

Modification of Nanocrystal-based Network Structures

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The transformation of colloiddally dispersed nanocrystals into porous network structures, called gels, can be seen as way to bring these nanoscopic particles into the macroscopic world without losing their size-dependent properties. This means one is able to generate a macroscopic structure which still has the high surface to volume ratio and tunable optics inherent to the nanoparticulate building blocks. However, the generated networks are usually mechanically fragile. We aim to address this weakness by encasing the whole continuous network in a thin shell, e.g. made from silica (see Figure 1a-c).

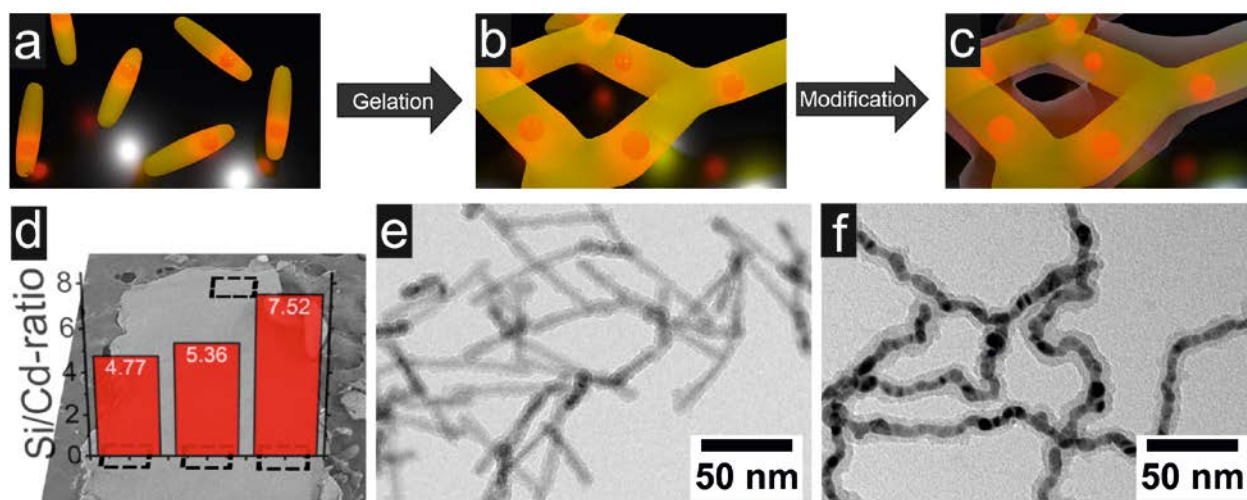


Figure 1. Modification of nanocrystal-based network structures. Schematic depiction of the process from colloidal nanocrystals (a) to the network (b) to the silica shell modified network structures (c). SEM and local elemental measurements (d) as obtained from center of the gel (left) to outside of the gel (right). TEM micrograph of silica shell modified CdSe/CdS dot-in-rod (e) and gold-silver mixed (f) nanoparticle-based network structures.

Network structures were generated from two types of nanoparticles, semiconducting (here: CdSe/CdS dot-in-rod particles) and metallic (mixture of gold and silver particles), and successfully surrounded by silica shell in a Stöber process based method (see Figure 1e,f). This modification could also be expanded to titania as shell material. All networks were supercritically dried afterwards to convert them into so called aerogels. This marks the first successful wet-chemical shell growth on a continuous nanoparticle network.

We are showing the macroscopic homogeneity of the generated shells by elemental measurements of different network areas. The elemental ratio of the cadmium from the core network to the silica from the shell is slightly lower in the center of the network (see Figure 1d) which can be attributed to the reduced transport inside the network. Additionally, the increased mechanical stability of the silica coated networks could be demonstrated by mechanical measurements as well as rehydration experiments simulating application of the network in electrolytes. Unmodified networks showed mechanical failure at relatively low compressions (harsh drops in the stress-compression curve, see Figure 2a) while modified networks withstand much higher compressions. The surface area of modified and unmodified nanocrystal-based aerogels was measured by krypton physisorption and in all cases the surface area of modified networks was ca. 60-80 m²/g higher than the unmodified samples indicating inner porosity of the grown shell.

The optical properties of the generated networks were studied in more detail. It has been shown earlier that CdSe/CdS dot-in-rod nanoparticle-based networks exhibit increased fluorescence lifetimes compared to their building blocks. This was attributed to the mobility of the excited electron inside the network structure leading to a decrease in recombination rate and therefore increase in lifetime. By tuning the synthesis sequence (i.e. swapping the modification and gelation step) we were able to generate two similar structures,

one in which the CdSe/CdS nanoparticles are separated by an isolating silica layer and one in which there is a connected CdSe/CdS nanoparticle network surrounded by silica. When comparing the optical properties of these two structures our initial assumption relating the particle contact inside the network to the increased lifetimes was confirmed (see Figure 2b,c). The structures where the CdSe/CdS building blocks were isolated by a silica layer in between each other indeed showed the lifetimes of the pristine building blocks while the structures with direct contact between the building blocks showed the increased lifetimes as in earlier studies. By theoretical calculations and low-temperature spectroscopy it could be shown that the increase in fluorescence lifetime is caused by the influence of higher excited energetic states inside the structure.

