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# Photoluminescent Aerogels from Quantum Wells

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**ABSTRACT:** Highly porous self-supported three dimensional aerogel monoliths are synthesized from strongly quantum confined quantum wells, namely 5 monolayer thick CdSe and CdSe/CdS core/crown nanoplatelets. The aerogels are synthesized by hydrogelation of the aqueous quantum well solutions and subsequent supercritical drying. The aerogels are optically characterized by UV-Vis absorption spectroscopy, emission spectroscopy, and PL decay analysis. Morphological and structural characterizations are achieved by transmission electron microscopy, scanning electron microscopy, and X-ray diffractometry. The macroscopic aerogels exhibit extremely low densities of  $0.038 \pm 0.007 \text{g} \cdot \text{cm}^{-3}$  and a significantly high specific surface area of 219 m<sup>2</sup>·g<sup>-1</sup> with nearly entirely (111) as the exposed crystal facet. Moreover, the aerogels feature properties related to quantum confinement comparable to those of their original building blocks with photoluminescence quantum yields up to 10.3%.

#### 1. Introduction

Metal-chalcogenide nanoparticles, such as colloidal quantum dots, rods, tetrapods, octapods, nanowires, nanoribbons, nanoplatelets (NPLs) or nanosheets (sometimes also referred to as quantum wells), have attracted the attention of many scientists due to their interesting size and shape dependent optoelectronic properties.<sup>1-6</sup> By controlling the shape of the nanocrystals, the exciton (electron-hole pair) can be confined in three dimensions e.g. in quasi-spherical crystals, in two dimensions such as in nanorods and nanowires and in one dimension, namely in quantum wells such as NPLs. In recent years, a variety of only few monolayer (ML) thick NPLs, core/shell NPLs or core/crown NPLs of various compositions, such as CdSe,<sup>4, 7-10</sup> CdSe/CdS,<sup>5, 11</sup> CdSe/CdS/CdZnS,<sup>12</sup> PbSe/PbS,<sup>6</sup> ZnSe/ZnS,<sup>13</sup> and CdSe/CdTe<sup>14</sup> have been reported, with unique optoelectronic properties such as high photoluminescence quantum yields (PLQYs), extremely narrow emission band widths, ultrafast fluorescence decays and reduced Stokes shifts. As for applications, electroluminescent emitters, reversible oxygen sensing, and room temperature lasing with low energy threshold have already been reported.<sup>15-18</sup> Furthermore, the CdSe NPLs were assembled into close-packed pileshaped products emitting polarized light.<sup>8</sup> Instead, the assembly of the NPLs into self-supported, highly porous 3D bulk architectures, which would be of interest for a variety of possible applications, such as in photovoltaics, sensors for detecting chemicals and photocatalysis, has not been reported so far.

In earlier studies, porous aerogels from quasi-spherical CdS

nanoparticles were obtained by controlled destabilization of the colloidal solution.<sup>19</sup> Since then research efforts have been dedicated to extend this technique to other colloidal semiconductor building blocks of various cadmium chalcogenide compounds including quasi-spherical and rod-like shapes.<sup>20-26</sup> 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.<sup>21, 27</sup> More recently, also mixed aerogels e.g. from Au and CdTe,<sup>28, 29</sup> and aerogels solely from metal nanoparticles (such as Pt, Au, Ag)<sup>30-36</sup> have been reported. Here, we present to the best of our knowledge for the first time the assembly of fluorescent quantum wells to form selfsupported highly porous, extremely lightweight, macroscopic 3D aerogels with large specific surfaces. The destabilization of the here employed anisotropic 5 ML thick CdSe and CdSe/CdS core/crown NPL building blocks in aqueous medium was achieved by hydrogen peroxide induced ligand oxidation. The impact of variable amounts of H<sub>2</sub>O<sub>2</sub> on the gelation process and on the optical properties of the resulting hydrogels and aerogels is investigated. A diagram representing the synthesis steps from the pristine colloidal NPLs in hexane solution over phase transfer to aqueous solution, and over hydrogelation to fluorescent aerogel monoliths is shown in scheme 1.

The aerogels reported here exhibit intense photoluminescence and might in future serve as an effective material for highly sensitive sensing devices. For example, Lorenzon et al.<sup>17</sup> have observed that CdSe based NPLs have unique capability of



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.

photoluminescence based reversed oxygen sensing (and other gases such as CO and CO<sub>2</sub>) attributing this property to the large specific surface of the particle increasing the probability for the creation of surface trap states which are necessary for this type of reversed gas sensing. The assembly of NPLs into a highly porous and accessible large surface superstructure (as achieved in the present work) might help making gas sensing devices from such nanoscopic building blocks, since the aerogels are self-supported in gaseous environments. The high porosity and mesoporous character of the hydrogel and aerogel materials developed in the present work might allow possible reactant molecules to access the large specific surface area, and hence such gels are potentially also applicable for superior electro-catalytic activity.<sup>37</sup> A different example for possible applications, in which the porous arrangement of CdSe based NPLs, was suggested by the Dubertret group<sup>38</sup> in their work about the employment of NPLs in electrolyte gated field effect transistors. It was found that porous arrangement leads to much higher currents due to a better chemical interface, and it was suggested that even more porous arrangements could improve this effect. Therefore, a gel-type assembly as synthesized in our present work would be of high interest also for this type of applications. Moreover, aerogels of the NPLs exhibit solely (111) as the exposed crystal facet, providing the

opportunity to perform facet dependent chemical reactions on its surface. Furthermore, the here developed aerogel materials might be applicable in optical sensing, photovoltaics, light emitting diodes (LEDs), or as a catalyst.

#### 2. Experimental Section

*Reagents.* Cadmium nitrate tetrahydrate (99.999 %), cadmium acetate dihydrate (98.0 %), sulphur powder (> 99 %), sodium myristate (> 99 %), 11-mercaptoundecanoic acid (MUA) (95 %), hydrogen peroxide (30 %), 1-octadecene (90 %) (ODE), oleic acid (90 %), methanol (99.5 %), ethanol (99.5 %), *n*-hexane (> 99 %), and acetone (> 99 %) were purchased from Sigma Aldrich. Selenium powder 200 meshes (99.999 %), nitric acid (> 69 %) and hydrochloric acid (> 37 %) were purchased from Fluka. Indium foil, thickness 0.1 mm,  $\geq$  99.995 % trace metal basis was purchased from Sigma-Aldrich.

