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White/blue-emitting, water-dispersible CdSe quantum dots prepared by counter ion-induced polymer collapse

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ABSTRACT

The synthesis and characterization of water-dispersible, luminescent CdSe/ZnS semiconductor quantum dots that exhibit nominal “white” fluorescence emission and have potential applications in solid-state lighting is described. The nanomaterials, prepared through counter ion-induced collapse and UV cross-linking of high-molecular weight polyacrylic acid in the presence of appropriate aqueous inorganic ions, were of ~2–3 nm diameter and could be prepared in gram quantities. The quantum dots exhibited strong luminescence emission in two bands, the first in the blue-region (band edge) of the optical spectrum and the second, a broad emission in the red-region (attributed to deep trap states) of the optical spectrum. Because of the relative strength of emission of the band edge and deep trap state luminescence, it was possible to achieve visible white luminescence from the quantum dots in aqueous solution and in dried, solid films. The optical spectroscopic properties of the nanomaterials, including ensemble and single-molecule spectroscopy, was performed, with results compared to other white-emitting quantum dot systems described previously in the literature.

1. Introduction

Improvements in the optical and electronic properties of semiconductor materials used for solid-state lighting applications have the potential for major economic impact, both in terms of net energy efficiency and for improved longevity of lighting devices such as light emitting diodes (LEDs) [1]. A key goal in the development of semiconductor solid-state lighting is the construction of devices that emit “white” light, and various approaches to accomplish this, ranging from mixing of multiple coloured LEDs, to tailoring of different phosphor materials have been devised. Amongst the various semiconductor materials used for such devices, luminescent CdSe-based colloidal particles (or quantum dots; QDs) are of significant potential value because of their strong optical output and because their spectroscopic properties can be synthetically tuned through a combination of size-control (through quantum confinement effects) coupled with appropriate chemical functionalization of the quantum dot surface with organic stabilizer ligands [2,3]. This suggests the possibility of developing white light emitting devices that use a single semiconductor material as the active optical medium, which would lead to considerable cost-savings over devices based upon mixing of multiple coloured materials. While environmental toxicity concerns exist about the use of Cd-based materials for solid-lighting applications, there have been a number of promising advances in tailoring properties of CdSe QDs for white-light applications that bear further investigation.

A number of different examples of CdSe-based QDs that exhibit white emission have been described in the literature (Refs. [4–7] and others). Of particular recent interest are “magic-sized” QDs, first reported and explored in detail by the Rosenthal group [5,6,8,9]; these materials consist of ultra-small (<2 nm), highly-monodisperse CdSe particles, which exhibit a typical sharp band edge emission feature at low emission wavelengths, a broad “deep trap” emission band in the red-region of the optical spectrum and additional novel features at intermediate wavelengths which have been attributed to defect surface states. While the band edge and deep trap spectral features are commonly observed in many CdSe QD preparations, with the deep trap states resulting from chalcogenide defect sites in the semiconductor [10,11], the novel intermediate surface trap states are unique to the ultra-small systems. The large surface area-to-volume ratio of the ultra-small particles enhances the relative contribution of these defect sites to the overall emission of the particles, resulting in white net emission. While the works by Rosenthal’s group are an important contribution to the field of white-emitting nanomaterials, monodisperse, ultra-small particles are not a necessary requirement

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for achieving white emission in CdSe QDs. Baker et al. [4] have synthesized, using a hot injection approach, trioctylphosphineoxide–dodecylamine functionalized ~2.8 nm CdSe QDs, and through ligand-exchange reactions with 3-mercaptopropionic acid (MPA), tuned the relative intensities of the band-edge and deep trap emission to achieve a range of fluorescence emission colours, including white. The intensity of the deep trap emission was strongly dependent on the extent of MPA binding, thus providing a chemical handle to achieve tunable emission without requiring further changes to particle size. In a related study, Vempati et al. [7] prepared ~3.2 nm diameter, white light emitting CdS QDs through a standard CdS precipitation reaction in the presence of a poly (vinyl pyrrolidine) stabilizer ligand. White light emission was attributed to replacement of non-radiative surface trap channels with new, radiative pathways in the polymer-functionalized QD. In general, careful tuning of surface trap states with a number of different surface ligands allows for the preparation of white emitting QDs of a variety of particle sizes.

In this work, we have developed an alternative approach to synthesizing white-emitting QDs using purely aqueous chemistry under ambient conditions and have characterized the optical spectroscopic properties of the resulting nanomaterials. The synthetic approach, similar to that reported previously in the synthesis of water-dispersible CdTe/CdS QDs [12,13], involves a three-step process: (i) Cd^{2+}-induced collapse of an aqueous polymer in solution followed by photochemical cross-linking to form a nanometer-scale template for particle deposition; (ii) formation of CdSe by addition of appropriate Se-based salts to the mixture; and (iii) formation of a nominal ZnS capping layer by addition of appropriate Zn-based salts along with thioacetamide. The resulting QDs are water-dispersible and upon photoexcitation, emit visibly white light. A detailed characterization and spectroscopic evaluation of these materials, including steady-state and time-resolved optical spectroscopy, as well as single-molecule fluorescence spectroscopy, is described below.

