Continuous real-time monitoring of quantum dot synthesis within microfluidic reactors

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Abstract

Currently, one of the primary challenges associated with the synthesis of quantum dots or nanoparticles in bulk reaction chambers is the ability to control the nucleation and growth of clusters. Consequently, the ability to monitor particle formation in real time is highly desirable. Herein we demonstrate a strategy based on continuous-flow microfluidic reactors to monitor CdSe nanoparticle formation in real time.

Keywords: Confocal spectroscopy, Quantum dots, Microfluidic reactors, real-time monitoring

1. Introduction

Semiconductor quantum dots (QD) are currently a subject of intense research. QDs describe materials with dimensions in transition regime between molecules and bulk solids. Due to quantum confinement effects QDs show unique physical and chemical properties such as size-dependent band gap shifts and size dependent photoluminescence. Consequently, there is considerable interest in synthesis routes that yield nanoparticles of well-defined sizes [1]. Currently, one of the primary challenges associated with the synthesis of QDs in bulk reaction chambers is the ability to control the growth of the clusters. Consequently, the ability to monitor the formation of particles in real time is highly desirable. Herein we demonstrate a strategy based on continuous-flow microfluidic reactors and confocal spectroscopy to synthesize and monitor CdSe nanoparticle formation in real time.

The ability to monitor the formation of particles in real time is highly desirable. Herein we demonstrate a strategy based on continuous-flow microfluidic reactors and confocal spectroscopy to synthesize and monitor CdSe nanoparticle formation in real time. Current real time microfluidic monitoring techniques are typically based on using flow cells coupled to a micromixer. Although this approach is viable, dead volumes are generally much greater than when monitoring a reaction directly within the walls of a microfluidic reaction chamber. An example of this was demonstrated by Edel et al. CdS nanoparticles...
synthesized by hydrodynamically delivering the reactants into a microfluidic channel network at various flow rates (1-600 µL/min) [2].

2. Experimental

CdSe particles were synthesized as follows. Selenium powder (9.5 mg) was dissolved in trioctylphosphine (TOP, 2 mL) under dry nitrogen with vigorous stirring. Cd(OAc)$_2$ (6.5 mg) and trioctylphosphine-oxide (TOPO) (300 mg) were then added to the solution. A syringe pump (PHD 2000, Harvard Instruments) was then used to deliver the precursor solution into the microfluidic channel at a variety of flow rates (0.1–10 µL/min). Nucleation and nanoparticle growth is initiated by heating the entire chip substrate to between 180 and 290 °C. Residence times within the microfluidic chip ranged from 10 – 200 s. Reaction products were monitored on-line using a home built confocal fluorescence spectrometer (CFS).

A schematic of the spectrometer is shown in Figure 1. Precise details of the experimental system are described elsewhere [3]. A picosecond pulsed diode laser (at 438 nm) was used for all fluorescence lifetime measurements. Since fluorescence decaytimes were greater than 200 ns a laser repetition rate of 600 kHz was used. Fluorescence emission spectra were obtained using the 458 nm line from a multi-line CW air-cooled argon ion laser.

![Figure 1. Schematic of the confocal spectrometer](image)
3. Results and discussion

Figure 2 shows photoluminescence (PL) spectra of CdSe nanoparticles synthesized and monitored in real-time at a temperature of 290 °C. It is interesting to note that as the reactant flow rate is decreased spectra gradually shift to higher energies. This is a result of reactants spending increased times within the microfluidic system (yielding longer nucleation times) and forming larger nanoparticles. PL spectra provide a direct method of sizing nanoparticles as peak maxima are governed by the average particle size and the full width half maximum of the emission is directly related to the polydispersity of the particle population. Figure 3 shows a fluorescence decay of a CdSe particles synthesized at 290 °C and at a flow rate of 2 µl/min. Analysis of the decay profile yielded a tri-exponential decay law with component lifetimes of 274 ns, 72.9 ns, and 7.55 ns.

Figure 2. Photoluminescence spectra of CdSe nanoparticles synthesized at 290 °C and at flow rates ranging from 0.5 – 2 µl/min.

Figure 3. Fluorescence lifetime decay of CdSe nanoparticles synthesized at 290 °C and a flow rate of 2 µl/min within a microfluidic channel.
QDs tend to be highly photostable and fluorescence decay lifetimes range from nanoseconds to microseconds and hence, these particles would appear to be ideal for single molecule spectroscopy due to its improved spectral properties over typical organic dyes such as R-Phycoerythrin or rhodamine 6G. QD's such as CdSe also tend to have a much narrower full width half maximum (FWHM) and much more symmetrical emission spectra when compared to their organic counterparts. The benefits can be clearly seen in the single CdSe solution state burst spectra shown in Figure 4. This was obtained using the same confocal spectrometer described above. The overall signal to noise is much higher as well as the burst widths are more uniform than when compared to single molecule spectra of organic dyes such as rhodamine.

Figure 4. Single molecule detection of CdSe within a microfluidic channel

4. Conclusions

In this publication we have demonstrated a method for the monitoring the formation of quantum dots in continuous real-time using confocal spectroscopy. The same confocal fluorescence spectrometer was also used to show single molecule detection capability of the CdSe nanocrystals in the solution state.

References