Synthesis of 5 ML thick CdSe NPLs. Quasi 2D, 5 ML thick CdSe NPLs were prepared according to the procedure described in literature with little modifications.<sup>5, 39</sup> A total amount of 170 mg cadmium myristate,  $Cd(myr)_2$  (0.3 mM)

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and 14 mL ODE were placed in a 25 mL three neck round bottom flask. The mixture was degassed at 100 °C for one hour at constant stirring conditions. A clear solution of cadmium myristate dissolved in ODE was obtained. Under argon flow, the temperature of the solution was raised to 250 °C. Then 1 mL of a 0.15 mM Se solution (prepared by dispersing 12 mg Se powder in 1 mL ODE), was quickly injected into the mixture. Subsequently, one minute after the selenium solution injection, a total amount of 120 mg (0.9 mM) Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O was added to the mixture. The reaction was continued at a constant temperature of 250 °C for 10 min. Finally, 0.5 mL 10 oleic acid was injected into the mixture, and the reaction tem-11 perature was lowered down to room temperature by placing a 12 water bath under the flask. The NPLs were separated from all 13 other byproducts (mainly CdSe cubes and spheres) by adding 14 20 mL of a mixture of hexane : ethanol = 3:1 and centrifug-15 ing for 15 min at 3800 g (rcf). The dark red precipitate of the 16 CdSe NPLs was collected from the bottom of the centrifuge 17 vial and dispersed in 2 mL hexane. 18

Synthesis of 5 ML thick CdSe/CdS core/crown NPLs. The growth of a CdS crown on these CdSe NPLs was performed following a modified method of Tessier *et.al.*<sup>5</sup> A synthesis mixture for the growth of the CdS crown was prepared by placing 480 mg Cd(OAc)<sub>2</sub>.2H<sub>2</sub>O together with 340 µL oleic acid and 2 mL ODE in a three neck flask. The temperature of the mixture was increased to 150 °C, and the reaction was continued for 15 min under air with constant stirring and sonication. The light grev mixture of the cadmium oleate was cooled down to room temperature, and subsequently 3 mL of a 0.1 M sulphur precursor solution prepared previously by dissolving 19 mg of elemental S in 6 mL ODE was added. The whole mixture was then transferred to a syringe. The entire product of the previously prepared 5 ML CdSe NPLs were placed inside a 25 mL three neck round bottom flask with 10 mL ODE. The temperature of the reaction flask was increased to 100 °C, and the mixture was degassed under vacuum for 30 min to remove the hexane completely. Under Ar flow, the mixture was heated up to 240 °C. The crown growth mixture (prepared previously) was continuously injected at a rate of 8 mL/h for 7.5 min by means of a syringe pump. The heating mantle was removed and the solution was allowed to reach room temperature and after that 15 mL ethanol was added. The whole mixture was transferred to a centrifuge vial, and the NPLs were precipitated by centrifugation at 3800 g (rcf) for 15 min. The supernatant was discarded and the CdSe/CdS core/crown NPLs were dispersed in 3 mL hexane.

Phase transfer of 5 ML thick CdSe and CdSe/CdS NPLs. The NPLs were transferred to aqueous medium following a procedure described by Kodanek et.al.<sup>40</sup> Briefly, a mixture of 61 mg MUA together with 4 mL methanol and 0.05 g KOH was placed in a vial and sonicated for 3 min. The entire hexane solution of the CdSe NPLs (Cd ion concentration is 25 mM as determined from AAS) synthesized above was added to the vial with the phase transfer reagent and shaken overnight. The hexane phase was removed by means of a separation funnel and the MUA capped CdSe NPLs in the methanolic phase were precipitated by centrifugation. Afterwards, the whole product was dispersed in 4 mL of a 0.1 M KOH solution. Finally, the phase transferred NPLs were washed twice with

distilled water. The CdSe/CdS NPLs were transferred to aqueous medium following the same procedure as mentioned above.

Hydrogelation of the CdSe/CdS core/crown and CdSe NPLs. In the first set of experiment the effect of H<sub>2</sub>O<sub>2</sub> concentration on the time required for the appearance of hydrogel formation was studied. Therefore, eight 2 mL micro-centrifuge tubes were filled with 400 µL of the aqueous NPLs solution. The Cd ion concentration of the NPLs solution was kept constant at 1.77 mM. Thereafter, a series of different concentration of H<sub>2</sub>O<sub>2</sub> solutions (0.1 %, 0.15 %, 0.25 %, 0.5 %, 0.75 %, 1 %, 1.5 % and 2 %) were prepared and 20 µL of each was added to the vials containing NPLs, which led to molar ratios of  $[H_2O_2]: [Cd^{2+}] = 1.2:1, 1.8:1, 3.0:1, 5.8:1, 8.7:1,$ 11.6: 1, 17.4: 1 and 23.2: 1 respectively. All the sample vials were placed in an oven (already heated) at 80 °C for 2 min in order to initiate the gelation process and subsequently placed under ambient conditions in the dark. The time required for the first appearance of the hydrogel was 1.5 h for  $[H_2O_2]$ :  $[Cd^{2+}] = 23.2$ : 1 and (NPLs are completely bleached) and more than 14 days for  $[H_2O_2]$ :  $[Cd^{2+}] = 1.1$ : 1. In case of molar  $[H_2O_2]$ :  $[Cd^{2+}]$  ratios 1.8:1, the gelation time was approximately one week. In all other cases gelation time was found to vary between 3-8 h. The extent of bleaching of the NPLs was found to increase with higher molar ratios of  $[H_2O_2]$ :  $[Cd^{2+}]$ . Hence, the optimum gelation condition lies between molar ratio  $[H_2O_2]$  :  $[Cd^{2+}] = 3.0 : 1$  to 5.5 : 1, where the gelation time is 6-8 h and the NPLs are least oxidized.

