Emission-tunable microwave synthesis of highly luminescent water soluble CdSe/ZnS quantum dots†

Marc D. Roy,[a] Andrew A. Herzing,[b] Silvia H. De Paoli Lacerda[a] and Matthew L. Becker*[a]

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Water soluble CdSe/ZnS nanoparticles with emission maxima from 511 nm to 596 nm and quantum efficiencies ranging from 11% to 28% are synthesized in a facile two-step method in ambient atmospheric conditions using a commercially available microwave reactor.

Uses for efficient and stable water soluble quantum dots are abundant, especially within biological applications.[1] However, conventional synthetic routes for producing such materials require significant time, skill[2] and typically rely upon a post-synthetic ligand exchange,[3] silica shell encapsulation,[4] or surface ligand interdigitation[5] procedure. These processes have been shown to significantly alter the luminescence, stability and ''blinking'' behavior of the as-synthesized material.[6] Simpler approaches for the synthesis of water soluble quantum dots have been reported, yet these protocols involve considerable preparative time or require custom starting materials that are not commercially available.[7] Recently, biological molecules have also emerged as a tool to template quantum dot nucleation and growth;[8] however the luminescence of these materials is lower than those prepared using conventional ligands.

Microwave syntheses for organic soluble CdSe/ZnS[9] and CdTe[10] nanocrystals have been reported previously, but have relied on inert atmospheres. Microwave-assisted synthesis has been used increasingly to significantly reduce the time and temperature involved with many chemical reactions.[11] Extending this approach, we have devised a facile, tunable synthetic procedure involving commercially available starting materials for the preparation of stable, highly luminescent, water-soluble CdSe/ZnS quantum dots in ambient atmospheric conditions.‡

Briefly, cadmium acetate ($Cd(CH_3COO)_2$) is dissolved by heating in trioctyl phosphine oxide (TOPO) and hexadecylamine (HDA) and allowed to cool. Separately, elemental selenium powder is added to trioctylphosphine (TOP) and mixed vigorously until dissolved. Next, the selenium solution is added to the cadmium containing mixture and mixed thoroughly. The sample is then heated and irradiated—while stirring—to allow for nucleation and growth of the nanoparticles. Unlike conventional syntheses, each step of this procedure is performed on the benchtop under normal atmospheric conditions. After the initial irradiation, the core CdSe particles are allowed to cool and are immediately precipitated with methanol and dried under vacuum. The addition of a zinc sulfide shell and water solubilization is then achieved using a strategy similar to that reported by Wang and coworkers.[12] Specifically, dried core CdSe nanoparticles are resuspended in 1-methyl-2-pyrrolidinone (NMP), 3-mercaptopropionic acid (3-MPA), hexamethyldisilathiane and butylamine. Separately, butylamine, 3-MPA and diethyl zinc (in heptane) are added to NMP and heated to dissolution. The solution is allowed to cool to room temperature, after which the CdSe particle solution is added. This mixture is then heated at 70 °C to facilitate shell formation. The core/shell CdSe/ZnS nanoparticles are then extracted three times with hexanes and precipitated with toluene.

Precipitated particles are dried under vacuum and re-suspended in phosphate buffered saline (PBS). Employing this approach, nanoparticles with emission maxima ranging from 511 nm to 596 nm (Fig. 1) were synthesized by simply altering the time and/or temperature applied (Table 1). The reactions are performed at ambient atmospheric conditions over a period of minutes and at lower temperatures than used conventionally in the preparation of CdSe/ZnS nanoparticles.

Under the prescribed conditions, the particle size distribution—as measured by TEM—is nearly monodisperse, with the polydispersity increasing slightly as the time of synthesis is increased. Most importantly however, these nanoparticles exhibit spectral properties in the emission range desirable for many fluorescence-based microscopy applications. Specifically, luminescence quantum efficiency values range from 11% to 28% in PBS, while the FWHM emission properties vary from 70 nm to 36 nm. Following four months of storage under ambient temperature and atmospheric conditions, the spectral properties were reassessed to gauge the stability of the nanocrystals. The only sample to exhibit blue-shifted emission and luminescence loss typical of oxidative degradation was sample **1**. Here, an em_{max} shift from 511 nm to 465 nm was observed and the PLQE value was measured to be 6 ± 1%. The respective emission peak positions, FWHM and PLQE of **2–5** remained unchanged. The utilization of other capping

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[a] *Polymers Division, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, USA*
[b] *Surface and Microanalysis Science Division, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, USA. E-mail: mlbecker@nist.gov; Fax: +1 301 975-4977; Tel: +1 301 975-6842*

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‡ Although reactions were performed under ambient atmospheric conditions, the reaction vessels and microwave reactor were maintained in a chemical fume hood for safety. This is important to consider for groups not used to working with reactive inorganic materials, including diethyl zinc.

