

Surfactant-Imposed Interference in the Optical Characterization of GaP Nanocrystals

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We report on the complications in optical characterization of GaP nanoparticles grown by colloidal chemistry. It is demonstrated that upon exposure to relatively mild heating conditions, the surfactants utilized to arrest growth and/or agglomeration lead to thermal decomposition products, which exhibit optical properties similar to those observed for nanocrystals with broad size distributions. The origin of this photoluminescence is still unknown; however, photoluminescence measurements of surfactants of different purities indicate that the impurities may be responsible for the emission. The results of this study demonstrate the potential complications associated with studying the optical properties of GaP nanocrystals prepared in the presence of commonly utilized surfactants. They suggest that more reliable assignment of the spectral features of nanocrystals can be afforded by a more detailed understanding of the optical properties associated with the surfactants and or their thermal decomposition products.

Colloidal growth is an established method for the preparation of semiconductor nanocrystals and typically involves heating the precursors in the presence of a surfactant and/or coordinating solvent.^{1–6} A variety of both II–VI and III–V semiconductor nanocrystals have been successfully prepared by this method. Although trioctylphosphine oxide (TOPO) and trioctylphosphine (TOP) are most widely utilized, other surfactants such as hexadecylamine (HDA), trioctylamine (TOA), etc., have found use as well. In addition to controlling the growth of the nanocrystals, the surfactants passivate their surfaces, thereby limiting surface traps and the agglomeration of the nanocrystals. However, to obtain highly crystalline nanocrystals, it is necessary to conduct the reactions at relatively high temperatures, 100–200 °C^{2,4} for the II–VI (such as CdSe) ionic semiconductor nanocrystals, and in excess of 270 °C for several days for III–V covalent semiconductors such as InP.^{3,5,6}

At the temperature at which the semiconductor nanocrystals are prepared, thermal decomposition of the surfactant results in the formation of unidentified products in addition to the nanocrystals. In most cases, isolation of the nanocrystals and the removal of excess surfactant is achieved by washing with methanol or acetone. To our knowledge, there has been no report in the literature where the surfactant utilized in the preparation of the nanocrystals has been completely removed from the nanocrystal surface. In fact, the maximum surfactant exchange has been reported to be between 80 and 90%.^{9,10} Therefore, it is important to understand the nature of the optical properties associated with the thermal decomposition products associated with these surfactants in order to separate their contribution to the absorption and emission spectra of the solutions containing nanocrystals. We have successfully prepared GaP nanoparticles using methods previously described,^{1–6} intended to be incorporated into hybrid inorganic/organic devices such as OLEDs. Toluene solutions of GaP nanocrystals capped with TOPO exhibit a broad photoluminescence (PL) spectrum upon UV

excitation (350 nm) with the maximum of the emission intensity in the blue region as expected for GaP. However, our photoluminescence (PL) and photoluminescence excitation (PLE), as well as time-resolved photoluminescence (TRPL) measurements of toluene solutions containing just the heated TOPO, exhibited a broad emission spectrum extended over the entire visible region with a maximum located at a wavelength shorter than 500 nm. The PLE spectra and carrier recombination dynamics are very similar to those expected from nanocrystals with a broad size distribution. Under these circumstances, the identification of the feature associated with carrier recombination in the semiconductor nanocrystals becomes problematic, especially where the emission of the nanocrystal is expected at wavelengths shorter than 500 nm.

GaP nanocrystals were prepared by reacting GaCl₃ with P(SiMe₃)₃ in TOPO (90%) following a method similar to the one presented in refs 1–6. Continuous wave (CW) PL and PLE spectra were acquired in the frontal geometry using a Jobin Yvon Fluorolog-3 spectrofluorometer equipped with a 400 W Xe lamp as an excitation source and a Hamamatsu R928 photomultiplier (PMT) tube as a detector. All spectra were corrected for the PMT response and/or the lamp emission spectrum. The excitation source used for measuring the photoluminescence intensity decay was the frequency-doubled 400 nm, 200 fs pulses output from a Coherent Rega 9000 regenerative amplifier with a 250 kHz repetition rate. The solutions containing the heated surfactants were diluted with toluene, and their emission was collected from solutions in quartz cuvettes using conventional optics in the frontal geometry. The photoluminescence signal was spectrally and temporally resolved by a Chromex 250IS monochromator equipped with a Hamamatsu C4334 streakcamera having a typical jitter of 50 ps.

