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Oleic-capped CdSe nanocrystals silver-doped in the course of synthesis

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Determination of doping level by XRF

The determination of Ag doping level in CdSe nanocrystals through XRF was conducted as follows. First, a series of standard samples was prepared in form of dodecane solutions, containing 40 mM of both cadmium oleate and trioctylphosphine selenide. The concentration of silver in these samples varied from 0 to 1,6 mM, silver was presented in form of silver oleate. Some cluster formation was observed, but it didn't disrupt the homogeneity of samples on micrometric level.

The XRF measurements were performed on Bruker M1 MISTRAL spectrometer, the beam energy was 50 keV. The measurements were performed with Mo filter to diminish the background signal. Both standard samples and QD samples were employed as dodecane solutions and sols (diluted to cadmium concentration of 40 mM) and placed in polyethylene cuvettes for measurements. The analytical signal was determined as relation of Ag K line integral intensity to Cd K line integral intensity. A calibration curve was obtained from standard samples' measurements. The detection limit is 60μM, the limit of quantification is 120μM, that correspond to doping levels of 0,15% and 0,3% respectively. Relative error mid-curve is 3%. Doping levels in QD samples were determined from the calibration curve (Fig. S1).

To exclude the possibility of Ag existing in samples in form of metalorganic byproducts, the NCs were precipitated with acetone and dispersed again in hexane several times. Also, for selected samples the stabilizer exchange on pyridine was performed to completely ensure accurate determination of doping level. This didn't lead to significant changes in determined doping levels.

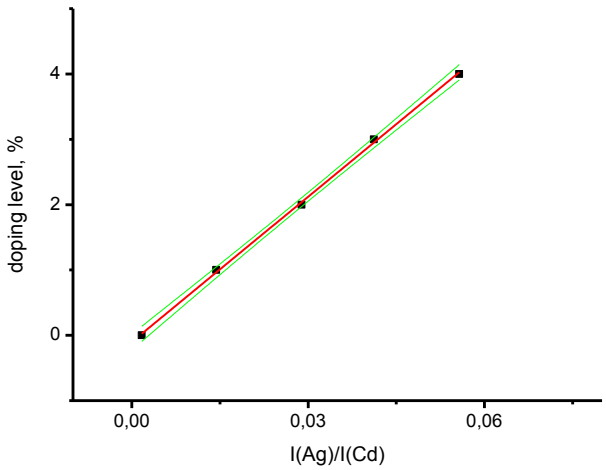

Figure S1 Calibration curve for determination of Ag doping level in CdSe QDs *via* XRF technique.

Powder X-ray diffraction

X-ray powder analyses were carried out using DRON-4-07 diffractometer (CuKα radiation). The samples were prepared as films on <111>-oriented Si substrates. Phase analysis was performed with use of "WinXPow" software

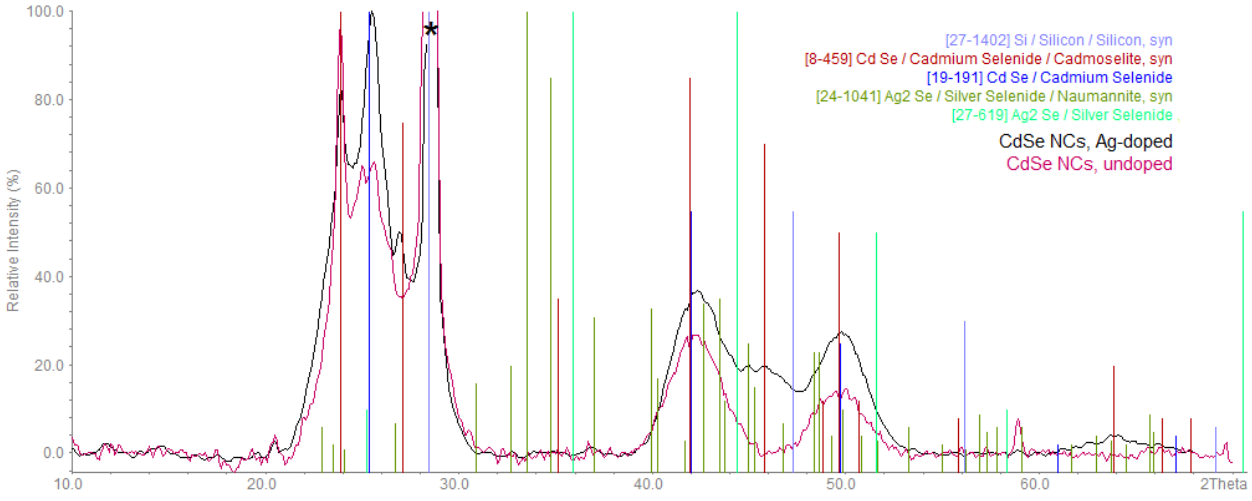

Figure S2 Powder XRD data on Ag-doped (black line) and undoped CdSe QD (violet line) compared to ICDD data on wurtzite (red drop-lines) and sphalerite (blue drop-lines) CdSe modifications and Ag_2Se modifications (dark-green and cyan drop-lines) (* marked reflex originates from Si substrate).

