Full-Color Emission and Temperature Dependence of the Luminescence in Poly-*P*-phenylene ethynylene–ZnS/Mn²⁺ Composite Particles

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The synthesis of a nanocomposite material composed of anionic poly(phenylene ethynylene) (aPPE) polymer particles and ZnS/Mn²⁺ nanoparticles is described, and its luminescence properties are investigated. aPPE particles have two emissions, one in the blue (460 nm) and the other in the green (490 nm), that are assigned to the 0-0 transition and an excimer, respectively. ZnS/Mn²⁺ nanoparticles have an emission at 596 nm that is due to the ${}^{4}T_{1}-{}^{6}A_{1}$ transition of Mn²⁺ and an emission at 706 nm that is ascribed to defect-related luminescence. The blue, green, yellow, and red emissions make the composite a potential material for full-color displays. More interestingly, the relative intensities of the different emissions may be varied by changing the excitation energy. Infrared spectra reveal that interactions exist between the two particles; however, photoluminescence excitation and emission spectra as well as observations of luminescence lifetimes indicate that there is negligible energy transfer from the polymer particles to the ZnS/Mn²⁺ nanoparticles. Temperature studies reveal that the ZnS/Mn²⁺ nanoparticles in the nanocomposite have a significantly reduced thermal quenching energy relative to that of bare ZnS/Mn²⁺ nanoparticles. In addition, between room temperature and 90 °C, the luminescence of the ZnS/Mn²⁺ nanoparticles at 596 nm increases in intensity with increasing temperature. This surprising phenomenon is attributed to thermoluminescence and thermal curing of the particle surface upon heating.

1. Introduction

Currently, nanostructured materials form a new branch of materials science that is under extensive investigation. For semiconductor nanoparticles, perhaps the most striking property is the massive change in optical properties as a function of size, which is most notably observed as a blue shift in the absorption spectrum with the decrease in the particle size.¹ As the particle size approaches the exciton Bohr radius, there are drastic changes in the electronic structure and physical properties such as a shift of the energy levels to higher energy, the development of discrete features in the spectra, and the concentration of the oscillator strength into just a few transitions.² These novel characteristics enable semiconductor nanoparticles to have a bright future in practical applications such as lasers, flat-panel displays, optical storage, single-electron transistors, and biological probes.³

Often during nanoparticle preparation, organic polymers are used to terminate growth.⁴ This allows for the fabrication of a new type of composite material—nanocomposites consisting of an organic polymer and inorganic nanoparticles. In these nanocomposites, the function of the organic polymer is not only to stabilize the nanoparticles, but the coupling of the organic and the inorganic components usually results in some novel properties with potential applications. Nanocomposite structures have been used to create optically functional materials. Incorporating semiconductor nanoparticles such as CdS into a polymer such as poly(N-vinylcarbazole) (PVK) may enhance the photoconductivity of the polymer resulting from charge generation, charge transfer, and charge separation at the interfaces between the polymer and the nanoparticles.⁵ Semiconductor-polymer nanocomposites may show larger nonlinear susceptibilities relative to those of bulk semiconductors and may exhibit a higher refractive index than the polymer alone.⁶ Therefore, these nanocomposites may find applications in optical amplification, optical storage, antireflection coatings, and optical lenses.⁶ Nanocomposites have been used for flat-panel displays by taking advantages of luminescence from both the semiconductor nanoparticles and the luminescent polymers.⁷⁻¹⁰ Recently, highly fluorescent polymer particles composed of anionic poly-(phenylene ethynylene) have been used to capture Cy-5-labeled oligonucleotides.¹¹ By using the subsequent fluorescence quenching of the complex, a detection sensitivity of over 2 orders of magnitude relative to that of direct Cy-5 excitation has been realized.¹¹ In addition to chemical sensors, aPPE particles may find applications in displays and lighting because they have a strong blue emission peaking at 460 nm.^{11,12} In this paper, we describe the formation and luminescence of a composite luminescent thin film composed of aPPE blue polymer particles and ZnS/Mn²⁺-doped nanoparticles with emission in the orange and attempt to develop these composite luminescent materials for applications in displays and temperature sensing.

2. Experimental Section

2.1. Preparation of Poly(*P*-**phenylene ethynylene**). Anionic poly(phenylene ethynylene) (aPPE) particles possessing pendant sulfonate groups were prepared by the copolymerization of

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SCHEME 1



SCHEME 2



sulfonated monomer (B) and glycol monomer (C) with pentiptycene monomer (D) (Scheme 1).

The synthesis of B, 1,4-(bis-3-sulfopropyloxy)-2,5-diiodobenzene, is described below (Scheme 2).

The syntheses of monomers C and D have been reported elsewhere.¹³ Reagents and solvents were purchased from Aldrich. ¹H NMR (400 MHz) spectra were obtained from Spectra Data Services (Champaign, IL).

