Quantum yield excitation spectrum (UV-visible) of CdSe/ZnS core-shell quantum dots by thermal lens spectrometry
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I. INTRODUCTION

Fluorescence quantum efficiency (or quantum yield, $\eta$) parameters can be obtained by conventional photoluminescence (PL) or fluorescence lifetime methods. However, the photothermal spectroscopy methods, as the thermal lens spectrometry (TLS), has been shown to be an alternative way to obtain $\eta$ with accurate precision, by measuring the fraction of absorbed energy converted into heat ($\varphi$) in the sample. The measurement of $\varphi$ is complementary to the purely optical methods, such as PL and lifetime measurements. The main advantage of photothermal spectroscopy is that they do not require comparison with a standard sample, a process that generates large random uncertainty as well as systematic effects due to difference in solvents, calibration of spectrometers, detectors, etc. Among the photothermal techniques, TLS has been shown to be particularly interesting due to its simplicity, high reproducibility, and sensitivity. Mainly two approaches based on TLS have been used for $\eta$ measurements in liquids and solids, reference sample (RS) and multiwavelength (MW). In the first method, the thermal-optical properties of the sample must be known or else, the solvent of the solution (or the undoped matrix) with negligible fluorescence should be used as a reference. The second routine (MW) can be used when $\eta$ is independent on the excitation wavelength in some wavelength range, which occurs usually for a broad absorption band like in rhodamine 6G, or when all excited states decay very fast to a single emitting metastable level, which is the case of Nd$^{3+}$ and other rare earth ions. In this case, where the nonradiative transitions are used as an internal reference, the thermal-optical parameters and $\eta$ are directly obtained from the dependence of the thermal lens (TL) signal with the excitation wavelength. Nowadays, the mode-mismatched dual-beam (pump-probe) TLS configuration is the most applied one. In our view, the main drawback of this configuration is that the results depend critically on the beam waists, their values and positions, which results in the major source of experimental uncertainty. Recently, Marcano et al. presented another mode-mismatched dual-beam TLS configuration, which optimizes the technique and requires no calibration since the results does not depend critically on the beam parameters. Besides that, the sensitivity is improved because large samples can be used (up to 100 cm was demonstrated).

Quantum dots (QDs) or semiconductor nanoparticle materials have a variety of new applications, for example, in biomedical tags, light-emitting diodes, lasers, photonic devices, sensor material, etc. It is established that capping a core material with a shell reduces nonradiative recombination, when the shell inorganic material is a semiconductor with wider band gap than the core semiconductor. Fluorescence quantum efficiency and related aging and photodegradation effects are therefore of utmost importance in the development and applications of the QDs materials. QDs were also used to probe local-field effects on the spontaneous emission rate.

In this study, the recent TLS configuration, which is cited above and named here as optimized, was applied to measure $\eta$ of cadmium selenide/zinc sulfide (CdSe/ZnS) core-shell semiconductor nanocrystals in solution using both RS and MW methods. We demonstrated that this arrangement is especially advantageous to obtain the photothermal excitation spectrum. The two methods (RS and MW) were applied in QDs suspended in two different solvents at ultra-violet and visible (UV-vis) range. For poly(methyl methacrylate) (PMMA)-encapsulated CdSe/ZnS QDs suspended in THF, the aging effect on TLS results was observed. In addi-
ion, conventional PL measurements were applied to obtain a relative quantum yield, which was compared to the TLS results.

II. THEORETICAL BACKGROUND

In TLS experiments, the heat source profile $Q(r)$ is proportional to the Gaussian intensity profile of the excitation beam expressed as $I_{ex}(r) = (2P_{ex}/\pi w_{ex}^2) \exp(-2r^2/w_{ex}^2)$, where $P_{ex}$ is the excitation beam power, which has a radius $w_{ex}$ at the sample. The temporal evolution of the temperature profile $\Delta T(r,t)$ in the sample can be obtained by the heat conduction equation. In experiments with short excitation pulses, heat diffusion can be neglected and the temperature profile, $\Delta T(r,t)$, is proportional to the Gaussian intensity profile of the excitation beam $I(r)$. However, for long pulses or continuous wave experiments, the effect of heat diffusion is important and consequently $\Delta T(r,t)$ is wider than $I_{ex}(r)$.

