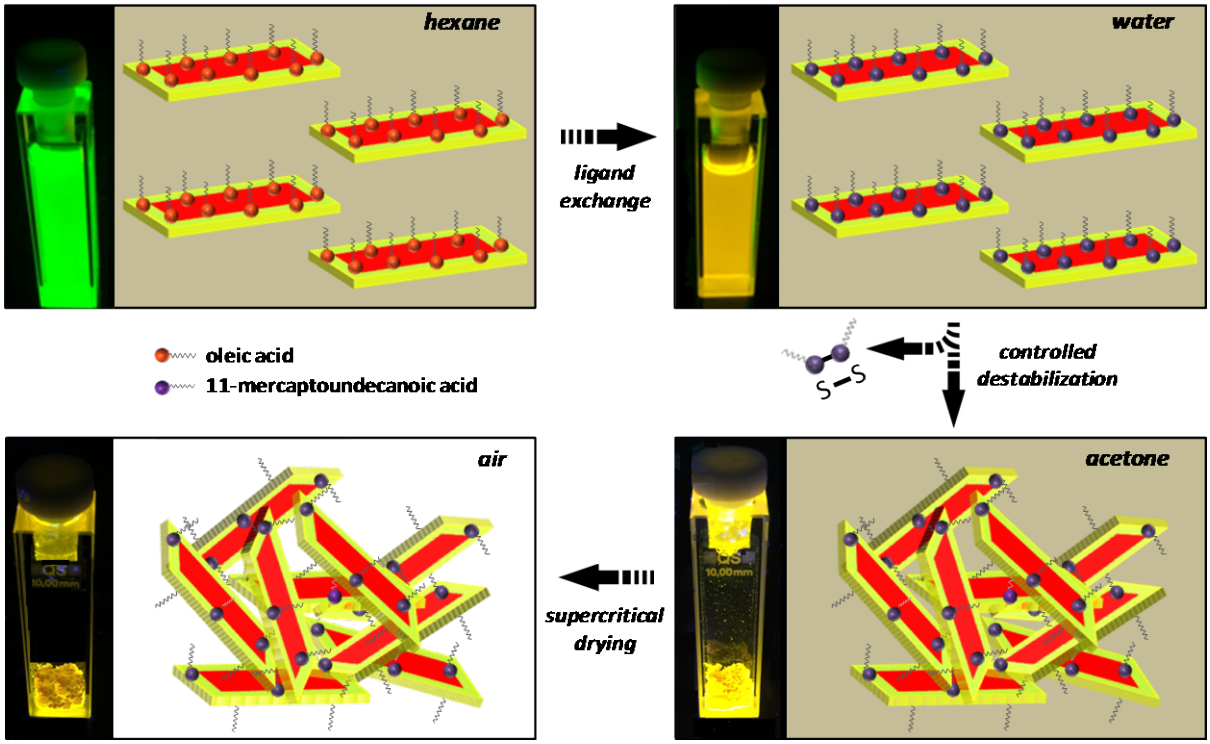
Abstract. We report on the synthesis of highly porous, self-supported inter cross-linked, 3D aerogel superstructures from 5 monolayer (ML) thick CdSe/CdS core/crown and CdSe core nanoplatelets (NPLs). Controlled partial oxidative removal of the thiol ligands from the surface of the NPLs is achieved with variable amounts of H_2O_2. The wet gels of CdSe and CdSe/CdS are converted to aerogels by exchanging the solvent with liquid CO_2 followed by supercritical drying. A comparative study of the optical properties of the aqueous NPLs solution to those of the hydrogels and the aerogels is carried out using UV-vis absorption, photoluminescence (PL) emission and PL decay measurements. The aerogels exhibit inherent quantum confined properties comparable to those of the aqueous solution of the NPLs. Compared to a densely packed NPLs film, aerogels exhibit higher (absolute) quantum yield and longer PL decay time. The interconnected porous network type morphology of the aerogels is characterized by transmission electron microscopy (TEM) and also by scanning electron microscopy (SEM). The monolithic aerogels are extremely lightweight (density < 0.038 g cm^{-3}) with a very high BET specific surface area of 219 m^2 g^{-1} and consist of only (111) as the exposed crystal facet.

Introduction

In recent years, aerogels from metal chalcogenide nanoparticles, such as CdSe,[1] CdTe,[2] CdSe/ZnS dots[3] and CdSe/CdS rods[4] even mixed metal-semiconductor, e.g., Au-CdTe[5] has attracted attention of the scientists due to their high porosities, large specific surface areas and quantum confinement properties. Regarding possible applications, metal chalcogenide aerogels for capturing radioactive elements and enzyme encapsulated quantum dot hydrogels for the development of biosensors have already been demonstrated. More recently, quasi 2D CdSe[6] or CdSe/CdS core/crown[7] or core/shell NPLs[8] of only few monolayer (ML) thicknesses have been reported with unique optoelectronic properties such as high PL quantum yield, extremely narrow emission band width, ultrafast radiative lifetime and reduced Stokes shift. Various possible applications of these NPLs, such as room temperature lasing, polarized light emission, reverse oxygen sensing are discussed in literature.[9, 10] The self-assembly of the NPLs to achieve porous 3D aerogels, while maintaining the quantum confinement properties, which would be of high interest, has not been reported so far.