1,4-(Bis-3-sulfopropyloxy)benzene, A. NaH (60% in oil; 9.9 g, 0.248 mole) was placed in a clean, oven dried, three-necked round-bottom flask that was then sealed and purged with argon. Anhydrous THF (50 mL) was added to disperse the NaH, and the oil was extracted from the resulting dispersion. Hydroquinone (13.36 g, 0.121 mole) was placed in a clean oven-dried flask and dissolved in 50 mL of anhydrous THF. The hydroquinone solution was added slowly to the NaH dispersion over 1 h, resulting in vigorous gas evolution and the formation of a white gelatinous precipitate. An additional 100 mL of anhydrous THF was added to form a free flowing, white slurry that was stirred for an additional hour. Propanesultone (22.4 mL, 0.255 mole) was added slowly via syringe, and the mixture was stirred for 1 h. The mixture was quenched cautiously with water until gas evolution ceased, and then the reaction volume was doubled by adding additional water. Initially, a white precipitate formed but dissolved on dilution and stirring. The mixture was acidified with concentrated HCl, yielding a clear, light-brown solution. The product was recovered by precipitation in 1.5 L of acetone and subsequent filtration. The crude product was recovered as a fine, off-white powder (37.4 g, 85% yield) and was used without further purification in the subsequent iodination. ¹H NMR (D₂O): δ 6.88 (s, 4H), 4.01 (t, 4H), 2.96 (appt. t, 4H), 2.06 (appt. p, 4H).

1,4-(Bis-3-sulfopropyloxy)-2,5-diiodobenzene, B. A 1-L, three-necked round-bottom flask with an affixed reflux condenser was charged with compound A (37.4 g, 0.106 mole), KIO₃ (9.0 g), and iodine (53.6 g). To this, 290 mL of acetic acid, 35 mL of deionized water, and 2 mL of concentrated sulfuric acid were added. The contents of the flask were heated with stirring to reflux for 6 h. After the mixture was allowed to cool to room temperature, residual iodine was consumed by the addition of 20% sodium hydrosulfite. A fine silt-like precipitate was collected by filtration and recrystallized twice from deionized water to yield large needle-like crystals (16 g, 20% yield). ¹H NMR (D₂O): δ 7.53 (s, 2H), 4.24 (t, 4H), 3.24 (t, 4H), 2.29 (appt. t, 4H). The lithium salt was prepared by heating B (1.0 g) and LiOH (0.075 g) in approximately 15 mL of deionized water until both dissolved. On cooling, fine white needle-like crystals formed and were collected by filtration and dried under vacuum.

aPPE Particles. A Schlenk reaction tube equipped with a magnetic stirbar was charged with monomers B (14.8 mg, 2.40 $\times 10^{-5}$ mole), C (15 mg, 2.40 $\times 10^{-5}$ mole), and D (22.9 mg, 4.79 $\times 10^{-5}$ mole). The reaction tube was transferred into an inert atmosphere glovebox where Pd(P(C₆H₅)₃)₄ (5.5 mg) and CuI (5.5 mg) were added and the tube was sealed. Argon sparged 2:3 (v/v) diisopropylamine/dimethylformamide (3 mL total) was added via cannula. The reaction mixture was heated to 65 °C with stirring for 20 h. At the end of the polymerization, the copolymer was recovered by precipitation in ~150 mL of acetone. The yellow-green, fluffy solid was collected by filtration and dried under vacuum. On drying, the solid turned black. The molecular weight was determined by GPC using 0.1 M LiBr in DMF as the eluent and monodispersed poly(methyl methacrylate) standards with $M_n = 17\ 000/M_w = 123\ 000$.

2.2. Preparation of ZnS/Mn²⁺ **Nanoparticles.** The ZnS/ Mn^{2+} nanoparticles were prepared as follows: The contents of a four-necked flask charged with 400 mL of deionized water and 2 g of poly(vinyl alcohol) (PVA) were stirred under N₂ for 2.5 h. An aqueous solution of 1.6 g of Na₂S and an aqueous solution of 5.8 g of Zn(NO₃)₂·6(H₂O) and 0.26 g of Mn(NO₃)₂ (Mn²⁺/Zn²⁺ molar ratio 5:95) were prepared and added to the first solution simultaneously via two different necks. After the addition, the resulting solution was stirred constantly under N₂ at 80 °C for 4 h, and a white colloid of ZnS/Mn²⁺ was formed. The pH value of the final solution was 4. This relatively low pH value is required to prevent the precipitation of unwanted Mn species.¹³ The nanoparticles were separated from the solution by centrifugation and dried in vacuum at room temperature.

