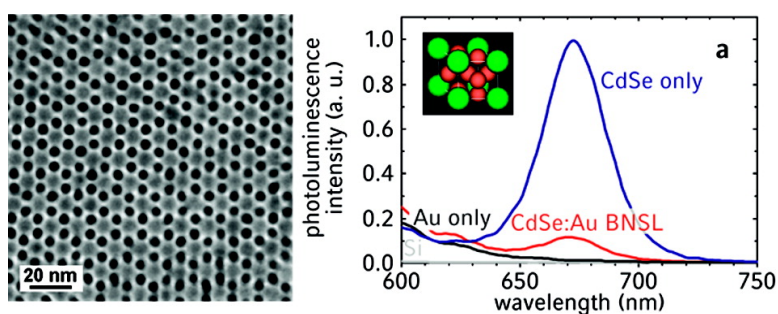


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Self-Assembled Binary Superlattices of CdSe and Au Nanocrystals and Their Fluorescence Properties

Elena V. Shevchenko,[†] Moritz Ringler,[‡] Alexander Schwemer,[‡] Dmitri V. Talapin,^{*,†} Thomas A. Klar,[‡] Andrey L. Rogach,^{*,‡} Jochen Feldmann,[‡] and A. Paul Alivisatos[†]

The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720 and Photonics and Optoelectronics Group, Physics Department and Center for Nanoscience (CeNS), Ludwig-Maximilians-Universität München, Amalienstr. 54, 80799 Munich, Germany

Received November 27, 2007; E-mail: andrey.rogach@physik.uni-muenchen.de; dvtalapin@uchicago.edu

Semiconductor and metal nanocrystals (NCs) and their assemblies have attracted significant interest from many branches of science and technology. Hybrid assemblies built of semiconductor and noble metal NCs are expected not only to combine the properties of the constituent building blocks but also to generate new, collective phenomena based on interparticle interactions at the nanoscale,¹ particularly the coupling of excitons in semiconductor NCs with plasmon resonances in their metal counterparts. Understanding of interaction mechanisms between optically active species like semiconductor NCs and neighboring metal nanoparticles can help establish conditions either for quenching of the fluorescence of semiconductor NCs through the creation of an additional nonradiative decay channel via resonant energy transfer to metal NCs² or for metal-enhanced fluorescence of chromophores³ similar to the SERS mechanism.⁴ Regular superstructures of nanoparticles with well-defined geometrical parameters offer the unique possibility to control coupling between excitons and plasmons in three-dimensional metamaterials.⁵ Studies of collective optical properties of hybrid materials comprising semiconductor and metal NCs are ideally conducted on samples with a high degree of ordering, where not only the size of the NCs but also the mutual arrangement of the NC building blocks and the spacing between them are controlled on a large scale. Glassy solids⁶ or layer-by-layered assembled structures⁷ of differently sized semiconductor NCs do not provide long-range order achievable in self-assembled NC superlattices.^{8,9} In particular, binary nanoparticle superlattices (BNSLs) of monodisperse semiconductor and noble metal NCs⁹ are appealing objects for studying the collective optical excitations. In this letter, we report for the first time on the preparation and the fluorescence spectroscopy study of long-range ordered BNSLs, self-assembled from CdSe NCs emitting in the visible spectral range and gold NCs with a nanoparticle plasmon resonance in the visible spectral range.

Monodisperse 8.7 nm CdSe NCs and 5.5 nm Au NCs were synthesized following the procedures reported in refs 10 and 11, respectively. For structural analysis, BNSLs of CdSe and Au were self-assembled (see ref 9 for details) from the toluene solutions on ultrathin carbon films supported by a copper grid (type A, Ted Pella, Inc.). TEM studies revealed that four different structural types of BNSLs (Figure 1a–d) could be obtained by varying relative concentrations of CdSe and Au NCs. A BNSL isostructural with the AuCu intermetallic compound has been formed using a particle number ratio of CdSe:Au of 1:0.7 (Figure 1 a,e). A BNSL isostructural with AlB₂ was obtained from a solution containing an excess of Au NCs (~1:5 CdSe/Au particle ratio) (Figure 1 b,f). The same particle ratio led to the formation of CaCu₅-type (Figure 1 c,g) and cub-AB₁₃-type (Figure 1 d,h) superlattices when small