For $t \approx t_c$ (characteristic heat diffusion time), the on-axis temperature rise is proportional to the absorbed excitation power ($P_{abs}$) and inversely proportional to the thermal conductivity ($\Delta T \propto P_{abs}/k$) but it does not depend on $w_{ex}$. The TL effect is created when the excitation laser beam passes through the sample and the absorbed energy is converted into heat, changing the refractive index of the material, and consequently causing a thermal phase shift, whose amplitude is

$$\theta = - \varphi \frac{P_{abs} \ dn}{k\lambda_p dT}.$$  

(1)

Here, $\varphi$ is the fraction of absorbed energy converted into heat (denominated absolute nonradiative quantum efficiency), $\lambda_p$ is the probe beam wavelength, $k$ is the thermal conductivity, $dn/dT$ is the temperature coefficient of the refractive index, and $P_{abs} = P_{ex}(1 - e^{-\alpha b})$ is the absorbed excitation beam power, where $\alpha$ is the linear optical absorption coefficient at the excitation wavelength $\lambda_{ex}$ and $L$ is the sample thickness (optical path length). Using the diffraction theory, it can be shown that the variation in the probe beam on-axis intensity is

$$I(t) = I(0) \left[ 1 - \frac{\theta}{2} \tan^{-1} \left( \frac{2mV}{(1 + 2m)^2 + V^2} \right) \right]^2,$$

(2)

where $m = (w_p/w_{ex})^2$, and $w_p$ and $w_{ex}$ are respectively the probe and excitation beam radius at the sample; $V = z/Z_{op} + (Z_{op}/Z_2)[1 + (z/Z_{op})^2]$, where $Z$ and $Z_2$ correspond respectively to the positions of the sample and the aperture with regard to the probe beam waist; and $Z_{op}$ is the probe beam Rayleigh range; $t_c = w_{ex}^2/4D$, where $D = k/\rho C_p$ is the thermal diffusivity, $\rho$ is the density, and $C_p$ is the specific heat. $I(0)$ is the on-axis intensity when $t$ is zero (the instant when the excitation beam is turned on). The propagation of a probe laser beam through this TL in a liquid sample will result in either a spreading ($dn/dT < 0$) or a focusing ($dn/dT > 0$) of the beam, depending on the temperature coefficient of the sample refractive index.

Usually, Eq. (2) is used to fit the experimental data in order to determine the parameters $\theta$ and $t_c$. The optimized TLS configuration, however, allows obtaining $\theta$ without requiring such fits. In this case, the probe beam is much wider than the excitation’s, and their waists are at the same position. Thus, in steady-state $\langle I(\infty) \rangle$, the inverse tangent in Eq. (2) reaches its maximum value $(\pi/2)$, so the TL signal becomes

$$S = \langle I(\infty) - I(0) \rangle / I(0) = - (\pi/2) \theta.$$  

(3)

This way the parameter $\theta$ can be directly obtained, simply by taking the beam intensity before and after the TL effect. On the other hand, to acquire $t_c$ (and consequently $D$) even in the optimized TLS configuration the transient TL signal has to be recorded and fitted with Eq. (2). Nevertheless, in this case, the fitting result is more accurate than in standard TLS configuration since the transient TL signal in the optimized configuration does not depend critically on the beam waists, their values, and positions. This is especially important when the wavelength requires be changed, for example, to obtain spectra as following.

For fluorescent materials, the nonradiative quantum efficiency is

$$\varphi = 1 - \eta \langle \lambda_{ex} / \lambda_{em} \rangle,$$

where $\langle \lambda_{em} \rangle$ is the average emission wavelength. It is interesting to rewrite Eq. (1) introducing a new parameter $\Theta$

$$\Theta = - \frac{\theta}{P_{abs}} = \Theta_o \left( 1 - \frac{\lambda_{ex}}{\lambda_{em}} \right),$$

(4)

where $\Theta_o = (dn/dT)/k\lambda_p$ is a factor that depends on the thermo-optical properties of the solution. In many cases, the emission spectrum does not change for a certain $\lambda_{ex}$ range, then $\langle \lambda_{em} \rangle$ is constant, and the linear dependence of $\Theta$ versus $\lambda_{ex}$ [Eq. (4)] should provide both $\eta$ and $\Theta_o$. This method is named MW, and has been applied in liquids and solids.

For dilute solutions, the parameter $\Theta_o$ of the solution in general is practically the same as the pure solvent. In this case, the solvent parameter can be used in Eq. (4) to determine $\eta$ by

$$\eta = \left( 1 - \frac{\Theta}{\Theta_o} \right) \frac{\lambda_{em}}{\lambda_{ex}}.$$  

(5)

This method is denominated RS. Also, a nonfluorescence solution could be prepared with the same solvent to be used as reference.

