Supplementary material (ESI) for Chemical Communications

Supporting Information

Emission-Tunable Microwave Synthesis of Highly Luminescent Water Soluble CdSe/ZnS Quantum Dots.

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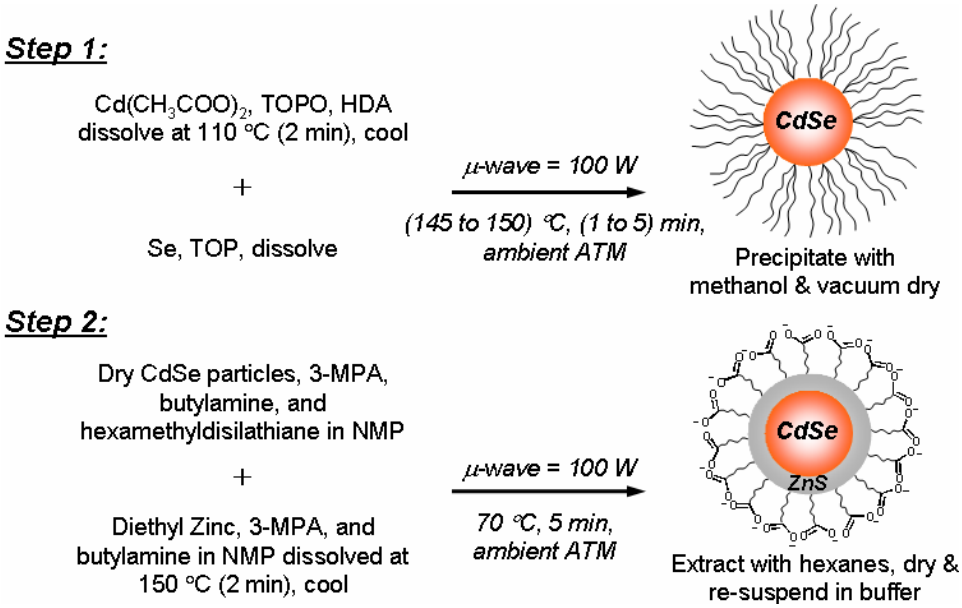

Scheme 1. Two step microwave synthesis of water soluble CdSe/ZnS quantum dots. TOPO = trioctylphosphine oxide, HDA = hexadecylamine, TOP = trioctylphosphine, 3-MPA = 3-mercaptopropionic acid, NMP = 1-methyl-2- pyrrolidinone

[*]Identification of a commercial product is made only to facilitate reproducibility and to adequately describe procedure. In no case does it imply endorsement by the National Institute of Standards and Technology or imply that it is necessarily the best product for the procedure.

Experimental Section

SAFETY NOTE

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.

Materials

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Cadmium Acetate (99 %), selenium (200 mesh) (99.9 %), trioctylphosphine (TOP) (99 %), hexadecylamine (HDA) (98 %), 1 mol/L diethyl zinc in heptane, 3-mercaptopropionic acid (3-MPA) (99 %), butylamine (99.5 %), anhydrous 1-methyl-2-pyrrolidinone (NMP) (99.5 %), and hexamethyldisilathiane were used as received from Aldrich. Trioctylphosphine oxide (TOPO, 99 %) was obtained from Alfa. Anhydrous methanol, toluene, hexanes and chloroform were purchased from Aldrich and used without further purification. Dulbecco's phosphate buffered saline (PBS) was purchased from Invitrogen.

Microwave synthesis of CdSe nanocrystals

In a typical synthesis of CdSe/ZnS water soluble quantum dots the core CdSe particles were first prepared under normal atmosphere by combining 100 μmol of cadmium acetate with 13 mmol of TOPO and 10 mmoles of HDA in a 50 mL round bottom flask and irradiated at 100 W power to 100 °C over 1 min at 100 W, followed by heating to 150 °C for 1 min and holding at 150 °C for 2 min. This solution was allowed to cool to 37 °C. Separately, 600 μmol of elemental selenium powder (200 mesh) was added to 2.0 mL of TOP under normal atmosphere and mixed vigorously until dissolved. Next, the selenium solution was added to the cadmium containing mixture and mixed thoroughly. The sample was then irradiated, while stirring, to 100 °C over 1 min at 100 W, followed by heating at 100 W power to the specified temperature for 1 min and holding at that temperature for the designated time. After heating the core CdSe particles were allowed to cool slowly and were immediately precipitated with methanol, and dried under vacuum. The preparation of the mixtures was carried out on the benchtop, while microwave heating was performed in a fume hood. In all cases the samples were under ambient atmospheric conditions.