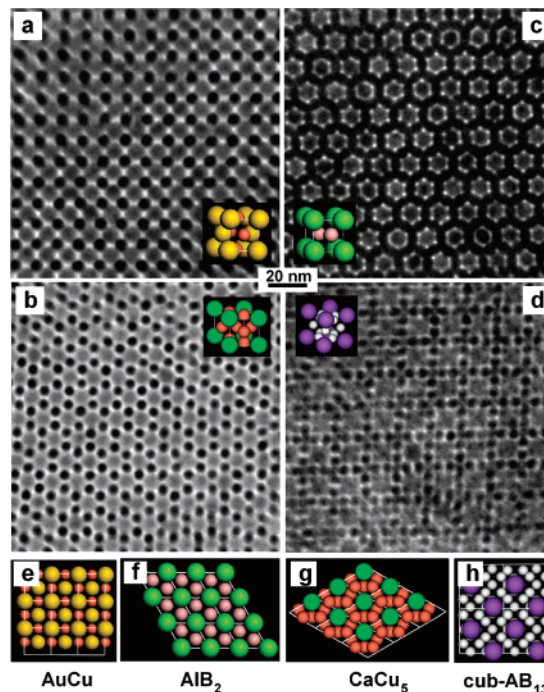


Figure 1. TEM images of (001) projections of BNSLs self-assembled from 8.7 nm CdSe and 5.5 nm Au NCs and isostructural with (a) AuCu, (b) AlB₂, (c) CaCu₅ intermetallic compounds and (d) cub-AB₁₃.²⁹ Insets in (a–d) depict the unit cells of subsequent structures. (e–h) Modeled (001) projections of AuCu, AlB₂, CaCu₅, and cub-AB₁₃ lattices, respectively.

amounts of dodecanethiol and trioctylphosphine oxide have been added to the colloidal solutions of NCs, respectively.

For optical studies, BNSLs were grown on hexamethyldisilazane-treated silicon substrates with a 250 nm thick SiO₂ layer by evaporating 5 μ L of a toluene solution of CdSe and Au NCs (~1:2.5 CdSe/Au particle ratio) at 45 $^{\circ}$ C under ambient conditions. Reference samples of Au-only and CdSe-only close-packed superlattices were grown in a similar manner on the same type of substrate. High-resolution scanning electron microscopy (HRSEM) studies of as-deposited structures revealed the excellent long-range ordering extending over micron-size domains (Figures 2 and S1). Both CaCu₅- and AlB₂-type superlattices can appear very similar in SEM if represented solely by their (001) planes. In order to assign the BNSL to a certain crystallographic space group we performed elemental analysis using EDX spectroscopy (Figure S2). We found that the CdSe/Au particle ratio in long-range ordered periodic structures was $1:2.2 \pm 0.18$, indicative of an AlB₂ structure.

Optical studies¹² have been performed on BNSLs of CdSe and Au NCs isostructural with AlB₂ and on the reference samples of

[†] The Molecular Foundry.

[‡] Ludwig-Maximilians-Universität München.

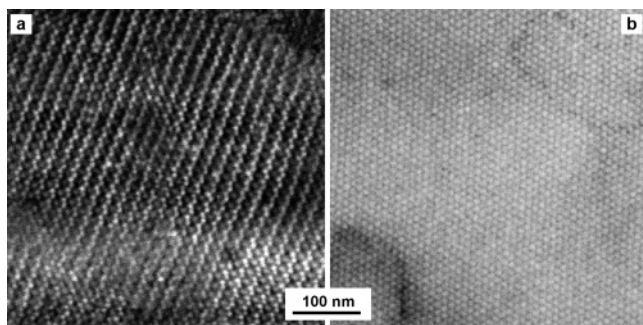


Figure 2. HRSEM images of fragments of (a) AlB₂-type binary superlattice consisting of 8.7 nm CdSe and 5.5 nm Au NCs and (b) CdSe-only superlattice of 8.7 nm CdSe nanoparticles.