III. EXPERIMENTAL

A. Material

The samples studied were as follows: (a) green CdSe/ZnS core-shell nanocrystals with $(2.4 \pm 0.2)$ nm core size suspended in toluene $(C_8H_{18})$ at a $3.14 \mu$mol/l concentration and (b) fort Orange CdSe/ZnS core-shell nanocrystals encapsulated into PMMA with $(3.5 \pm 0.5)$ nm core size and $74 \mu g/nmol$ molecular weight dissolved in THF (tetrahydrofuran, $C_8H_{18}O$) at a 15 mg/ml concentration. Core-shell suspended in THF was prepared by mixing the QDs with the solvent under constant magnetic stirring. Both the CdSe/ZnS
QDs encapsulated in PMMA (in powder form) and the CdSe/ ZnS QDs suspended in toluene (in solution form) were obtained from Evident Technologies.19

Figure 1 shows the absorption and PL spectra of the nanoparticles suspended in toluene. The emission spectrum does not depend on the excitation wavelength at the UV-vis region. From this spectrum, the average value of the emission wavelength \( \langle \lambda_{\text{em}} \rangle = 527 \text{ nm} \) was obtained. The first and second absorption peaks shown in Fig. 1 (centered at 510 and 455 nm) correspond to the transitions 1S\(_{3/2}\)1S\(_{\text{e}}\) and 2S\(_{1/2}\)1S\(_{\text{e}}\), respectively.20,21

Figure 2 shows the absorption and PL spectra of the PMMA-encapsulated nanoparticles suspended in THF. The average value of the emission band (solid line) is centered at \( \langle \lambda_{\text{em}} \rangle = 587 \text{ nm} \) and the full width at half maximum (FWHM) of \( \sim 41 \text{ nm} \). The PL spectrum for the QDs in THF is broader than for the QDs in toluene (FWHM \( \sim 28 \text{ nm} \)). The enlargement of the emission band for QDs in THF compared to the QDs in toluene is probably due to a more inhomogeneous distribution of crystallite size and/or impurities of the QDs solution.22,23 As oppose to the solution in toluene, the solution of PMMA-encapsulated QDs in THF was inhomogeneous, with PMMA microparticles that could be seen by naked eye. These inhomogeneities perturbed the reproducibility of the measurements. In order to improve the reproducibility, we set the solution to rest at room temperature (\( \sim 22 ^\circ \text{C} \)) so that the heaviest particles precipitated. The process was very slow and took over one week to reach a stationary state, when a much more homogeneous solution was obtained. After this long period of time at room temperature, the absorption spectrum changed as shown in Fig. 2. Two following main effects can be observed: absorption decrease and blueshift of both absorption and emission (dashed line). The absorption decrease can be attributed to the precipitation process, so a decrease in QDs concentration was estimated as \( \sim 30\% \). By shaking the aged sample, the concentration is expected to be nearly the same as in the original one, so that the difference between the new absorption spectrum (dotted line) and that for the fresh sample (solid line) was attributed only to the QDs degradation effect. The emission spectrum for this shaken sample was the same as the precipitated sample. The peak of the emission spectrum blue shifted by 17 nm, and the FWHM increased \( \sim 32\% \). A similar blueshift in the PL was observed on single CdSe/ZnS QDs and attributed to photoinduced oxidation of the CdSe crystallites.17

**B. Setup and procedure**

All the TLS measurements were performed with a quartz cuvette of length \( L = 5 \text{ mm} \) at room temperature (\( \sim 22 ^\circ \text{C} \)), using the optimized TLS configuration, whose experimental setup is described elsewhere.10 A He–Ne laser (632.8 nm) was used as the probe beam, and either another He–Ne laser (543 nm) or an Ar\(^+\) Laser (with lines at 335, 351, 364, 457, 465, 472, 476, 488, 496, 501, 514, or 528 nm) was used as the excitation beam. A typical transient TL signal for QDs suspended in THF is present at Fig. 3. The behavior of this curve indicates a negative \( dn/dT \) (as expected for most liquids), i.e., the TL effect causes a defocusing of the probe beam. The theoretical fit, by Eq. (2), provides the parameters \( \theta \) and \( t_c \). Then, the thermal diffusivity can be found by \( D = w_{\text{ex}}^2/4t_c \). The excitation \( (w_{\text{ex}}) \) and probe \( (w_p) \) beam radius at the sample position were measured with an Omega Meter beam profiler from Thorlabs Inc. The TL signal shown in Fig. 3 is an average obtained from five transient signals. In order to improve the precision, this average TL signal was measured as a function of \( P_{\text{ex}} \) for each \( \lambda_{\text{ex}} \). Figure 4 shows that the plot of \( \theta \) versus \( P_{\text{ex}} \) presents a linear behavior (for small \( \theta \)) as expected by Eq. (1).
Since the concentrations of the samples are relatively low, the parameters $k$ and $dn/dT$ of both solvents could be used in Eq. (5). For THF, however, a lack of parameters from literature required an additional study. The temperature dependence of the refractive index was then measured with a Pulfrich-Refractometer PR2 refractometer at 435.8, 546.1, and 587.6 nm, for both the pure THF solvent and the QDs suspended in THF (Table I). The refractive indexes were measured for approximately 23 different temperature values, between ~15 and 35 °C. The fit was made by the least square method, and the correlation coefficient was as good as R = 0.999 (confidence level 95%). The thermal conductivities ($k$) were calculated from the thermal diffusivities ($k = \rho C_p D_l$), which in turn was determined by fitting the transient TL signal as in Fig. 3.

