

Supplementary Information

Reversible Cation Exchange on Macroscopic CdSe/CdS and CdS Nanorod Based Gel Networks

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Energy dispersive X-Ray spectroscopy of initial CdSe/CdS and CdS NR aerogels (Fig. S1 A) show the typical lines of Cd, S, and Se. EDXS spectra of copper chalcogenide based aerogels (Fig. S1 B) show typical lines of Cu, S, and Se. In both spectra cadmium (< 1 at%) can also be found which we attributed to residual cadmium salts which were formed via cation exchange and is insoluble in methanol and acetone. From the EDXS spectra of the back-exchanged CdSe/CdS and CdS NR aerogels also the typical lines of Cd, S, and Se are visible. These spectra exhibit no copper line, so that a complete back-exchange has taken place.

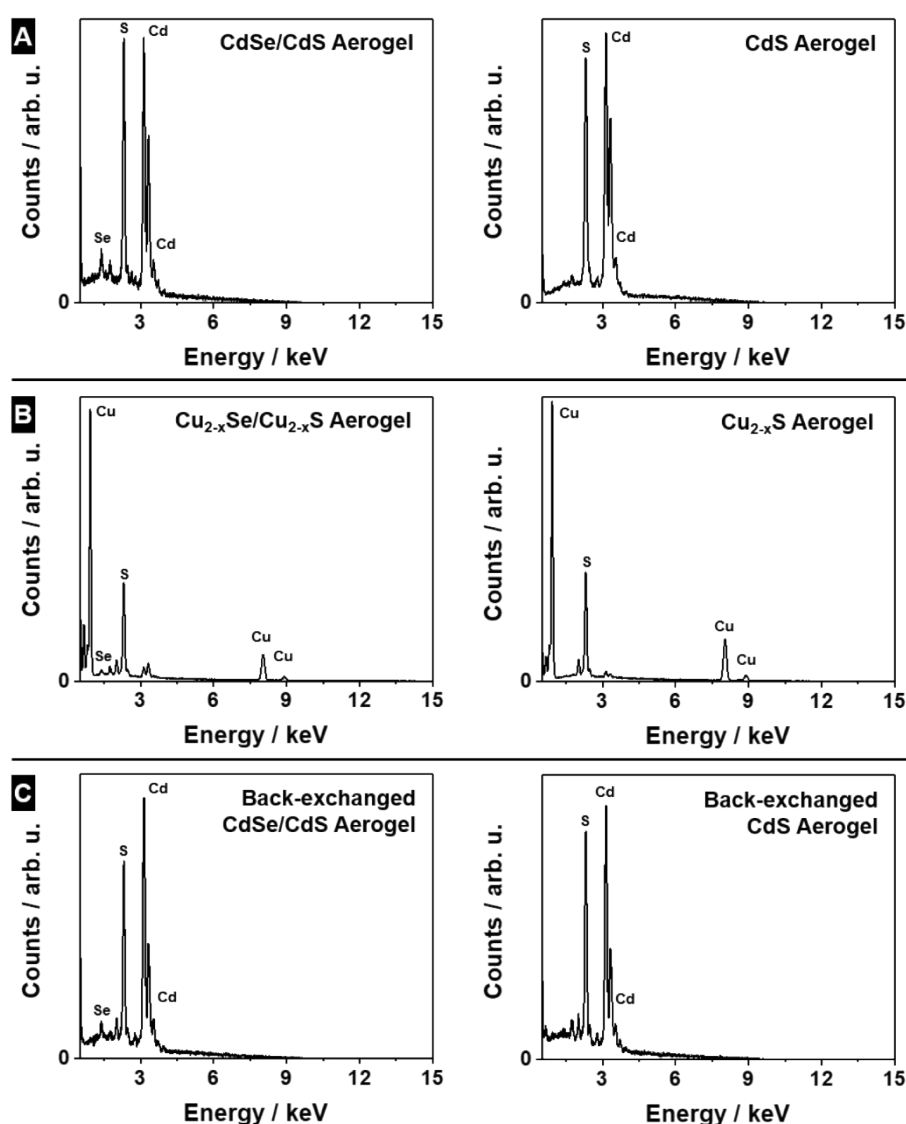


Fig. S1 EDX spectra of CdSe/CdS and CdS aerogels before cation exchange (A), Cu_{2-x}Se/Cu_{2-x}S and Cu_{2-x}S aerogels (B), and back-exchanged CdSe/CdS and CdS aerogels (C) recorded with SEM.

