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Cathodoluminescence and photoluminescence of highly luminescent CdSe/ZnS quantum dot composites

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We report room-temperature cathodoluminescence and photoluminescence spectra originating from ZnS overcoated CdSe nanocrystals, 33 and 42 Å in diameter, embedded in a ZnS matrix. The thin-film quantum dot composites were synthesized by electrospray organometallic chemical vapor deposition. Cathodoluminescence and photoluminescence are dominated by the sharp band-edge emission characteristic of the initial nanocrystals. The emission wavelength can be tuned in a broad window (470–650 nm) by varying the size of the dots. The cathodoluminescence intensity depends on the crystallinity of the ZnS matrix and the voltage and current density applied. © 1997 American Institute of Physics. [S0003-6951(97)01016-4]

Semiconductor nanocrystals smaller than the exciton Bohr radius exhibit unique optical properties due to confinement of the electron excitations.¹ The optical absorption and emission can be tuned across the visible spectrum by changing the size of the nanocrystals, making these materials attractive for applications in optoelectronics and nonlinear optics. Macroscopic quantities of nearly monodisperse II–VI semiconductor nanocrystals organically capped with trioctylphosphines can be synthesized by solution techniques.² The quantum yield of CdSe quantum dots (QDs), as prepared, is ~10%–15% with the yield typically being limited by the existence of surface defects, which lead to nonradiative paths for the electron–hole pair recombination. Solution chemistry growth of a thin ZnS overlayer on the surface of the CdSe particles passivates the defects and raises the quantum yield to values between 40% and 50% for particles ranging in size from 20 to 60 Å in diameter.^{3,4}

ZnSe films containing CdSe QDs have been previously prepared by electrospray organometallic chemical vapor deposition (ES-OMCVD).⁵ In this method, the QDs are transferred from a liquid dispersion into the gas phase by electrospray,⁶ and the transferred particles are subsequently codeposited with a wide band-gap compound semiconductor matrix grown by OMCVD. Since the luminescence wavelength and properties are characteristic of the embedded quantum dots, the wavelength can be tuned from ~470 to ~650 nm. The incorporation of nearly monodisperse luminescent quantum dots into wide band-gap semiconductor matrices offers an alternative route for the fabrication of new optoelectronic device structures.⁷ The conductivity of the matrix can be controlled by *in situ* doping during the

OMCVD process. These structures may offer significant advantages over polymer-based light emitting devices, which require extensive synthetic procedures to change the emission wavelength, and have short lifetimes operating under ambient atmosphere. Other approaches for *in situ* fabrication of III–V QDs have been reported using selective area OMCVD, strain-induced self-organized growth of QDs, or molecular beam epitaxy.^{8–10} These techniques provide a convenient route for the synthesis of small-size nanocrystals. However, control of the nucleation process is difficult and the broad-size distributions result in inhomogeneous broadening of the optical transitions.

Cathodoluminescence (CL) and photoluminescence (PL) typically are used to explore the potential of these new composites as phosphor materials in light emitting devices or cathode ray tubes. In particular, CL provides information about the excitation and deexcitation mechanism involved during device operation, and about the optimum acceleration range and current densities under which these materials can be used. In this letter, we demonstrate cathodoluminescence from ZnS overcoated CdSe quantum dots of 33 and 42 Å diameter embedded in an inorganic matrix of ZnS grown by OMCVD. This study aims at taking advantage of the size-dependent properties of the quantum dots and the robust ZnS matrix to generate CL emissions at various wavelengths.

The ZnS overcoated CdSe quantum dots were prepared as described elsewhere.^{3–5} The quantum yield of the dots in hexane was around 45%. The trioctylphosphine (TOP)/trioctylphosphine oxide (TOPO) surface cap was exchanged by pyridine (lowering the quantum yield to ~10%–15%) and dispersed in anhydrous pyridine under nitrogen and mixed with acetonitrile (1:2) to achieve stable operation of the electrospray. The CdSe/ZnS quantum dots were incorporated by ES-OMCVD, carried out in a tubular up-flow

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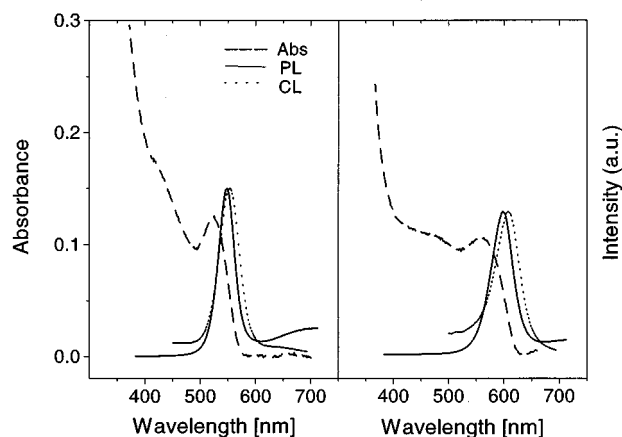