2.3. Formation of aPPE Particles–**ZnS/Mn**²⁺ **Composite Particles.** A polymer particle solution was made by dissolving 0.05 g of aPPE particles in 5 mL of DMF and 10 mL of water. The particle size of the polymer prepared in this way is about 500 nm.¹¹ A semiconductor nanoparticle solution was made by dissolving 0.5 g of the PVA-stabilized ZnS/Mn²⁺ nanoparticle powder in 10 mL of water and 10 mL of ethanol. The two



Figure 1. HRTEM image of the aPPE–nanoparticle composite. The estimated size of the ZnS/Mn^{2+} nanoparticles is about 4.5 nm. The (111) lattice planes of the ZnS nanoparticles can be observed in some of the particles.

solutions (1:1) were mixed, stirred, and heated to 60 °C under nitrogen protection for 1 h. A thin film was made by dropping the solution on a glass substrate and drying at room temperature.

2.4. HRTEM, Infrared Spectra, and Luminescence of $aPPE-ZnS/Mn^{2+}$ Nanocomposites. The composite material was dissolved in a water solution by sonication and was placed onto holey-carbon-covered copper grids for high-resolution TEM (HRTEM) observations. The HRTEM images of the particles were obtained with a JEM-4000EX electron microscope (400 kV) with a structural resolution of 0.16 nm.

IR spectra of aPPE, ZnS/Mn²⁺, and aPPE–ZnS/Mn²⁺ composite particles were recorded on a Nicolet Magna FTIR spectrometer using a liquid-nitrogen-cooled detector. Solid samples were prepared as KBr pellets. The photoluminescence excitation and emission spectra at different temperatures were recorded on a SPEX fluorolog 3 fluorescence spectrophotometer. The fluorometer was equipped with a 450-W xenon arc lamp, double monochromators (SPEX 1680) for excitation and emission, and a cooled photomultiplier tube. The nanoparticle sample was mounted on the coldfinger of a liquid-helium flow-through cryostat using indium metal for thermal contact. The coldfinger was equipped with a heating element, and the temperature was controlled by a Lakeshore model 330 temperature controller that monitored the temperature with a calibrated silicon diode attached to the indium metal near the sample position.

A pulsed nanosecond optical parametric oscillator/amplifer (OPO) (Spectra-Physics MOPO-730) operating at a 10-Hz repetition rate was used to collect the photoluminescence (PL) lifetime data. The output of the OPO was frequency doubled in KDP to produce the PL excitation light. The excitation light was directed onto the particles, and emission was collected at right angles to the excitation and focused into a 1/8-m mono-chromator equipped with a standard photomultiplier tube. The photomultiplier tube output was directed into a digital oscilloscope to record the emission decays. The response time of the system was measured to be about 15 ns fwhm.

3. Results and Discussion

Figure 1 shows a HRTEM image of the aPPE-ZnS/Mn²⁺ particles prepared in dispersions. ZnS particles of 4.5-nm



Figure 2. HRTEM image of the aPPE-nanoparticle composite showing a dark, carbon-like material that is likely formed by the decomposition of PVA.



Figure 3. Absorption spectrum (--) and luminescence spectrum (-, excitation at 275 nm) of aPPE.

average size are easily observed. In each image, the (111) lattice planes of some ZnS/Mn²⁺ particles can be observed. The (111) lattice spacing of the particles was estimated to be around 0.31 nm from the HRTEM images. This is consistent with the (111) spacing of bulk ZnS (0.312 nm). In some areas, as shown in Figure 2, a carbon-like material can be observed. This material is likely produced by the dissociation of PVA during heating.¹⁴ Because of the large size (~500 nm) and likely low contrast of the polymer, aPPE particles are not observed in the HRTEM images.

Figure 3 shows the absorption and emission spectra of aPPE particles in DMF. The strongest peaks in the absorption spectrum around 430 nm and in the emission spectrum at 460 nm are attributed to 0-0 band absorption and emission, respectively.^{11,12} The green emission shoulder at 490 nm may be from an excimer formed within the polymer,^{11,12} and the emission band peaking at 370 nm is due to the solvent, DMF.

Figure 4 shows the photoluminescence excitation (PLE) and emission spectra of ZnS/Mn²⁺ nanoparticles. The emission at 590 nm is attributed to the ${}^{4}T_{1}-{}^{6}A_{1}$ transition of Mn²⁺.¹³ The absorption band in the excitation spectrum is due to the bandto-band transition of ZnS. Energy transfer from the ZnS exciton trapped at the Mn²⁺ site leads to efficient excitation of the Mn²⁺ center. In ZnS/Mn²⁺-doped nanoparticles, the Mn²⁺ ions may occupy either Zn²⁺ sites or surface sites. The presence of the Mn²⁺ emission at 590 nm following excitation into the absorption band of ZnS indicates that Mn²⁺ ions occupy Zn²⁺ sites.



Figure 4. Excitation (a) and emission (b) spectra of ZnS/Mn^{2+} nanoparticles. The peak at 330 nm in the excitation spectrum is due to the band-band transition of ZnS. The emission at 590 nm is attributed to the ${}^{4}T_{1}-{}^{6}A_{1}$ transition of Mn²⁺.



Figure 5. Infrared spectra of aPPE, ZnS/Mn²⁺, and aPPE–ZnS/Mn²⁺ nanocomposite particles.