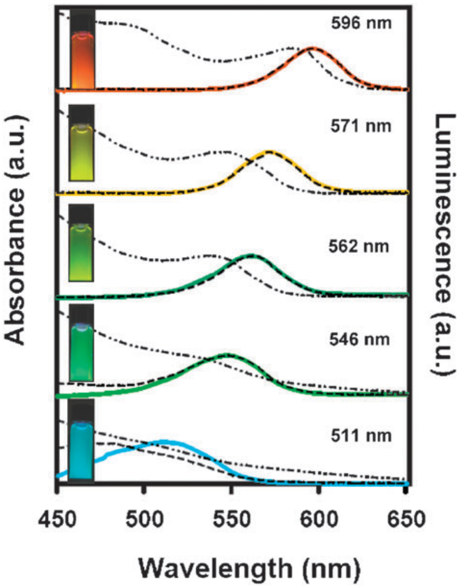

Fig. 1 Absorbance (dotted) and luminescence spectra of CdSe/ZnS nanoparticles in PBS buffer. Numbers indicate the emission maximum of each sample. Dashed black lines represent fluorescence spectra after 120 days of storage in PBS under ambient temperature and atmospheric conditions.

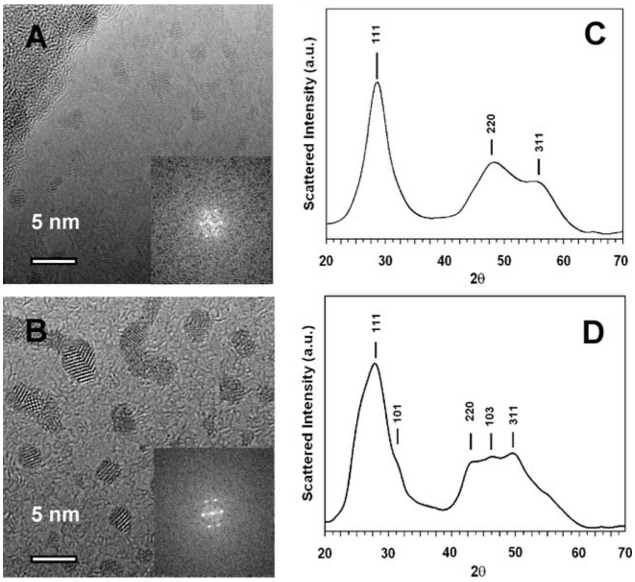

Fig. 2 Representative HRTEM images of CdSe/ZnS quantum dots **1** (A) and **5** (B). FFT diffractogram analyses of individual dots (inset) suggest that they exhibit the cubic zinc blende structure. X-Ray diffraction patterns of CdSe/ZnS particles exhibiting emission maxima of (C) 511 nm and (D) 596 nm.

Table 1 Fabrication conditions for water-soluble CdSe/ZnS particles. Values for full width half maximum (FWHM), average diameter and photoluminescence quantum efficiency (PLQE) are listed

	$\mathrm{Em_{max}}$/nm	Temp./°C	Time/min	FWHM/nm	Diameter/nm[a]	PLQE (%)[ab]
1	511	145	1.25	70	1.66 ± 0.28	14 ± 1
2	546	145	2.00	52	2.04 ± 0.45	11 ± 1
3	562	145	2.50	44	3.35 ± 0.32	27 ± 1
4	571	150	2.00	39	4.08 ± 0.51	28 ± 1
5	596	150	3.00	36	5.49 ± 0.59	24 ± 1

[a] Error represents standard deviation from the mean. [b] Photoluminescent quantum yield in comparison to fluorescein at 470 nm (0.93).[13]

agents which afford water soluble dots possessing functional handles and their stability in other biological buffers is the subject of a subsequent study.

High resolution TEM (HRTEM) imaging (Fig. 2) of samples **1** and **5** confirmed the size data obtained at lower magnification. Electron diffractograms produced *via* fast Fourier transform (FFT) of the lattice images of single dots indicated that, regardless of size, the samples exhibited the cubic, zinc blende structure with a majority of the particles lying in the [110] orientations with respect to the beam (Fig. 2A and B, insets). Finally, a number of the larger particles observed in **5** were found to be twinned, as is typical for particles in this size range (≈ 5nm).

X-Ray diffraction patterns representing samples **1** (Fig. 2C) and **5** (Fig. 2D) support the structural data obtained from the single particle diffractograms. The three characteristic reflection peaks—(111) at ≈28°, (220) at ≈48° and (311) at ≈56°—indicative of a zinc blende arrangement are well-defined in **1** (Fig. 2C). Under conditions that generate larger particles, **5**, additional peaks which are attributed to the wurtzite (101) and (103) reflections are observed (Fig. 2D). However, the wurtzite structure was not observed during the HRTEM analysis. Considering the higher temperature and longer time associated with the synthesis of larger particles, it is not surprising that a fraction of the population may possess the hexagonal arrangement, which has been established in the literature with conventional syntheses.[14]

In summary, we report a microwave-assisted approach for the synthesis of water soluble CdSe/ZnS quantum dots ranging in emission maxima from 511 nm to 596 nm. This method utilizes commercially available starting materials, short reaction times, lower reaction temperatures and is performed under ambient atmospheric conditions. The products obtained from our approach possess a high degree of crystallinity, high quantum efficiencies, narrow FWHM, and have demonstrated stability in aqueous buffer for more than four months.

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