FIG. 1. Absorption (dashed lines), photoluminescence, and cathodoluminescence (dotted lines) spectra for thin-film quantum-dot composites containing 33 Å (a) and 42 Å (b) diameter ZnS overcoated CdSe nanocrystals. The PL is strongly redshifted from the absorption spectrum due to extensive agglomeration of the quantum dots inside the thin films, leading to energy transfer to the larger dots. Sample (b) has an optical density almost three times larger than (a) and a broader size distribution, which leads to the larger redshift. Cathodoluminescence spectra were recorded at 30 kV, 20 nA. PL excitation wavelength was at 480 nm.

OMCVD reactor equipped with an external resistive heater. The transferred QDs were combined with the matrix precursors, hydrogen sulfide (25 $\mu\text{mol}/\text{min}$), DEZn or DMZn (2.5 $\mu\text{mol}/\text{min}$), and the carrier gas H_2 in the mixing zone at the reactor inlet. The growth temperature range from 100 to 250 °C and the total pressure was maintained at 600 Torr. The composites were grown on glass substrates with film thicknesses ranging from 0.5 to 1 μm . A thin ($\sim 0.1 \mu\text{m}$) ZnS layer was grown before the thin-film composite, and the composite was covered by a similar ZnS film to ensure complete coverage of the quantum dots.

PL measurements were carried out at room temperature in a Spex Fluorolog-2 spectrometer with front-face collection. CL experiments were conducted at room temperature in a scanning electron microscope (SEM) equipped with an Oxford Mono-CL spectrometer. The electron-beam energy and current ranged between 1 and 40 kV and 1 and 160 nA, respectively.

Figure 1 shows room-temperature absorption, photoluminescence, and cathodoluminescence of thin-film composites containing CdSe/ZnS QDs of 33 (a) and 42 Å (b) diameter. Quantum confinement shifts the peak of the smaller crystallites to higher energies and shows that CL and PL near band-edge spectra originate from the same state of the nanocrystals and not from the polycrystalline ZnS matrix. The band-edge PL spectra have narrow bandwidths (30–40 nm) and are redshifted from the absorption maximum. The QDs incorporated inside the thin films show a redshift of the PL emission when compared to the same nanocrystals in solution. This is caused by aggregation of the nanocrystals inside the inorganic matrix during the ES-OMCVD process,⁵ and energy transfer to the larger particles in the agglomerate.¹¹ The PL quantum yield (QY) has been obtained by comparing the PL signal of the thin-film composites to rhodamine 640 in methanol. A background correction to subtract the contribution from the ZnS matrix in the absorption

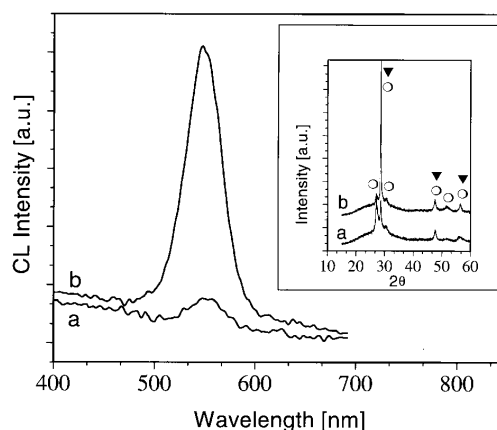


FIG. 2. Dependence of the CL intensity on the growth temperature, (a) 100 °C and (b) 250 °C, of the thin-film quantum-dot composites. CL was performed at 30 kV, 40 nA. (Inset) x-ray diffraction profiles, obtained with Cu K α radiation, of both samples showing the difference in crystallinity. The zinc blende and wurtzite diffractions of ZnS are labeled \blacktriangledown and \circ , respectively.

spectra has been done for each of the films. Quantum yields between 10% and 15% were measured, although the roughness of the films (2000–4000 Å) makes it difficult to obtain an accurate number due to the scattering of the light. These values agree with the PL quantum yield of the ZnS overcoated CdSe quantum dots dispersed in pyridine. The high PL QY values obtained mean that when illuminated with a low power UV lamp, the thin films glow at the wavelength characteristic of the quantum dots at ambient light. The room-temperature CL is nearly identical to the PL, with a small redshift (~ 6 nm) and wider linewidths (40–50 nm). A similar spectral shift has already been observed in the electroluminescence of quantum-dot/polymer composites,⁷ and in the luminescence of quantum dots under high electric fields,¹² which can be attributed to a quantum-confined Stark effect.