Otherwise, the Mn²⁺ emission is observed at 350 nm if Mn²⁺ ions exist at the surface sites.¹⁵

Figure 5 shows the infrared spectra of aPPE, ZnS/Mn²⁺, and aPPE-ZnS/Mn²⁺ composite particles, respectively. ZnS is an IR window material that is transparent in this measurement range; therefore, the IR peaks from ZnS/Mn²⁺ arise from the stabilizer (PVA) incorporated into the nanoparticles. The fingerprint region ($600-1500 \text{ cm}^{-1}$) is quite different for the three samples. The spectrum of the aPPE $-ZnS/Mn^{2+}$ particles is not simply a superposition of the individual spectra of aPPE and the nanoparticles. This indicates that there are likely interactions between aPPE and ZnS/Mn²⁺ particles. The alkyl C-H stretch peaks of aPPE and PVA in the ZnS/Mn²⁺ nanoparticles at 2865 cm⁻¹ are shifted to 2850 cm⁻¹ in the composite material, which may be due to the coupling between the two kinds of particles. In addition, some new IR peaks appear in the nanocomposite particles. These new IR peaks might arise from the coupling or new chemical bonding between the polymer particles and the semiconductor nanoparticles. The strong, broad -OH peak from 3100 to 3600 cm⁻¹ in the ZnS/ Mn²⁺ sample is most likely due to residual water in the sample and the -OH group in PVA. Most likely, the coupling between the polymer particles and ZnS/Mn²⁺ nanoparticles is via chemical bonding through the stabilizer (PVA).

Figure 6 shows the excitation and emission spectra of aPPE– ZnS/Mn²⁺ composite particles. Four emission peaks are observed at 460, 490, 596, and 706 nm. As before, the two emission peaks at 460 and 490 nm are assigned to aPPE particles, and the emission at 596 nm is assigned to the ${}^{4}T_{1}$ –



Figure 6. aPPE–ZnS/Mn²⁺ nanocomposite excitation spectra monitoring the luminescence at 590 nm (590-nm PLE), 490 nm (490-nm PLE), and 460 nm (460-nm PLE). Also shown is the luminescence spectrum obtained following 370-nm excitation (370-nm PL).

 ${}^{6}A_{1}$ transition of Mn²⁺. When monitoring the emissions of aPPE particles at 460 or 490 nm, only the 420-nm peak is observed in the excitation spectra, indicating that the 420-nm excitation peak is from aPPE particles. When monitoring the emission of Mn^{2+} at 596 nm, two excitation peaks are observed at 330 and 420 nm. The 330-nm peak is due to the ZnS band-to-band transition. The 420-nm peak may be due to a variety of sources. First, energy transfer from the aPPE particles to Mn²⁺ would result in increased Mn²⁺ luminescence. Second, the aPPE emission is broad, and the tail extends well into the red region of the spectrum. Excitation at 420 nm causes increased aPPE luminescence in the red (as well as blue) region of the spectrum, leading to an observed peak in the excitation spectrum. Third, the peak in the excitation spectrum may be due to a d-d transition in Mn²⁺ because it is consistent with a known d-d transition in ZnS/Mn²⁺ particles. Two results indicate that there is little or no energy transfer from aPPE particles to Mn²⁺ in the ZnS/Mn²⁺ nanoparticles or that the energy transfer is a minor contribution to the Mn²⁺ luminescence in the nanocomposite. The first is that very little Mn²⁺ emission is observed following excitation at 420 nm whereas the emission of aPPE particles is the highest at this excitation wavelength. The second is that in the aPPE-ZnS/Mn²⁺ nanocomposite the luminescence quantum efficiency of Mn²⁺ is not influenced by the concentration of aPPE particles. Therefore, it is likely that the 420-nm peak in this excitation spectrum is due to either a d-d transition in Mn²⁺ and/or the red tail of the aPPE particle emission.

A new emission band is observed at 706 nm. This emission band has not been reported in ZnS/Mn²⁺ nanoparticles; however, an emission at 709 nm has been reported in undoped ZnS nanoparticles and has been assigned to impurities.¹⁶ In addition, in CdS/Mn²⁺ nanoparticles, an emission around 700 nm has been observed and attributed to a defect-related CdS emission.¹⁸ This emission is strongest at temperatures below room temperature; above room temperature, it is quenched rapidly. This behavior is similar to the luminescence of most defects in semiconductors.¹⁷ Accordingly, the emission at 706 nm in the aPPE–ZnS/Mn²⁺ composite is assigned to an impurity or a defect in the ZnS nanoparticles.

