"In-Situ" Monitoring of CdSe/ZnS Quantum Dot Growth During Microwave Synthesis

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ABSTRACT

We have studied the use of in-situ fluorescence spectroscopy for the optimization of a microwave synthesis of CdSe/ZnS core-shell quantum dots. In this research we demonstrate the usefulness of coupling a fluorescence spectrometer to the microwave reactor to quickly determine a range of appropriate temperatures and times to further optimize from. In contrast to previously published work, we determined that the microwave reaction temperature does not affect the fluorescence properties of our CdSe/ZnS particles within a range of 130 to 155 °C. Additionally, through more careful optimization, we have improved our previously published quantum yield of 13% to 19%.

Keywords: quantum dots, synthesis, microwave, in-situ monitoring

1 INTRODUCTION

Quantum dots, fluorescent nanoscale semiconductors, have many potential uses in biology and materials science due to their high quantum yields and resistance to photo bleaching that affects organic dyes. The high costs of these materials make them less likely to be commercialized into new technologies, so there is a current effort to develop simplified, highly scalable synthesis methods. One such method is to synthesize the particles in a microwave reactor. This has led our lab to develop a fast, "one-pot" synthesis that produces stable, aqueous CdSe/ZnS core/shell quantum dots [1]. While they are significantly less expensive to produce, these particles have a lower quantum yield, 15%, than we have measured for comparable commercially produced quantum dots, 90%.

In order to gain a better understanding of the microwave synthesis and fully optimize it, we have coupled our microwave reactor to a fluorescence spectrometer via fiber optic cables (set up shown in Figure 1). This allows for the particles to be monitored as they are synthesized. To our knowledge this is the first time that nanoparticle synthesis has been monitored in real-time in a microwave reactor.

2 EXPERIMENTAL DESCRIPTION

2.1 Materials

Cadmium chloride hemipentahydrate (CdCl2·2.5 H2O, >98 %) and sodium borohydride (NaBH4, 99 %) were obtained from Aldrich (Milwaukee, WI, USA). Zinc chloride (ZnCl2, 99.99 %), 3-mercaptopropionic acid (MPA), and selenium powder (Se, 99.5+ %, 200 mesh) were obtained from Acros (Geel, Belgium). Sodium hydroxide (NaOH) and ammonium hydroxide (NH4OH, 28 – 30 %) were obtained from Mallinckrodt Chemicals (Phillipsburg, NJ, USA). All chemicals were used without further purification. The H2O used in this study was purified by a Barnstead NANOpure Infinity ultrapure water system (Dubuque, IA, USA).

2.2 Quantum Dot Synthesis

Cadmium selenide core/zinc sulfide shell quantum dots were produced with a negatively charged capping agent, 3-mercaptopropoionic acid (MPA), in a previously reported microwave synthesis [1]. Briefly, fresh solutions of NaHSe were prepared by mixing $NaBH_4$ with H_2O followed by the addition of Se powder under an inert environment (N_2). The components reacted for roughly 3 hours, and then supernatants containing NaHSe were diluted to 20 mM using N_2-saturated H_2O. A solution of Cd-MPA was created by mixing MPA in H_2O with 5.0 mM $CdCl_2 \cdot 2.5\ H_2O$ stock solution, adjusting the pH to 9.5 using 1 M NaOH, and held at room temperature until needed. Last, a 60 mM $Zn(NH_3)_4^{2+}$ stock solution was prepared by dissolving $ZnCl_2$ in H_2O and titrating with NH_4OH, and was stored at 4°C. Nucleation of CdSe dots occurred when the NaHSe stock was injected into Cd-MPA solution. This mixture was stirred for one hour prior to the addition of the $Zn(NH_3)_4^{2+}$ stock solution. These contents were then microwave irradiated at various temperatures and times.

2.3 In-Situ Fluorescence Spectroscopy

In-situ fluorescence measurements were made with a Discover SP (CEM) microwave system and Horiba Jobin Yvon Fluorolog 3 Fluorometer during quantum dot synthesis. The Discover SP system is configured with a port hole for use with a camera attachment to image the sample during heating. Figure 1 shows the fiber optic attachment of the Fluorolog 3 fluorometer inserted into the Discover SP microwave. A fitting was fabricated to hold the fiber optic cable in place. No further modifications were necessary to

obtain fluorescence measurements from the microwave reaction chamber.

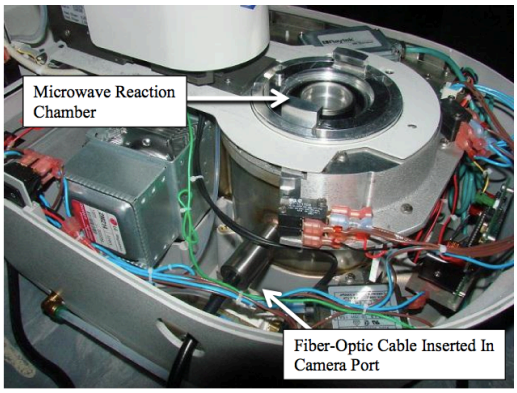

Figure 1: Fluorometer/Microwave Reaction Coupling

Batch runs were set up using the fluorometer software to take spectra throughout the microwave heating. A significant fluorescence emission near 500 nm was present when using the typical 375 nm excitation wavelength used in characterizing the synthesized quantum dots. This peak was also observed when the microwave chamber was empty. Moving the excitation wavelength from 375 nm to 480 nm eliminated the background fluorescence of the chamber, and still excited quantum dot emission. A 6 nm band width was used for both the excitation and emission monochromators. The emission wavelength was scanned from 500 to 750 nm.

