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Fluorescence spectroscopy and transmission electron microscopy of the same isolated semiconductor nanocrystals

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We present a method to establish a correlation between the crystalline structure and the fluorescence properties of isolated semiconductor nanocrystals. By using ultrathin silicon nitride substrates with markers, we have localized and investigated the same particles in both a high-resolution transmission electron microscope (TEM) and a confocal optical microscope. We have found that the observation of strong fluorescence emission does not require single domain particles. Additionally, we have correlated the size and shape of a particle as determined by TEM and its spectral properties like emission wavelength and spectral diffusion. © *2002 American Institute of Physics.*
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The development of nanotechnology strongly depends on a detailed understanding of the physical properties of matter in the transition regime between molecular species and the solid state. Since small changes in the size and structural as well as morphological properties of nanoscopic objects can already lead to large changes in their electronic and optical properties, the investigation of nanoscale ensembles is often severely aggravated by sample inhomogeneities. This can very clearly be seen for semiconductor nanocrystals, which can be synthesized via a wet chemical approach in a size regime between 1–10 nm in diameter leading to a variation of the band gap by more than 1 eV.[1] Although, e.g., CdSe particles can be prepared with a size distribution of less than 5%, sample inhomogeneities due to slight differences in size, crystallographic orientation, and also in the chemical nature of the particle surface influence most physical measurements.

Therefore, several microscopic techniques have been employed to explore structural and electronic properties of individual particles. For the structural part, high-resolution transmission electron microscopy (HRTEM) has proven to be the most powerful tool to determine the size and shape as well as the crystal structure and orientation of nanocrystals.[2,3] Likewise, fluorescence microscopy of single particles has revealed many interesting optical properties which usually are hidden in the ensemble average.[4] For example, it could be shown that the fluorescence intensity of single particles is fluctuating which is attributed to a redistribution of charges in and around the particles.[5] However, the investigation of one and the same nanocrystal in both a transmission electron microscope (TEM) and also a fluorescence microscope has not been reported so far.

The CdSe nanocrystals (NCs) were prepared following standard methods and covered with nominally 3 monolayers of ZnS.[6] Absorption and fluorescence measurements of toluene solutions of the particles have indicated an average core diameter of 6.5 nm[7] and a fluorescence quantum yield of more than 50%. For a combined investigation of the same individual particles in both, a TEM and an optical microscope, the choice of the substrate is of major importance. First, the substrate needs to be suitable for both kinds of measurements, i.e., it has to be highly transparent for the electron beam and it should neither show any autofluorescence nor quench the fluorescence of the particles. Second, the substrate need to be labeled with markers to trace the same particles in the different microscope. For this purpose, we used ultrathin (20 nm) silicon nitride (Si_3N_4) membranes with Pd/Au electrodes as markers.[8] Si_3N_4 is transparent at the laser excitation wavelength hence showing a low fluorescence background and also gives a low contrast in the TEM micrographs. For sample preparation a small droplet (50 μl) of a colloidal solution of nanocrystals ($\sim 10^{-8}$–10^{-9} mol NCs/l) was carefully placed onto the Si_3N_4 membrane and allowed to evaporate leading to well separated matrix free NCs on the substrate. Although the absence of a matrix to embed the particles (typically a polymer film) was mandatory for the TEM measurements, it

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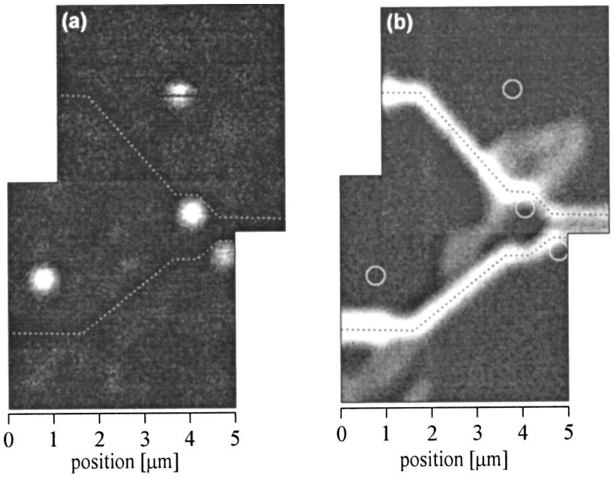

FIG. 1. Localization of CdSe/ZnS NCs in the optical microscope. The fluorescence image (a) shows fluorescence signals of four (single) emitters ($\lambda_{ex} = 488$ nm, $I = 58$ W/cm^2, 256×256 pixel^2,2 ms/pixel). The reflection image (b) shows the position of the marker electrodes.

