Synthesis and characterization of positively capped CdTe quantum wires that exhibit strong luminescence in aqueous media†

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The novelty of the current work lies in the versatile synthesis of highly luminescent water-soluble CdTe quantum rods (QR) which to the best of our knowledge are the first known water-soluble QR carrying positively charged stabilizer.

Semiconductor nanocrystals have attracted considerable attention during the past decade. This is mainly due to their shape- and size-dependent physicochemical properties[1] and their tunable optoelectronic properties.[2] As an important example of photonic applications, semiconductor nanocrystals are expected to potentially contribute to an easier and cheaper photovoltaic conversion of solar energy.[3] Several different approaches are reported in the literature: hybrid nanocrystal–polymer[4] and all inorganic nanocrystal solar cells[5] are just two concepts. In light of the current work, powerful approaches that integrate versatile water-soluble organic–inorganic nanocomposites that are held together by electrostatic interactions should be considered. Notably, various strategies are described that put functionalized fullerene derivatives and/or carbon nanotubes (CNT) to use. The electronic nature of such nanostructured carbon materials renders them suitable for photoinduced electron transfer processes, where they act as electron accepting building blocks.[6] In these organic–inorganic nanocomposites, size-quantized, anionic-stabilized CdTe nanodots acted as excited state electron donors. Due to their quantum confinement, nanorods (QR) are expected to provide a better conduction path for charge carriers – electrons and holes – than that typically found for nanodots (QD). Ultimately, the use of QR will be beneficial for the function and performance of such assemblies.[7]

In this paper, we report on CdTe nanorods that were prepared using a procedure modified from that of previous work for positively charged QD.[8]‡ The key difference is the addition of L-cysteine (cys) as a second stabilizer (*i.e.*, besides 2-(dimethylamino)ethanethiol), which is expected to promote the one-dimensional growth along a particular lattice plane, although dipole–dipole interactions may also contribute to the linear growth.[7a,9]

The first insight into the structural features of CdTe QR came from transmission electron microscopy (TEM). Initially, TEM images were acquired for the CdTe QD precursors – making up the QR. During the initial period of the reaction only well-dispersed CdTe QD were noticed. Nevertheless, Fig. 1a also documents that some accumulation is discernable. Following this period, formation of rod-like structures, in which smaller fragments align in preferred directions, seems to dominate. For example, after 5 hours, monodimensional CdTe QR of uniform lengths (*i.e.*, ~8–12 μm) and diameters (*i.e.*, 40–60 nm) are observed – see Fig. 1b. With continuing growth these QR tend to aggregate further, affording bundle-like structures with diameters that reach 180–200 nm.

The composition of both CdTe QD and QR was qualitatively determined by means of energy disperse X-ray analysis (EDS) measurements (see Fig. 1c). Quantitative information about the crystallinity of the CdTe nanocrystals was deduced from high resolution transmission electron microscopy (HRTEM). In particular, magnifying selected areas, for which an example is shown in Fig. 2, the lattice planes are visualized within the crystal structure. The interplanar spacing in several CdTe QR was measured to be 370–380 pm, which corresponds to the characteristic (220) lattice plane in cubic zinc blende CdTe, values that resemble previous reports.[9]

Independent, but qualitative, proof of the cubic zinc blende crystal structure of the CdTe QR came from selected area electron diffraction patterns (SAED). In Fig. S1 (ESI)†, which documents a

