Optical Properties of Fluorescent Mixtures: Comparing Quantum Dots to Organic Dyes

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Optical Properties of Fluorescent Mixtures: Comparing Quantum Dots to Organic Dyes

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Semiconductor nanocrystals, or quantum dots (QDs), exhibit size-dependent optical properties *(1)*. Both emission and absorption are affected by the size of the particle, so that these attributes are easily tuned during synthesis. Because of the simple relationship between size and fluorescence in QDs, optical tunability is controlled by growth time during the reaction, and a single preparation of particles can yield samples that are fluorescent over a range of colors from blue to red. Eye-catching QDs are therefore attractive candidates for both classroom demonstrations and laboratory experiments. The synthesis and analysis of QDs in undergraduate laboratories has been recently described *(2),* while separate articles targeted at upper-level undergraduates discussed the size dependence of QD emission as a qualitative comparison to the quantum mechanics of a particle-in-a-box in classroom *(3)* and laboratory *(4)* environments. This article is intended for use as a lecture demonstration to display the unique properties of QD mixtures or, alternatively, to provide a hands-on laboratory experiment for both less-experienced and more-advanced students.

Quantum dots have unique advantages compared to typical fluorescent materials: QD fluorescence is synthetically tunable across a broad wavelength range, and mixtures of different sizes (i.e., colors) have the unique property of additive color. That is, all QD particles in a mixture are photoexcited using a *single* UV excitation wavelength, leading to fluorescence emission that appears to be their combination: a blend of red, green, and blue fluorescing QDs will produce white light. This is fundamentally different from a mixture of common fluorophores, such as organic dyes, which typically fluoresce a single color from one component owing to difference in the energy required to excite the different dye molecules. These differences can be easily seen using a simple store-bought black light as the UV excitation source so that the QDs can be used in both classroom demonstration and lab environments.

This article (and the Laboratory Documentation in the Supplemental Material[W]) explores the optical properties of mixtures of quantum dots and compares these results to fluorescent organic dyes. We discuss the differences in absorption and fluorescence between quantum dots and organic dyes and analyze the results with descriptions from the perspective of general chemistry to more advanced energy transfer and quenching mechanisms. QDs are thus a platform for introducing spectroscopy and nanometer-scale materials: we divide the Laboratory Documentation[W] into three sections of variable complexity as follows. For high school students with little spectroscopy background, QDs can be used as a classroom demonstration (section 1: Classroom Demonstration) and understood from simple principles: when an excited molecule relaxes it may emit energy in the form of light. A general chemistry (undergraduate or advanced high school) class can use measurements and visualization of QD optical properties to understand electronic transitions and the relative energies involved in absorption and fluorescence (section 2: Beginning Student Lab). Guided by the ideas presented in the context of the laboratory, students apply analytical techniques and use experimental data to understand the properties of nanomaterials. Advanced undergraduates can combine these tools with a synthetic section (section 3: Advanced Student Lab) in a comprehensive experiment that includes synthesis, analysis, and application. This experiment may also be tailored to teach material outside the scope of traditional courses, including nanomaterials, semiconductor physics, and quantum mechanics, using the physical properties of quantum dots. Despite the advanced applications envisaged for quantum dots, they can be analyzed using relatively simple observations (i.e., color changes that are easily seen by the eye) and quantitatively measured in basic UV–vis absorption and fluorescence spectroscopy experiments.

Experimental

Nanocrystal Synthesis

A recent report in this *Journal (2)* provides a concise experiment for the synthesis of CdSe nanocrystals; an alternative synthesis is provided here.[1]

Chemicals Required

CdSe quantum dots, toluene, organic fluorophore dyes.

Fluorescence and Absorption Measurements

Fluorescence and absorption measurements can be used in addition to simple visual inspection to analyze the samples. The color changes in the mixtures are easily detected by the eye and with careful addition of two components the mixing process can be observed. For a more quantitative analysis, absorption and fluorescence spectra of samples and samples mixtures are measured using the appropriate spectrophotometers.[2]

Equipment and Instrumentation

These experiments can be tailored to suit the needs of the course and availability of equipment and instrumentation. In addition to general glassware and supplies, the following is a list of the equipment and instrumentation for the completion of the lab. The minimum requirements call for at least two colors of QDs (either synthesized or purchased from commercial sources) and a fluorescent black light to allow an instructor to demonstrate the mixing of QDs and their additive emission. For a complete lab experiment, at least four colors of QDs, four colors of organic dyes (or other fluorophores), and a fluorescent black light are necessary. While examples of spectra are provided in the Supplemental Material,[W] a UV–vis absorption spectrophotometer and a fluorometer[2] are needed for students to acquire their own spectral data.