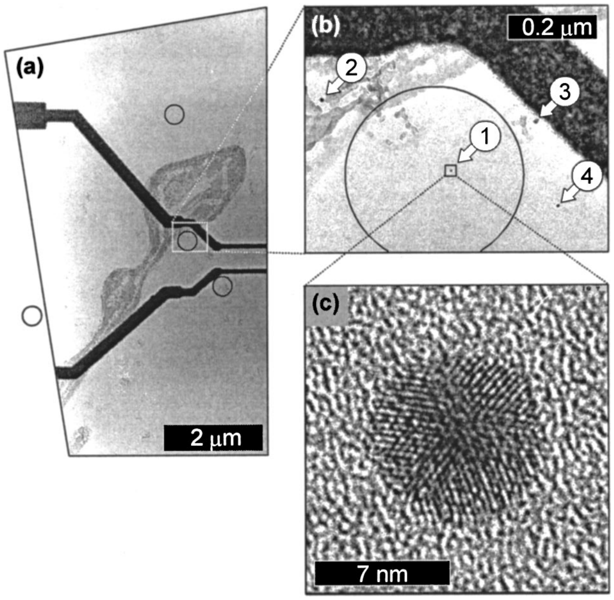

FIG. 2. Localization of single CdSe–ZnS NCs in the TEM. (a) Same sample area as in Fig. 1 (Phillips CM20,×6,6k, 120 kV). The circles denote the positions of fluorescing particles. (b) Maginified area of the substrate, where a luminescing NC is expected. (c) High resolution TEM of the particle marked in (a) (JEOL 4000 FX,×1350k, 400 kV).

caused a problem in the optical measurements due to increased irreversible photocorrosion of the particles. To mediate this problem, all optical measurements were conducted under a continuous argon flow at room temperature.[9]

The confocal optical microscope is based on an inverted microscope equipped with a piezoscanner as described in detail elsewhere.[9] For coarse approach, the sample is illuminated in a wide field mode where the markers on the substrate can clearly be seen and the piezoscanner including the sample is positioned with an x/y translation stage. To record a fluorescence image, the microscope was used in the confocal mode and the sample was raster scanned through the excitation focus with the piezoscanner. The fluorescence light was collected with the same microscope objective (Zeiss Epiplan, 100×,$NA = 0.9$), separated from back reflected excitation light by a glass longpass filter (OG 590) and guided to a photon counting module and a spectrograph equipped with a charge coupled device camera.

The sequence of the microscopic investigations turned out to be of crucial importance, because no fluorescence could be detected from particles, which had been investigated by TEM before. This effect might be caused by the detachment of the molecular ligands under electron bombardment in the TEM since it is well known that molecular ligands have a strong influence on the fluorescence quantum yield even though the particles are covered by ZnS.[10] Therefore, the optical investigations were always performed before the TEM measurements.

In the optical image in Fig. 1(a), four isolated fluorescing nanocrystals can be seen. The electrode pattern of the same sample area can clearly be seen in Fig. 1(b), where the longpass filter was replaced and the image is dominated by the backscattered excitation light. Since the same substrate areas are scanned in Figs. 1(a) and 1(b), both images can be overlaid to determine the position of the luminescing spots with respect to the electrodes. The size of the fluorescing spots is about 400 nm [full width at half maximum (FWHM)] but the position, i.e., the center of the spot can, in principle, be determined with a much higher accuracy.[11] However, due to a nonsystematic shift between the fluorescence and the reflection image, the position of the luminescing particles could only be determined with an accuracy of ±200 nm.