The GaP nanocrystals were characterized by transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), and electron diffraction. The TEM image shown in Figure 1a indicates that the nanocrystals are spherically shaped with an average diameter of 14 nm and a large size distribution

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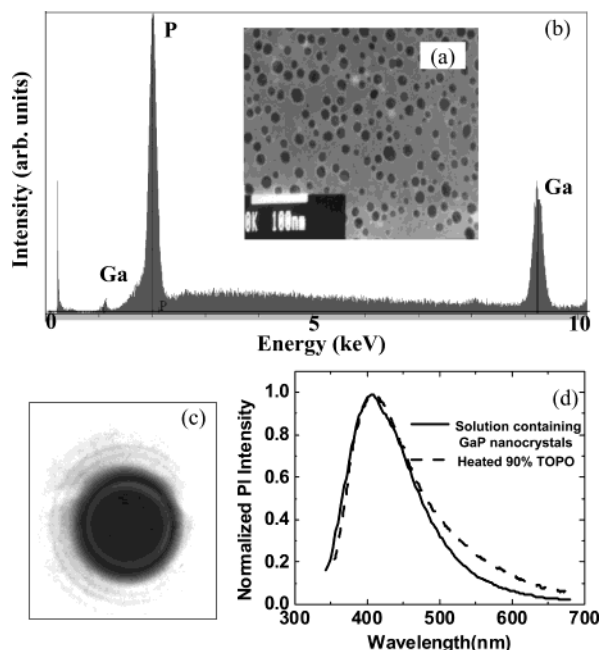


Figure 1. (a) Transmission electron microscopy image (b), energy dispersive spectrum, and (c) electron diffraction pattern of GaP nanocrystals grown by colloidal chemistry. The particles are characterized by an average diameter of 14 nm and a broad size distribution ($\pm 50\%$). (d) Comparison between the photoluminescence spectra of heated 90% TOPO (dashed curve) and a solution containing GaP nanocrystals (solid curve).

($\pm 50\%$). The EDS spectrum (Figure 1b) exhibits an excess of phosphorus, suggesting the presence of either excess surfactant or other phosphorus-containing compounds. Electron diffraction performed on the same grid exhibits a ring pattern as shown in Figure 1c. Fourier transform far-infrared spectroscopic studies on the same sample confirmed the crystallinity of the GaP nanoparticles through the presence of transverse optical bulk-like TO(Γ) phonon modes.⁸

Our preliminary results encouraged us to investigate the optical properties of the nanocrystals. The photoluminescence spectrum of a toluene solution containing the GaP nanocrystals is presented in Figure 1d. The emission is broad and extends over the entire visible spectrum with a maximum intensity in the blue region as expected for GaP nanocrystals. A brief statement made by Micic et al. alluded to the fact that the heated surfactant (90% TOPO) might be emitting in the same wavelength range as the GaP nanocrystals they fabricated.⁶ However, no detailed studies of the optical properties of these heated surfactants have been reported in the literature.

Since the same surfactant was used in the growth of the nanoparticles discussed here, we measured, for completeness, the PL spectrum of TOPO (90%) heated under the same conditions as the growth process and diluted in toluene. The spectrum is represented by the dashed line in Figure 1d. Clearly the two spectra in this figure are essentially the same and suggest the entire emission observed in the solution containing the GaP nanoparticles is due to the surfactant as a result of being heated. The observation of emission from heated surfactants points that caution has to be exercised in assignment of the observed emission to GaP nanocrystals.

Recently, a similar spectrum, measured for a mixture of TOPO and HDA, has been reported in connection with the optical studies of CdSe nanoparticles.⁷ However, unlike III–V semiconductors, photoluminescence spectra from II–VI semiconductor nanocrystals typically exhibit sharp and strong

