

Enhancement of the Photoluminescence of CdSe Nanocrystals Dispersed in CHCl_3 by Oxygen Passivation of Surface States

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ABSTRACT

An unusual enhancement of photoluminescence from CdSe nanocrystals (NCs) dispersed in air-saturated CHCl_3 was observed as a function of time. Within two weeks, for samples kept in the dark, the photoluminescence intensity increased by as much as a factor of 6, based on the peak height, with no change in peak position or width. This enhancement can be attributed to the reaction of nanocrystals with dissolved oxygen, which results in surface passivation. CdSe NCs kept in the growth solution (TOP/TOPO) showed no photoluminescence increase.

Semiconductor nanocrystals (NCs), or quantum dots, have been extensively studied because of their unique size dependent electronic, magnetic, optical, and electrochemical properties.^{1–4} Highly luminescent semiconductor NCs have gained increasing attention for use in light-emitting devices and tagging applications.^{5,6} For these applications, the efficiency and line width of the photoluminescence (PL) are important factors, and these PL properties are very sensitive to the nature of the particle surface. For example, CdSe NCs when passivated with a shell of a larger band gap semiconductor, such as ZnS, ZnSe, or CdS, show an improved PL quantum efficiency.^{6–9} Nevertheless, the effect of surface on the emissions is not fully understood.¹⁰

In a previous report, we described electrogenerated chemiluminescence (ECL) and electrochemical properties of CdSe NCs synthesized by the hot trioctylphosphineoxide (TOPO) method.¹¹ After PL and UV measurements, the CdSe NCs dispersed in CHCl_3 were kept in a dark condition for further experiments. Interestingly, these solutions showed a large enhancement of PL as a function of time. In this report, we describe these results and discuss the effect of oxygen on the enhancement.

CdSe NCs were synthesized and purified according to procedures described elsewhere.^{11,12} Briefly, monodisperse nanocrystals were synthesized at 330 °C using TOPO and trioctylphosphine (TOP) as capping agents and Cd-acetate

and Se powder as precursors. After purification by precipitation, centrifugation, and decantation, the vacuum-dried CdSe NCs were dissolved in CHCl_3 and kept in the dark until UV and PL measurements.

Ellis and co-workers have shown that the band edge PL intensity of *n*-CdSe single crystals can be altered through surface adduct formation.¹³ For example, adsorption of Lewis bases on the surface enhanced PL intensity, while Lewis acids produced a PL decrease. Buratto and co-workers demonstrated that PL from ordered monolayers of a film of CdSe quantum dots capped with hexadecylamine increased during irradiation in wet air or nitrogen atmospheres (but not in dry atmospheres) and ascribed the increase to adsorbed water molecules.¹⁰ We found similar results from CdSe NCs dispersed in CHCl_3 with some distinct differences.

CdSe NCs dissolved in CHCl_3 showed substantial improvement in PL as a function of time without any change in emission or absorption maximum. Figure 1 shows typical PL and absorption (inset) spectra of CdSe NCs dissolved in air-saturated CHCl_3 . As described before,¹¹ the sharp UV and PL spectra indicate a highly monodisperse sample, with a particle size of <3.2 nm, as estimated from the absorption maximum at 534 nm. Also shown are the emission spectra red shifted by ~10 nm, reflecting the size distribution of the sample.

Simply by leaving the particles in the CHCl_3 solution in the dark, the PL increased by a factor of more than 6 (based on peak height) after two weeks without any change in maximum wavelength or peak width. The PL increased

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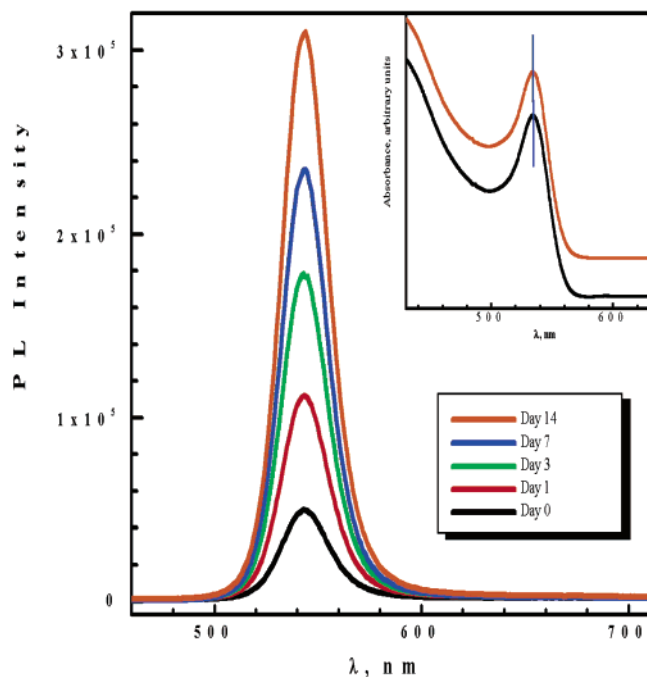