As displayed in Figure 7, the overall emission color of the nanocomposite changes for different excitation wavelengths because the relative emission intensities of Mn^{2+} and aPPE particles change. As shown in the inset of Figure 7, as the excitation wavelength varies from 280 to 420 nm, the orange (596-nm) emission intensity of Mn^{2+} decreases, and the blue (460-nm) and green (490-nm) emissions of aPPE particles



Figure 7. Photoluminescence spectra of the aPPE–ZnS/Mn²⁺ nanocomposite following excitation at different wavelengths. The inset displays the variation in luminescence intensity of the different emissions as a function of excitation wavelength.

increase. This change in intensity is related to the energy structure of ZnS/Mn²⁺ nanoparticles and aPPE particles in the composite. The conduction band of aPPE particles partially overlaps with the excited states of ZnS/Mn²⁺ nanoparticles, and the energy gap of ZnS/Mn²⁺ nanoparticles (around 330 nm) is larger than that of aPPE particles (around 420 nm). In this case, if the excitation energy is greater than the energy gap of ZnS/ Mn²⁺ nanoparticles, then the induced emission is mainly from Mn²⁺ particles and the emission of Mn²⁺ is stronger than that of aPPE particles in intensity. If the excitation energy is less than the energy gap of the ZnS/Mn²⁺ nanoparticles but greater than the energy gap of aPPE particles, then the induced emission is mainly from aPPE particles. In semiconductors, it has been demonstrated that the excitation rate is greater when the excitation energy is closer to the absorption edge.¹⁷ This may explain why the emission intensity of aPPE particles increases with increasing excitation wavelength from 280 to 420 nm. If the excitation energy is less than the energy gap of ZnS/Mn²⁺ nanoparticles, then the emission of Mn²⁺ may be due to the excitation of d-d transitions of Mn2+. Because the d-d absorption cross section of Mn2+ is smaller than the bandband transition of ZnS, the d-d excited luminescence is weaker in intensity than that from the band-band excitation. This phenomenon provides a possible mechanism for adjusting the emission color of the composite by varying the excitation wavelength, thus making these materials useful in applications involving emission displays.

Luminescence lifetime measurements (not shown) reveal that the majority of the luminescence from aPPE particles decays on a time scale faster than the instrument response (<15 ns), although there is a smaller amplitude component with a lifetime of ~200 μ s. Previous aPPE luminescence results have also shown subnanosecond lifetimes for both emissions.¹² The luminescence lifetime of Mn²⁺ emission in the ZnS/Mn²⁺ nanoparticles is likewise multiexponential, as has been observed previously, with the longest lifetime (~1.5 ms) consistent with nanoparticles of similar size.^{19,20} There is, therefore, no evidence of energy transfer in the luminescence decay data, consistent with the results from the excitation and emission spectra.

Figures 8-10 show the emission spectra, emission wavelength maxima, and the emission intensity at different temperatures. All of the emission bands shift to the red with decreasing temperature although the shift in the peak position is not very dramatic. All of the emissions decrease in intensity with



Figure 8. Luminescence spectra of the aPPE $-ZnS/Mn^{2+}$ nanocomposite at different temperatures ranging from 11 to 276 K.



Figure 9. Emission-energy maxima of the defect (\blacklozenge), Mn²⁺ (\blacksquare), 490-nm aPPE (\ast), and 460-nm aPPE (\blacktriangle) emissions at different temperatures below room temperature.



Figure 10. Emission intensity of the defect (\blacklozenge), Mn²⁺ (\blacksquare), 490-nm aPPE (\ast), and 460-nm aPPE (\blacktriangle) emissions at different temperatures below room temperature. The error is within 2%.

increasing temperature, with the decrease of the Mn^{2+} emission at 596 nm being much larger than the decrease of the emissions of aPPE particles.

As in bulk ZnS/Mn²⁺, the emission-energy shifts of Mn²⁺ in ZnS/Mn²⁺ nanoparticles with temperature can be described by crystal field theory.^{21,22} The red shift of the Mn²⁺ emission wavelength with decreasing temperature is due to the enhancement of the crystal field strength at lower temperatures resulting from crystal lattice contraction. As a consequence, the emitting

TABLE 1: Simulated Parameters for the Temperature Dependence of Emissions in ZnS/Mn²⁺-aPPE Particle Nanocomposites

wavelength (nm)	460	490	596	706
a	1.9 ± 0.8	27 ± 27	6 ± 1	29 ± 7
$E_{\rm b}~({\rm meV})$	27 ± 8	49 ± 16	27 ± 3	47 ± 4
I_0	$1.04 \pm 0.03 \times 10^{5}$	$4.9\pm0.3 imes10^4$	$1.43 \pm 0.03 \times 10^{5}$	$3.15 \pm 0.05 \times 10^4$

state, ${}^{4}T_{1}(G)$ of Mn^{2+} , shifts to lower energies with decreasing temperature, shifting the emission to longer wavelengths.