Therefore, in this work, we have synthesized aerogels from colloidal solution of 5 ML thick CdSe and CdSe/CdS core/crown NPLs with varying amounts of H_2O_2 as destabilizing agent.[11] The consecutive reaction pathways such as, ligand exchange, controlled destabilization and supercritical drying, to obtain porous aerogels are shown in Scheme 1. After synthesis of the NPLs in colloidal organic medium, the surface ligands are exchanged with 11-mercaptoundecanoic acid, and the NPLs are transferred to aqueous medium.[12] Controlled destabilization of the aqueous NPLs solution is experimented with variable molar ratios of $[H_2O_2]/[Cd^{2+}]$ ranging from 1.2:1 to 23.2:1, and it is found that the optimum gelation conditions (retention of PL emission properties) are between the molar ratios 3.0:1 to 5.5:1.[11] The resulting hydrogels (voluminous monolithic aggregation of the NPLs) are kept in dark for 4 days for aging and the solvent is gradually exchanged with dry acetone. The wet gels are then transferred to a supercritical drying boat under dry acetone environment. After inserting the boat inside the supercritical dryer chamber, acetone is replaced with liquid CO_2. Finally, after supercritical drying, monoliths of aerogels are obtained, which show bright emission upon UV light irradiation (see photographs in Scheme 1).[11]



Scheme 1. Schematic diagram of the aerogel formation from CdSe/CdS core/crown NPLs. First, ligand exchange is performed in order to transfer the quantum wells to aqueous solution. Controlled destabilization by means of hydrogen peroxide addition results in the formation of hydrogels, which are subsequently transferred to aerogels by supercritical drying. The photographs on the left of the schemes display the quantum wells in the respective solutions and in the gels under UV illumination. (Reprinted with permission from "Naskar, S.; Miethe, J. F.; Sánchez-Paradinas, S.; Schmidt, N.; Kanthasamy, K.; Behrens, P.; Pfnür, H.; Bigall, N. C. Photoluminescent Aerogels from Quantum Wells. Chem. Mater. ***2016,*** *DOI: 10.1021/acs.chemmater.5b04872." Copyright {2016} American Chemical Society).*

The structural morphologies of the aerogels are investigated with SEM and TEM microscopy and the results (for CdSe/CdS NPLs) are shown in Figure 1. The SEM micrographs reveal that the aerogels are enormously voluminous with high porosity and consist of fractal-type network. The diameter of the pores ranges from the mesoporous (2-50 nm) to the macroporous (> 50 nm) regime. The TEM micrographs also prove that the self-supported porous network is formed by the coalescence of the NPLs edges (see inset of Figure 1D).

The hydrogels and the aerogels obtained with variable molar ratios of $[H_2O_2]/[Cd^{2+}]$ = 3.0:1 to 5.5:1 are also characterized with optical spectroscopic techniques. A comparison between a densely packed thin film of CdSe/CdS NPLs and the aerogel (both having similar optical density of 1.1 at 440 nm) reveals that the aerogel exhibits higher absolute quantum yield (10.3% vs 5.5%) and longer PL decay time (9.5 ns vs 3.6 ns) than the film. This can be attributed to the porous morphologies of the aerogels, which cause less interaction between the neighboring NPLs in the aerogels. The hydrogel and the corresponding aerogel with molar ratio of $[H_2O_2]/[Cd^{2+}]$ = 3.0:1 exhibit the highest absolute quantum yield of 12.1% and 10.3%, respectively. The quantum yield as well as the PL decay time of the hydrogels and the corresponding aerogels are found to decrease regularly with increasing amount of H_2O_2, and we suggest a homogeneous quenching mechanism to explain this effect.[11] Further increase in the H_2O_2 concentration, e.g., $[H_2O_2]/[Cd^{2+}]$ = 17.4:1 leads to dissolution of CdSe core in CdSe/CdS NPLs and results in morphologies of interconnected rectangular hollow CdS NPLs rings, without any CdSe domain. The XPS analysis of the aerogels obtained with higher H_2O_2 concentration shows no Se peak, which supports the findings from TEM analysis and our interpretation of the dissolution of CdSe under these conditions.[11]

