

Size-tunable infrared (1000–1600 nm) electroluminescence from PbS quantum-dot nanocrystals in a semiconducting polymer

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Nanocomposites consisting of PbS nanocrystals in a conjugated polymer matrix were fabricated. We report results of photo- and electroluminescence across the range of 1000 to 1600 nm with tunability obtained via the quantum-size effect. The intensity of electroluminescence reached values corresponding to an internal quantum efficiency up to 1.2%. We discuss the impact of using different-length capping ligands on the transfer of excitations from polymer matrix to nanocrystals.

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Polymer–quantum-dot nanocomposites have been investigated for visible spectral region luminescence and photovoltaic properties. If extended to the infrared, they could potentially enable planar-integrable active optical elements—sources, modulators, channel monitors, and switches—at telecommunications wavelengths from 1.3 to 1.6 μm . Related progress in this direction includes embedding InAs/ZnSe nanocrystals into a polymer matrix¹ and using erbium-based small-molecule organics to extend the success of rare-earth-doped glass into a semiconducting matrix for electroluminescence (EL).² In the present work we suggest using, for this purpose, another material: lead sulphide nanocrystals embedded into a polymer matrix.

Among the lead chalcogenides, PbS has a larger band gap than PbSe and PbTe and thus does not require ultrasmall nanocrystals to adjust the effective gap in the spectral region suitable for applications in telecommunications. PbS nanocrystals of suitable size for telecommunications-wavelength applications have been fabricated, as well as PbS nanocrystal–polymer composites.^{3–5} Nonlinear optical studies in these materials have yielded promising third-order ultrafast Kerr coefficients,^{3,6} photorefractive effects,⁴ and devices exploiting absorption saturation.⁷ All observed luminescence and gain^{8,9} from PbS quantum dots have to date been achieved using optical excitation of nanocrystals in a noninjecting glass matrix. Previously-reported nanocrystals in polymers¹⁰ and sol-gels¹¹ have exhibited a very high density of surface states, yielding no detectable luminescence at room temperature.

We present herein results on fabrication and investiga-

tion of EL nanocomposites containing PbS nanocrystals in conducting conjugated polymers.

Colloidal PbS nanocrystals were synthesized in a solution phase organometallic method.¹² Lead oxide (PbO) was dissolved in oleic acid ($\text{C}_{18}\text{H}_{34}\text{O}_2$) at 150 °C under Ar to which bis-trimethylsilylsulfide in trioctylphosphine was injected. The resulting PbS nanocrystals were stabilized with a capping layer of oleate ligands coordinated to the Pb atoms. The particle size was tunable by variations in reaction parameters and growth conditions. A post-synthetic ligand exchange was performed to replace the ligands with a shorter chain alkyl amine, thereby reducing the length of the insulating capping layer. The precipitated PbS nanocrystal powder was dissolved in a small amount of octylamine ($\text{C}_8\text{H}_{19}\text{N}$), the solution was heated at 50 °C for 24–48 h, and the octylamine-capped nanocrystals were isolated by precipitation with a polar solvent. The procedure was repeated to ensure uniform ligand exchange. After the second exchange, the final precipitate was dispersed into the desired organic solvent for polymer composite fabrication. The two different sets of samples will herein be referred to as C_{18} and C_8 , which are the number of carbon atoms in the chain, corresponding to the oleate- and the octylamine-capped nanocrystals, respectively.

Figure 1 presents a transmission electron microscope (TEM) image of nanocrystals with the C_{18} capping ligand dissolved in toluene. The average size of the nanocrystals is 5 nm, with polydispersity of 12%.