In the second set of experiment, the effect of variable  $[H_2O_2]$ :  $[Cd^{2+}]$  molar ratio on the optical properties of the resulting gel was investigated following the above mentioned optimum reaction conditions. Therefore, 5 µL, 7 µL, 9 µL, 11  $\mu$ L and 13  $\mu$ L of a 0.5 % H<sub>2</sub>O<sub>2</sub> solution were added to each micro-centrifuge tubes containing 400 µL aqueous NPLs solution (molar ratio  $[H_2O_2]$  :  $[Cd^{2+}] = 3.0 : 1, 3.7 : 1, 4.3 : 1,$ 4.9:1 and 5.5:1 respectively). Once the appearance of the hydrogels was observed, the supernatant solvent was exchanged with deionized water for 7-8 times in order to remove excess H<sub>2</sub>O<sub>2</sub> and reaction byproducts from the system. Subsequently, the samples were kept at ambient conditions in the dark for 3 days (aging). Thereafter, the solvent was gradually exchanged with mixtures of 10 %, 20 %, 40 %, and 60 % (v/v) acetone in water, and finally the samples were washed with pure acetone (7 to 8 times). In order to remove residual water, the vials were filled with dry acetone and were placed inside a desiccator with anhydrous CaCl<sub>2</sub> to avoid the contamination of moisture from air. The desiccator was evacuated until the acetone slightly boiled, and left at these conditions for 8 h. The acetogels were then transferred to a supercritical drying boat in anhydrous acetone environment. The boat was inserted in the critical point dryer chamber (E3100 from Quorum Technologies), where acetone was replaced with liquid CO<sub>2</sub>. After storage in liquid CO<sub>2</sub> for one day, the temperature of the chamber was raised above the critical point of  $CO_2$  (31.5 °C and 1100 psi), and the CO<sub>2</sub> present in the system was released as a gas. A volume shrinkage of roughly 30 % to 40 % was observed during the conversion of hydrogels to aerogels. The monolithic aerogels of the CdSe and CdSe/CdS core/crown NPLs were stored under ambient conditions.

Measurement of density of the aerogels. The aerogels are irregular in shape, which makes it difficult to estimate the exact volume. We have calculated the volume via inserting small aerogel pieces in a cylindrical vial with known inner diameter. From the filling height of the aerogel inside the vial (several measurements are taken to obtain an average height) the volume has been calculated. From the mass of the aerogel (measured with a Sartorius balance measurement accuracy  $\pm 0.0001$ g) the density has been evaluated. We have taken into account a maximum of 20 % error in the measurement.

Atomic absorption spectroscopy. The Cd ion concentration of the CdSe NPLs and the CdSe/CdS NPLs solution was determined by atomic absorption spectroscopy (AAS) using a Varian AA140 instrument equipped with an air/acetylene flame atomizer. The samples were prepared by digestion with aqua regia. Five standard  $Cd^{2+}$  solutions were measured to obtain a calibration curve. A 1 % HNO<sub>3</sub> solution was used in order to correct the background signal.

*Scanning electron microscopy*. Scanning electron microscopy (SEM) was carried out on a JEOL JSM 6700F equipped with cold field emission gun electron source. The samples for SEM imaging were prepared by deposition of small pieces of the aerogels on adhesive carbon films.

Transmission electron microscopy. The morphologies of the gels were investigated by transmission electron microscopy (TEM) using a FEI Tecnai G2 F20 TMP ( $C_s = 2 \text{ mm}$ ,  $C_c = 2 \text{ mm}$ ), equipped with a 200 kV field emission gun. Micrographs were taken in bright field mode. Each sample was purified 3 to 4 times by precipitation with ethanol (CdSe NPLs) and CdSe/CdS NPLs) followed by centrifugation and redispersion in hexane, prior to TEM grid preparation. Subsequently, 10 µL of the purified sample were dropcasted on a 300 mesh carbon coated copper TEM grid, purchased from Quantifoil. In case of aqueous solution, 10 µL of the sample was dried on the TEM grid using an IR lamp for 20 min. The TEM samples of the aerogels were prepared by carefully touching the aerogels with the TEM grid.

Spectroscopic characterization. UV-Vis absorption spectra of the samples were recorded using an Agilent Cary 5000 absorption spectrophotometer. Emission spectra of the samples were recorded using a Horiba Fluoromax-4 spectrometer. The PLQY (in absolute mode) of the samples in solution, the hydrogels and the aerogels were measured with a Horiba-DUAL FL spectrophotometer equipped with a Quanta- $\phi$  integrating sphere (Horiba). All absorption and emission spectra of the samples were measured in a 1 cm quartz cuvette using toluene, hexane (UV-Vis spectroscopy grade), water or 0.1 M KOH as solvents. Time-correlated single photon counting (TCSPC) measurements were performed using a Fluoromax-4 combined with the Fluorohub TCSPC unit. A nanosecond pulsed LED with full width at half maxima (FWHM) around 1.2 ns was used as the excitation source. The excitation wavelength was 368 nm for CdSe NPLs in hexane medium and 454 nm for all other samples.

X-ray photoelectron spectroscopy (XPS). A Leybold Heraeus XPS analyzer with Al  $K_a$  x-ray beam was used as the excita-

tion source to analyze the surface of the aerogel. A small amount of aerogel sample was pressed onto an indium foil (~1.7 cm<sup>2</sup>). The conductive, soft surface of the indium foil holds the sample adequately and prevents specimen charging.<sup>21</sup> The samples were incubated in vacuum ( $10^{-8}$  mbar) for 18 h before the measurements. All the binding energy peaks were calibrated with measured carbon 1s peak (binding energy 284.6 eV). The raw data from XPS analysis was fitted with Gaussian/Lorentzian curve fitting using XPS 4.1 software.

*Nitrogen physisorption measurements.* Nitrogen sorption isotherms were measured at 77 K on a Quantachrome Autosorb-3 instrument. The samples were degassed under vacuum at 25 °C for 24 h before the start of the sorption measurement. Surface areas were estimated by applying the Brunauer-Emmett-Teller (BET) equation.<sup>41</sup> The pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method.<sup>42</sup> The total pore volume was estimated using the single point method at  $p/p_0 = 0.99$ .

