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Application News

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Spectrophotometric Analysis

Measuring Fluorescence Quantum Efficiencies of Quantum Dots using the Shimadzu RF-6000 Fluorescence Spectrophotometer

■ Background

Quantum dots are nanoparticles whose fluorescence excitation/emission properties are largely governed by their dimensions. In general, the emitted wavelength on fluorescence increases as the quantum dot diameter increases. Tight manufacturing controls allow for very tunable quantum dot size distributions resulting in very predictable and selectable emission wavelength maxima. Researchers have found applications for quantum dots in material science, nanoparticle, renewable energy, and medical imaging sectors.

Quantum dots with a cadmium selenide (CdSe) core and a zinc sulfide (ZnS) shell are commercially available in 25 to 35 nm sizes appropriate to achieve emission maxima between 400nm and 750nm. Ligands can be attached to the shells of quantum dots to achieve solubility, binding efficiency, or other desired particle interaction properties. Pharmaceuticals including biologics can also be bound to quantum dot shells, so fluorescence imaging techniques can be used to precisely examine how they interact with healthy or diseased cells.

The Shimadzu RF-6000 fluorescence spectrophotometer with integrating sphere is ideal to characterize the optical properties of quantum dots. These instruments can be used in the R&D, manufacturing, and QA/QC process to measure product quality, and batch to batch uniformity. This paper looks at the 3D fluorescence and the fluorescence quantum efficiency characteristics of several commercially available CdSe / ZnS quantum dots.

■ Method for the Determination of Fluorescence Quantum Efficiency

An RF-6000 fluorescence spectrophotometer (*figure 1*) was equipped with a 100mm internal diameter integrating sphere (*figure 2*). The integrating sphere was set in the direct excitation position, so the excitation beam would be incident on the sample. Fluorescent photons were "captured" by reflecting inside the integrating sphere and ultimately emitted out of the emission window to the detector.

Figure 1: RF-6000 fluorescence spectrophotometer

Figure 2*:* Top view of the integrating sphere (open position) within the sample compartment of an RF-6000, cuvette holder is in direct excitation position.

To determine the optimal wavelength to be used in quantum efficiency measurements, a 3D fluorescence spectrum (Fluorescence Excitation-Emission matrix) was acquired for each sample using the 3D module of Shimadzu LabSolutions RF software. The excitation wavelength resulting in the highest emission was chosen. Rayleigh scatter and second order Rayleigh scatter peaks were easily identified and ignored using the emission/excitation 3D matrix (*figure 3*).

Quantum efficiency measurements were performed in two steps using the Quantum Efficiency module of LabSolutions RF software. First, a measurement was conducted with an empty integrating sphere. This measurement captured characteristics of the excitation beam and instrument and integration sphere optical conditions. Second, a measurement was conducted with a sample in place. From these two data sets, LabSolution RF calculated the absorbed fraction and internal and external quantum efficiencies.

- Irradiated Light Area (S_{rd}) = Integration of peak centered at excitation wavelength of blank.
- Scattered Light Area (S_{sc}) = Integration of peak centered at excitation wavelength of sample.
- Baseline Area (S_{bl}) = Integration of peak on emission wavelength range of blank.
- Emission Area (S_{em}) = Integration of peak on emission wavelength range of sample.
- Absorbed Fraction
$$AF = \frac{S_{rd} - S_{sc}}{S_{rd}}$$
- Internal Quantum Efficiency
$$QE_{in} = \frac{S_{em} - S_{bl}}{S_{rd} - S_{sc}}$$
- External Quantum Efficiency
$$QE_{ex} = \frac{S_{em} - S_{bl}}{S_{rd}}$$

Absorbed fraction (AF) expresses the ratio of photons that are absorbed by a sample to the total available excitation photons. For example, an AF of 0.9500 indicates that 95% of the excitation photons are absorbed by the sample. Internal quantum efficacy (QE_{in}) expresses the ratio of the fluorescent light emitted by a sample to the excitation light absorbed by it. For example, a QE_{in} of 0.4000 indicates that 40% of the excitation photons absorbed by a sample are emitted at a longer wavelength. External quantum efficiency (QE_{ex}) expresses the ratio of the fluorescent light emitted by a sample to the excitation light incident upon it. For example, a QE_{ex} of 0.3000 indicates that 30% of the excitation photons incident on a sample are emitted at a longer wavelength.