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From the TEM images (Fig. S2) of silver chalcogenide aerogels deformed nanorod building blocks are visible with some contamination of spherical nanoparticles. During the exchange from copper to silver the replaced copper ions can reduce the excess of silver ions with the results of *in-situ* grown Ag nanoparticles which are indicated as black spheres on the TEM images. In future this circumstance can be avoid by lowering the silver ion exchange concentration while simultaneously increasing of the exchanging steps. TEM micrographs of the obtained HgSe/HgS and HgS aerogels show connected nanocrystals, which have da different shape compared to the initial nanorods.

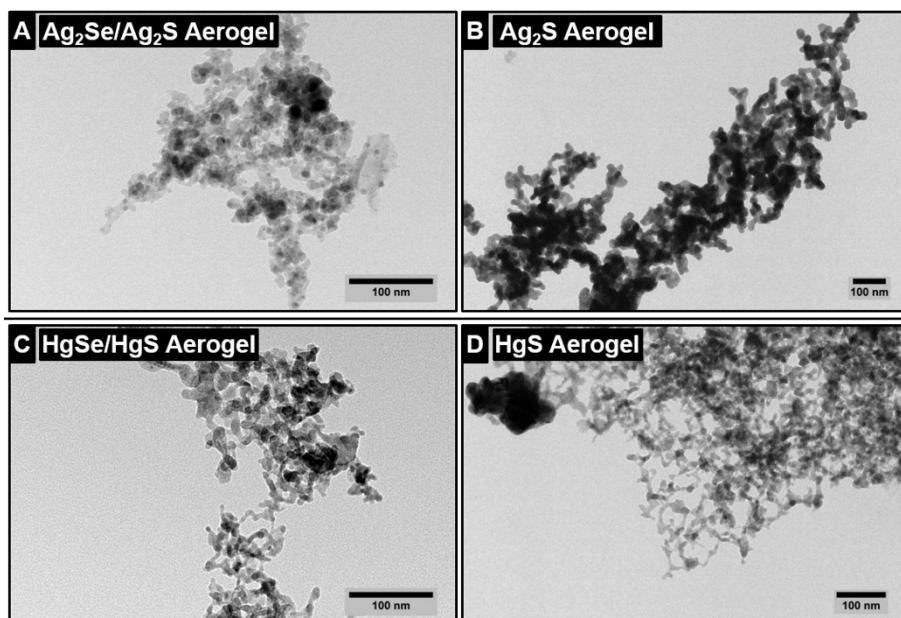


Fig. S2 TEM micrographs of cation exchanged $\text{Ag}_2\text{Se}/\text{Ag}_2\text{S}$ (A), Ag_2S (B), HgSe/HgS (C), and HgS (D) aerogels.

Powder X-Ray diffraction pattern of the silver chalcogenide ($\text{Ag}_2\text{Se}/\text{Ag}_2\text{S}$ and Ag_2S) aerogels and mercury chalcogenide (HgSe/HgS and HgS) aerogels are shown in Fig. S3 A. The PXRD pattern of silver chalcogenide show that both samples exhibit in the monoclinic Ag_2S crystal structure. Beside the silver sulfide phase reflections of the pristine cubic Ag crystal structure are visible, which is in good agreement with the TEM micrographs. Powder X-Ray diffraction pattern of the mercury chalcogenide-based aerogels show the hexagonal HgS crystal phase (Fig. S3 B). Beside the reflection of the hexagonal HgS phase sharp reflections are visible. These reflections can be attributed to the Hg_2Cl_2 crystal phase. Here, we also assume an oxidation of Cu^+ to Cu^{2+} while the simultaneous reduction of Hg^{2+} to Hg^+ . Due to the excess of chloride ions (use of mercury(II) chloride precursor) the Hg_2Cl_2 salt can be precipitated which is insoluble in alcoholic solutions.