#### 3. Results and discussion

After the NPL synthesis and prior to gelation, both CdSe NPLs and the CdSe/CdS core/crown NPLs were transferred to water following a procedure described in a previous work.<sup>40</sup> The TEM micrographs of the anisotropic NPLs as well as the optical characterizations, measurements from UV-Vis absorbance, emission and PL decay are shown in figure SI-1 and figure SI-2 and discussed in detail in the Supporting Information. These NPLs in aqueous solution were employed as building blocks for the gel synthesis.

Prior studies reveal that hydrogels of conventional (such as dots or rods) metal chalcogenide nanoparticles are obtained by controlled destabilization of the system employing  $\rm H_2O_2$  or tetranitromethane as the oxidizing agents.  $^{21,\ 22,\ 26,\ 43\cdot45}$  The gelation process is initiated via partial removal of the surface ligands by oxidation, which reduces repulsion between the nanoparticles and results in partial aggregation to form the gel-like network.<sup>25, 26</sup> In the present article, hydrogelation of the CdSe NPLs and the CdSe/CdS NPLs was achieved employing the same technique using H<sub>2</sub>O<sub>2</sub> as chemical oxidizing agent. The effect of H<sub>2</sub>O<sub>2</sub> amount on the CdSe/CdS (aq) NPLs gelation process was investigated by adding a defined amount of  $H_2O_2$  in concentrations varying from 0.1 % to 2 %, while keeping the amount of MUA ligands and NPLs constant (see experimental section). With 0.1 % concentration (a molar  $[H_2O_2]$ :  $[Cd^{2+}]$  ratio of 1.2 : 1) the initial gelation effect, i.e. a voluminous monolithic aggregation with a clear supernatant, was only observed after 2 weeks with reduced fluorescence intensity (PLQY =  $4.3 \% \pm 0.2 \%$ ). For larger molar  $[H_2O_2]$ :  $[Cd^{2+}]$  ratios below 3.0 : 1, hydrogelation took also relatively long time (approximately one week). For such low hydrogen peroxide amounts probably only insufficient ligands were removed from the surface of the NPLs. Furthermore, for these low hydrogen peroxide concentrations the hydrogels obtained exhibited low photoluminescence, and the gel consistency is not enough to enable transfer to the supercritical drying boat for further processings. In case of higher oxidant concentrations (i.e. molar  $[H_2O_2]$ :  $[Cd^{2+}]$  ratios of 11.6 to 23.2:1), a rapid gelation of the NPLs (within 1.5 h) was ob-

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58 59 60 served. However, with these larger amounts of  $H_2O_2$ , the emission of the wet gel was found to be completely quenched. The optimum gel formation was found to take place with molar  $[H_2O_2]$ :  $[Cd^{2+}]$  ratios of 3.0 : 1 to 5.5 : 1. In these cases, also bright photoluminescence was observed. Photographs of the hydrogels and the corresponding aerogels under daylight and upon UV light irradiation are shown in figure 1. In this parameter range, the gelation time was 6-8 h, which is slightly longer, but at the same time there was only negligible loss of the deep orange color and fluorescence properties with respect to the original aqueous solution. The hydrogel and the corresponding aerogel with a molar  $[H_2O_2]$ :  $[Cd^{2+}]$  ratio of 3.0 : 1 exhibited the highest photoluminescence intensities. For further increasing of hydrogen peroxide content, the photoluminescence intensity was found to decrease more and more.



Figure 1. Photographs of the hydrogels (A and B) and aerogels (C and D) obtained from the CdSe/CdS (aq) NPLs with variable molar ratios of  $[H_2O_2]$ :  $[Cd^{2+}]$  ranging from 3.0 : 1 to 5.5 : 1.(left to right, respectively). All monoliths (both hydrogels and aerogels) exhibit intense fluorescence upon irradiation with a UV lamp (wavelength 365 nm). The hydrogel and the corresponding aerogel with  $[H_2O_2]$  :  $[Cd^{2+}] = 3.0 : 1$  and 5.5 : 1 have the highest and lowest PLQY, respectively. The scale bar is in centimeter. Notably, the surfaces of the hydrogels inside the micro centrifuge tubes are curved inward which means that the volumes of the aerogel and hydrogel cannot be compared directly.

As a reference experiment, the gelation of CdSe (aq) NPLs was also investigated following the same reaction conditions. We observed similar time scales for the hydrogel formation even though the photoluminescence was found to be completely quenched (a fact which is already observed for the aqueous CdSe NPL building block solutions caused by the phase transfer via ligand exchange).

In all gelation experiments, after the formation of the initial wet gel, a washing step is crucial to remove excess oxidant and soluble byproducts e.g. disulphides.<sup>26, 44</sup> Consecutive washing and aging allows the NPLs with their partially bare facets to come closer to each other and hence to form the

