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

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Silver-doped CdSe quantum dots with a prominent size-independent long-wavelength feature in photoluminescence spectra and an improved quantum yield were synthesized using a modified oleate colloidal technique.

Semiconductor nanocrystals (NCs) or quantum dots (QDs) based on II–VI Group elements have been intensely studied.[1,2] Attention has been focused on obtaining NCs with desired optical and electronic properties by doping.[3,4]

Doped NCs are of interest in bioimaging because the introduction of dopant atoms can cause the emergence of non-excitonic intracenter luminescence band with a long lifetime. Long lifetime of carriers on dopant-related levels can also provide an inverted population of electrons, which might be used in constructing QD-based lasers.[5] Quantum dots are promising for use in photovoltaics as an engineered bandgap material for tandem solar cells. The most interesting are NCs doped with heterovalent impurities, the introduction of such impurities to exchange sites in a lattice leads to the p- or n-type conductivity of QDs, needed to create junctions. The doping of NCs may protect them against UV photooxidation in solar cells, as excitation from absorbed photons can be efficiently transferred to the impurity, suppressing undesirable reactions on the NC surface.[6]

The heterovalent doping of colloidal QDs is performed by cation exchange[7] based on the diffusion of impurity atoms into NC, the addition of an impurity precursor during the NC growth[8] and a three-part core-shell synthesis.[9]

While the incorporation of Ag into cadmium chalcogenide NCs has received moderate attention, the study of this system is by no means thorough. Early studies featured exposing cadmium chalcogenide NCs to cation exchange with a silver precursor. The exchange process is very thermodynamically efficient[7] and leads to high degrees of exchange. Maximum bulk solubility of Ag_2Se in CdSe is 0.94 mol% (1063 K), though it drops sharply at lower temperatures.[10] Low bulk solubility can be explained by larger Ag atoms inducing high tensions to dense-packed CdSe lattice. In principle, these tensions can be relaxed more easily in NCs, which, in conjunction with NCs being fundamentally non-equilibrium, can lead to a higher possible Ag content. However, in case of unhindered exchange, multiphase NCs or silver chalcogenide NCs are formed.[7] In the former, Ag atoms are capable of migrating inside a cadmium chalcogenide lattice. This leads to the formation of silver chalcogenide domains at high concentrations.[11]

In the current studies of single-phase silver doped CdSe [CdSe(Ag)] NCs the same synthetic approach is used, where the silver impurity is introduced through cation exchange.[12,13] The QDs were doped[12] by adding ethanolic $AgNO_3$ to a toluene dispersion of NCs with mild heating. Trioctylphosphine was added to the silver precursor solution to diminish the exchange effectiveness. Thus, doped NCs were achieved with a doping level (Ag-to-Cd ratio) varying from 0.2 to 4%. $AgNO_3$ in a dilute aqueous solution of mercaptopropionic acid (MPA) was employed.[13] The role of MPA is that it lowers the exchange effectiveness through ligation with silver ions. In this case, the doping level was 0.45%. The doped NCs are stable at doping levels lower than 4%. Higher impurity concentrations cause NCs to decompose gradually with the formation of microcrystalline silver and Ag_2Se.[12] Doping CdSe NCs with silver through cation exchange does not notably affect crystallinity, UV-VIS absorption spectra or size distribution.[12,13]

The data on the photoluminescence of CdSe(Ag) NCs are rather contradicting. Both studies indicate the emergence of a dopant-related size-dependent feature in the long-wavelength part of spectra. However, the dopant-related feature[12] is prominent only at cryogenic temperatures, whereas the long-wavelength feature[13] is dominating at room temperatures and 'band-edge' emission is non-existent. This discrepancy can be accounted for different positions of the dopant. Sahu et al.[12] supposed that dopant-related emission is caused by the recombination of photo-excited electrons with Ag-bound holes; thus, silver is acting like a p-type dopant at higher concentrations. At a low doping level, silver just provides a positively charged centre, being an n-type dopant. The addition of one or two silver impurity atoms per NC improves the luminescence quantum yield from 14 to 27%.[12]