Figure 1. Temporal behavior of photoluminescence and UV spectra (inset) of CdSe nanocrystals dispersed in CHCl_3 . Excitation wavelength: 370 nm.

quickly in the initial stage followed by a gradual increase. During the first three days, the PL increased by almost 3 times, with the remaining enhancement occurring during the next 11 days. The size of the nanocrystals remained unaltered during the PL enhancement, as indicated by the same maximum wavelength. Moreover, the same full width at half-maximum (fwhm) of the PL spectra before and after PL enhancement indicates that size distribution of NC remained unaltered during this period.¹⁴

The PL from CdSe NCs dispersed in CHCl_3 remained enhanced upon complete drying and redispersion. When the CdSe NCs in CHCl_3 solution were vacuum-dried and redispersed in a fresh CHCl_3 , there was no change in the previously enhanced PL intensity. This implies that the PL enhancement is irreversible and can be attributed to effects on the particle rather than the bulk solution. Unlike NCs kept in CHCl_3 , CdSe NCs kept in the growth solution (containing TOPO, TOP, and few mL of CHCl_3) showed no significant changes in the UV and PL spectra. That is, the maximum wavelengths and PL intensities remained the same during the two-week time span. However, once purified and kept in CHCl_3 , CdSe NCs showed an increase in PL as described above.

Considering properties of solvents and experimental conditions, the influence of oxygen on the PL enhancement was first investigated. A photoeffect was not considered, since all of the solutions were kept in the dark except during the PL measurement. As described earlier by Alivisatos,^{15,16} oxygen reacts with CdSe NCs, with the possible formation of surface CdO and SeO_2 . To determine if this contributes to the PL enhancement, CHCl_3 solutions containing CdSe NCs were purged with oxygen for 1 h without any water trap. As shown in Figure 2A, the PL increased more than

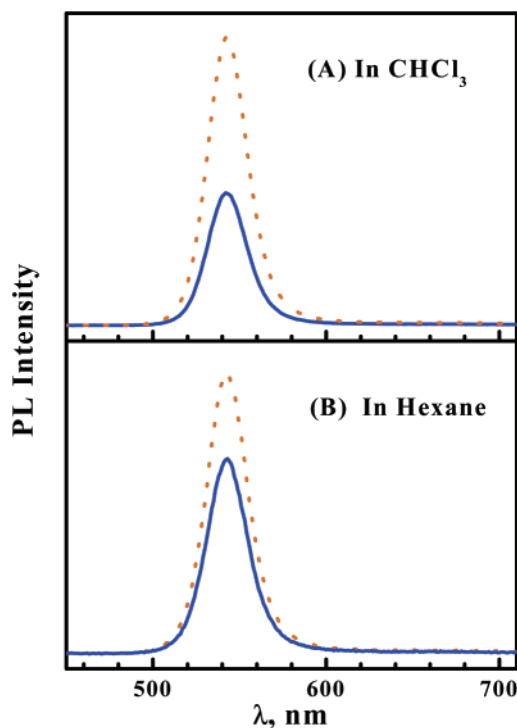


Figure 2. The room-temperature photoluminescence of CdSe nanocrystals dispersed in (A) CHCl_3 and (B) hexane before (—) and after (---) bubbling with oxygen in the dark for 1 h.

twice without any change in peak shape. One hour in air-saturated solution (without oxygen bubbling) showed a smaller PL enhancement (much less than the one in Figure 2A). Similar results were observed in the case of hexane, although the PL enhancement was relatively small (Figure 2B). In addition, the spectra in Figure 2 show no changes in fwhm, which indicates, again, no alteration of particle size distribution.

Although thermodynamic considerations suggest that adsorbed oxygen molecules react with CdSe to create surface oxides,^{15,16} it is difficult to identify the exact nature of the oxide. However, comparison of spectra indicates insignificant change of particle size. From the above data, it is suggested that irreversibly adsorbed oxygen molecules on the CdSe NC surface passivate surface states that are not blocked by the capping agent (TOPO), which results in PL enhancement. However, adsorbed oxygen molecules do not create a macroscopic oxide layer, which can result in smaller NCs and also a loss in PL efficiency. In addition, we carried out experiments monitoring the change in the PL intensity for CdSe NCs dispersed in CHCl_3 solutions containing TOPO at various concentrations, to see if TOPO in solution would prevent the luminescence increase by maintaining surface capping. However, in these solutions, held in the dark, the CdSe NCs did not appear to be stable; the absorbance showed a blue shift and the PL decreased.

Buratto and co-workers, on the basis of measurements of an irradiated CdSe NC film in various gases, suggested that water molecules adsorbed on the surface increased the PL from CdSe quantum dot monolayers.¹⁰ However, preliminary experiments on the effects of water on the PL intensity

revealed that addition of a small amount of distilled water to the CHCl_3 solution containing the CdSe NCs reduced PL intensity (in the absence of photoactivation). More detailed experiments are under investigation in this lab.

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