Photoluminescence studies of inter-particle silver exchange

This experiment was conducted to examine the possibility of inter-particle silver exchange in CdSe QDs. Two samples of different mean sizes (2.3 nm for undoped NCs and 3.2 nm for Ag-doped) were employed so as to distinguish their "band-edge" luminescence. This is essential for clear observation of changes, induced in undoped QDs after mixing with doped sample. Sols of these samples were prepared with concentrations, meeting the following conditions: absorbance of lower than 2.5 in 500−1100 nm wavelength region; equal intensity of luminescence of two "band-edge" bands upon mixing in 1:1 proportion. After mixing the sols we studied changes in PL spectrum of the mixture in time, for these studies samples of mixture were taken and diluted 50-fold (this results in absorbance lower than 0.05, necessary to exclude self-absorption and cross-absorption).

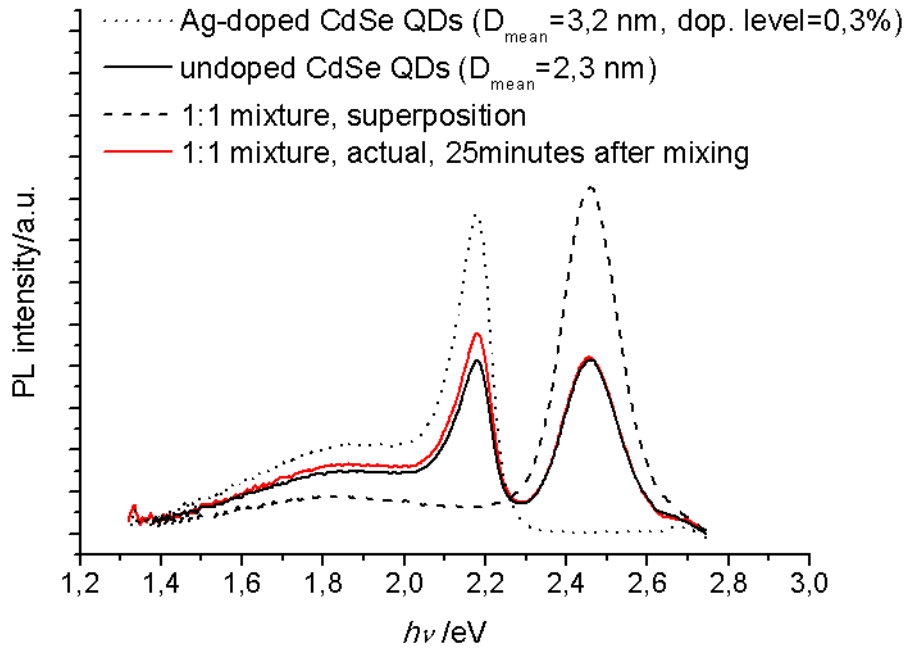

Figure S3 Photoluminescence spectra of sols of undoped CdSe QDs with mean diameter of 2.3 nm (dashed line), Ag-doped CdSe QDs with mean diameter of 3.2 nm (dotted line); superposition of above spectra, corresponding to 1:1 in volume mixture of samples (black solid line); actual spectrum of this mixture (red line).

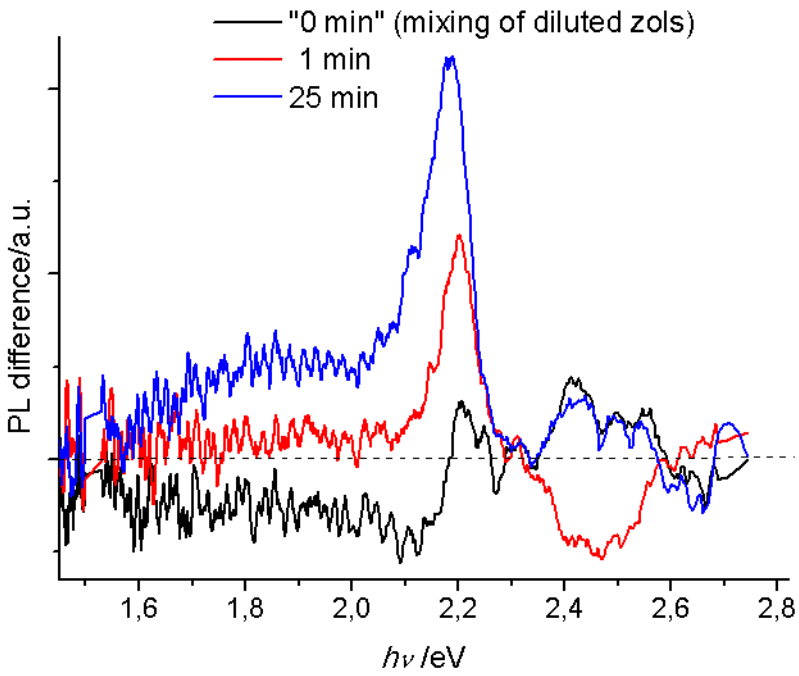

Figure S4 Difference spectra of mixture of doped and undoped QDs (in comparison to superposition spectrum): mixture of diluted sols (black line), mixture of concentrated sols – 1 minute after mixing (red line), 25 min after mixing (blue line).