stable network (as was suggested for conventional nanoparticles<sup>25</sup>). During the aging period, a little volume loss (around 5 %) can be observed. The hydrogels obtained in this way are stable monoliths as shown in figure 1. In order to obtain voluminous aerogels, the hydrogels were supercritically dried following Kistler's method<sup> $\frac{46}{6}$ </sup> (see experimental section). This method allows the network to retain its structure without any major changes since cappillary forces do not occur during this drying process. The aerogels obtained after supercritical drying were monoliths of interconnected NPLs. However, it should be noted that careful handling is necessary to avoid mechanical stress and electrostatic charging which might break the monoliths into smaller pieces. The resulting aerogels of CdSe/CdS core/crown NPLs are highly fluorescent (PLQY up to 10.3 %, which is only slightly lower than that of the corresponding hydrogel with 12.1 %). However, we observe a loss in PLOY during gelation (the PLOY of the aqueous solution is 18 %). We explain the loss of PLQY as follows: The addition of  $H_2O_2$  leads to three effects: i) The peroxide radical can generate active Se<sup>-</sup> (in case of CdSe) or S<sup>-</sup> and Se<sup>-</sup> (in case of CdSe/CdS) at the surface of the NPLs, which in turn facilitates to form the interconnection of the NPLs through chalcogenide bonding.<sup>20, 22</sup> ii) The peroxide radical can help to generate a disulphide bonding between two MUA surface ligands, which is a soluble byproduct. When ligands desorb from the NPLs, unsaturated surface states can cause lowering of the PLQY.<sup>20, 22</sup> iii) Excess amount of  $H_2O_2$  can also cause the oxidation of CdSe to form a soluble oxide species, (e.g. CdSeO<sub>4</sub>) which is washed out after hydrogelation by solvent exchange (see XPS measurements proving the absence of other Se components than Se<sup>2-</sup> in the aerogels). This explains the dissolution of the CdSe core of the CdSe/CdS core crown NPL (which is observed by TEM by the generation of NPLs rings for higher H<sub>2</sub>O<sub>2</sub> concentrations, see figure 6). With higher oxidant concentration the CdSe crystallites are more and more dissolved. Kinks, lattice defects and hence unsaturated surface states are therefore more and more created. Since the PL emission of the platelets only comes from the CdSe part (for both CdSe and CdSe/CdS NPLs) due to the specific band structures of the two materials, dissolution of the CdSe also goes along with reducing the PLQY of the samples. Therefore, effects ii) and iii) can explain why the PLQY decreases with increasing hydrogen peroxide concentrations.

The aerogels from CdSe/CdS core/crown NPLs exhibit extremely low densities of  $0.038 \pm 0.007$  g·cm<sup>-3</sup> representing 0.8 % of the density of bulk CdS (4.82 g  $\cdot$  cm<sup>-3</sup>) and 0.69 % of bulk CdSe  $(5.816 \text{ g} \cdot \text{cm}^{-3})$  respectively. Similarly, also the aerogels from CdSe NPLs exhibit low densities of  $0.036 \pm 0.007 \text{ g} \cdot \text{cm}^{-3}$  corresponding to 0.62 % of the bulk CdSe. A small piece of the CdSe/CdS core/crown NPL aerogel (molar ratio  $[H_2O_2 : Cd^{2+}] = 3.0 : 1$ ) was investigated by SEM to visualize the morphology of the solid structure. Figure 2 (A-C) shows the SEM micrographs of the CdSe/CdS NPLs aerogel in different magnifications. At lower magnifications, it is evident that the aerogel superstuctures have pores in the macroporous regime (with pore size > 50 nm). The higher resolution SEM micrograph also proves the presence of an enormously voluminous and branched 3D network having many pores with diameters extending from the mesoporous



Figure 2. Morphological characterization of an aerogel. (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 (250 nm).

(2 to 50 nm) to the macroporous (> 50 nm) regime. From the comparison of the lower and higher resolution SEM images, it can be derived that these aerogels consist of a fractal-type network. The SEM and TEM micrographs of the aerogels from solely CdSe (aq) NPLs also show highly porous morphology similar to the core/crown NPLs (see Supporting Information figure SI-3). We have also investigated the morphology of xerogels which are obtained by drying the hydrogels under ambient conditions (see figure SI-4). It should be noticed that the volumes of the xerogels are drastically reduced to only 1-2 % of their corresponding hydrogels. This is most likely due to capillary forces, generated during the liquid evaporation process, breaking down the porous morphology to a much more compact structure.

 The TEM micrographs of the aerogel from CdSe/CdS core/crown NPLs are shown in figure 2D. In accordance with the previous observations, here also a porous interconnected network of the NPLs is observed. Most of the CdSe/CdS NPLs

are assembled in a non-ordered 3D arrangement, where the NPLs coalesce in a random fashion. The NPLs are mostly bended, and sometimes rectangular sheets with edge-to-edge connections can be found. A closer look on the high resolution TEM (HRTEM) micrographs (figure SI-5) of the gelated NPLs (through fast fourier transformation, FFT) reveals a distance of  $\sim 0.34$  nm between the lattice planes, which accounts for the presence of (111) facets of the NPLs. Due to the extremely low thickness (~1.5 nm) of the building blocks and rather random connections between the NPLs, by HRTEM we are unable to find out whether the interparticle connections are crystalline-type or not. Indeed, we assume the interplatelet connections to be of non-crystalline type. The assumption of an amorphous connection is based on the outcome of a previous work on aerogels from CdSe core CdS shell nanorods,  $\frac{26}{10}$  in which prolonged PL lifetimes resulted from crystalline type connections, which is not the case in the present work (as shown later). If the connections between the neighboring NPLs would be crystalline-type, we would expect the possibil-

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ity that excited electrons could travel to their next neighbors which would lead to a lower recombination probability and therefore a prolonged radiative lifetime.<sup>26</sup>

In order to characterize the surface of the aerogel, whether  $H_2O_2$  causes any surface oxidation to produce CdO or any other complex oxides, the aerogel sample (with molar  $[H_2O_2] : [Cd^{2+}] = 4.9 : 1$  and 17.4 : 1 respectively) are analyzed using XPS spectroscopy and is shown in figure 3.



Figure 3. XPS spectra of the CdSe/CdS aerogel with molar ratios  $[H_2O_2]$ :  $[Cd^{2+}] = 4.9 : 1$  (red line) and 17.4 : 1 (blue line). The position of the characteristic peaks confirms the presence of Cd is in +2 oxidation state (A) and Se and S are in -2 oxidation state (B and C, respectively). High amount of oxidant causes dissolution of CdSe from the centre of the CdSe/CdS NPL and hence the intensity of binding energy peak for Se is near to noise level for the aerogel with molar  $[H_2O_2]$ :  $[Cd^{2+}] = 17.4 : 1$ .