Here, we propose the *in situ* doping of CdSe NCs with silver during the colloidal synthesis as an alternative to cation exchange. An analogous technique was employed previously to dope CdSe NCs with copper.[8] Using $Cu_4I_4(PPh_3)_4$ as a complex precursor yielded doped NCs with a doping level up to 5%. Obtaining higher doping levels was deterred by formation of a copper selenide phase in this case. Higher doping levels (up to 15%) can be achieved with more sophisticated copper precursors.[14]

For the syntheses of NCs, we employed a modified oleate technique.[15,†]

† The source of cadmium was cadmium oleate prepared beforehand from cadmium acetate and oleic acid and dissolved in diphenyl ether. The selenium precursor was a 1 M solution of trioctylphosphine selenide (TOPSe) in trioctylphosphine (TOP) prepared by dissolving selenium powder in TOP. The typical synthetic procedure was as follows: cadmium precursor solution containing 0.5 mmol of Cd was put in a reactor flask with a calculated amount of $Ag_4Cl_4(PPh_3)_4$ (synthesized as described in ref. 16); upon adding two or three drops of TOP, the reaction mixture was heated to 200 °C under an argon flow with vigorous stirring. Immediately after reaching the desired temperature, 0.48 ml of a Se precursor were injected to induce supersaturation and QD formation. All syntheses proceeded for 5 min exactly at 200 °C; after that, the reaction mixture was cooled to room temperature. The presence of organic phosphines, which are capable of forming strong complexes with silver, is necessary for slowing the rate of reaction between Ag and Se precursors and thus decreasing the amount of undesirable bulk Ag_2Se formed. The post-synthetic treatment