■ Measuring the Quantum Efficiency of Quantum Dots

Samples of cadmium selenide core, zinc sulfide shell quantum dots suspended in a urethane polymer and cast in plastic cuvettes were acquired from a commercial source. Measurements followed the following procedure.

1. With nothing in the integrating sphere and the sample compartment closed to prevent stray light, instrument was autozeroed.
2. Sample was placed in the cuvette holder of the integrating sphere in the direct excitation position. Integrating sphere and sample compartment lids were closed.
3. 3D scan was performed using method parameters in *table 1*.
4. Excitation wavelength resulting in a maximum emission was found and the emission spectrum was extracted.
5. Sample was removed from integrating sphere.
6. Steps 2 through 5 were repeated for the rest of the samples.
7. Quantum efficiency scan was measured using method parameters in *table 2* with an empty integrating sphere.
8. Sample was placed in the cuvette holder of the integrating sphere in the direct excitation position. Integrating sphere and sample compartment lids were closed.
9. Quantum efficiency scan was measured also using method parameters in *table 2*.
10. LabSolutions RF automatically integrated all peaks and calculated AF, QE_{in}, and QE_{ex}.
11. Steps 7 through 10 were repeated for the rest of the samples.

Table 1: 3D scan method parameters.

Parameter	Value
Measurement Type	Emission/Excitation 3D
EX Wavelength Start	350.0 nm
EX Wavelength End	800.0 nm
Data Interval	5.0 nm
EM Wavelength Start	375.0 nm
EM Wavelength End	825.0 nm
Data Interval	5.0 nm
Scan Speed	6000 nm/min
EX Bandwidth	5.0 nm
EM Bandwidth	5.0 nm
Sensitivity	Low

Table 2: Quantum efficiency method parameters.

Parameter	Value
Excitation Wavelength	470 nm (Set to max from 3D plot)
Emission Wavelenght Range	Automatically set
Data Interval	1.0 nm
Scan Speed	6000 nm/min
Excitation Bandwidth	5.0 nm
Emission Bandwidth	5.0 nm
Sensitivity	Auto

A representative 3D fluorescence spectrum is shown in *figure 3*. It shows a maximum excitation at 470.0 nm. The extracted emission spectrum is shown in *figure 4*.

The quantum efficiency spectra are shown in *figure 5*. Maximum excitation wavelengths and quantum efficiencies results are presented in *table 3*.

