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EXPERIMENTAL DETERMINATION OF PHOTO LUMINESSCENSE QUANTUM YIELD OF CDSE QUANTUM DOTS

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Abstract. *The fluorescence quantum yield or the efficiency of the fluorescence process is defined as the ratio of the number of photons emitted to the number of photons absorbed. In this report the experimental method to determinate photo luminescence (PL) quantum yield (QY) of CdSe quantum dot will be described. The experimental condition which depends on QY will be investigated. The QY values of CdSe which were prepared at Nano Materials Physics Laboratory Research Center for Dielectric and Advanced Matters Physics Pusan National University will be carried out and compared with the commercial CdSe sample.*

I. INTRODUCTION

Semiconductor quantum dots (QDs) have received tremendous attention due to considerable potential for a diverse range of technological applications. In contrast to many binary semiconductor quantum dots, CdSe QDs are readily synthesized with narrow size distributions and possess excellent photochemical stability when passivated properly [1, 2]. In addition, they demonstrate size-dependent photoluminescence that encompasses the visible region of the electromagnetic spectrum, and high luminescence quantum yield. Hence, CdSe represents an archetypal system for numerous QD applications.

Basics of fluorescence

Fluorescence is a several-step process that begins when a relatively high-energy photon is absorbed by a system (typically an atom or molecule). The system may then release some of the energy internally (e.g. in increased vibrational motion of the atoms in a molecule). This is followed by a transition to an energy level close to the original one, with the emission of a photon; this photon constitutes the fluorescence emission. Since some of the absorbed photon's energy is released through internal conversion, the emitted (fluorescence) photon must have lower energy than the absorbed photon. This process is illustrated in the left-hand diagram in Fig. 1 below. This energy shift is known as Stokes' Law, and is commonly observed in fluorescent systems. In many

commercial applications (e.g. enhanced "day-glo" colors), the absorbed photon is in the UV, while the emitted photon is in the visible region.

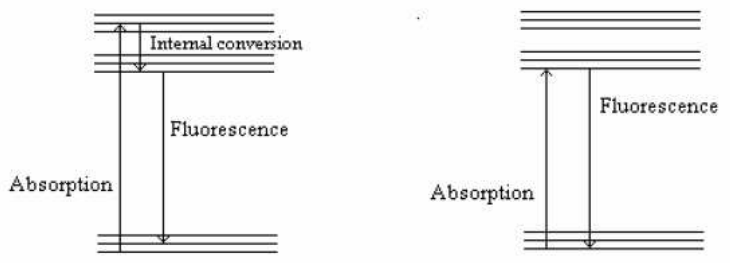

Fig. 1. Typical processes involving fluorescence

Quantum yield

The luminescence quantum yield is given as the ratio of the number of photons emitted to the number of photons absorbed by the sample:

$$QY = \frac{photon_{em.}}{photon_{abs.}}. \tag{1}$$

Absolute measurements of QY are difficult, but it is straight forward to find the ratio of the QY for two substances, denoted by 1 and 2.

$$QY2/QY1 = [F2/A2]/[F1/A1] = [F2/F1][A1/A2] \tag{2}$$

where, $F1$ is integrated intensity of the substance 1 fluorescence spectrum, $F2$ is integrated intensity of the substance 2 fluorescence spectrum, $A1$ is absorbance at wavelength λ a for the substance 1 absorption spectrum, $A2$ is absorbance at wavelength λ a for the substance 2 absorption spectrum.

It is easier to determine the "relative" quantum yield of a fluorophore by comparing it to a standard with a known quantum yield. Some of the most common standards are listed in Table 1.

II. EXPERIMENTAL

The CdSe NQDs were synthesized with CdO and Se as precursors by the colloidal chemical process at Laboratory Physics of Nano Materials Pusan National University, Korea, an other commercial CdSe sample also was used to compare

Fluorescence spectra of CdSe QD arising from excitation by incident λ_a light from xenon lamp which was dispersed by the first monochromator, the fluorescence signal was collected into second monochromator and detected by PMT. The reference sample is Rhodamine 6G with quantum yield about of 95%. Absorption spectra will also be taken, including a quantitative determination of the absorbance at the UV excitation wavelength. The absorption and fluorescence spectra for the reference sample and for the quantum dots will be compared and their relationship examined in the light of the usual Stokes' law behavior. Also, the quantum yield of the quantum dot sample will be expressed in terms of the quantum yield of the dye standard and evaluated quantitatively based on the accepted value for the standard.