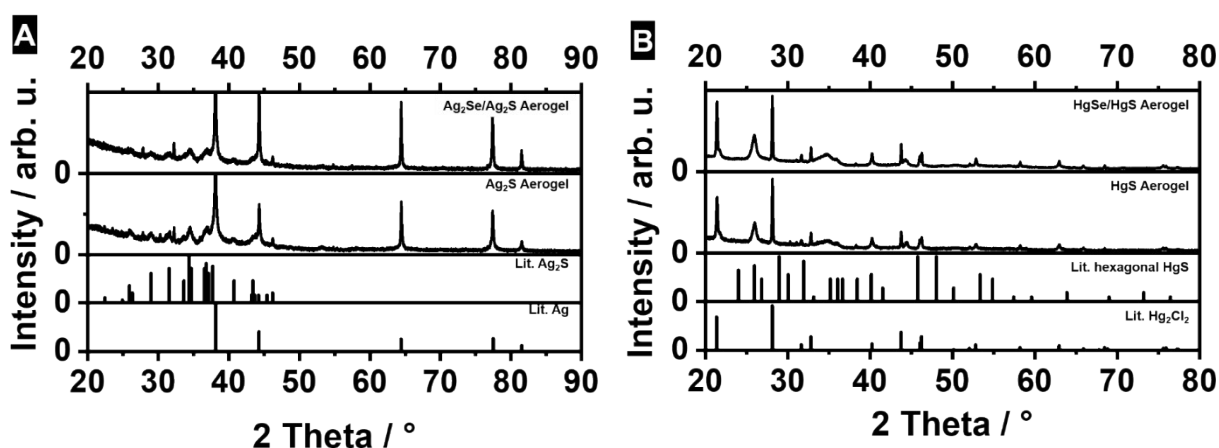


Fig. S3 PXRD patterns of exchanged $\text{Ag}_2\text{Se}/\text{Ag}_2\text{S}$ and Ag_2S aerogels (A). Reference XRD patterns of monoclinic Ag_2S (Card No.: C14-72) and cubic Ag (Card No.: C4-783). PXRD patterns of exchanged HgSe/HgS and HgS aerogels (B). Reference XRD patterns of hexagonal HgS (Card No.: 00-019-0798), and Hg_2Cl_2 (Card No.: C26-312).

EDXS spectra of silver chalcogenide based ($\text{Ag}_2\text{Se}/\text{Ag}_2\text{S}$ and Ag_2S) and mercury chalcogenide (HgSe/HgS and HgS) based aerogels are illustrated in Fig. S4. The EDXS spectra of silver chalcogenide based aerogels show peaks of selenium, silver and

sulfur for $\text{Ag}_2\text{Se}/\text{Ag}_2\text{S}$ aerogel and silver, and sulfur peaks for Ag_2S aerogels. The EDXS spectra of mercury chalcogenide based aerogels beside the peaks of selenium, sulfur, and mercury additional peaks of copper. The residual presents of copper after ion exchange is also known from literature.^[1]