Figure 2(a) shows a low-resolution TEM micrograph of the same sample area as in Fig. 1 with the positions of the fluorescing spots marked by circles. The blur elongated feature is due to residues on the back side of the Si_3N_4 membrane related to the substrate fabrication. The TEM image in Fig. 2(b) shows an enlarged part of the sample where, according to the optical image [see Fig. 1 (a)], one of the fluorescing nanocrystals is expected. Actually, within the range of the position uncertainty of the fluorescence spot marked by the circle, a single dark spot is found, the HRTEM image [Fig. 2(c)] of which gives clear evidence for a nanocrystal. Outside the range of the circle drawn in Fig. 2(b), the arrows point to three further dark spots in the image. In this context, it is noted that a recent correlation of optical and force microscopy has shown that, in general, only a fraction of 30%–50% of the particles fluoresce at all[12] which might also be true for the particles investigated in this study. However, the TEM investigation has shown that, e.g., the features labeled 2 and 3 in Fig. 2(b) are not semiconductor nanocrystals but might rather be formed during the substrate preparation or marker deposition.

The HRTEM image of the luminescing semiconductor particle in Fig. 2(c) shows a pattern of lattice fringes which can not be explained by a single-crystal domain. A detailed analysis of the nature of the involved stacking faults can be performed by calculating TEM pictures of a given crystal structure[13] and is currently in progress.[14] Irrespective of this analysis the results clearly demonstrate that a fluorescence intensity sufficient for single-particle detection does obviously not require a single-domain structure for the nanocrystal. This finding has been corroborated by studies of further particles, where stacking faults or even polycrystallinity did not prevent efficient fluorescence emission.[14]

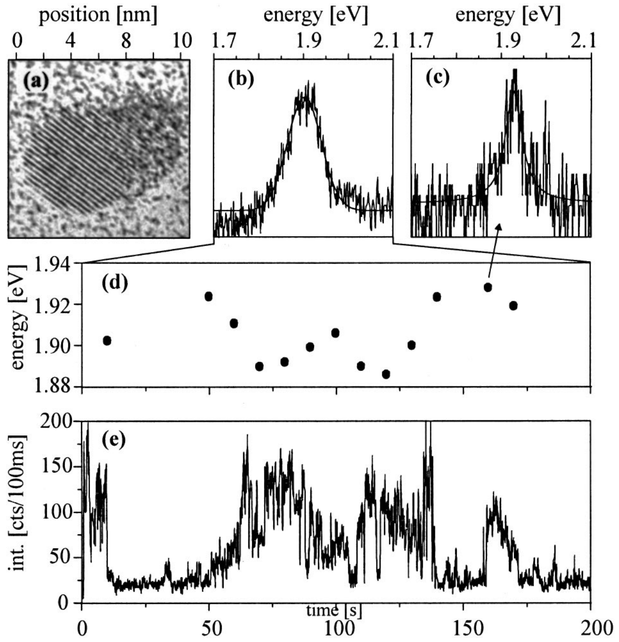

FIG. 3. Combined TEM and fluorescence investigations (a) HRTEM picture of a CdSe/ZnS core shell particle with coherent lattice fringes (Technai F30ST, ×900k, 300kV). The shadow on the upper right-hand side might be due to an imperfect ZnS shell. (b) and (c) Fluorescence spectra of the same particle as in (a) recorded for 200 and 10 s, respectively. (d) Spectral and (e) intensity fluctuations recorded simultaneously by guiding half of the fluorescence light to an avalanche photodiode and a spectrograph, respectively.

In Fig. 3, the TEM image of another nanocrystal is displayed together with the fluorescence spectra and the intensity transient of the same particle. This particle could be measured for more than 3 min while the fluorescence spectrum of the particle shown in Fig. 2(c) could not be recorded, probably due to rapid photocorrosion. The TEM micrograph in Fig. 3(a) reveals an almost spherical particle with a blurred shadow on the upper right-hand side part probably due to imperfectly grown ZnS. The spherical part shows 24 coherent lattice fringes in diagonal consistent with a diameter of of 8.9 nm since the lattice spacing of CdSe (100) layers is 0.37 nm. The average of 20 fluorescence spectra (10 s each) of this particle in Fig. 3(b) is centered at around 1.9 eV. An accurate correlation between the CdSe core size and the emission wavelength is difficult because the layer thickness of the ZnS shell is not precisely defined. However, based on theoretical considerations and experimental results,[7] the value of 1.9 eV should correspond to a CdSe core diameter of 7.5 nm. Accordingly, the thickness of the epitaxially grown ZnS shell around the particle should be close to two monolayers.