The absorption and PL spectra of the samples were performed using an Ocean Optics USB2000 spectrometer, with resolution of 1.3 nm. To obtain a better accuracy, the absorption coefficient was determined also by direct laser transmission measurements, where Beer’s law was applied and the reflections at the sample surface were considered for each excitation wavelength. The determination of the QDs core sizes was performed by considering the absorption spectrum of the samples.24

The PL experiment was performed collecting the light emitted in the direction perpendicular to the laser beam. The integrated emission spectrum was normalized by the rate of absorbed excitation photons ($P_{abs}/hv_{ex}$) in order to obtain relative quantum efficiency, so that it is not a calibrated measurement. Therefore, in order to compare the results, the relative PL was arbitrarily equalized to the absolute TLS quantum yield at $\lambda_{ex} = 355$ nm.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>THF</th>
<th>QDs in THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>435.8</td>
<td>⋯</td>
<td>−4.1</td>
</tr>
<tr>
<td>546.1</td>
<td>−4.3</td>
<td>−4.2</td>
</tr>
<tr>
<td>587.6</td>
<td>−4.1</td>
<td>−4.0</td>
</tr>
</tbody>
</table>

TABLE I. $dn/dT \times 10^4$ K$^{-1}$ values obtained by reflectometer for pure THF solvent and QDs/PMMA suspended in THF (±0.1 uncertainty, 95% confidence level).

The spectrum of the TL signal amplitude ($\theta$) normalized by the excitation power ($P_{ex}$) for the sample of QDs in toluene is shown in Fig. 5(a). Compared to the absorption spectrum, the parameter $\theta/P_{ex}$ is larger for shorter wavelength ($\lambda_{ex}$) because the fraction of absorbed energy released as heat ($\varphi$) increases with the excitation photon energy ($hc/\lambda_{ex}$). This effect is clearly seen in Fig. 5(b), where $\Theta(k_{ex})$ presents a nearly linear behavior, as expected by Eq. (4). Using the MW method, the linear fit of Fig. 5(b) results in $\eta=0.79 \pm 0.06$ and $\Theta_{ex}^{\text{TL}}=(7.0 \pm 0.2) \times 10^3$ W$^{-1}$, with correlation coefficient R = 0.97 (confidence level 95%). This factor $\Theta_{ex}^{\text{TL}}$ is in good agreement with $\Theta_{ex}^\text{calc}=6545$ W$^{-1}$ calculated using the literature data for toluene ($k = 0.134$ W/K m, $dn/dT = -5.6 \times 10^{-4}$ K$^{-1}$ at 632.8 nm).25 Since the concentration of QDs in toluene is relatively low, the parameters $k$ and $dn/dT$ of the sample are supposed to be nearly the same as the solvent. Since $\Theta_{ex}^\text{calc}$ is previously known, the RS method can also be used to obtain $\eta$ by Eq. (5), as shown in Fig. 5(c). The quantum yield obtained by this method is nearly constant for the whole UV-vis excitation range (335–528 nm), with an average value $\langle \eta \rangle = 0.76 \pm 0.02$, where the uncertainty corresponds to the measurement standard deviation (confidence level ~68%). Therefore, the agreement between the results obtained with RS and MW methods is very good. Figure 5(c) compares the quantum yield spectra obtained by the RS method and by conventional PL technique. The fluctuation of the data obtained by PL is about five times larger than that from TLS. The quantum yield values obtained by TLS (with a ~3%
error) is at least 50% larger than the one provided by the manufacturer, obtained by conventional PL technique using a dye as a reference.