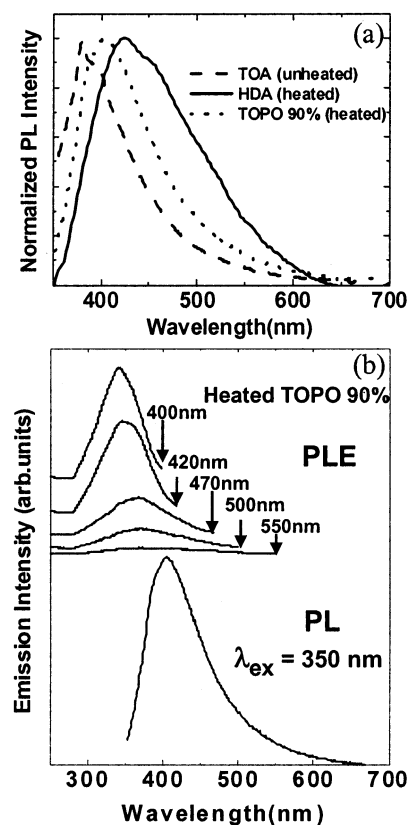


Figure 2. (a) Photoluminescence spectra from three different surfactants commonly used in nanocrystals colloidal chemistry growth, and (b) PLE spectra for the 90% TOPO heated at 150 °C taken at different wavelengths across the PL feature. The peak of the PLE spectra shifts as a function of wavelength, indicating the presence of several emitting components in the heated TOPO solution.

features that are distinguishable from the broad emission observed for the surfactants.

Typical photoluminescence spectra obtained from three different solutions containing heated TOPO (90%) and HDA as well as unheated fresh TOA are presented in Figure 2a. The excitation wavelength was 350 nm for all samples. The emission is broad and extends over the entire visible region and is similar in character to the emission from nanocrystals characterized by a broad size distribution.^{11–14} Therefore, upon heating at high temperatures, TOPO, HDA, and/or other potential decomposition products exhibit photoluminescence properties. In some cases (for example TOA), the surfactant exhibits an emission without any heating.

We have further investigated the optical properties of these heated surfactants by recording the PLE spectra at several wavelengths across the PL feature. The results of the measurements are presented in Figure 2b. The excitation wavelength corresponding to the maximum emission intensity changes at different emission wavelengths, suggesting that there are several emitting species present in the solution. This type of behavior is also exhibited by semiconductor nanocrystals^{15–17} in the quantum confinement size regime, where the maximum of the PLE spectrum depends on the nanoparticle size. This behavior is often utilized to identify the emission attributed to the nanocrystals. Therefore, the heated surfactants not only exhibit emission in the expected wavelength range for GaP nanocrystals, but they also exhibit PLE spectral features similar to those associated with nanocrystals.

The CW PL and PLE studies were found to be insufficient to establish the nature of the photoluminescence or to isolate

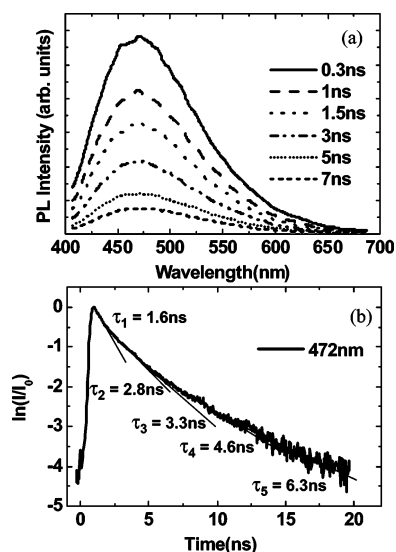


Figure 3. (a) Time-resolved PL spectra of 90% heated TOPO at different delay times under 400 nm excitation, and (b) the PL intensity decay as a function of time for the wavelength corresponding to the peak PL intensity. A multicomponent fit to this decay shows that the emission lifetimes are very similar to carrier radiative lifetimes for semiconductor nanocrystals

the spectral components related to nanocrystals. Therefore, we performed time-resolved photoluminescence measurements on the same 90% TOPO solution using a 400 nm femtosecond pulsed excitation. The measured time-resolved spectra at different delay times are presented in Figure 3a. The PL peak is red-shifted when compared to the CW spectrum obtained with 350 nm excitation. Such a shift is expected considering the PLE results, which show that different excitation wavelengths are resonantly pumping different species, which contribute to the broad PL feature. A plot of the PL intensity decay as a function of time at the wavelength corresponding to the emission intensity peak in Figure 2a is shown in Figure 3b. The decay has a nonexponential character and can be attributed to the existence of several different emitting species. The emission lifetimes resulting from a multicomponent fit to this decay are in the nanosecond range and are similar to the radiative recombination lifetimes in direct band gap semiconductors. Again, this spectroscopic technique has provided results that are similar to those expected for nanoparticles. The nonexponential character of the decay has been encountered in the time-resolved studies^{18–20} of carrier recombination in nanocrystals and is a result of the carrier lifetime dependence on the nanoparticle size.