The binding energy peaks at  $\approx 405.2$  eV and at  $\approx 412$  eV can be attributed to Cd 3d<sub>5/2</sub> and 3d<sub>3/2</sub> doublets from CdSe respectively. The absence of a binding energy peak  $(3d_{5/2})$  near 404 eV confirms there are no CdO or other complex oxides e.g. CdSeO<sub>4</sub> present on the surface of the aerogel.<sup>21, 48</sup> The 3d and 2p<sub>3/2</sub> binding energy peaks appearing at 163 eV and at 54.2 eV (figure SI-6B and C) confirm the presence of sulphur and selenium in -2 oxidation state respectively. A very weak energy peak  $\approx 58$  eV might be due to the presence of tiny amount of SeO<sub>2</sub> that resulted due to the etching of the CdSe NPL by H<sub>2</sub>O<sub>2</sub>. Notably, in case of higher oxidant concentration (molar the  $[H_2O_2]$ :  $[Cd^{2+}] = 17.4 : 1)$  the binding energy peak from  $Se^{2}$  is absent which confirms nearly complete dissolution of the CdSe core of the NPL under this conditions, which is consistent with the TEM micrographs shown in figure-7. We assume that such kind of oxidized products are washed out due to their water solubility and therefore cannot be determined in XPS. However, the results from optical spectra and TEM (dissolution of the CdSe domains for higher H<sub>2</sub>O<sub>2</sub> concentration) are in good agreement with the missing CdSe signal in XPS.

For an overall comparison of the optical properties of the resulting hydrogels and aerogels with respect to their initial building blocks, UV-Vis absorption and emission spectra were recorded. The high optical density and strong scattering behavior of the gels do not allow one to measure the optical properties in transmission mode. Therefore, absorption and emission spectra and absolute PLQY measurements were performed using an integrating sphere. A comparison of the absorption spectra of the initial oleic acid capped CdSe/CdS core/crown NPLs in hexane (CdSe/CdS (hex)), the phase transferred MUA capped CdSe/CdS core/crown NPLs in aqueous medium (CdSe/CdS (aq)) and the resulting hydrogel and aerogel (with molar ratio  $[H_2O_2]$ :  $[Cd^{2+}] = 3.0:1$ ) is shown in figure 4A. From the absorption onset of the hydrogels and aerogels, it can be inferred that the CdS band gap is

not significantly changed compared to their aqueous building blocks, which means that the quantum confinement properties are retained, even though the discrete heavy and light holes are not distinguishable and smeared out. A saturation effect in the shorter wavelength regime can be observed due to the inhomogeneity of the samples inside the cuvette, where the excitation beam cannot be adjusted to only hit the sample, rather a part of the light passes besides the gels. The emission maxima of the hydrogels and aerogels likewise those of the NPLs in solution (figure 4B) can be attributed to recombination from the CdSe band edge. The emission peak of the CdSe/CdS hydrogels (black line) is 6 nm shifted towards the lower energy regime with an increased FWHM of 24 nm in comparison to the CdSe/CdS (aq) NPLs building block solution (with a FWHM of 17 nm). This effect could be due to the assembly of the CdSe/CdS NPLs, which allows energy transfer processes to occur between neighboring NPLs causing a slight shift of the emission peak to the lower energy regime.<sup>24, 26</sup> Also the emission peak of the hydrogels is broadened in comparison to that of the corresponding aqueous solution. In addition, for the hydrogels and aerogels, an elongated tail in the emission spectrum in the longer wavelength regime can be observed, which is attributed to trap state emission. The trap state generation could be due to partial surface dissolution of the NPLs by peroxide radical, producing unsaturated valences on the Cd atoms present on the surface. Noticeably, there was no trap state emission of the NPL solutions observed, neither in aqueous nor in organic medium. It should also be noted that the emission maximum of the aerogel is shifted to shorter wavelengths with a slight further broadening of the FWHM compared to the corresponding hydrogel. While the phenomena of shifting to shorter wavelengths and broadening of absorption and emission spectra is not yet perfectly understood, it could



Figure 4. (A and B) Comparison of the absorption and emission spectra of the CdSe/CdS NPLs before and after gelation. Inset of (B) shows the magnification of the selected region of the spectra. (C) comparison of the absorption and emission spectra and (D) PL decay of the CdSe/CdS NPLs in aqueous solution, as thin film and as an aerogel.

be caused by an interplay of partial dissolution of platelets, partial loss of ligands, the change in dielectric constant in combination with tilting, overlaying and broadening of the nanoplatelets. The broadening might be explained by partial dissolution, removing parts of the CdSe crystallites, which results in slight variations of the thickness of the quantum wells.

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At this point it is interesting to compare the optical properties of the highly porous self-supported network of the same NPLs with those of denser packed NPLs. In order to do so, the optical properties of a NPL film with similar optical density as the aerogel was investigated (1.1 and 1.2 at 300 nm, respectively, measured in scattering free absorption mode at similar areas exposed to the beam). The film was prepared by drying the CdSe/CdS (aq) NPLs solution on a glass slide. The spectra are shown in figure 4C and D. Here, we observe that the shape of the absorption and the emission spectra of the film and of the aqueous solution are very similar. In case of aerogel the CdS absorption onset appears in the same wavelength regime (compared to the film and the solution), while the CdSe absorption band is broadened. Compared to the film, the emission spectrum of the aerogel was also found to be broadened. However, it should be noticed that the PLQY of the film is only 5.5 % with photoluminescence lifetime ( $\tau$ ) of 3.6 ns whereas, the aqueous solution has 18 % ( $\tau = 11$  ns) and the aerogel has the PLQY of 10.3 % ( $\tau = 9.5$  ns). This short lifetime and low PLOY of the film is most likely due to the dense packing of the NPLs which increases the occurrence of various nonradiative recombination pathways in the system. Nevertheless, the aerogels from the core/crown NPLs, as shown in the manuscript, have higher PLQY (10.3 % for the lowest amount of H<sub>2</sub>O<sub>2</sub> used) as well as longer PL-decay times compared to the densely packed film. We attribute this to the highly porous morphology, where the NPLs are loosely packed (compared to the film) and the interactions with the neighboring NPLs are limited.

