Investigation of the photocatalytic hydrogen production of semiconductor nanocrystal-based hydrogels

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One of the main challenges in recent decades is the transformation toward a sustainable energy system. Hydrogen is a widely discussed alternative to fossil fuels and besides the yet industrially applied electrolysis, photocatalytic hydrogen production could be a method to supply hydrogen. A variety of materials, e.g., TiO_2, MoS_2, CdS, SiC or g-C_3N_4, has been investigated to find a suitable candidate to use sunlight efficiently for photocatalytic hydrogen production. Nanomaterials in comparison to the bulk material in general provide a large surface-to-volume ratio leading to a high amount of catalytically active surface in an overall low amount of material. To broaden the possible applications of these nanomaterials a novel class of materials with an interesting morphology are nanocrystal-based gel structures. Nanocrystal-based gel structures undergo a controlled destabilization of the ligand-stabilized nanocrystal solution to form a three-dimensional, highly porous network which retains the properties of the nanocrystal building blocks.

In this work, we present the influence of gel network formation of different semiconductor nanocrystal building blocks on the photocatalytic hydrogen production in aqueous solutions in comparison to their non-gelated nanocrystal building block counterparts. As semiconductor material beside others a heterostructure made of a CdSe core with a CdS rod like shell. To destabilize the ligand-stabilized nanocrystal solutions, an oxidative method using H_2O_2 was used. Removal of the ligands from the surface leads to the formation of a hydrogel with more freely accessible surface and different surface properties, such as the formation of sulfate sites, compared to the ligand-stabilized nanocrystals.

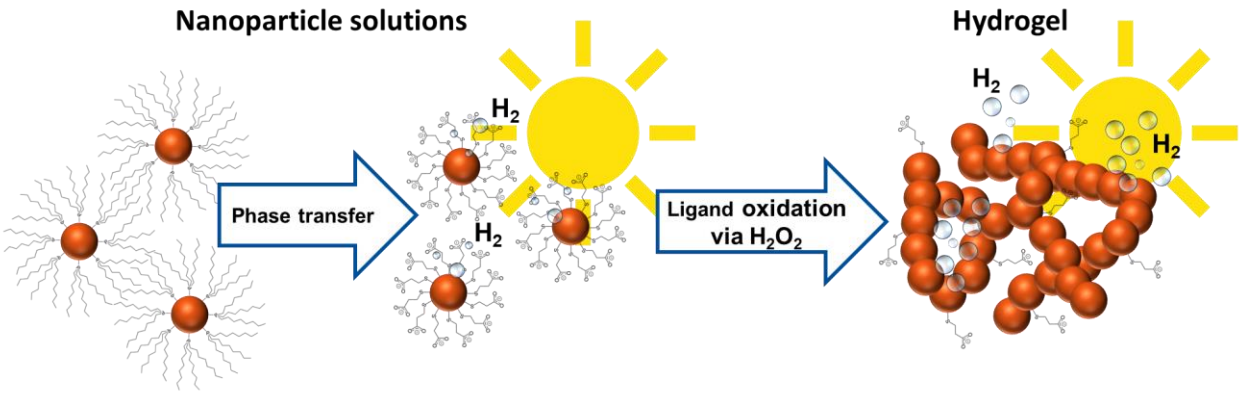

Figure 1: Schematic illustration of the synthesis of nanoparticle based hydrogels including phase transfer and the colloidal destabilization with H_2O_2. Further, it shows the photocatalytic hydrogen production which is possible using an aqeous nanoparticle solution and hydrogels.

Hydrogen production measurements of nanocrystal solutions as well as their respective hydrogels showed up to five times higher hydrogen production rate when using the hydrogel instead of nanocrystals in solution. As hole scavenger a solution of Na_2S and Na_2SO_3 has been the most efficient compared to aqueous solutions of methanol, ascorbic acid or triethanol amine. The higher photocatalytic activity of the nanocrystal-based hydrogels compared to the nanocrystals in solution could be explained by optical, XPS and electrochemical measurements. Removal of the ligands during the oxidative destabilization with H_2O_2 leads to an accessible semiconductor surface without the obstacle of organic ligands. These ligands additionally form hole trap states that reduce the charge carrier separation, so that their absence possibly results in a better charge carrier separation and longer charge carrier lifetimes. In addition to the influence of surface properties, the interconnection of the NCs in the hydrogels enables charge delocalization beyond one NC building block and thus also extends the charge carrier lifetimes. Longer charge carrier lifetimes make the photocatalytic reaction more probable leading to more efficient photocatalysts. Furthermore, the controlled destabilization and hydrogel formation ensures a high surface area which would not be the case by an uncontrolled agglomeration which can be observed using the nanocrystals in solution. As shown above the explanation of the interestingly higher hydrogen production rates using a hydrogel is off several factors. The differentiation of which factor has how many of an impact could not be determined.

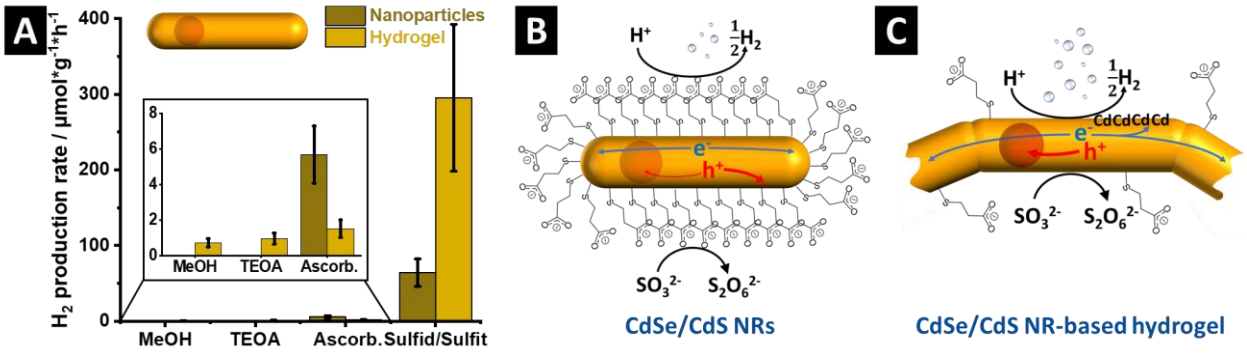

Figure 2: (A) Hydrogen production rate of CdSe/CdS nanorods as nanoparticles in solution and hydrogels in different hole scavenger solutions. (B) and (C) schematic difference between nanoparticles in solution and hydrogels.