To isolate the possibility of optical absorption directly by the ligands independent of the nanocrystals, we measured separately the optical absorption of the pure ligand solution. The measurements were made using the Cary 500 UV-Vis-NIR spectrophotometer. The onset of absorption for C_{18} oc-

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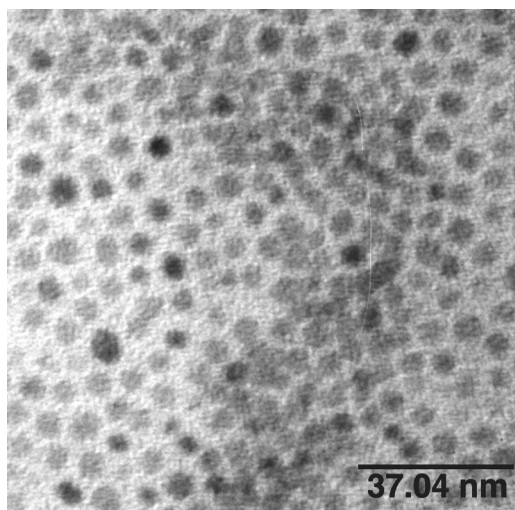


FIG. 1. TEM image of PbS nanocrystals with the C_{18} capping ligand.

curs at lower energy (~ 4 eV) than for C_8 (~ 5 eV). The C_{18} ligand offers a lower potential barrier to the capture of at least one, and possibly both types of carriers into the nanocrystals.

Polymer–nanocrystal composites were obtained by mixture a polymer precursor with a solution of nanocrystals in toluene followed by vacuum annealing at 80°C . Commercially available (American Dye Source Inc.) poly(2-methoxy-5-(ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) and poly(2-(6-cyano-6'-methylheptyloxy)-1,4-phenylene) (CN-PPP) were used as matrix materials. The structures for measurements comprise quartz or glass substrates covered by an indium-tin-oxide (ITO) layer used as the anode contact, nanocomposite layers 100–150 nm thick, and upper cathode contacts fabricated by vacuum evaporation of Mg protected from the ambient atmosphere with a thin capping Ag film.

The absorption spectra of the composites and of the capped nanocrystals in solution essentially coincide in the long-wavelength regime. In this range, the nanocrystals themselves are thus primarily responsible for absorption in the composite as well as in the solution. Figure 2 shows typical absorption spectra for the same nanocrystals in two different polymer matrices. They show similar behavior, with the absorption maximum around 1200 nm. This differs dra-

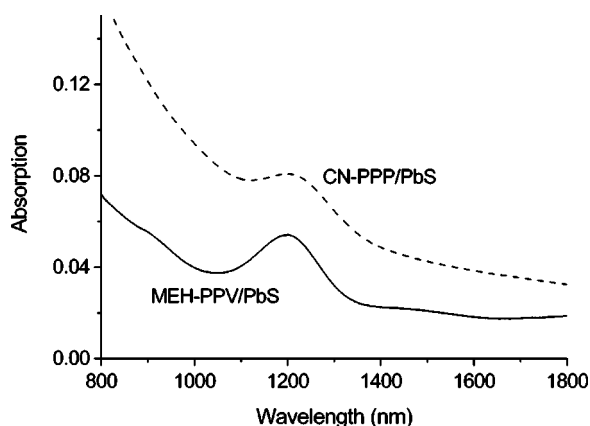


FIG. 2. Absorption spectra of the MEH-PPV/PbS and CN-PPP/PbS nanocomposites with the same nanocrystal size.

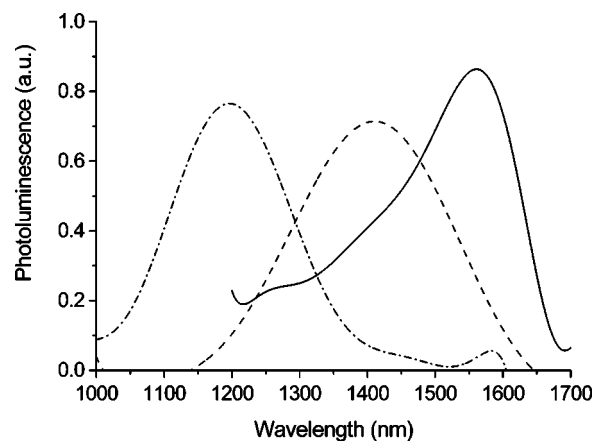


FIG. 3. PL spectra of PbS–polymer nanocomposites with three different nanocrystal diameters for the C_{18} ligand. Suppression of the long-wavelength ($\lambda \geq 1700$ nm) spectral wing is an artifact caused by the drop in photodetector sensitivity.

matically from the 3000-nm absorption edge of bulk PbS and confirms strong size quantization in nanocrystals¹³ in both solution and in the solid state.