The temperature dependence of the Mn^{2+} emission intensity in ZnS/Mn²⁺ nanoparticles has been discussed,^{22–25} and the proposed mechanisms can reasonably explain the temperature behavior of Mn^{2+} emission observed here. On the basis of the theory of thermal quenching, the temperature dependence of the emission intensity, I(T), can be described by²⁶

$$I(T) = \frac{I_0}{1 + a e^{-E_b/kT}}$$
(1)

where E_b is the activation energy (thermal quenching energy), k is the Boltzmann constant, a is a constant related to the ratio of the nonradiative rate to the radiative rate, and I_0 is the emission intensity at 0 K. The solid lines in Figure 10 represent a simulation of the intensities using this theory. The parameters used to fit the four emissions are shown in Table 1. The excellent agreement between theory and experiment suggests that the intensity decrease of the emissions with increasing temperature is mainly due to thermal quenching.

The thermal quenching energy is related to the bound exciton binding energy.²³ For bulk ZnS/Mn²⁺, the exciton binding energy is about 60 meV.²⁴ This value is very close to the thermal quenching energy (57 meV), as estimated from the temperature dependence of Mn²⁺ luminescence in bulk ZnS/Mn²⁺.²⁴ Recently, however, a markedly lower value of 23 ± 5 meV has been reported for the thermal quenching energy of bulk ZnS/ Mn^{2+,27} For ZnS/Mn²⁺ nanoparticles with an average size of 3.5 nm, the thermal quenching energy reported for the ${}^{4}T_{1}$ - ${}^{6}A_{1}$ transition of Mn²⁺ is ~70 meV,²⁵ which is larger than the exciton binding energy in the bulk. This increase in exciton binding energy has been attributed to the increase in the overlap of the electron and hole wave functions as a result of quantum size confinement. The thermal quenching energy for the ${}^{4}T_{1}$ - $^{6}A_{1}$ transition of Mn^{2+} emission in the ZnS/Mn²⁺-aPPE nanocomposite film is approximately 27 meV, which is significantly less that the result from 3.5-nm ZnS/Mn²⁺ nanoparticles.²⁵ Most likely, this large difference is related to the interaction of Mn²⁺ with aPPE particles in the nanocomposite as well as the surface characteristics and defects in the nanoparticles. The exciton binding energy in nanoparticles is related not only to the particle size but also to their surface characteristics.²⁸ The differences in surface coating and structure may cause differences in the lattice strain and therefore differences in the binding energy of up to 0.1 eV.²⁸ In addition, the temperature dependence of the emission in a material such as PbWO₄ has been attributed to traps or defects in the material.²⁹ Photoinduced carriers (electrons or holes) may be trapped at these defects or traps, and at certain temperatures, the trapped carriers may be released to the conduction band, resulting in luminescence.³⁰ Because of the smaller surface/ volume ratio, 4.5-nm particles are expected to have fewer surface traps relative to 3.5-nm particles.²¹ The aPPE polymer may affect the nature and number of defect or surface states in the nanocomposite; consequently, these factors will affect the temperature dependence of the luminescence and the thermal quenching energy (exciton binding energy).



Figure 11. Intensity—temperature dependence of the aPPE emission at 460 nm and the Mn^{2+} emission from room temperature to 60 °C. The 460-nm emission decreases in intensity upon heating (**I**); however, the intensity does not recover upon subsequent cooling (**I**). The Mn^{2+} emission increases upon heating (**A**) but only partially recovers upon subsequent cooling (**V**). The error is within 2%.



Figure 12. Intensity-temperature dependence of the aPPE emission at 460 nm and the Mn^{2+} emission from room temperature to 140 °C following one cycle of heating and cooling described in Figure 11. Above 60 °C, the emission of aPPE upon heating (\blacklozenge) decreases steadily and is completely quenched at 140 °C. The luminescence intensity does not recover following subsequent cooling (×). The Mn^{2+} emission intensity also decreases from 60 to 140 °C (+), upon which it is completely quenched. The intensity also does not recover upon cooling (*). The error is within 2%.

Figures 11 and 12 show the luminescence intensity temperature dependence of the emission at 460 and 596 nm at temperatures above room temperature for the nanocomposite material. Figure 11 shows the dependence from room temperature to 60 °C. It is surprising to observe that the emission of Mn^{2+} at 596 nm (Figure 11, \blacktriangle) increases while the emission of aPPE particles at 460 nm (Figure 11, \blacksquare) decreases with increasing temperature. Upon subsequent cooling, the emission intensity at 596 nm (Figure 11, \blacktriangledown) decreases, although the intensity does not recover to its original value. Similarly, the intensity of the aPPE emission at 460 nm (Figure 11, \bigcirc) does not recover to its initial value upon cooling. Figure 12 shows the intensity dependence up to 140 °C following one cycle of heating and cooling described above. The blue emission of aPPE particles decreases gradually with increasing temperature (Figure 12, \blacklozenge). However, the luminescence of Mn²⁺ at 596 nm increases with increasing temperature up to 90 °C (Figure 12, +). When the temperature is higher than 90 °C, the luminescence is quenched rapidly. At 140 °C, both the emissions of aPPE particles and the Mn²⁺ emission are quenched completely. In either species, the luminescence does not recover following subsequent cooling (Figure 12, ×, *).