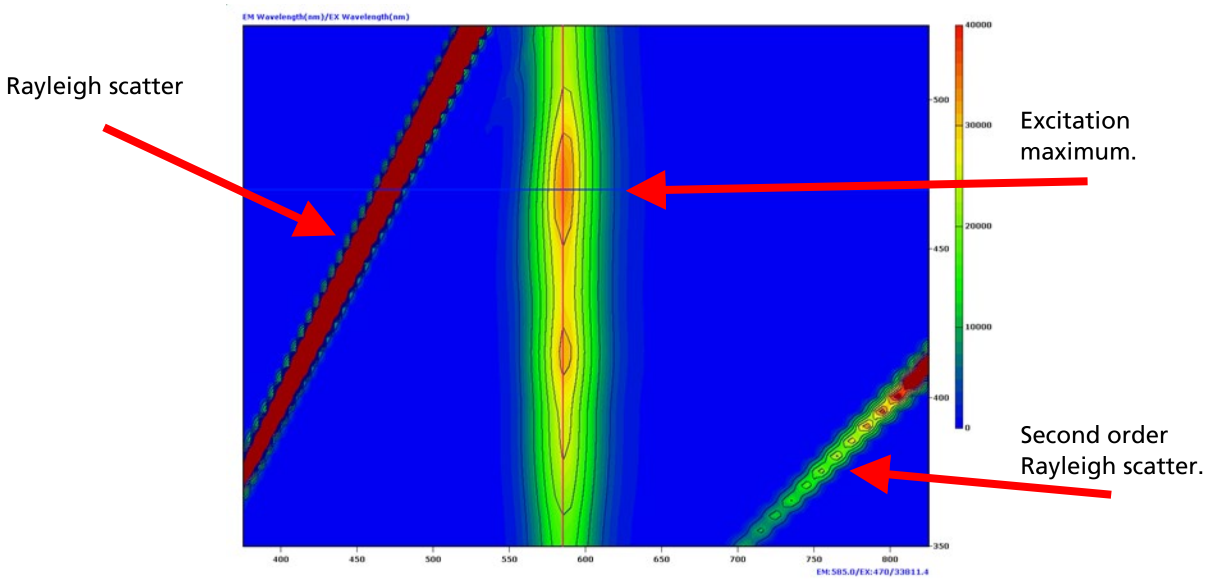

Figure 3*:* 3D spectrum of quantum dot sample.

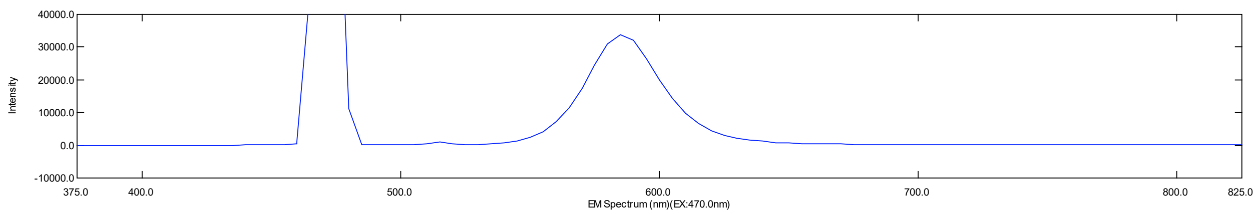

Figure 4: Emission spectrum of quantum dot sample.

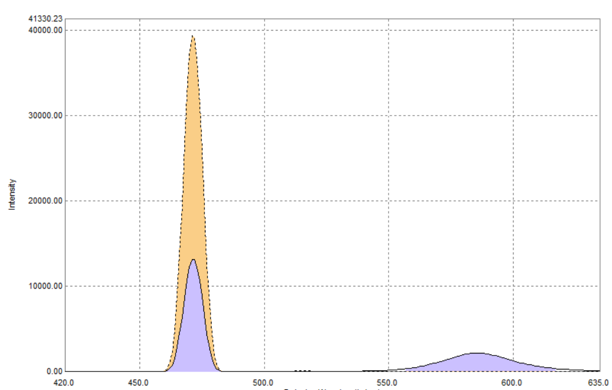

Figure 5: Quantum efficiency spectrum of quantum dot sample.

Table 3: Quantum efficiency results for quantum dot samples. Saturated peak around 480 nm is due to Rayleigh scatter.

Quantum Dot	Ex Max	AF	QE_{in}	QE_{ex}
Sample 1	405 nm	0.9493	0.0337	0.0320
Sample 2	420 nm	0.7215	0.1759	0.1269
Sample 3	470 nm	0.6668	0.2997	0.1998
Sample 4	505 nm	0.6637	0.0960	0.0637
Sample 5	555 nm	0.8398	0.0336	0.0282

■ Conclusion

The 100 mm integrating sphere seamlessly integrates with the RF-6000 fluorescence spectrophotometer and LabSolutions RF software to provide a simple and streamlined workflow for measuring 3D fluorescence and fluorescence quantum efficiencies.

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SHIMADZU

SHIMADZU Corporation
www.shimadzu.com/an/

SHIMADZU SCIENTIFIC INSTRUMENTS
7102 Riverwood Drive, Columbia, MD 21046, USA
Phone: 800-477-1227/410-381-1227, Fax: 410-381-1222
URL: www.ssi.shimadzu.com