Figure 2 shows CL spectra from films grown at 100 and 250 °C and the corresponding x-ray diffraction patterns. The difference in CL emission shows that the crystallinity of the inorganic host matrix has a significant effect on the quality of the cathodoluminescence spectrum. ZnS thin films grown by ES-OMCVD at temperatures around 100 °C are poorly crystallized, showing broad x-ray diffraction features and the presence of a hexagonal phase. When the growth temperature is increased to 250 °C, the structure is predominantly zinc blende and the x-ray diffraction spectrum shows well-defined peaks. The amorphous contribution to the x-ray diffraction profile in spectra **a** and **b** of the inset of Fig. 2 originates mainly from the glass substrate due to the small thickness of the ZnS films (~ 0.5 –1 μm). We attempted to increase the CL intensity by improving the crystallinity of the ZnS thin-film composites grown at low temperatures by annealing the samples at ~ 300 °C. However, these temperatures are high enough to alloy the CdSe dots with the surrounding ZnS matrix, decreasing the photoluminescence quantum yield, but still too low to modify the crystallinity of the ZnS matrix.

Figure 3 shows the influence of the electron-beam energy and current flow on the CL of the thin-film composites.

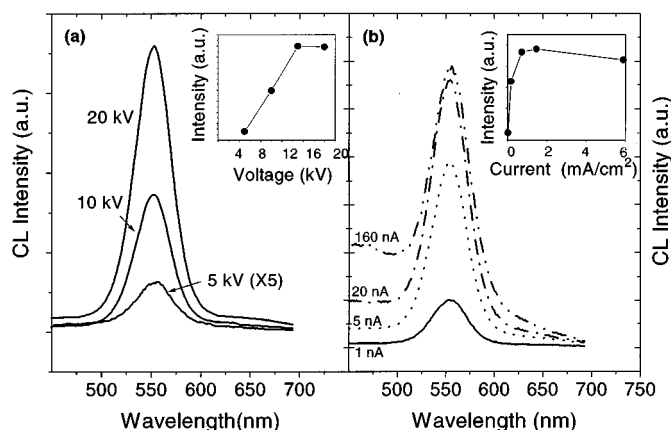


FIG. 3. Room-temperature cathodoluminescence spectra of a thin-film composite containing 33 Å ZnS overcoated CdSe nanocrystals at different applied voltages (a) and currents (b). (Inset) plot of the integrated intensities vs voltage (a) and current (b).

The increase in CL signal with both acceleration voltage and current density is related to the generation of secondary electrons inside the ZnS matrix. The formation of the electron/hole (e/h) pairs is not uniform,¹³ the majority of the excitons being generated near the surface within a relatively small radius. The saturation of CL with voltage could be explained in terms of the small thickness (0.5–1 μm) of the films. Increasing the voltage shifts the maximum efficiency of the e/h pair generation towards the substrate, leading to a saturation of the CL intensity. The saturation is not due to charging, since SEM images confirm that charging effects are absent for these samples, and similar results are obtained on thin-film composites deposited on Si(100) substrates. With increasing current density, light emission also saturates.

Electron-beam irradiation at high voltages or current densities produced a decrease of the CL intensity over time. This decay is faster in the poorly crystallized samples grown at 100 °C than in the ones grown at 250 °C. Glassy films formed by casting the quantum dots from solution on a Si wafer show faster decay times, proving the importance of the ZnS matrix in protecting the quantum dots. Annealing of an irradiated sample at 100 °C for 3 h produced a partial recovery of the CL signal. By analogy to the optical darkening effect of semiconductor-doped glasses when exposed to laser

irradiation,¹⁴ the decrease of the CL intensity over time may be attributed to electron ionization of the quantum dots, followed by trapping of the ejected electrons at deep traps inside the ZnS matrix.

We have reported the CL and PL of 33 and 42 Å diam ZnS overcoated CdSe nanocrystals embedded in polycrystalline ZnS matrices. The ZnS matrix provides surface passivation and significantly reduces the CL quenching of the quantum dots. CL and PL of the CdSe/ZnS thin-film composites originate from the same state in the nanocrystals. Therefore, the whole visible spectrum, from red through green to blue, can be realized by changing the size of the ZnS overcoated CdSe nanocrystals. The results obtained in the CL experiments show the potential of quantum dot composites in inorganic optoelectronic devices.

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