

# Control Over Structure and Properties in Nanocrystal Aerogels at the Nano-, Micro- and Macroscale

*Pascal Rusch, Dániel Zámbo, Nadja C. Bigall\**

Institute of Physical Chemistry and Electrochemistry, Leibniz Universität Hannover,  
Callinstraße 3A, 30167 Hannover, Germany

Cluster of Excellence PhoenixD (Photonics, Optics, and Engineering – Innovation Across  
Disciplines), 30167, Hannover, Germany

\*Corresponding Author: [nadja.bigall@pci.uni-hannover.de](mailto:nadja.bigall@pci.uni-hannover.de)

Within this supporting information certain aspects of the ideas presented in the main article will be discussed in more detail. These more in-depth views provide additional complementary information as well as technical details for the interested reader.

### **Spectroelectrochemical investigation of CdSe/CdS dot/rod gel networks**

Spectroelectrochemistry provides analytic methods that allow a deeper understanding of the processes within NC-based network structures especially with regards to the charge carrier transport. Accordingly, they were applied to study CdSe/CdS dot/rod-based gels as these show the fascinating optical properties mentioned in the main article which were attributed to the enhanced charge-carrier mobility in the network. By means of linear sweep voltammetry (LSVs) and intensity modulated photocurrent spectroscopy (IMPS), the enhanced mobility of electron within the interconnected networks was confirmed. By measuring the photocurrent with changing the applied bias potential, a clear influence of gel thickness on the electrochemical properties can be observed. Very thin gels show both positive and negative photocurrents depending on the bias potential, while thicker gels only exhibit positive photocurrent. This can be explained by the special electronic structure of the networks. Negative photocurrent can only be generated by the particles in direct contact with the transparent conductive oxide (TCO) electrode, while positive photocurrent can originate even further away from the electrode inside the gel network, because excited electrons are able to travel within the CdSe/CdS network (and can reduce  $H^+$  to  $H_2$ ) and hence contribute to the photocurrent also from thicker layers. The holes are confined to the respective CdSe core and can only contribute to the photocurrent when consumed by the hole-scavenger (if they are further away and not in contact to the electrode). For thicker networks, processes generating negative photocurrent therefore become less influential. A CdSe/CdS dot/rod network structure therefore exhibits essentially diode behavior as illustrated in Figure 3f of the main article.<sup>1</sup> The electron transfer processes could also be investigated by intensity modulated photocurrent

spectroscopy (IMPS) which gives further insight into the charge carrier mobility in the gel structures. The occurrence of two distinguishable charge carrier transport mechanisms, visualizing as two semicircles, was observed. A sub-monolayer of particles only exhibits one process due to the lack of direct particle-particle contacts (see Figure 3g of the main article).<sup>1</sup> Therefore, the processes were attributed to the transition at the (a) electrolyte-particle contact on the gel surface (which is part of every electrochemical circle) and (b) the particle-particle contact within the network (unique to network electrodes). The significantly increased mobility of the excited electrons in the networks also supports the findings discussed in the optical properties of such structures, namely the ultra-long exciton lifetimes and enhanced photoluminescence quantum yields.

### **Transferring Cation Exchange from Nanocrystals to Networks**

The cation exchange process usually introduces a lot of crystal defects into the structures which is beneficial for the exchange as it increases ion diffusion. However, the defects can later act as trap states, that opens new channels for non-radiative recombination *i.e.* quenching the fluorescence of the particle. Similarly, a loss in emission could also be caused by leftover copper-ions. Therefore, it was necessary to heat the networks over several days to heal out the defects, and by this annealing step it was possible to recover the fluorescence (see the spectroscopic data in Figure 4b). Importantly, the structure and porosity of the starting gel networks could be retained in all cases. As a testament to the difficulty of applying techniques developed for solution to gel substrates, it has to be mentioned that minor contaminations with side products of the exchange process in the form of Hg salts or Ag nanocrystals (NCs) were observed. This is most likely due to the incredibly high “concentration” of NCs inside a given volume of the network compared to a similar volume in colloidal NC solutions and similar contaminations could be found when applying the exchange procedure adapted to gels to a comparable NC solution.<sup>2</sup>

The cation-exchange is only possible with gels in reasonable reaction times because the preserved dimensions of the nanoscopic building blocks and the porosity of the gel substrates limit the length of solid-state ion diffusion, and since the hierarchical pore geometry typical for gels results in a good accessibility of the solid backbone to exchange ions. Overcoming the limitations and optimizing the exchange procedure conditions, gel networks of numerous new materials ( $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ ,  $\text{HgSe}/\text{HgS}$ ,  $\text{PbSe}/\text{PbS}$ ,  $\text{Ag}_2\text{Se}/\text{Ag}_2\text{S}$ ) have been achieved starting from the  $\text{CdSe}/\text{CdS}$  NC network.