Theoretically, luminescence will decrease in intensity with increasing temperature because of thermal quenching²⁶ and the increase in the nonradiative rate as a result of a stronger electron—phonon interaction.^{31,32} Three possible reasons may cause the increase in luminescence intensity with increasing temperature observed here: energy transfer, thermal luminescence, and thermal curing of the nanoparticle surface. We have demonstrated that there is negligible energy transfer from aPPE particles to Mn²⁺. Most likely, the luminescence enhancement of Mn²⁺ with increasing temperature up to 90 °C is due to thermoluminescence and surface curing. Upon heating, carriers at some traps are released to the conduction band and contribute to the luminescence; as a result, the luminescence increases with increasing temperature. As the trapped sites are emptied, the luminescence enhancement decreases in intensity.

In addition, ultraviolet curing has been observed to increase the luminescence of ZnS/Mn²⁺ nanoparticles.³³ This is due to polymerization and surface passivation that occurs along with the polymerization. Similarly, heating can induce polymerization and surface passivation, resulting in luminescence enhancement. Therefore, it is reasonable to assign the luminescence enhancement of Mn²⁺ in the nanocomposite to thermoluminescence and surface curing with increasing temperature up to 90 °C.

The luminescence quenching of both emissions at increased temperature may be due to phonon quenching and/or chemical dissociation or oxidation of the compounds in the composite. Phonon quenching has already been discussed, and the same arguments apply above room temperature. If phonon quenching were solely responsible, then the luminescence intensity would be expected to return to its original value upon cooling from elevated temperatures. However, this is not the case with either the aPPE or Mn²⁺ luminescence. Therefore, it is likely that the luminescence quenching is mainly due to chemical dissociation or oxidation of the compounds in the composite. It is more likely that some decomposition occurs within the aPPE particles, decomposing the polymer into species that serve as efficient energy quenchers. From our measurements, as the polymer begins to decompose, there is quenching of the aPPE luminescence. There may also be some quenching of the Mn²⁺ luminescence, but this may be masked by the increase due to the thermal curing and thermoluminescence. At temperatures above 90 °C, the Mn²⁺ luminescence is quenched rapidly. Thus, the ZnS/Mn^{2+} nanoparticles may be more stable with respect to thermal decomposition, but the byproducts of aPPE decomposition have a significant quenching effect on the Mn²⁺ luminescence as well. Once full quenching has been achieved, the process is not reversible for either species. Thus, although this nanocomposite is not well suited for elevated temperature applications, the change in the relative intensities of the polymer particles and the semiconductor particles with temperature makes this nanocomposite a potential temperature indicator below room temperature. The measurement of the peak ratio could be much easier and more reliable than a single peak-intensity measurement in practical applications. Variations of the optical path, such as the bend of an optical fiber or skin penetration, could change the detected fluorescence intensity easily, but the ratio of the two peak intensities is much less dependent on such factors.³⁴ This potential application is particularly interesting and suitable for temperature measurement in laser cooling systems where temperature detection is still an unsolved problem.³⁵ In addition, the nanocomposite exhibits properties that may make it practical for use in full-color displays.

4. Summary

A composite material composed of aPPE polymer particles and ZnS/Mn²⁺ nanoparticles is described, and its luminescence properties are investigated. The composite has blue (460-nm), green (490-nm), orange (596-nm), and red (706-nm) emissions, and the relative intensities of the three emissions change with the excitation energy. Observations of luminescence lifetimes as well as excitation and emission spectra indicate that there is little or no energy transfer from the blue polymer particles to ZnS/Mn²⁺ particles. However, infrared investigation reveals that there are interactions or coupling between the two particles. Temperature studies suggest that the ZnS/Mn²⁺ nanoparticles are more stable than the aPPE polymer particles with respect to decomposition and that the thermal quenching energy of ZnS/ Mn²⁺ nanoparticles within the composite is smaller than that for naked nanoparticles. From room temperature to 90 °C, the luminescence of ZnS/Mn²⁺ nanoparticles at 596 nm increases in intensity with increasing temperature. This interesting result is attributed to thermoluminescence and thermal curing of the particle surface upon heating. At temperatures higher than 90 °C, the luminescence is quenched, and the emissions from both the polymer particles and the nanoparticles are quenched completely at 140 °C.

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References and Notes

(1) Wang, Y. In *Advances in Photochemistry*; Neckers, D. C., Volman, D. H., von Bunau, G., Eds.; Wiley and Sons: New York, 1995; Vol. 19, p 179.

(3) Handbook of Nanostructured Materials and Nanotechnology: Optical Properties; Halwa, H. S., Ed.; Academic Press: San Diego, CA, 2000; Vol. 4.

(4) Wang, J.; Montville, D.; Gonsalves, K. E. J. Appl. Polym. Sci. 1999, 72, 1851.