In order to investigate the impact of the H<sub>2</sub>O<sub>2</sub> amount used during gelation on the optical properties of the resulting hydrogels and the corresponding aerogels, we have compared the spectra of the samples with four different  $[H_2O_2]$ :  $[Cd^{2+}]$ molar ratios, namely 3.0 : 1, 3.7 : 1, 4.3 : 1, and 4.9 : 1 (figure 5, black, red, blue and green line, respectively). It can be clearly derived that the UV-Vis absorption spectra have sharp absorption onsets and have contribution from both CdSe and CdS with band gaps considerably larger than the corresponding bulk semiconductors. In case of the emission spectra it should be noticed that there is a small shift of the emission maximum towards the shorter wavelength region with increasing  $H_2O_2$  amount. This can partly be explained by the fact that larger amounts of H<sub>2</sub>O<sub>2</sub> can oxidize more thiol ligands (MUA) from the surface of the CdSe/CdS (aq) NPLs leading to a decrease of the exciton probability function in the thickness direction. Furthermore simultaneously the dissolution of the CdSe domain occurs. This occurrence of a parallel reaction effecting the CdSe domains is proven by employing a higher molar ratio of  $[H_2O_2]$  :  $[Cd^{2+}] = 17.4$  : 1. From the TEM images of the corresponding gel shown in figure 6A and B it can be derived that the CdSe is nearly completely vanished from the centre of the NPLs leaving holes inside the residual CdS NPL rings. Hence it is likely that also with the small amounts of H<sub>2</sub>O<sub>2</sub> which we employ in our fluorescent quantum well gelation, we can expect that partial local thinning (not the complete monolayer) of the CdSe platelets occurs, which leads to a slightly reduced (and inhomogeneous) thickness. This results in the shift of the emission peak to shorter wavelengths. In addition, it should be noted that with higher H<sub>2</sub>O<sub>2</sub> concentration, the trap state emission increases, which is in agreement



Figure 5. Optical characterization of the hydrogels and the corresponding aerogels with four different  $[H_2O_2]$ :  $[Cd^{2+}]$  molar ratios of 3.0 : 1, 3.7 : 1, 4.3 : 1, and 4.9 : 1 (black, red, blue, and green line, respectively). (A and B) and (C and D) represent UV-Vis absorption and emission spectra of the corresponding hydrogels and aerogels, respectively. Insets of (C and D) represent magnified spectra of the selected region. (E and F) represents the PL decay curves of the hydrogels.

to an increased degree of ligand oxidation and the creation of e.g. dangling bonds (imperfect saturation of surface). The lifetime of the (presumably) trap state emission was found to be in the order of tens of microseconds, which is in agreement with previous observations for trap state emission of assembled CdSe nanocrystals (see figure SI-6).<sup>47</sup>



Figure 6. (A and B) TEM micrographs of CdSe/CdS aerogel in two different magnifications with  $[H_2O_2]$ :  $[Cd^{+2}] = 17.4 : 1$ . Higher amount of  $H_2O_2$  causes etching of CdSe and produces holes inside the rectangular NPLs. Schematic models inside the figures are drawn to guide the eye.

The measured PLQYs and the corresponding PL lifetimes for both hydrogels and aerogels are shown in figure 7A and B. The QY (in case of monoexponential PL decay) can be expressed as the ratio of the rate constants of the radiative and nonradiative processes as  $QY = k_{rad} / (k_{rad} + \sum k_{non-rad})$  where  $k_{rad}$  and  $k_{non-rad}$  being radiative and non-radiative rate constants, respectively. The PLQY of the CdSe/CdS NPLs in aqueous solution is 18 % with corresponding PL lifetime of 11 ns.



Figure 7. (A and B) PLQY and fluorescence lifetime of CdSe/CdS hydrogels and aerogels with variable molar ratios of  $[H_2O_2]$ :  $[Cd^{2+}]$ .

It should be noticed from figure 7A, that the PLQY as well as the measured fluorescence lifetime of the hydrogels decreases with increasing H<sub>2</sub>O<sub>2</sub> amount. Similar trend was also observed for the corresponding aerogels (figure 7B). This decrease in PLOY is most likely due to dissolution of the CdSe with higher amounts of hydrogen peroxide and due to the presence of less and less ligands on the surface, both effects resulting in the creation of unsaturated surface states and hence nonradiative recombination pathways (or lower-energetic trap state emission).<sup>26</sup> The decay curves can be reasonably fitted with a mono-exponential decay, measured with the lifetime  $\tau_{\text{measured}} = 1 / (k_{\text{rad}} + \sum k_{\text{non-rad}})$ . The extent of decrease in lifetime of the exciton is quite consistent with the decrease in PLQY. Hence, we can conclude that the system undergoes a homogeneous quenching mechanism: which means that all individual fluorescent NPLs of a given ensemble undergo similar quenching upon H<sub>2</sub>O<sub>2</sub> addition (for a brief explanation of the terms homogeneous and inhomogeneous quenching, please see Supporting Information).

In a recent publication of our group, exceptionally long radiative lifetime (56 ns with a PLQY of 29%) of aerogels from CdSe seeded CdS nanorods have been observed.<sup>26</sup> In that case, according to our interpretations, tip-to-tip connections of the CdSe/CdS nanorod crystallites open up the possibility for the excited electrons to travel to the connected nanoparticles while the holes are confined in the CdSe leading to a delay in the recombination of the exciton and hence longer radiative lifetime. Instead, in the present article, we do not observe that kind of tip-to-tip connections; rather here the NPLs are randomly attached with their neighbors. We assume that the connections of the NPLs are not through crystal points and together with that bending of the NPLs reduces the probability of the electron delocalization. In addition, an overall increase in the nonradiative recombination pathways results in shorter photoluminescence lifetime. However, also this work shows similarly to the above-mentioned article that the PLQY can be high in aerogels; in the present case it is e.g. approximately twice higher than in the denser packed films of similar optical densities.