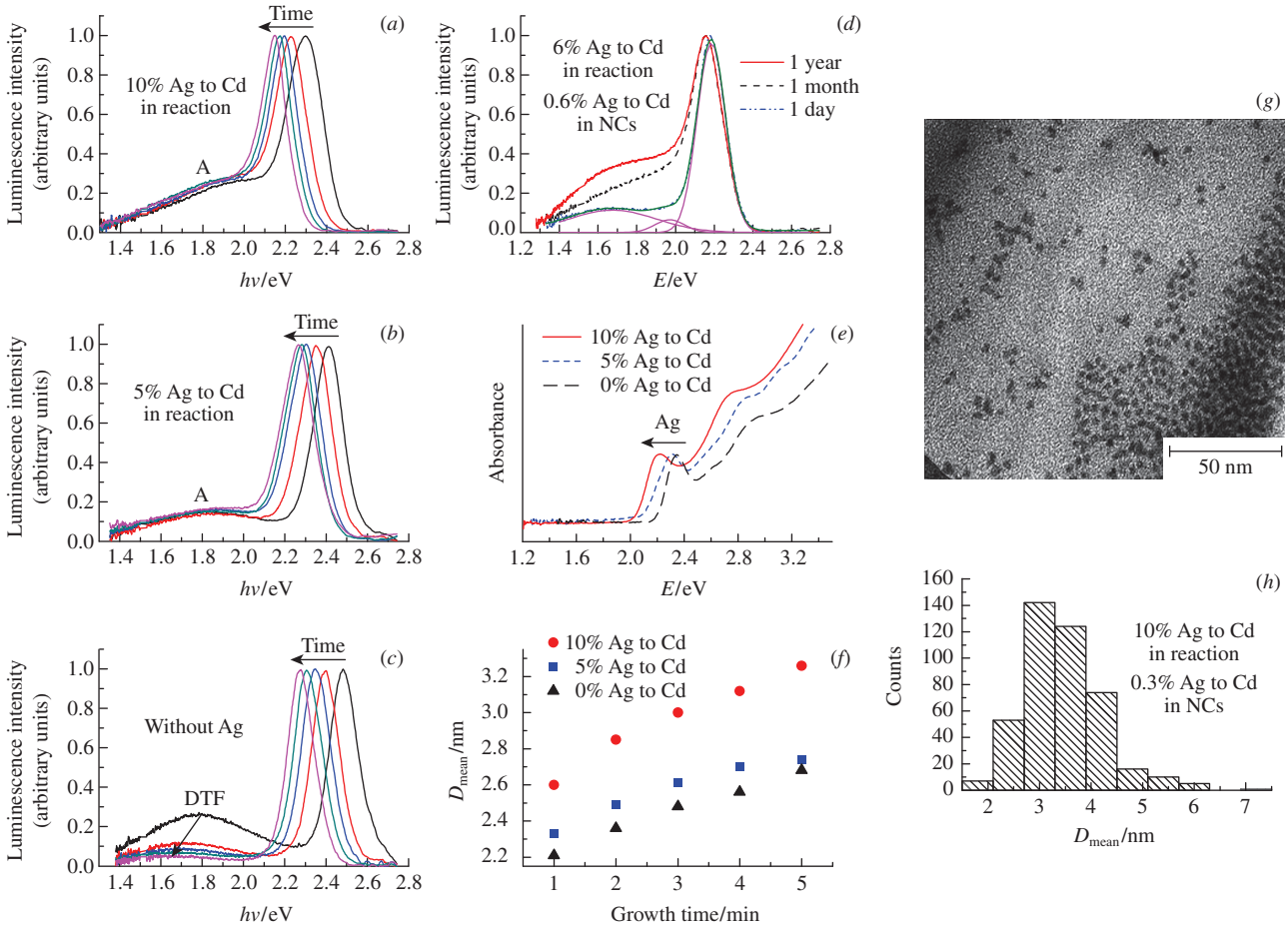

Figure 1 (*a*)–(*c*) Photoluminescence spectra of samples taken from the reaction mixture 1, 2, 3, 4 and 5 min after TOPSe injection. Excitation at 3.06 eV. (*d*) Changes in the photoluminescence spectrum of a silver-doped sample with time. (*e*) UV-VIS absorption spectra of synthesized NCs. (*f*) Dependence of mean NC size on the growth time for different Ag-to-Cd atomic ratios in synthesis. (*g*), (*h*) TEM image and size distribution of CdSe(Ag) NCs sample.

Unlike the case of copper doping, the usage of a similar complex Ag precursor $Ag_4Cl_4(PPh_3)_4$ allowed us to obtain CdSe(Ag) NCs with a doping level of only 0.6% (1.4 Ag atoms per NC). For this sample, the atomic ratio of Ag to Cd in reaction mixture was 6%. A further increase in $Ag_4Cl_4(PPh_3)_4$ quantity led to a lowered doping level; the atomic ratio of Ag to Cd of 10% yields NCs with a 0.3% doping level (1.4 Ag per NC due to an increased size). Excessive silver precipitated as Ag_2Se during the synthesis. An atomic ratio of 5% in synthesis resulted in a 0.5% doping level in NCs (0.9 Ag per NC). Upon studying CdSe(Ag) NCs with X-ray diffraction, we discovered that the only crystalline phase in samples is CdSe (Figure S2, Online Supplementary Materials). Note that Ag_2Se NCs do not exhibit luminescence in the optical region.[7]

Photoluminescence spectra of synthesized NCs [Figure 1(*a*),(*b*)] consist of a 'band-edge' maximum and a long-wavelength feature caused by the presence of Ag (A-band) close to the 'band-edge' peak. Addition of small quantities of an Ag impurity enhances the luminescence quantum yield (combined of 'band-edge' peak and A-band) from 8–10% for the undoped CdSe NCs to 20% for CdSe(Ag) with a doping level of 0.6%, which is in good agreement with other studies. Analysis of our results and published data[12] led us to the conclusion that the growth of quantum yield in this case can be accounted for binding of excessive surface selenium with silver, negating the selenium surface quenching, as the effect in question is most prominent in samples synthesized in the presence of excessive amounts of a Se precursor.

The UV-VIS absorption spectra of our samples [Figure 1(*e*)] are similar to the spectra of undoped CdSe QDs. The sample with 5% impurity atomic ratio in reaction exhibits a long-wavelength absorption tail originating from the high defectiveness of particles.

The evolution of mean size of NCs during a growth stage was calculated from first absorption maximum position[17] [Figure 1(*f*)]. Increasing amounts of silver precursor in synthesis accelerates the NC growth. TEM data [Figure 1(*g*)] show that NCs of the sample with 10% Ag-to-Cd in reaction are compact but not perfectly spherical. The size distribution [Figure 1(*h*)] has a maximum at 3 nm, which is in good agreement with the mean size calculated from absorption spectra.