Table 1. List of common standards for fluorescence quantum yield measurements.

Quantum Yield [Q.Y.] Standards	Q.Y. [%]	Conditions for Q. Y. Measurements	Excitation [nm]	Ref.
Cy3	4	PBS	540	[2]
Cy5	27	PBS	620	[2]
Cresyl Violet	53	Methanol	580	[3]
Fluorescein	95	0.1 M NaOH, 22˚C	496	[3]
POPOP	97	Cyclohexane	300	[3]
Quinine sulfate	58	0.1 M H_2SO_4, 22˚C	350	[3]
Rhodamine 101	100	Ethanol	450	[4]
Rhodamine 6G	95	Water	488	[4]
Rhodamine B	31	Water	514	[4]
Tryptophan	13	Water, 20˚C	280	[3,5]
L-Tyrosine	14	Water	275	[3,5]

The total number of fluorescence photons emitted is proportional to the area under the intensity vs wavelength curve; the software in the fluorometer performs that integration to yield the quantity F. The total number of incident photons that are absorbed in the fluorescence process is proportional to the absorbance A at wavelength λ_a , which is measured in a separate experiment using the UV-Vis absorption spectrometer. For best results in determining quantum yields, the two substances should have absorption peaks at approximately the same wavelengths, and their fluorescence spectra should overlap as much as possible.

General Experimental Considerations

Reference samples. The reference samples should be chosen to ensure they absorb at the excitation wavelength of choice for the test sample, and if possible, emit in a similar region to the test sample. The reference samples must be well characterised and suitable for such use.

Cuvettes. Standard 10 mm path length fluorescence cuvettes are sufficient for running the fluorescence measurements. In order to minimise errors in calculating the absorbance of each solution, it is advisable to use absorption cuvettes with extended path lengths

Concentration range. In order to minimise re-absorption effects absorbance in the 10 mm fluorescence cuvette should never exceed 0.05 at *and above* the excitation wavelength. Above this level, non-linear effects may be observed due to inner filter effects, and the resulting quantum yield values may be perturbed.

III. RUSULT AND DISCUSSION

Calculation

The relative quantum yield is generally determined by comparing the wavelength-integrated intensity of an unknown sample to that of a standard. The quantum yield of the unknown sample is calculated using:

$$Q = Q_R \frac{I}{I_R} \cdot \frac{OD_R}{OD} \cdot \frac{n^2}{n_R^2}, \tag{3}$$

where Q is the quantum yield, I is the integrated intensity, n is the refractive index, and OD is the optical density. The subscript R refers to the reference fluorophore of known quantum yield.

Fig. 2 show the absorption spectra and fluorescence spectra of CdSe and R6G. These spectra were recorded in the same condition. The line 488 indicate the excited wavelength for fluorescence spectra. The QY depend on excited wavelength and slit width of monochormator were investigated.

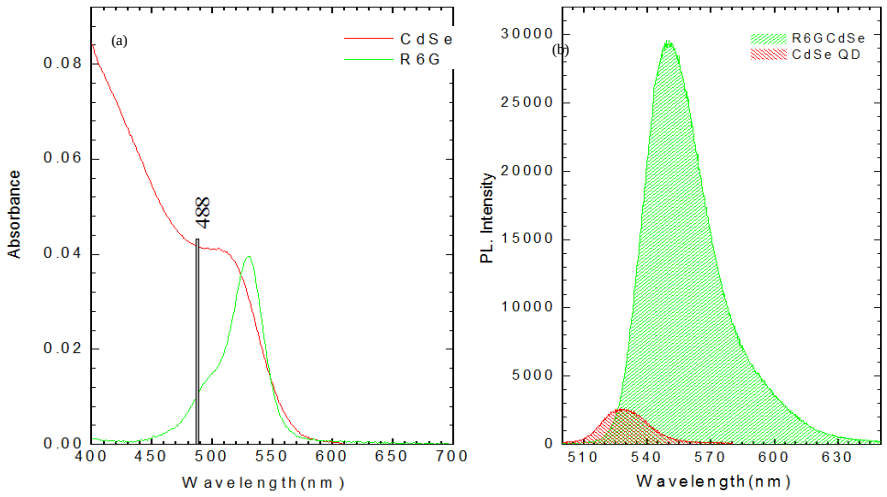

Fig. 2. Absorption spectra of CdSe and R6G (a) and Fluorescence spectra of CdSe and R6G (b), line 488 indicate the excited wavelength