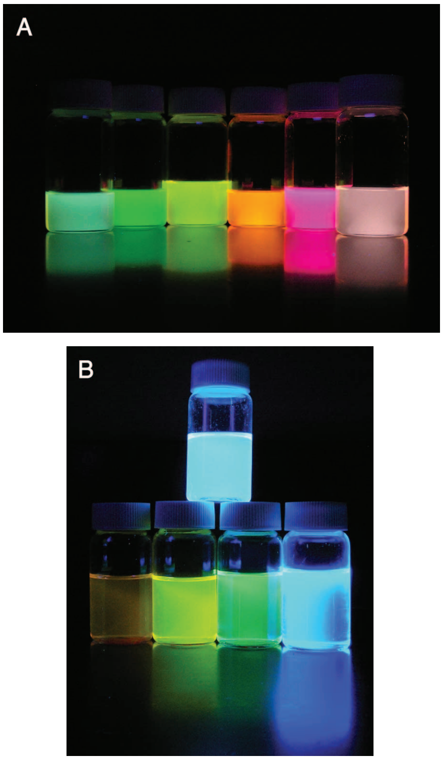

Figure 1. (A) A series of CdSe QDs prepared in this experiment (5 vials on left) and a mixture of these components (right) illuminated with a black light and (B) a series of dyes (bottom: rhodamine 610, rhodamine 590, coumarin 6, and coumarin 460), and a mixture of the dyes (top) illuminated with the same black light (see p 1235 for colored versions of these images).

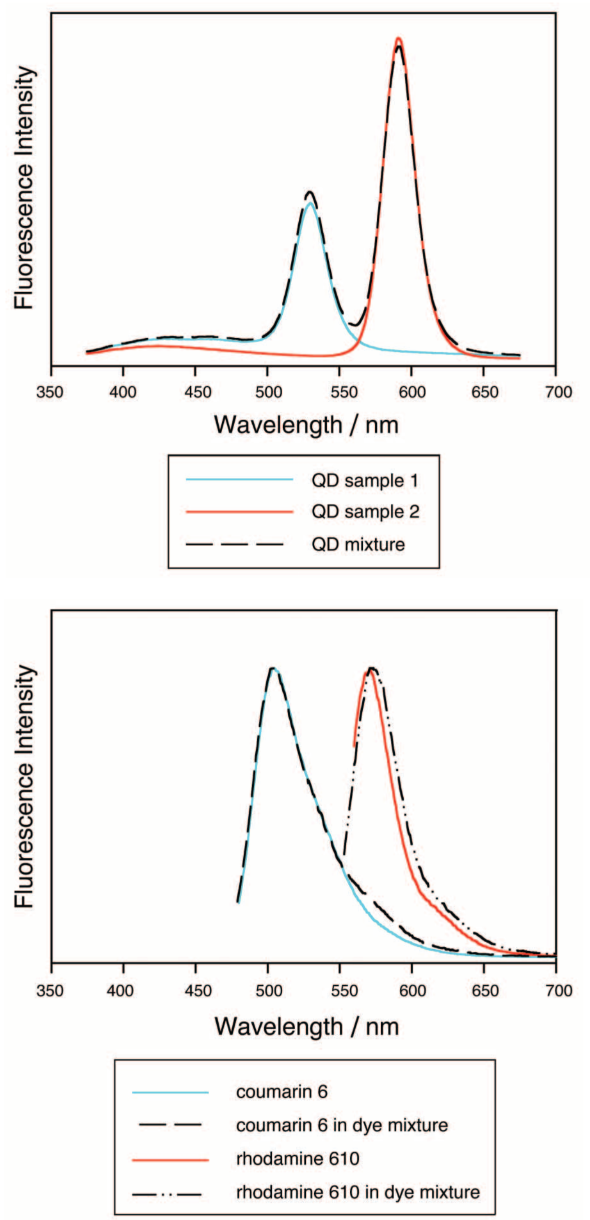

Figure 2. Fluorescence emission spectra of two different mixtures: (A) QD mixture containing two sizes of QD, excited at 350 nm, and (B) a mixture of coumarin 6 and rhodamine 610 that were excited at 469 nm and 543 nm, respectively.