A fit to the average fluorescence spectrum yields an almost Gaussian line shape with FWHM = 90 meV [Fig. 3(b)] which is relatively broad for a single-quantum dot even at room temperature.[15] In contrast, for each of the 10 s spectra, we find an almost Lorentzian line shape. For the spectrum shown in Fig. 3(c), the linewidth amounts to 45 meV but it is changing from spectrum to spectrum. Even more pronounced are the fluctuations of the emission maximum (spectral diffusion) and intensity (blinking) plotted as a function of time in Figs. 3(d) and 3(e). In low-temperature experiments, spectral diffusion in semiconductor nanocrystals has been explained by a reorganization of local electric fields in or around the particles[16] while crystal defects have been discussed to be a reason for spectral diffusion in single self-assembled epitaxially grown dots.[17] Considering the TEM micrograph of the particle in Fig. 3(a), the blurred feature which was attributed to an imperfect growth of ZnS easily could constitute a defect structure in this particular nanocrystal and might cause the spectral and intensity fluctuations.

To get more supporting evidence of such a picture, it will be most important to study the spectral features of nanocrystals free from defects. In addition, further experiments of combined optical and TEM work will focus on the correlation of crystal structure and orientation of the emission dipole for the same individual nanocrystals.

[1] A. D. Yoffe, Adv. Phys. **50**, 1 (2001).
[2] J. J. Shiang, A. V. Kadavanich, R. K. Grubbs, and A. P. Alivisatos, J. Phys. Chem. **99**, 17417 (1995).
[3] X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich, and A. P. Alivisatos, Nature (London) **404**, 59 (2000).
[4] S. A. Empedocles, R. Neuhauser, K. Shimizu, and M. G. Bawendi, Adv. Mater. **11**, 1243 (1999).
[5] M. Nirmal, B. O. Dabbousi, M. G. Bawendi, J. J. Macklin, J. K. Trautman, T. D. Harris, and L. E. Brus, Nature (London) **383**, 802 (1996).
[6] B. O. Dabbousi, J. Rodriguez-Viejo, F. V. Mikulec, J. R. Heine, H. Mattoussi, R. Ober, K. F. Jensen, and M. G. Bawendi, J. Phys. Chem. B **101**, 9463 (1997).
[7] M. Kuno, J. K. Lee, B. O. Dabbousi, F. V. Mikulec, and M. G. Bawendi, J. Chem. Phys. **106**, 9869 (1996).
[8] G. Philipp, T. Weimann, P. Hinze, M. Burghard, and J. Weis, Microelectron. Eng. **46**, 157 (1999).
[9] F. Koberling, A. Mews, and T. Basché, Adv. Mater. **13**, 672 (2001).
[10] O. Schmelz, A. Mews, T. Basché, A. Hermann, and K. Müllen, Langmuir **17**, 2861 (2001).
[11] T. D. Lacoste, X. Michalet, F. Pinaud, D. S. Chemla, A. P. Alivisatos, and S. Weiss, Proc. Natl. Acad. Sci. U.S.A. **97**, 9461 (2000).
[12] Y. Ebstein, T. Mokari, and U. Banin, Appl. Phys. Lett. **80**, 4033 (2002).
[13] A. Mews, A. V. Kadavanich, U. Banin, and A. P. Alivisatos, Phys. Rev. B **53**, R13242 (1996).
[14] F. Koberling, U. Kolb, I. Potapova, G. Philipp, T. Basché, and A. Mews (unpublished).
[15] G. Schlegel, J. Bohnenberger, I. Potapova, and A. Mews, Phys. Rev. Lett. **88**, 137401 (2002).
[16] R. G. Neuhauser, K. T. Shimizu, W. K. Woo, S. A. Empedocles, and M. G. Bawendi, Phys. Rev. Lett. **85**, 3301 (2000).
[17] J. Seufert, M. Obert, R. Wigand, T. Kummell, G. Bacher, A. Forchel, K. Leonardi, and D. Hommel, Phys. Status Solidi B **224**, 201 (2001).