Figure 2 shows an example plot of the fluorescence during a 150 °C microwave synthesis. The x and y axes are emission wavelength and fluorescence intensity, and the z axis is time. The initial spectrum is prior to microwave heating. An intermediate species with an emission peak at approximately 502 nm is noted, and its relevance is being examined.

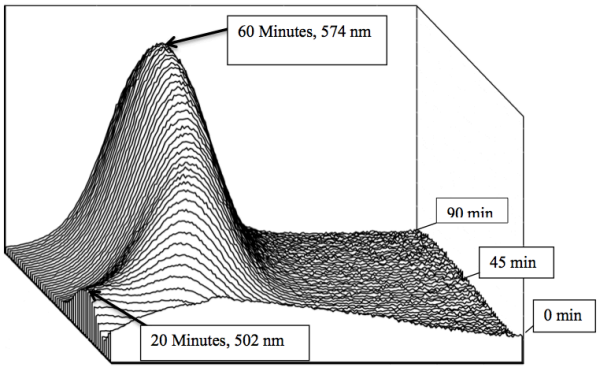

Figure 2: Time Dependent Fluorescence of QDs During Microwave Synthesis

2.4 Temperature Optimization

To determine the optimal temperature of synthesis, the reactants were heated at temperatures varying between 125 and 160 °C in 5-degree increments. The 125 and 160 °C reactions did not result in any fluorescent products, so only the reactions between 130 and 155 °C were compared. An appropriate reaction time for each temperature was determined by choosing the time at which the fluorescence of the quantum dot peak stopped increasing, as demonstrated in Figure 3. Reaction times varied from 27 minutes at 155 °C to 4 hours and 20 minutes at 130 °C. A synthesis was then carried out at each determined temperature and time, and a quantum yield was measured for each sample. The results are summarized in Table 1.

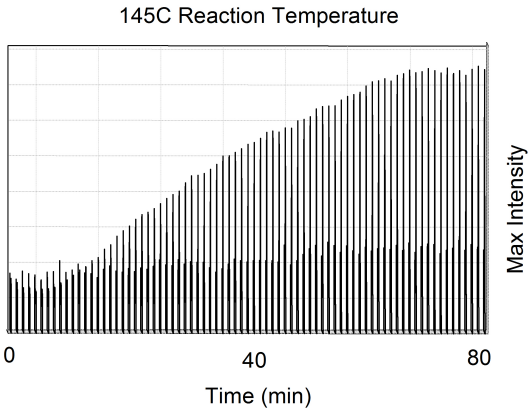

Figure 3: Max Intensity vs. Time for 145 °C Reaction Temperature

Synthesis Temperature (°C)	Synthesis Time (min)	Quantum Yield (%)
155	27	4.1
150	51	5.8
145	72	7.7
140	88	6.7
135	122	6.4
130	260	9.4

Table 1: Temperature Optimization Data

2.5 Time Optimization

To determine the optimal time of synthesis, several reactions were completed at times varying from 4 to 6.5 hours. Quantum yields were measured for each synthesis. This data is summarized in Table 2.

Synthesis Time (hrs)	QD/TS Peak Ratio	Quantum Yield (%)
4	6	6.5
4.5	12	11
5	17	12
5.5	17	11
6	19	14
6.5	11	11

Table 2: Synthesis Time Optimization for 130 °C

Because this resulted in the same quantum yield as previously obtained with the published 150 °C reaction, we also optimized our highest temperature, 155 °C, to determine if the temperature has any effect on the fluorescence of the quantum dots. This data is summarized in Table 3.

Synthesis Time (min)	QD/TS Peak Ratio	Quantum Yield (%)
30	11	7.1
35	8	8.2
40	11	9.4
45	18	19
50	11	10

Table 3: Synthesis Time Optimization for 155 °C

3 DISCUSSION

Our initial optimization at 130 °C yielded particles which were the same as our previously published 150 °C synthesis. This indicates that the temperature does not affect the quality of the particles. To test this, we also optimized at our highest temperature, 155 °C. While this temperature did result in a higher quantum yield of 19%, this is still significantly lower than the current commercialy available particles (90%).

We believe that the higher quantum yield of the 155 °C synthesis is the result of a higher degree of precision in its optimization, within 5 minutes, compared to the 30 minute intervals of the slower 130 °C synthesis. We conclude that within this range, the temperature of microwave irradiation only affects the speed of the synthesis, not the quantum yield of the particles.

We have demonstrated for the first time the potential utility of optimizing a microwave reaction by in-situ fluorescence spectrometry. In this case we have studied a previously optimized reaction. This method could be used to easily determine an optimal time and temperature for any microwave synthesis which results in fluorescent particles. This could also be expanded to take advantage of other spectroscopic properties such as UV-Vis or infrared absorbance.

REFERENCES

[1] Schumacher W., Nagy A., Waldman W.J., & Dutta P.K. Direct Synthesis of Aqueous CdSe/ZnS-Based Quantum Dots Using Microwave Irradiation. *The Journal of Physical Chemistry C* **113**, 12132-12139 (2009).