Hazards

CdSe nanocrystal samples contain toxic materials including cadmium, selenium, and toluene. Elemental selenium is toxic by inhalation, contact, and ingestion. Cadmium is a probable carcinogen and toxic by inhalation and contact. Toluene is harmful or fatal by ingestion and inhalation, and is a probable carcinogen. Some organic dyes may be toxic or carcinogenic and appropriate precautions should be taken. Always wear gloves and safety goggles. Waste should be collected for proper disposal.

Results and Discussion

Solutions of mixtures of QDs of different sizes emit colors that are the sum of the fluorescence wavelengths of the individual QD components. Both binary and ternary mixtures exhibit this additive emission that is possible to see with the naked eye using a black light excitation source. For example, when students mix red and yellow quantum dots, the resulting solution emits orange light. When mixed in the appropriate relative quantities some QD mixtures emit nearly white light (Figure 1A). On the other hand, when organic dyes are mixed, the black light excites only a single species and so only one emission color is observed (Figure 1B). Why would that be?

To understand why mixtures of quantum dots and organic dyes have different appearances, their optical properties are quantitatively measured using absorption and fluorescence emission spectroscopy. The wavelength of maximum peak in the fluorescence spectrum corresponds to the color of light that is emitted *(5)*. The fluorescence spectrum of a binary mixture of QDs (such as red and green) compared to those obtained of its individual components are shown in Figure 2A: two peaks are observed in the mixture, one corresponding to each individual component. In contrast, the fluorescence emission spectrum of a binary mixture of organic dyes (rhodamine 610 and coumarin 6), shown in Figure 2B, contains only one dominant peak that depends on the excitation wavelength rather than the components in solution. The emission spectra are consistent with the colors observed with the black light: all mixtures of organic dyes have one dominant emission peak in their spectrum and therefore only one is visually observed. The emission spectra of QD mixtures contain as many peaks as the number of particle components, and because light is emitted at each of those wavelengths, we visually observe the sum of all of them. It is therefore only possible to produce white light emission using mixtures of QDs and *not* organic dyes.

This experiment has been used as a lecture demonstration or a complex lab for advanced chemistry students and may be adapted as a simple experiment for beginning undergraduate students using the provided materials (see the Supplemental Material^W^). As part of the development of the laboratory component, an advanced undergraduate spectroscopy class (16 students in 4 groups) performed the synthesis and characterization experiments described in the Supplemental Material.^W^ Quantum dot synthesis was performed in one lab session, and the mixtures were prepared and analyzed in a second lab session. In addition to characterizing the synthesized materials and measuring the spectra of the mixtures, students applied their knowledge of electronic transitions to elucidate the differences in the spectroscopic behavior of the dyes and quantum dots.

Conclusions

These results and observations demonstrate that mixtures of QDs uniquely possess emission colors that are the sum the individual QD components so that even white light can be produced from simple mixtures. These are contrasted and compared to observations using mixtures of organic dyes, and the results interpreted using fluorescence emission spectra. Students are able use these experiments to both gain hands-on experience and deeper understanding of spectroscopy and fluorescence, and to manipulate nanomaterials with unique optical properties that are of intense interest in modern research and technology.

Acknowledgments

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^W^Supplemental Material

Notes for the instructor, demonstration techniques, handouts and answer keys for the beginning- and advanced-undergraduate student lab, and sample data are available in this issue of *JCE Online*.

Notes

1. Considerations for the difficulties of QD synthesis are further described in the Supplemental Material,^W^ as well as listings of commercially available QDs.

2. Student-built spectrophotometer experiments are found elsewhere *(6),* and may be used in the absence of a fully electronic fluorescence spectrometer.

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