Microwave synthesis of ZnS shell and water solubilization of CdSe nanocrystals

The core CdSe particles were reconstituted in 5.0 mL of NMP for shell preparation and water solubilization. Separately, 4.6 mmol of 3-MPA, 0.5 mmol of hexamethyldisilathiane and 3.0 mmol of butylamine were added to in 5.0 mL of NMP then mixed under ambient conditions with the CdSe particles in NMP. In a 50 mL round bottom flask 3.0 mmol of butylamine 4.6 mmol of 3-MPA and 0.5 mmol of diethyl zinc (1 mol/L in heptane) were added to 10.0 mL of NMP and heated while stirring to 100 °C over 1 min at 100 W, followed by heating at 100 W power to 150 °C for 1 min and holding at 110 °C for 2 min. This step should be performed in a fume hood with significant care, as the organo-metallic zinc is reactive with air. The solution was then allowed to cool to room temperature, after which the CdSe particle solution was added. This solution was then heated under normal atmospheric conditions at 100 W power to 50 °C for 1 min followed by heating to 70 °C for 1 min and holding that temperature for 5 min. The core/shell CdSe/ZnS nanoparticles were then extracted three times with hexanes and precipitated with toluene. Precipitated particles were dried under vacuum and resuspended in 1X phosphate buffered saline (PBS). Samples were stored at room temperature in the dark.

X-Ray Diffraction (XRD)

The crystal structure of the nanocrystals with (1.66 ± 0.28) nm (511 nm emission) and (5.49 ± 0.59) nm (596 nm emission) diameters were characterized by x-ray diffraction, using a 0.154 nm Cu Kθ Ni-filtered source. Diffractograms were recorded from purified and precipitated powder using a Rigaku reflectometer operated in reflectance mode at 1600 W, with an exit angle 2 ° and entrance slits. A 2θ diffraction angle was scanned from 20 ° to 70 ° in steps

of 0.01 °, with an acquisition time at each step equal to 12 s. Since some diffraction from the underlying aluminum sample holder was observed, a diffractogram of the empty holder was also recorded and subtracted from the sample diffractogram.

Transmission Electron Microscopy (TEM)

The size of the nanocrystals were measured by using TEM performed on a Philips EM 400T microscope operating at 120 kV equipped with a Soft Imaging System CCD camera (Cantega 2K). Samples were diluted equally to ≈ 0.1 a.u. at 470 nm and 500 uL were purified using YM30 Microcon tubes (Millipore, Billerica, MA) three times with pure 18.2 MΩ cm^2/cm water and reconstituted in 50 uL of pure water. Samples were prepared by dropping water soluble quantum dots onto a mica-coated 600-mesh carbon-coated copper grids. Reported particle sizes are an average of 50 individual measurements. The uncertainty is the standard deviation of the size distribution.

High-resolution (HR) TEM images were obtained using a FEI Titan 80-300 operating at 300 kV. Electron diffractograms from individual quantum dots were extracted by performing a fast Fourier transform (FFT) of the HRTEM lattice images using Digital Micrograph v. 3.9.5. Samples were prepared as described above.

Luminescence and Quantum Efficiency

Luminescence emission profiles were obtained on Cary Eclipse fluorescence spectrophotometer. Quantum yields are reported relative to a 50 nM fluorescein standard in 0.1 M NaOH (Φ= 0.93).[1] Absorbance values at the excitation wavelength (470 nm) were measured for each of the samples and dilutions were prepared to generate absorbance values ≤ 0.01 a.u. Absorbance values were obtained using a Cary Eclipse UV-Vis spectrophotometer. Fluorescence spectra were collected for three separate dilutions of each sample with an excitation source at 470 nm. Emission spectra were collected between 490 nm and 700 nm and the area under the curve was integrated. Raw photoluminescence quantum yield values were corrected relative to the fluorescein standard. At least three independent measurements were used to calculate the values and error reported.

References

(1) Teale, F. W.; Weber, G., *Biochem. J.* 1957, 65, (3), 476-82.