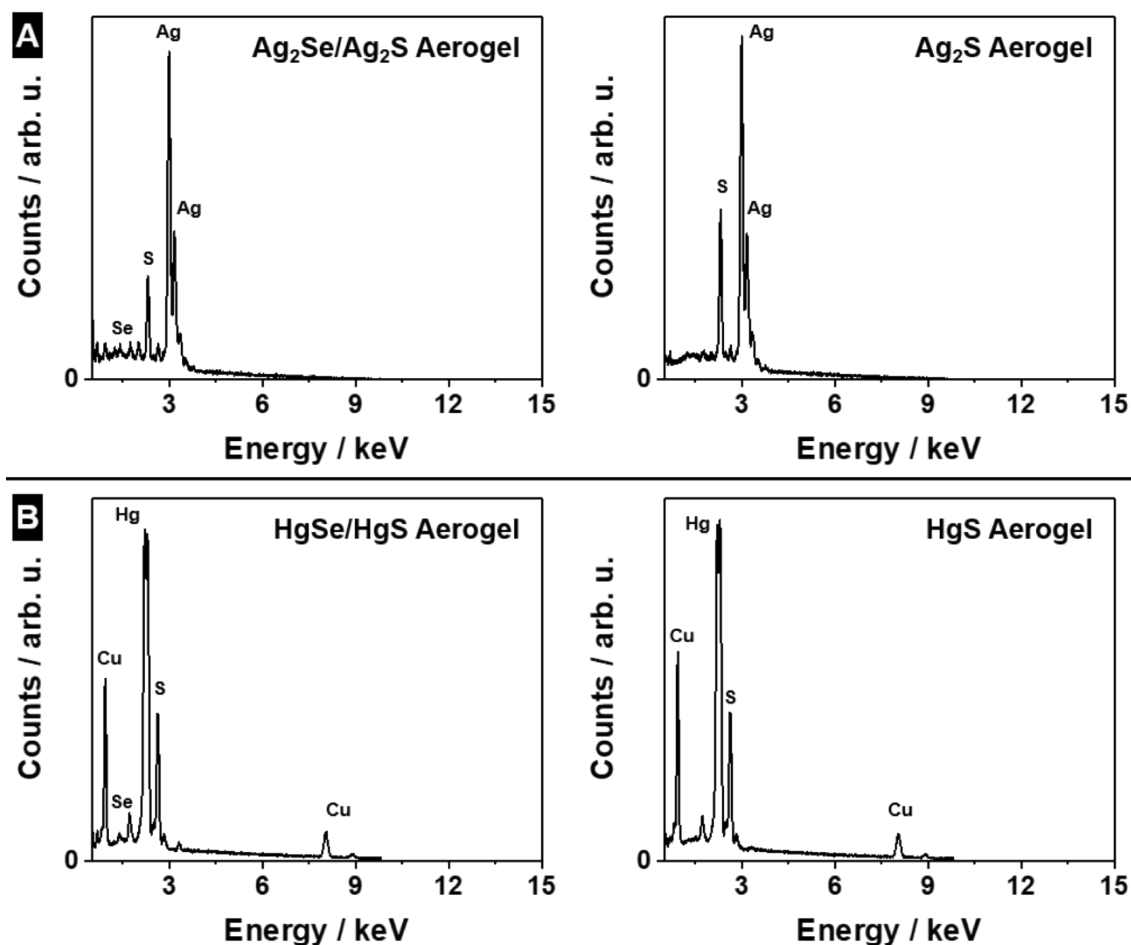


Fig. S4 EDX spectra of $\text{Ag}_2\text{Se}/\text{Ag}_2\text{S}$ and Ag_2S aerogels (A), and HgSe/HgS and HgS aerogels (B) recorded with SEM.

To understand the results from copper to silver and from copper to mercury on the macroscale, also cation exchange reactions at the nanoscale at pristine nanorods (only CdSe/CdS NRs) were performed. From the TEM images of copper exchanged $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ NRs (Fig. S5 B) a retained nanorod shape can be seen. The exchange from copper to silver leads to a reshaping of the nanocrystals and a simultaneous formation of pristine Ag NPs, which can be seen on the TEM image (Fig. S5 C). The results are also supported by the recorded PXRD pattern (Fig. S5 E), where in addition to the reflections of the monoclinic Ag_2S phase reflections of cubic Ag are present. As a reference experiment, the used methanolic copper ($[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$) and silver (AgNO_3) precursor solutions were mixed and analysed. From the TEM image (Fig. S5 F) fused strands of silver nanoparticles can be seen and the recorded PXRD pattern (Fig. S5 E) show reflections of the cubic Ag phase. The TEM image of the cation exchange from copper to mercury is shown in Fig S5 D. It can be seen, that a reshaping of the nanocrystal structure takes place, which results in ellipsoid shaped nanocrystals. In addition, small as well as larger nanocrystals are visible, which can be assumed to be Hg_2Cl_2 crystals or broken off HgS NPs. The PXRD pattern of the exchanged HgSe/HgS NRs show reflections of the hexagonal HgS crystal phase (Fig. S5 E) and a second phase, whose reflections can be attributed to the Hg_2Cl_2 crystal phase.

The different results compared to the literature are most likely caused by the tenfold higher starting material as well as precursor concentrations of the exchange solutions.^[2] The high precursor concentrations are however necessary to achieve complete ion exchange on the macroscopic gel structures.