(5) Cheng, J.; Wang, S.; Li, X.-Y.; Yan, Y.; Yang, S.; Yang, C. L.; Wang, J. N.; Ge, W. K. *Chem. Phys. Lett.* **2001**, *333*, 375.

(6) Caseri, W. Macromol. Rapid Commun. 2000, 21, 705.

⁽²⁾ Ekimov, A. I.; Efros, AL. L.; Onuschenko, A. A. Solid State Commun. 1985, 56, 921.

(7) Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P. Nature 1994, 370, 354.

- (8) Chen, W.; Grouquist, D.; Roark, J. J. Nanosci. Nanotechnol. 2002, 1, 47–53.
- (9) Schlamp, M. C.; Peng, X.; Alivisatos, A. P. J. Appl. Phys. 1997, 82, 5837.
- (10) Yang, X.; Xu, X. Appl. Phys. Lett. 2000, 77, 797.
- (11) Moon, J. H.; Deans, R.; Kruegger, E.; Hancock, L. Chem. Commun.
 2003, 1, 104.
 (12) Yang, J. S.; Swager, T. M. J. Am. Chem. Soc. 1998, 120, 11864.
- (12) Tang, S. S., Swager, T. M. S. Im. Chem. Boc. 1996, 126, 11664. Swager, T. Acc. Chem. Res. 1998, 31, 201.
- (13) Chen, W.; Sammynaiken, R.; Huang, Y. J. Appl. Phys. 2000, 88, 5188.
- (14) Oku, T.; Niihara, K.; Suganuma, K. J. Mater. Chem. 1998, 8, 1323.
 (15) Sooklal, K.; Cullum, B. S.; Angel, S. M.; Murphy, C. J. J. Phys. Chem. 1996, 100, 4551.
- (16) Denzler, D.; Olschewski, M.; Sattler, K. J. Appl. Phys. 1998, 84, 2841.
- (17) Moss, T. S. *Optical Properties of Semiconductors*; Butterworth Scientific Publications: London, 1959.
- (18) Bol, A. A.; Beek, R. V.; Ferwerda, J.; Meijerink, A. J. Phys. Chem. Solids 2003, 64, 247.
- (19) Smith, B. A.; Zhang, J. Z.; Joly, A.; Liu, J. Phys. Rev. B 2000, 62, 2021.
- (20) Chen, W.; Joly, A. G.; Zhang, J. Z. Phys. Rev. B. 2001, 64, 41202-(R).
- (21) Chen, W.; Sammynaiken, R.; Huang, Y.; Malm, J.-O.; Wallenberg, R.; Bovin, J.-O.; Zwiller, V.; Kotov, N. A. J. Appl. Phys. **2001**, *89*, 1120.

- (22) Joly, A. G.; Chen, W.; Roark, J.; Zhang, J. Z. J. Nanosci. Nanotechnol. 2001, 1, 295.
- (23) Yu, J. Q.; Liu, H. M.; Wang, Y. Y.; Fernandez, F. E.; Jia, W. Y. J. Lumin. **1998**, 76, 77, 252.
 - (24) Tanaka, M.; Masumoto, Y. Chem. Phys. Lett. 2000, 324, 249.
- (25) Chen, W.; Su, F.; Li, G. H.; Joly, A. G.; Malm, J.-O.; Bovin, J.-O. *J. Appl. Phys.* **2002**, *92*, 1950.
- (26) Jaszcyn-kopec, P.; Pinceaux, J. P.; Zigone, M.; Kenedy, J. M.; Stadtmuller, A. *Solid State Commun.* **1979**, *32*, 473. Seitz, F. *Trans. Faraday Soc.* **1939**, *35*, 79.
- (27) Su, F. H.; Ma, B. S.; Fan, Z. L.; Ding, K.; Li, G. H.; Chen, W. J. Phys.: Condens. Matter 2002, 14, 12657.
- (28) Tsunekawa, S.; Kang, J.; Asami, K.; Kawazoe, Y.; Kasuya, A. Appl. Surf. Sci. 2002, 201, 69.
- (29) Liu, B.; Shi, C.; Wei, Y.; Liao, J. Chem. Phys. Lett. 2002, 362, 296.
- (30) Chen, W.; Wang, Z. G.; Lin, Z. J.; Lin, L. Y. Appl. Phys. Lett. 1997, 70, 1465.
- (31) Dexter, D. L.; Klick, C. C.; Russell, G. A. Phys. Rev. 1955, 100, 603.
- (32) Bartram, R. H.; Stoneham, A. M. Solid State Commun. 1975, 17, 1593.
- (33) Bhargava, N.; Gallagher, D.; Hong, X.; Nurmikko, A. Phys. Rev. Lett. 1994, 72, 416.
- (34) Wang, S. P.; Westcott, S. L.; Chen, W. J. Phys. Chem. 2002, 106, 11203.
- (35) Mungan, C. E.; Gosnell, T. R. Adv. At., Mol., Opt. Phys. 1999, 40, 161.