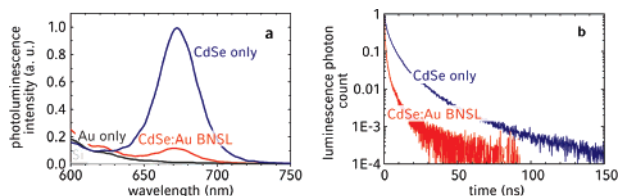


Figure 3. (a) Time-integrated fluorescence spectra and (b) time-resolved fluorescence transients of a close-packed CdSe NCs-only superlattice (blue curves) and of a BNSL of CdSe and Au NCs (red curves). Integrated fluorescence spectra of the Si substrate and of a superlattice of Au NCs are also shown in (a).

closely packed CdSe NCs-only and Au NCs-only superlattices. Dark field measurements on the BNSL of CdSe and Au NCs delivered a broad featureless scattering spectrum extending over the whole visible spectral range due to the strong coupling between the gold nanoparticle plasmons in the superlattice. Similar results have been obtained for the Au NCs-only superlattice. Time-integrated fluorescence spectra of the BNSL (Figure 3a) show that the fluorescence of CdSe NCs in the BNSL is only 5–15% of the fluorescence intensity of a CdSe NCs-only sample of an approximately comparable particle density, measured under the same excitation conditions.

Time-resolved emission transients of CdSe NCs show multiexponential recombination kinetics in both cases, the CdSe NCs-only and the BNSL samples (Figure 3b). Multiexponential fluorescence decays have been frequently observed for II–VI semiconductor NCs and are attributed to the distribution of nonradiative rates within the nanocrystal ensembles.¹³ The net emission lifetime, estimated as $\tau_{1/e} = 0.45$ ns, was considerably faster in the BNSL sample as compared to $\tau_{1/e} = 2.2$ ns in the CdSe-only superlattice (Figure 3b). Fluorescence quenching (Figure 3a) and a shortening of the fluorescence lifetime (Figure 3b) could be a result of the transfer of photoexcited charge carriers from the CdSe NCs to Au NCs. However, the distance between CdSe and Au NCs in the BNSL, which is determined by the length of the stabilizer molecules on CdSe¹⁰ and Au,¹¹ can be estimated as 1.5 nm. Charge tunneling should not play a major role at such distances.

There are four other interactions between CdSe NCs and Au NCs that can influence the fluorescence yield and the fluorescence lifetime of the CdSe NCs: First, the absorption cross section can be influenced because of field enhancement effects. Second, there is energy transfer from the CdSe NCs to the Au NCs, and third, the radiative rate of the CdSe NCs can be changed due to the

presence of the Au NCs.² Finally, the influence of Au NCs on the fluorescence intensity can be a trivial absorption of the exciting and emitted light by the Au NCs. The absorption cross section of the CdSe NCs should not be substantially changed by the Au NCs in BNSL samples, because we used the excitation wavelength of 405 nm and there were no plasmonic effects at this wavelength for Au NCs. The plasmon resonance of isolated Au NCs is located around 530 nm and further redshifts upon clustering of the Au NCs. We assume that a substantial part of the excitonic energy is transferred from the CdSe NCs to the Au NCs. This also leads to a shortened lifetime (Figure 3b) because energy transfer adds to the total nonradiative rate. The trivial absorption of exciting and emitted light by Au NCs would leave the fluorescence lifetime of CdSe NCs unchanged, which is not observed in our experiments. Therefore, the fluorescence of the CdSe NCs in the BNSL sample is actively influenced by the Au NCs due to energy transfer and, most probably, also due to a change of the radiative rate.

In conclusion, we employed self-assembly of monodisperse spherical NCs to create different types of BNSLs consisting of 8.7 nm CdSe and 5.5 nm Au NCs and conducted fluorescence spectroscopy studies of AlB₂-type BNSL of CdSe and Au NCs. We observed a considerably decreased fluorescence and a shortened fluorescence lifetime of the CdSe NCs in BNSLs compared to the CdSe NCs-only sample. The changed fluorescence lifetime clearly indicates that energy is transferred to surrounding Au NCs and that the Au NCs most probably also influence the radiative rate of the CdSe NCs.

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Supporting Information Available: Details of optical measurements on BNSLs. Figure S1, SEM images of AlB₂-type superlattices consisting of 8.7 nm CdSe and 5.5 nm Au NPs; Figure S2, EDX spectra of BNSL confirming their AB₂ stoichiometry.

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