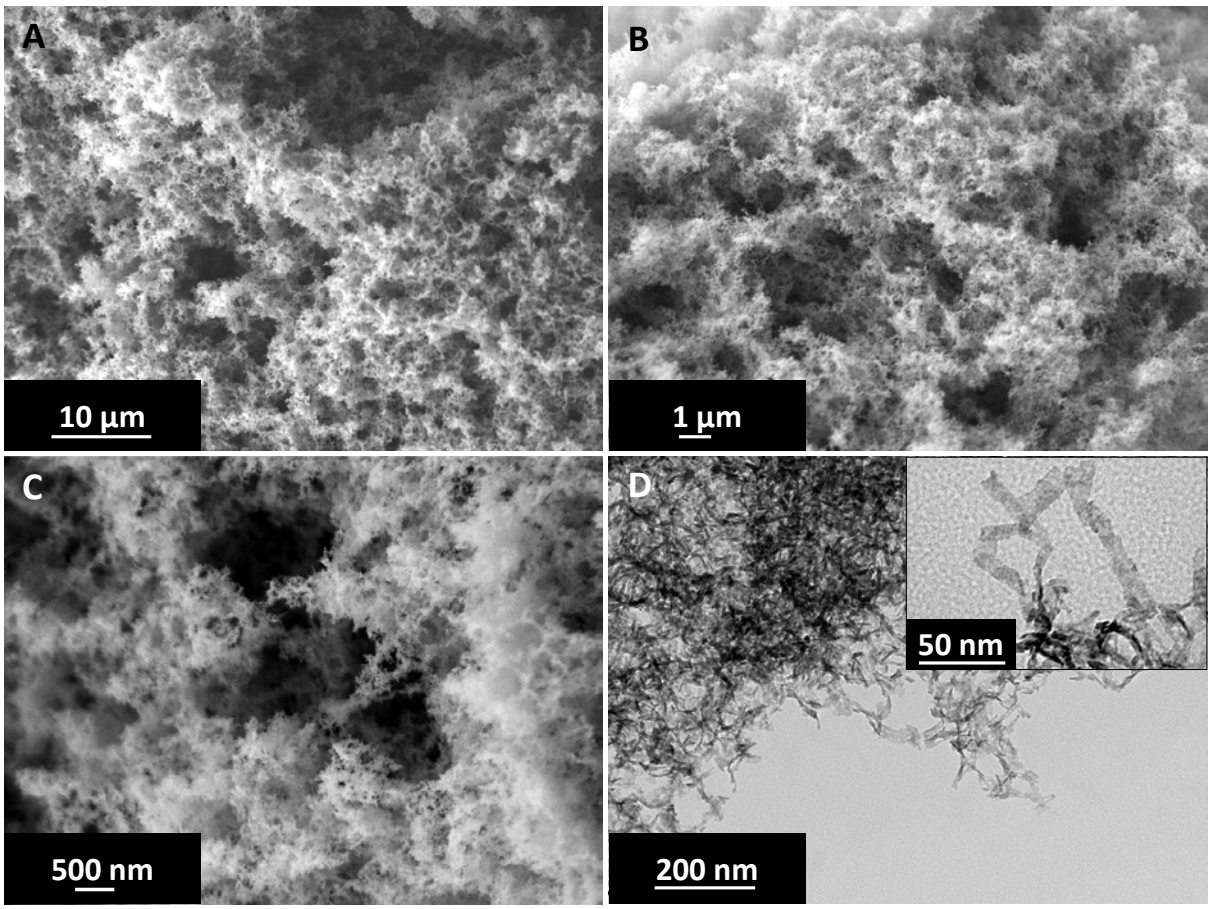


Figure 1. (A, B and C) SEM and (D) TEM micrographs of the aerogel from CdSe/CdS core/crown NPLs in different magnifications. Inset of figure (D) shows the orientation of the NPLs network inside the aerogel. The pore distribution ranges from mesopores (2-50 nm) to macropores (> 50 nm). (Reprinted with permission from "Naskar, S.; Miethe, J. F.; Sánchez-Paradinas, S.; Schmidt, N.; Kanthasamy, K.; Behrens, P.; Pfnür, H.; Bigall, N. C. Photoluminescent Aerogels from Quantum Wells. Chem. Mater. ***2016,*** *DOI: 10.1021/acs.chemmater.5b04872." Copyright {2016} American Chemical Society).*

The porosity and the inner specific surface area of the aerogels are obtained from N_2 physisorption experiments. The isotherms obtained are analyzed by BET (Brunauer-Emmett-Teller) method which show a combined IUPAC type II and type IV behavior. The BET surface area obtained is 219 $m^2 \cdot g^{-1}$ (for CdSe/CdS aerogel) and 189 $m^2 \cdot g^{-1}$ (for CdSe aerogel). These values are comparable to that of the highest specific area reported so far for metal chalcogenide nanocrystal aerogel systems and is equal to ~70% of the maximum possible surface area achievable with these NPLs. The high porosities of the here developed aerogels will allow the reactant molecules to pass through the pores with minimum hindrance, making them promising substrates for catalytic applications.

Conclusion

A synthetic strategy to obtain highly porous aerogels from quasi 2D 5 ML thick CdSe and CdSe/CdS NPLs is presented. The aerogels partially exhibit the quantum confinement properties of their initial building blocks with a highest absolute quantum yield of 10.3%. The aerogels solely exhibit (111) as the exposed crystal facet. This type of extremely lightweight aerogels with high porosities and BET specific surface areas (as high as 219 $m^2 \cdot g^{-1}$) are promising for future applications for e.g., facet dependent catalytic reactions or in sensing chemicals.

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Notes

This scientific work of Dr. Bigall and Prof. Behrens group has recently been published as a joint publication from LNQE, PCI and ACI in the journal of "Chemistry of Materials". Please see the following article for full reference "Naskar, S.; Miethe, J. F.;

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