The unique feature of our samples in comparison to previous studies is the independence of the A-band position of NC size. This terminates the possibility of it belonging to deep-trap fluorescence (DTF) characteristic of CdSe NCs. Luminescence spectra of CdSe NCs synthesized without an Ag precursor are shown in Figure 1(*c*) for comparison. One can observe a red

of samples consisted in iterative additions of acetone as an anti-solvent, resulting in the precipitation of QDs, and dispersing them in hexane. This was done to remove organic impurities and by-products. The samples were stored in glass vials, dispersed in hexane.

The doping level was determined *via* XRF with a Bruker M1 Mistral spectrometer (for details, see Online Supplementary Materials). The UV-VIS absorption was studied with a Varian Cary 50 spectrophotometer from 300 to 1000 nm. The fluorescence measurements were performed with a 405 nm laser and detected by an Ocean Optics 4000 USB spectrometer calibrated by a 2600 K W-lamp (450–1100 nm). The energy quantum yields were determined in diluted sols relative to rhodamine 6G solution of the same absorbance at 405 nm. Transmission electron microscopy (TEM) was performed on a LEO912 AB OMEGA microscope. Size distributions were obtained through manual calculations of QD images.

Table 1 Fit parameters for photoluminescence spectra of a selected sample (6% Ag/Cd ratio in synthesis) obtained during aging.

Peak		Time after synthesis								
		1 day			1 month			1 year		
		Relative area	Position/eV	Width	Relative area	Position/eV	Width	Relative area	Position/eV	Width
Peak 1	'band-edge'	1	2.19	0.15	1	2.17	0.16	1	2.17	0.16
Peak 2	A-band	0.07	1.97	0.15	0.22	1.97	0.20	0.26	1.97	0.20
Peak 3		0.36	1.68	0.45	0.72	1.75	0.45	1.01	1.71	0.45

shift of the DTF band maximum and a decrease in the relative intensity of the DTF band as the NCs grow. The A-band intensity of CdSe(Ag) NCs is independent of particle size. This excludes its connection to surface defects of NCs, as specific surface area is severely size-dependent. The A-band maximum is at 1.85 eV. It is not excited by irradiation at energies lower than 'band-edge' peak (we employed 1.88 and 1.92 eV lasers); therefore, no electrons are present on the lower of the levels of A-band transition until the particle is excited. This disproves the origination of A-band from larger NCs. We observed a high A-band intensity at room temperature, reaching 30% of the 'band-edge' peak (only 2% in ref. 12). As silver was introduced into NCs through the surface in all previous studies, it is logical to assume that the ratio of intrinsic Ag to surface Ag was higher in our case. Should A-band have the same origin as the long-wavelength feature from ref. 12, one can suppose that the A-band is caused by silver atoms in the bulk of NCs rather than surface atoms.

Obtained CdSe(Ag) NCs tend to age. After prolonged storage of sols of purified samples, we detected the growth of A-band intensity relative to 'band-edge' emission [Figure 1(*d*)]. Short-wavelength part of A-band grows in intensity faster than the long-wavelength part, which indicates a complex structure of the band. The luminescence spectra of CdSe(Ag) NCs can be well fit with a linear combination of three Gaussian functions (Table 1). Since ligand desorption mostly affects DTF, which is negligible in presented NCs, we assumed that the aging is resulted from inner and inter-particle redistribution of silver. A separate experiment on mixing Ag-doped and undoped NCs of different sizes has shown that, indeed, the inter-particle ligand-mediated Ag exchange is possible (Figure S3).

Thus, the addition of $Ag_4Cl_4(PPh_3)_4$ to oleate technique of CdSe NCs synthesis increases the size of the obtained particles. Unlike copper doping, doping with silver enhances the quantum yield of luminescence. While 'band-edge' peak persists in Ag doped NCs photoluminescence spectra, a broad long-wavelength feature appears with a maximum at 1.85 eV. Both the position and the relative intensity of this new band are independent of NC size. Prolonged storage of the sols of CdSe(Ag) NCs leads to their aging, perceived through spectrally irregular intensity growth of long-wavelength PL band.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2014.06.022.

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