Photoluminescence (PL) measurements employed excitation using the 488 line of an argon ion laser followed by a bandpass filter. The excitation energy was removed from the detected spectrum using long-pass filters following the monochromator. Spectra were acquired using a single grating monochromator TRIAX 320 coupled with a multichannel In-GaAs detector Hamamatsu G8163-512S. The shape of luminescence spectra associated with the nanocrystals did not vary with the polymer matrix. Figure 3 shows a series of PL spectra for nanocrystals of different size. No special size selection procedure was used to obtain monodispersed nanocrystals. The results of Fig. 3 are for the C_{18} family of capping ligands. We observed similar spectra and intensity of PL for the C_8 -capped nanocrystals.

Electrical measurements demonstrated asymmetric, strongly superlinear current–voltage characteristics similar to those of known polymer–nanocrystal composites emitting in the visible spectrum. EL was detected both by integrated and spectral means. The EL signal increased dramatically near 3 V. Figure 4 shows a close overlap between PL and EL spectra.

In contrast with PL, the intensity of EL depends dramatically on the type of capping. The results presented in Fig. 4

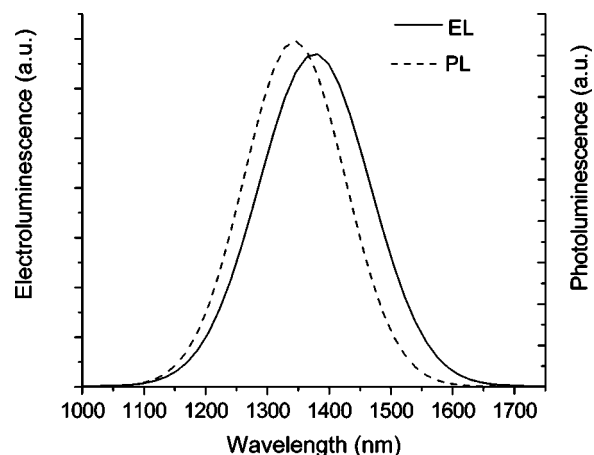


FIG. 4. PL and EL spectra of the MEH-PPV/PbS sample with the C_8 ligand.

are for C₈ samples; the C₁₈ samples demonstrated a much lower EL intensity in the wavelengths of interest. We attribute the distinction to the fact that excitations are generated inside the nanocrystals in PL, thus, internal efficiency is the main issue, and transport to or from the nanocrystal neither important nor desired. For EL, on the other hand, excitations generated entirely within the polymer matrix must be transferred to the nanocrystals, the rate of which is sensitive to the character of capping as well as the transfer mechanism. If excitation transfer is governed by the Förster mechanism, it is connected to the well-known $1/R^6$ dependence on the dipole–dipole distance,¹⁴ and for this reason will be dramatically suppressed for C₁₈ capping; the larger length of capping molecules will keep carriers at larger distances from a nanocrystal. The alternative hypothesis of a predominance of separate capture of electrons and holes requires tunnelling through the potential barrier formed by the capping molecules. This also decreases strongly (in this case exponentially) with the effective thickness of the capping layer.

We measured the quantum yield of EL of the light-emitting diode structures fabricated. Infrared integral radiation was measured using the Ophir Laserstar™ detector through the glass substrate. Without special measures for optimization, the internal efficiency^{15,16} is as high as 1.2%.

We have presented the results of infrared EL in nanocomposites of PbS in a conducting polymer. These results point to the possibility of using this composite system for creating light-emitting structures for optical communications photonic integrated circuits across the spectral region 1000–1600 nm.

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