### **Challenges in the Production of Core-Shell Networks**

In this endeavor, several key points have to be considered which underline important differences between NCs in solution and NC-based network structures as substrate: (i) the problem of the reaction medium and (ii) the problem of the diffusion of the reactants. One of the key points of gels is their heterogeneity, they are an insoluble, porous network, penetrated by a fluid. Luckily, the fluid can be chosen quite freely and adapted to the envisioned reaction, however, a lot of the established shell growth reactions employ micro-emulsion solvent systems.<sup>3</sup> These systems form micelles which might interfere with the filigree network of the gel. This simply means that some reactions are not adaptable for NC-based gel substrates, but there are plenty other options available from established literature methods of core-shell NC synthesis allowing the circumvention of this obstacle. The second problem of diffusion however cannot be avoided. While the porosity and thereby the accessibility of the single building blocks of a gel structure for molecules in the fluid medium is one of the key advantages of a gel over a dense packaging of said building blocks, the transport of material through the porous network is clearly hindered if compared to the free building blocks dispersed in a medium. To overcome this limitation, a homogeneously modified gel surface can only be obtained if the diffusion through the network structure is considerably faster than the reaction itself. This necessitates

the use of reactions that can either be tuned in their reaction kinetics to be very slow or can be initiated via external stimuli (e.g. heat), of course without destroying the network in the process.

The well-established sol-gel chemistry of silica does offer the required tunability. Starting from known procedures for the shell-growth onto NCs, key parameters like pH and water content have been adjusted to tune the hydrolyzation rate to produce homogeneous shells. To expand this method to other shell material which usually used much more reactive precursors other additives were needed to slow down the hydrolyzation to a point where a homogeneous shell could be achieved. Other substrates on the other hand, like noble metal NC-based networks require a linkage between the core network and the shell to prevent island-like shell growth.<sup>4</sup>

A different example of core-shell structured networks is mentioned in the main article. These bi- or trimetallic networks were built up from various metallic NCs (Pd alloyed with Au, Ni, Co, Cu in different concentrations) assembled into a nanowire-like network of connected NCs (as can be seen in Figure 6 of the main article) and afterwards used as substrate for electrochemical deposition of copper. In this case, the electrochemical deposition serves the purpose of circumventing the issues mentioned earlier and produce homogeneous shells. This resulted in multimetallic core-shell structured networks. The outside Cu shell could then be exchanged to platinum by galvanic replacement. The elemental mapping of the structures proves the successful preparation of these core-shell structured networks as shown in Figure 6a-c of the main article. Naturally, this also saves a considerable amount of material as the expensive platinum is only used for the outside shell layer (the region of great importance from catalytic point of view) while the inside backbone of the network can be made from lower-cost materials. These multimetallic aerogel structures have shown to be highly effective as ORR catalyst, more so than the conventional Pt/C catalyst. Interestingly, the catalytic activity could be shown to be dependent on the lattice parameter of the core network NCs in the form of a

volcano plot. This relation was attributed to the emerging lattice strain in the Pt shell which influences its catalytic activity.<sup>5</sup>

### **Technical details of gelation *via* inkjet printing process (GelVIP)**

The setup to deposit gels *via* ink-jet printing comprises a commercial ink-jet printer with CD printing capabilities with refillable cartridges. The cartridge is filled with an aqueous semiconductor NC-based ink and the appropriate gelation agent (dilute H<sub>2</sub>O<sub>2</sub> in this case) in two of the color chambers. The ratio between NCs and gelation agent can then be adjusted by the printing color according to the CMYK color model. This ratio is a key parameter, as the gelation must not be too fast to allow for the formation of a porous network but must also be fast enough to avoid the ink from bleeding which would limit lateral resolution. The humidity has to also be adjusted closely throughout the whole process to avoid an uncontrolled drying of the gel, especially before the gelation. The CD was replaced with the TCO substrate on which the gel was to be printed. In order to have inks from nanoparticles in water only, without additional additives, it was necessary to pre-treat the electrodes before the printing, otherwise the film homogeneity and printed shapes would be uncontrolled. This was achieved by the functionalization of the substrates by (3-mercaptopropyl)trimethoxysilane binding to the surface *via* the silicone while binding to the printed particles *via* the mercapto group.<sup>6,7</sup>

## References

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