Aerogels with very high porosity and large specific surface area are highly promising for catalytic as well as for sensor applications, as the reactant molecules or the analyte can easily diffuse through the pores with minimum hindrance. We analyzed the porosity and the specific surface area of the aerogels obtained from the CdSe NPLs and the CdSe/CdS core/crown NPLs using nitrogen physisorption experiments. The measured isotherms are shown in figure 8 and analyzed by the Brunauer-Emmett-Teller (BET) method. The isotherms for N<sub>2</sub> gas adsorption and desorption mainly show a multilayer adsorption behavior and can be designated with mixed IUPAC type II and type IV behavior. The multipoint BET measurements show very large specific surface areas and high porosities. The aerogels have BET surface areas of  $219 \text{ m}^2 \text{ g}^{-1}$  and 189 m<sup>2</sup> g<sup>-1</sup> for the CdSe/CdS NPLs and CdSe NPLs, respectively. These values are comparable with that of previously reported metal chalcogenide aerogels (typically in the range of 90 to 240 m<sup>2</sup> g<sup>-1</sup>).<sup>20-22</sup> However, care must be taken when comparing mass-specific surface areas of materials of different composition. As noted earlier<sup>49</sup>, such comparisons are biased by the influence of the molar mass of the compounds. For example, a typical silica aerogel with a mass-specific surface area of 500 m<sup>2</sup> g<sup>-1</sup> has a mole-specific surface area of 30.000 m<sup>2</sup> mol<sup>-1</sup> for comparison, a CdSe aerogel with a mass-specific surface area of 200 m<sup>2</sup> g<sup>-1</sup> has a mole-specific surface area of  $29.000 \text{ m}^2 \text{ mol}^{-1}$ .

This comparison shows that the semiconductor NPL aerogels described here has equally high specific surfaces as in classical oxide aerogels. It should be noted that the maximum surface area achievable (from rough geometrical estimations) with this system is ~ 290 m<sup>2</sup> g<sup>-1</sup> (considering all the NPLs are present separately). Hence, the specific surface area reported here is around 70 % of the maximum possible value. That means roughly 30 % of the surface is covered by overlaying of the NPLs surface to form 3D network. We have also evaluated the pore size distributions from the desorption branch of the isotherms, applying BJH (Barrett-Joyner-Halenda) theory.<sup>42</sup> The broad pore size distributions obtained, ranging from mesopores to macropores, are consistent with a highly porous disordered gel structure, as revealed by the SEM and TEM microscopic analysis. The cumulative pore volumes V<sub>3.0-245</sub> (lower subscript denotes the pore diameter) calculated for the CdSe/CdS core/crown NPL and CdSe NPL aerogels (at relative pressure  $P/P_0 = 0.99$ ) using BJH theory are 2.27 cm<sup>3</sup>·g<sup>-1</sup> and  $1.65 \text{ cm}^3 \cdot \text{g}^{-1}$ , respectively. The total pore volume  $V_t$  can be calculated using the equation  $V_t = (1/\rho_a) - (1/\rho_b)$ , where  $V_t$  is the total pore volume and  $\rho_a$  and  $\rho_b$  represent the density of aerogel and bulk solid material.<sup>50</sup> The total pore volume for the CdSe/CdS and for the CdSe aerogel are  $26.14 \text{ cm}^3\text{g}^{-1}$  and 27.60 cm<sup>3</sup>g<sup>-1</sup>, respectively. The average pore diameters estimated using the equation 4 x  $V_t/\sigma$  ( $\sigma$  represents the calculated BET specific surface area of the aerogel) are 477 nm and 584 nm for CdSe/CdS and CdSe aerogel, respectively.<sup>50, 51</sup> So, the average pore diameters calculated using the equation  $V_{\rm t} = (1/\rho_{\rm a}) - (1/\rho_{\rm b})$  are significantly higher than the average diameters as they were determined from the nitrogen adsorption data. This fact is an indication that the porosity results predominantly from the macropores, which is in accordance with the measured isotherms.

The crystallographic characterizations of the CdSe/CdS aerogel and the NPLs in solution (before and after phase transfer) were investigated using powder x-ray diffractometry (XRD) and are shown in the Supporting Information.



Figure 8. Nitrogen physisorption isotherms for (A) CdSe/CdS core/crown NPL and (B) CdSe NPL aerogels, as well as their pore size distributions derived from these data. (C) and (D) BJH cumulative pore volume distribution of the CdSe/CdS aerogel and of the CdSe aerogel.

#### 4. Conclusions

In conclusion, we have successfully developed a method to prepare highly porous aerogels from CdSe NPLs and CdSe/CdS core/crown NPLs with high PLQY up to 10.3 %. This is the first report on aerogels from colloidal quantum well building blocks. Notably, the aerogels of the NPLs have solely (111) as the exposed facet in the aerogel, which might be of high interest for facet selective catalysis or sensing. The aerogels from the NPLs partially retain the quantum confinement properties of the building blocks and have very large inner specific surface area of 219 m<sup>2</sup>/g which is close to the highest values reported so far for nanocrystal-based aerogels. Furthermore, the highly porous character would allow molecules to pass through with minimum hindrance, making them promising candidates e.g. detecting chemical agents.

## ASSOCIATED CONTENT

**Supporting Information**. TEM micrographs of the 5 ML CdSe/CdS core/crown NPLs before and after phase transfer, optical characterizations (UV-Vis absorbance, emission and PL decay) of the CdSe and CdSe/CdS core/crown NPLs in organic and in aqueous medium, , SEM micrographs of the aerogels from CdSe (aq) NPLs, SEM micrographs of the xerogel from CdSe/CdS core/crown NPLs, HRTEM of the aerogel from CdSe/CdS core/crown NPLs, XPS spectra of the CdSe/CdS

core/crown aerogel, PL decay analysis of the surface trap states, photograph of the film prepared by drying CdSe/CdS NPLs on a glass slide, X-ray diffraction pattern of the CdSe/CdS (aq) NPLs and of the hydrogels and aerogels obtained from CdSe/CdS NPLs. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Author Contributions

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### ABBREVIATIONS

NPL, nanoplatelet; MUA, 11-mercaptoundecanoic acid; PLQY, photoluminescence quantum yield; TEM, transmission electron microscopy; SEM, scanning electron microscopy; BET, Brunauer-Emmett-Teller; BJH, Barrett-Joyner-Halenda; XRD, x-ray diffractometry; FWHM, full width at half maximum; XPS, X-ray photoelectron spectroscopy.

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