**B. QDs suspended in THF**

From the transient TL signal (Fig. 3) and $t_c = u_{ex}^2/4D$, we obtained the thermal diffusivities as $D = (1.04 \pm 0.07) \times 10^{-3}$ cm$^2$/s and $(1.00 \pm 0.06) \times 10^{-3}$ cm$^2$/s, respectively, for PMMA-encapsulated CdSe/ZnS nanoparticles suspended in THF and pure THF solvent. This similarity in $D$ values is due to the small volume fraction of the QDs/PMMA in the solution. Considering the literature values, $\rho = 0.89$ g/cm$^3$ and $C_p = 1700$ J/kg K, the $D$ measurements imply in thermal conductivities of $k = DPC_p \approx 0.157$ and 0.151 W/m K, respectively, for the QDs solution and the pure solvent. For the QDs in THF, therefore, we used $k \approx 0.16$ W/m K. From Table I data, obtained by the refractometer, we estimated $dn/dT = -4.1 \times 10^{-4}$ K$^{-1}$ at 632.8 nm. Hence, the parameter $\Theta_0^{cal} = 4050$ W$^{-1}$ was calculated in order to obtain $\eta$ by Eq. (5). Figure 6 shows the spectrum of $\eta$ for the fresh and aged solutions. The $\eta$ average value was found to be $\eta = 0.43 \pm 0.07$ for fresh sample and $\eta = 0.16 \pm 0.04$ for the aged sample (error correspondent to the standard deviation). As mentioned before, the presence of PMMA microparticles increased the uncertainty of the TLS results, as can be seen comparing Figs. 5(c) and 6. In order to apply the MW method, $\Theta$ versus $\lambda_{ex}$ was plotted in Fig. 7. Through the linear fit (least square method), the parameters $\eta = 0.5 \pm 0.1$ and $\Theta_0^{TL} = (4.4 \pm 0.4) \times 10^3$ W$^{-1}$, and $\eta = 0.21 \pm 0.08$ and $\Theta_0^{TL} = (4.3 \pm 0.2) \times 10^3$ W$^{-1}$ were obtained, respectively, for fresh and aged samples. Considering the experimental uncertainty, the $\eta$ values determined by RS and MW methods are in conformity, which gives confidence on the main results observed. It is important to notice that the good agreement obtained between the parameters $\Theta_0^{cal}$ for the fresh and aged samples reveals that the thermal-optical parameters $k$ and $dn/dT$ do not change despite the aging effect. This fact was before adopted to obtain $\eta$ for the aged sample by the RS method.

The aging effect of PMMA CdSe/ZnS suspended in THF was studied also by measuring the parameter $\Theta$ in function of time. Figure 8 shows the evolution of the absorption decrease [Fig. 8(a)] as well as the increase in the parameter $\Theta$ [Fig. 8(b)] at $\lambda_{ex} = 457$ and 514.5 nm, for a period of more than one week. The evolution of the quantum yield [Fig. 8(c)] could be obtained using Eq. (5) with the above calculated parameter $\Theta_0^{cal}$. In a $\sim 200$ h period, the absorption dropped $\sim 40\%$ and $\Theta$ increased $\sim 50\%$, which corresponds to a fall of $\sim 60\%$ on $\eta$ at 514 nm.

Aging effects on PL intensity and quantum yield have been reported at literature for nanoparticles as CdS-capped and bare HgTe, PbTe, and Hg/CdTe nanocrystals. The CdSe aging effect on PL intensity was correlated with the purity of the nanocrystal samples, and defects as dislocation loop conglomerations induced in the QDs. For nanocrystals contained in porous silicon, the aging effects were found to modify the optical properties of the sample, as red-shift and width increase in PL spectra.

**V. CONCLUSIONS**

The optimized TLS configuration used in this study simplified the measurement procedure and improved its accu-
racy since it makes the fit of experimental data depend much less critically on the parameters of excitation and probe beams. The data were obtained by two different TLS methods for quantum yield (η) determination, the MW and the RS. The results of both methods are consistent, both for the quantum yield spectrum and the thermo-optical parameter (dn/dT)/k. Very good precision was obtained in the measurements of CdSe/ZnS QDs suspended in toluene. Varying the excitation wavelength between 335–543 nm, it was experimentally demonstrated that \( η = 76 ± 2\% \) does not depend on the excitation wavelength. The η data is approximately five times more precise than the result obtained by conventional PL technique. The aging effect in PMMA-encapsulated CdSe/ZnS QDs suspended in THF reduced η ~ 60% in a period of more than 200 h.

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