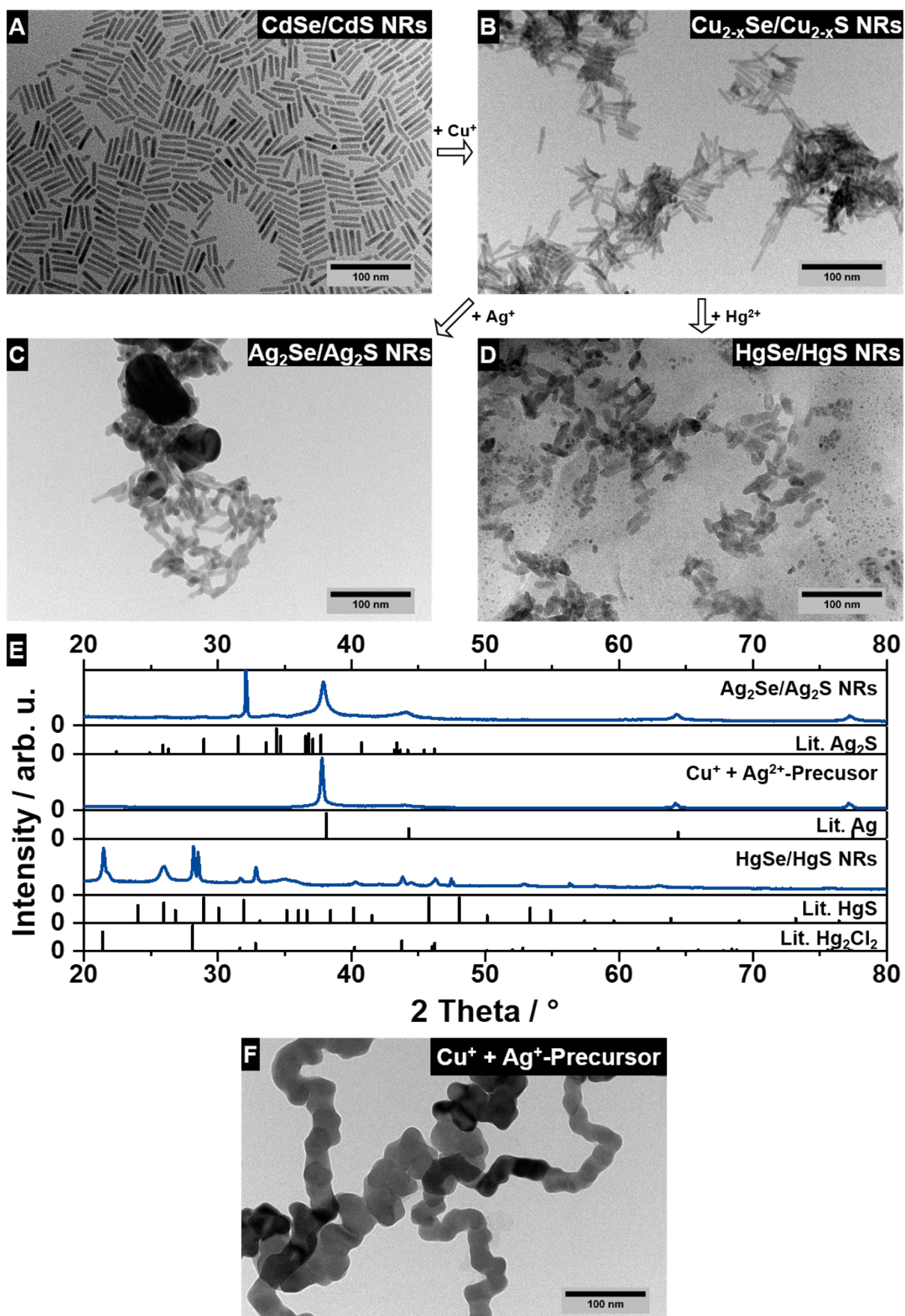


Fig. S5 TEM micrographs of CdSe/CdS NRs (A), $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ NRs after copper exchange (B), $\text{Ag}_2\text{Se}/\text{Ag}_2\text{S}$ NRs after silver ion exchange (C), HgSe/HgS NRs after mercury ion exchange (D), PXRD diffractograms of exchanged NRs (E), and TEM micrograph of an reference experiment where copper and silver precursor solution were mixed (F).

Experimental Section

Synthesis of CdSe Seeds

CdSe seeds were synthesized following the method of Carbone et al. with certain modifications.^[3] For the synthesis mixture 0.06 g CdO, 3 g TOPO and 0.17 g ODPA were placed in a 25 mL three-neck flask. The mixture was heated up to 150°C under vacuum and degassed for 1 h. Subsequently, the temperature was increased to 300°C under an argon atmosphere and 1.8 mL TOP was injected. The mixture was heated up to 380°C to obtain a clear solution. Then, 1.8 mL TOP:Se (0.4 mmol) solution was quickly injected into the reaction mixture. The temperature was allowed to recover to 380°C before quenching with 6 mL ODE. Red fluorescent CdSe seeds were obtained. After cooling the reaction mixture 5 mL toluene were added at 70°C and the CdSe seeds were precipitated by adding methanol and centrifuged (5,000 rpm, 3,775 RFC, 10 min). The CdSe seeds were purified twice with a toluene/methanol mixture and finally stored in 0.5 mL toluene.

