Aerogels from CdSe/CdS Nanorods with Ultra-long Exciton Lifetimes and High Fluorescence Quantum Yields

Sara Sánchez-Paradinas[1,*], Dirk Dorfs[1,*], Sebastian Friebe[1], Axel Freytag[1,*], Andreas Wolf[1,*], Nadja C. Bigall[1,*]

[1] *Institute of Physical Chemistry and Electrochemistry, Leibniz Universität Hannover, Callinstr. 22, 30167 Hannover, Germany*
[*] *Laboratory of Nano and Quantum Engineering, Schneiderberg 39, 30167 Hannover, Germany*

Abstract
Hydrogels and aerogels from CdSe/CdS nanorods have been fabricated. By precisely controlling the gelation process, gels with high photoluminescence quantum yield and ultra-long exciton lifetime can be obtained. Thus, this type of assemblies represents a very promising way to fabricate materials that present new or improved characteristics with respect to both the colloidal solution and the bulk.

Introduction
Nowadays, it is possible to produce a huge variety of nanoparticles (NPs) in colloidal solution with different interesting properties and a wide variety of sizes and shapes, but the fact of being in solution is sometimes a limitation for the envisioned applications. Assembly methods serve as a powerful tool to connect nanoscale materials into macroscopic materials, giving rise to superstructures, such as hydrogels and aerogels that retain the original *nanoproperties* [1].
In our work, we use semiconductor NPs, specifically CdSe/CdS nanorods, as building blocks for the fabrication of gels. This asymmetric core-shell system consisting of a CdSe core surrounded by a rod-shaped shell of CdS [2] is characterized by a high photoluminescence quantum yield (PLQY), due to the larger band-gap material in the shell that will force the exciton generated after illumination to recombine in the core [3].
The general methodology we follow to produced the gels consists of three main steps. The first one is a phase transfer of the NPs from the organic solvent to aqueous solution. Original TOP-TOPO ligands are exchanged by mercaptopropionic acid [4]. After the phase transfer, the NPs are subjected to a controlled oxidative process with hydrogen peroxide (H_2O_2) that removes part of the ligands in the surface of the NPs, they will interact with each other and they will form the hydrogels (Figure 1). In a last step the solvent in the pores (water) is removed by supercritical drying (SCD) to form aerogels (Figure 1). SCD is done in four main steps: the water in the gels is first replaced by acetone and then by liquid CO_2. Afterwards, the CO_2 is taken over its critical point and finally the gas is released. The gels were characterized by several techniques giving rise to very interesting results.

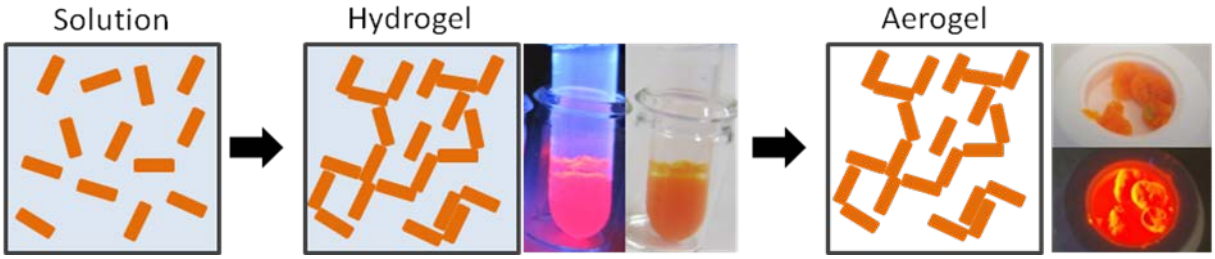

Figure 1. Scheme of the general methodology followed for the preparation of the gels.

Results and discussion
After analyzing the morphology of the gels by SEM and TEM it can be concluded that the gels have a highly porous structure, with pores ranging between 2 and more than 50 nm, and a nanoscopic morphology with connections between the rods mostly tip to tip, forming this network (Figure 2A).

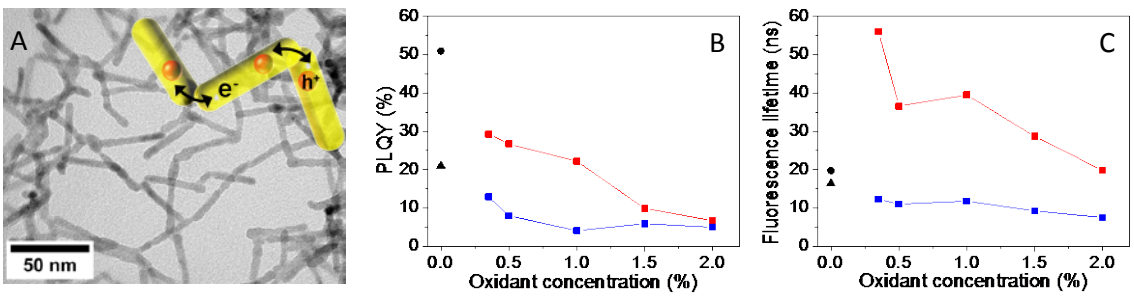

Figure 2. TEM image of an aerogel and a sketch of the corresponding model (A). PLQY (B) and fluorescence lifetime (C) of hydrogels (blue) and aerogels (red) generated with different H_2O_2 concentrations. 0% H_2O_2 corresponds to the organic (black circle) and aqueous (black triangle) solution of the nanorods.

The PLQY and the lifetime of the structures were measured as a function of the oxidant concentration (Figure 2B and C). It should be noted here that to our knowledge this is the first report on gels from CdSe/CdS nanorod system and moreover, that this is the first work reporting the PLQY of these structures, which due to their scattering nature are difficult to characterize. We observed that in all cases the PLQY of the aerogels is not only higher than the corresponding hydrogel but is also higher than the aqueous solution (at least for the three lower amounts of H_2O_2). Surprisingly, although we measure these high values of PLQY in the case of aerogels the values for the lifetime are extremely long. We have first a decrease in the non-radiative processes when going from hydrogel to aerogel and also the recombination process is slowed down in the aerogels. Taking all these things into account, we propose a model in which the NPs, that in colloidal solution are isolated, in the gels they form this network in which the inorganic parts are connected, creating a continuous structure in which the excited electron can be delocalized (sketch in Figure 2A). Consequently, lifetimes are strongly increased.
The results of this work are published in Advanced Materials [5], work to which the reader is encouraged to read for a more detailed information.

Conclusions

In this work we have fabricated gels from CdSe/CdS nanorods with high PLQY (up to 29% for the aerogel generated with 0.35% H_2O_2) and long lifetimes (56 ns for the aerogel generated with 0.35% H_2O_2), in comparison to those of the nanoparticle building blocks. When assembling nanoparticles into macroscopic superstructures, new interparticle interactions arise and fascinating changes of physical properties are expected, confirming the famous axiom "The Whole is Greater than the Sum of the Parts". Hence, CdSe/CdS nanorods gels are very promising as high-tech materials in light emitting diodes (LEDs), optical gain and sensors applications.

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