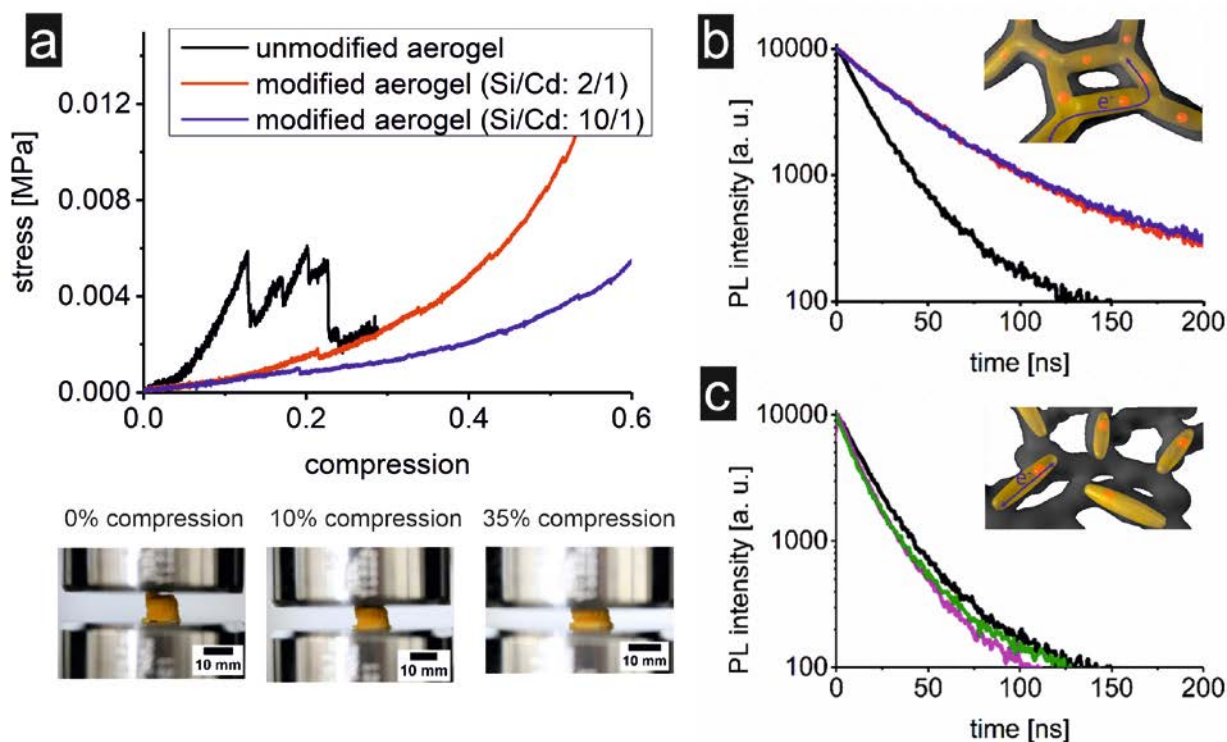


Figure 2. Mechanical and optical characterization of CdSe/CdS dot-in-rod nanoparticle-based aerogels. Compression test of different modified and unmodified aerogels (a) with photographs of a modified aerogel under different loads. Fluorescence lifetime measurements of aerogels with direct contact between the CdSe/CdS particles (b) and with insulating silica layer between the particles (c) respectively facilitating electron delocalization or confinement as indicated by schematics.

In short, the potential to modify nanoparticle-based network structures after their gelation was shown and realized. The improvement of their mechanical properties which is an important step in the way towards application of these structures could be demonstrated and these new structures allowed further insight into the electronic processes. In future studies we will focus on expanding the catalogue of materials for the inner network structure as well as the outer shell. Also, by further variation of network materials and in-depth spectroscopic experiments we aim to gain even more understanding into the electronic properties of these expanded semiconducting networks.

For more information see:

P. Rusch, F. Niemeyer, D. Pluta, B. Schremmer, M. Rosebrock, F. Lübke, M. Schäfer, M. Jahns, P. Behrens, N. C. Bigall, „Versatile route to core-shell reinforced network nanostructures”, *Nanoscale*, 2019, **11**, 15270-15278, <https://doi.org/10.1039/C9NR03645H>

P. Rusch, B. Schremmer, C. Strelow, A. Mews, D. Dorfs, N. C. Bigall, „Nanocrystal Aerogels with Coupled and Decoupled Building Blocks”, *J. Phys. Chem. Lett.*, 2019, **10**, 7804-7810, <https://pubs.acs.org/doi/full/10.1021/acs.jpcclett.9b02695>