Synthesis of CdS Seeds

CdS seeds were also synthesized following the method of Carbone et al. with certain modifications.^[3] For the synthesis mixture 0.1 g CdO, 3 g TOPO, and 0.6 g ODPA were mixed in a 25 mL three-neck flask, heated up to 150°C under vacuum, and degassed for 1 h. Subsequently, the solution was heated up to 320°C under an argon atmosphere following by the injection of 9.12 mL TBP consisting 0.6 mL (TMS)₂S. The synthesis was held at 250°C for 7 min, following by cooling down to room temperature. At 70°C 5 mL toluene were added, and the seeds were precipitated by the addition of methanol and centrifuged (5,000 rpm, 3,775 RFC, 10 min). The CdS seeds were purified twice with a mixture of methanol/toluene and stored in 0.5 mL toluene.

Synthesis of CdS Shells

CdS shells around CdSe seeds and CdS seeds were synthesized following the method of Carbone et al. with certain modifications.^[3] For the synthesis mixture 0.06 g CdO, 3 g TOPO, 0.16 g OPDA and 0.08 g HPA were placed in a 25 mL three-neck flask, heated up to 150°C under vacuum and degassed for 1 h. After switching to an argon atmosphere the temperature was increased to 300°C and 1.8 mL TOP were injected followed by increasing the temperature to 380°C. At that temperature 1.8 mL TOP:S (2.21 mmol) consisting the CdSe or CdS seeds (concentration of quantum dots in TOP was always 400 μM) was quickly injected and was heated for 8 min. After that time the reaction mixture were cooled down to room temperature by removing the heating mantle. The mixture was diluted with 5 mL toluene, precipitated by adding methanol and centrifuged (5,000 rpm, 3,775 RFC, 10 min). The purification step was repeated twice and the NRs were stored in 2.5 mL toluene.

Phase Transfer of CdSe/CdS NRs and CdS NRs

The phase transfer were performed according Kodanek et al..^[4] 750 μL of organic solution from CdSe/CdS NR or CdS NRs were precipitated with methanol, centrifuged and dissolved in 9.4 mL n-hexane. A second solution which consisted of 0.2 g KOH, 246 μL MPA and 9.4 mL methanol was mixed with the NR solution and the mixture was shaken overnight. Subsequently, the methanolic phase was separated with a syringe, centrifuged (5,000 rpm, 3,775 RFC, 10 min) and the CdSe/CdS NRs or CdS NRs were stored in 5 mL of a 0.1 M potassium hydroxide solution. The cadmium concentration of CdSe/CdS NRs is 21.8 mmol L⁻¹ and for CdS NRs 37.9 mmol L⁻¹.

Synthesis of acetogels and cation exchange reactions

In the following experimental section all information before the slash character addresses the synthesis with CdSe/CdS NRs and all information's behind the slash character belongs to the synthesis with CdS NRs. All cation exchange experiments take place in the glovebox under an argon or nitrogen atmosphere.

Synthesis of CdSe/CdS NRs and CdS NRs acetogels

CdSe/CdS and CdS NRs acetogels were prepared following the procedure of Sánchez-Paradinas et al..^[5] 800 μL / 1000 μL of the aqueous CdSe/CdS NRs or CdS NRs solution was mixed with 75 / 93.75 μL 0.35 wt% H₂O₂ solution following quickly shaking and heating for 1 min at 80°C. CdSe/CdS NR based hydrogels were gelled for 24 h and CdS NR based hydrogels were gelled for 48 h. After gelation and aging the hydrogels were washed 5 times with dist. water, 5 times with acetone and at least 5 times with dry acetone. Afterwards, the acetogels were brought inside a glovebox (working under an argon or nitrogen atmosphere) and washed again 5 times with extra dry acetone.

Cation exchange reactions (Cu, Ag, Hg) at CdSe/CdS NRs

For all experiments 400 μL of a CdSe/CdS NR solution (c(Cd) = 21.8 mmol L⁻¹) were used. For the copper exchange solution (Cd : Cu 1 : 10) 65 mg (0.34 mmol) [Cu(CH₃CN)₄]PF₆ was dissolved in 1.5 mL dry methanol and mixed with the CdSe/CdS NRs.

After 5 min the reaction mixture were centrifuged and the precipitated were stored in 1 mL toluene. For the silver exchange solution (Ag : Cu 1.8 : 1) 17.7 mg AgNO₃ (0.06 mmol) and for the mercury exchange solution (Hg : Cu 3 : 1) 35.4 mg HgCl₂ (0.13 mmol) were dissolved in 0.75 mL dry methanol and mixed with the Cu_{2-x}Se/Cu_{2-x}S NRs. After 5 min the mixture were centrifuged, redispersed in 400 μL toluene and mixed again with the silver or mercury exchange solution. The exchange step was in total repeated three times. The final product was stored in 1 mL toluene.

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