2. Experimental

2.1. QD synthesis and materials characterization

Polyacrylic acid (PAA; MW ~450,000) was obtained from Aldrich, while cadmium nitrate, sodium selenite, hydrazine and thioacetamide were obtained from Alfa Aesar. All chemicals were used as received without further purification. Aqueous solutions were prepared using ultrapure water (resistivity >18 MΩ cm).

PAA (2.0 g) was dissolved in 1 L of water and the pH of the solution was adjusted to ~6.8 with the addition of NaOH (10 M solution), and monitored using pH paper. To this slightly viscous solution was slowly added 1 L of $Cd(NO_3)_2$ (5 mM solution) to produce a clear colourless solution, which was subsequently exposed to 254 nm light from a Hg lamp for 1 h. The resulting solution (Cd^{2+}-PAA) was a pale yellow colour, with viscosity similar to water. A 1.3 L volume of Cd^{2+}-PAA solution was transferred into a round bottom flask and solutions of Na_2SeO_3 solution (13 mL, 50 mM) and hydrazine (6.5 mL; reducing agent) were added; this was refluxed for 2 h to yield the CdSe product (CdSe–PAA).

For purification, a 100 mL aliquot of the crude CdSe–PAA solution was mixed with NaCl (5 mL, 3 M solution) and shaken vigorously. To this was added 100 mL of ethanol (either absolute or 95%; results were consistent with each) and then shaken vigorously. The solution was centrifuged at 12,000 RCF for 15 min, and then decanted. The pellet was washed with 50% ethanol three times, and air-dried overnight at room temperature. The dried pellet was reconstituted with 20 mL of H_2O.

The CdSe–PAA solution (150 mL) was added to 1350 mL of H_2O, along with a $Zn(NO_3)_2$ solution (9.75 mL, 250 mM), and thioacetamide solution (0.975 mL, 250 mM), with the resulting solution at pH = 7.2. The mixture was refluxed for 20 h to yield the final product. The resultant materials were characterized using a combination of powder X-ray diffraction, transmission electron microscopy, atomic force microscopy and dynamic light scattering (see Supporting Information), as well as optical spectroscopic approaches which are described in more detail, below. Liquid samples were filtered through 0.2 μm syringe filters, in order to remove any aggregated material, prior to measurements.

2.2. Optical spectroscopic characterization of QDs

Steady-state absorption and fluorescence emission spectra of aerated solutions were collected using a Varian Cary 6000i UV–Vis spectrophotometer and a PTI Quantamaster spectrofluorometer, respectively. Fluorescence lifetimes were measured using the method of time-correlated single-photon counting (TCSPC) on an apparatus described elsewhere [14]. Lifetime decay parameters were extracted using a non-linear least-squares iterative convolution procedure based on the Marquardt algorithm. Data fitting quality was evaluated using reduced chi-squared values and through the distribution of weighted residuals.

Samples for single-molecule fluorescence experiments were prepared by drop-casting appropriately-diluted (with Millipore water) samples of QD solutions onto cleaned glass cover slips. Cover slips were cleaned by extensive rinsing with ethanol, followed by exposure to an air-based plasma generated in a bench-top plasma cleaner (Harrick Plasma) for at least half-an-hour.

Single-molecule fluorescence characterization of individual QDs was carried out using a custom-built epifluorescence microscope described previously [15]. The cw linearly-polarized output of a 405 nm laser diode (Dragon Lasers) was focused onto the back focal plane of a 1.4 NA microscope objective lens to provide sample excitation (~0.4 kW/cm^2), and the same objective lens was used to collect the resulting fluorescence emission from individual quantum dots. Fluorescence emission was passed through two 410 nm longpass emission filters to remove residual laser excitation. The fluorescence was passed through a dual-view image splitter (DV-2, Photometrics) equipped with a 505 nm dichroic beamsplitter and a "blue" bandpass filter (effective bandpass range was 455–485 nm) for one image channel and a "red" bandpass filter (effective bandpass range was 535–565 nm) for the second image channel, then directed onto an electron multiplying CCD camera (512F, Photometrics). In the Results and Discussion the first image channel is referred to as the "blue channel" and the second as the "red channel".

Single-molecule images of individual particles were converted into fluorescence time-trajectories by capturing a series of sequential images (time resolution of 300 ms) and determining the background-corrected integrated fluorescence emission for each discrete emitter per each image. The mean fluorescence intensity (in CCD counts) of each particle was determined by calculating the background-corrected average signal level per 300 ms integration bin during an "on" state.

3. Results and discussion

The synthetic scheme for the white-emitting QDs and images of the resulting product under visible and UV illumination are shown in Fig. 1. Aqueous samples had excellent long-term stability, with solutions retaining their spectral properties after many months of storage under ambient temperature and lighting conditions. Solid samples were equally robust, and could be reconstituted after many months storage to yield data comparable