To monitor the optical properties of heated TOPO as a function of heating time, a 0.5 mL aliquot was drawn every hour and dissolved in toluene. The spectra in Figure 4 show the resulting emission at various intervals of heating at 150 °C. The results indicate a significant emission after only 0.5 h of heating. Most importantly, the emission intensity increases as a function of heating time. The quantum efficiency was measured under 366 nm excitation using a solution of di-phenyl anthracene in toluene as a reference. After 24 h of heating, the quantum efficiency reaches 13.8%, which is similar to the efficiency reported for many quantum dots. It is important to note that most reported preparations of nanocrystals require heating times in excess of 24 h.

In an effort to determine the origins of the photoluminescence, we compared the emission intensities from two TOPO solutions of different purities: 90% and 99%. The emission intensity was found to decrease by a factor of 100 in the 99% TOPO, suggesting the photoluminescence properties might be related

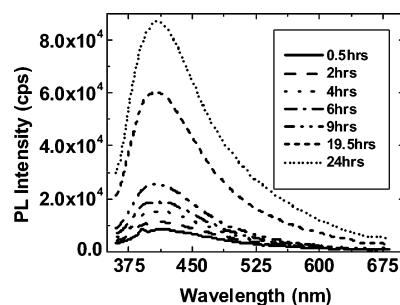


Figure 4. PL spectra for 90% TOPO heated to 150 °C, taken after different heating times. The emission intensity increases by a factor of 10 as the heating time increases from 0.5 h to 24 h. After 24 h, the quantum efficiency is of the same order as the one reported for nanocrystals.

to the thermal decomposition of the impurities present in the surfactant rather than the surfactant itself. The impurities present in commercial grade TOPO (90%) have been previously reported to be dioctylmonophosphonic acid, mono-octyldiphosphonic acid, dioctylphosphonic acid, and dioctylphosphinate.²¹ However, none of these reported species incorporates conjugated π -bonds, that could, upon heating, give rise to species expected to exhibit luminescence properties. In an attempt to identify the decomposition products that might be responsible for the observed properties, analytical tools such as ¹H NMR, FTIR, TLC, HPLC, and mass spectra were employed to study unheated and heated (150 °C \times 24 h) samples of 90% TOPO. In all these measurements, the results on both types of samples showed no apparent difference, indicating that any thermal decomposition product may be present in too small of a concentration to be easily identifiable by these techniques. For example, ¹H NMR spectra of both the heated and the unheated solutions in CDCl₃ show no apparent difference in the spectra and exhibit no resonances in the 3–8 ppm range. Thus, there is no evidence of the presence of any compounds exhibiting aromaticity. Admittedly, identifying the species responsible for such a substantially efficient photoluminescence behavior is important in order to minimize the interference due to surfactants on the optical properties of the nanocrystals. On the basis of the increasing intensity of PL with heating time, we believe that the concentration of the responsible species increases with the duration of heating.

In conclusion, surfactants widely used in the colloidal synthesis of semiconductor nanocrystals exhibit photoluminescence properties related to thermal decomposition. The emission spectra are very broad and extend over the entire visible region. Both the PLE and the TRPL spectra and dynamics are very similar to those expected for the GaP semiconductor nanocrystals. Therefore, common optical techniques utilized in the characterization of semiconductor nanocrystals cannot unambiguously distinguish between the PL resulting from the GaP nanocrystals or the surfactant thermal decomposition products. Furthermore, time-resolved photoluminescence studies could unambiguously isolate the component due to nanocrystals only if the emission is associated with surface or forbidden states, characterized by very long (tens or hundreds of nanoseconds) decay times. However, a short PL decay time does not necessarily indicate the absence of PL from nanocrystals. Careful and detailed PL, PLE, and TRPL studies of surfactants and/or solvents heated through a process that reproduces the growth conditions may help in isolating the surfactant component in the PL spectra. Detailed studies of the photoluminescence properties of surfactants are especially important for GaP nanocrystals, which are expected to emit at wavelengths shorter

than 500 nm. A detailed understanding of the optical properties associated with the solvents utilized in the nanocrystal preparation should permit more careful assignment of the spectral features associated with nanocrystals.

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