QY depend on excited wavelength

Fluorescence spectra of CdSe depend on excited wavelength, QY of CdSe QD were calculated with different excited wavelength. Figure 3 show fluorescence spectra of CdSe excited by different wavelength from 420 to 540 nm. The shape of spectra were changed but QY of CdSe (Fig. 4) almost do not change in region 470-520 nm.

Table 2. Comparison QY of CdSe QD prepared at laboratory and CdSe QD commercial

No	Sample	QY
1	CdSe ODE 12	0.071
2	CdSe ODE 14	0.022
3	CdSe ODE 25	0.139
4	CdSe ODE x5	0.077
5	CdSe ODE 5-1	0.08
6	CdSe ODE 16	0.034
7	CdSe ODE ex.	0.026
8	CdSe (Comm.)	0.913

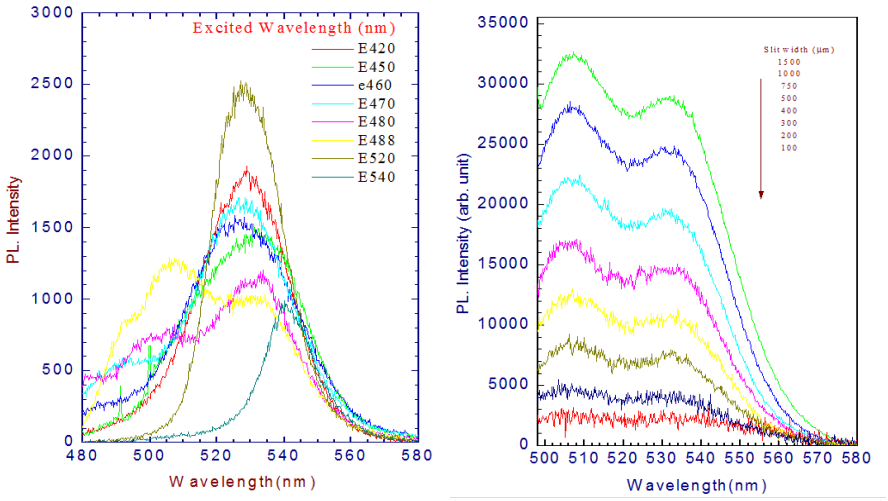

Fig. 3. Fluorescence spectra of CdSe QD measured with different excited wavelength (a) and different slit widths of monochromator (b)

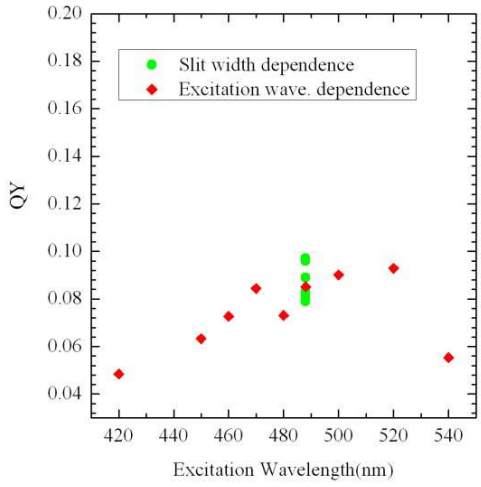

Fig. 4. QY of CdSe depend on excited wavelength and slit width

IV. CONCLUSION

Measurement of fluorescence QY can often be difficult and troublesome, and the need for absolute care during every step cannot be over emphasised. However, it is possible to make such measurements routinely, and we were success in investigation, determination QY of CdSe QD.

ACKNOLEGMENTS

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