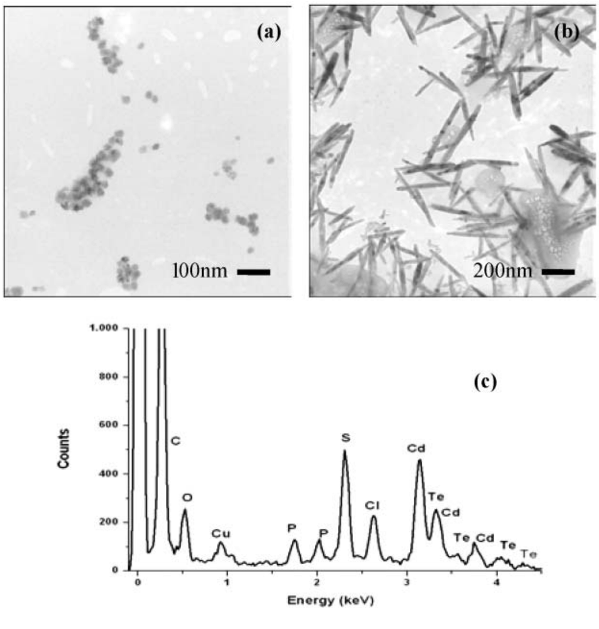

Fig. 1 TEM images of (a) linear aggregation of CdTe QD after 3 hours and (b) CdTe QR after 5 hours reaction time, confirming the monodimensional amalgamation of CdTe QD to yield CdTe QR during the course of 5 hours. (c): EDS pattern of CdTe QR (8 h reaction time) showing that the major elements of the nanowires were Cd, Te, and S.

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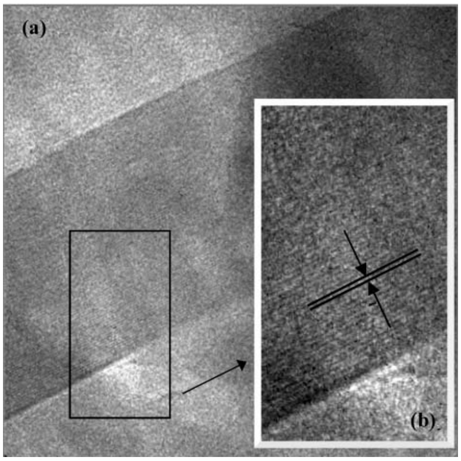

Fig. 2 HRTEM image of CdTe QR (a). The inset (b) highlights the typical interplanar spacing (376 pm), which corresponds to the (220) lattice plane in cubic zinc blende CdTe. The size of the view is 63.7 x 63.7 nm for (a) and 7.70 x 15.0 nm for (b).

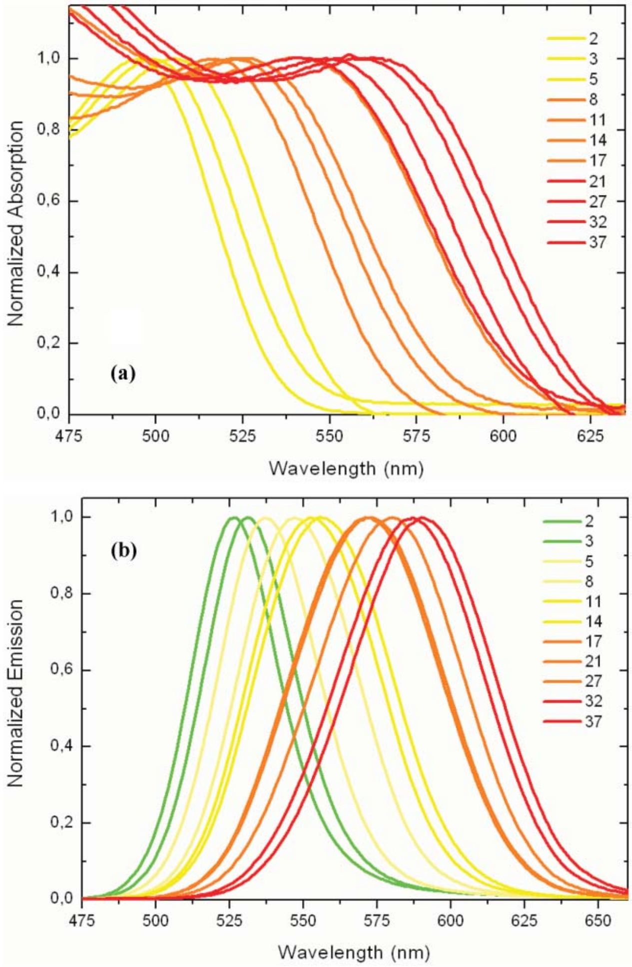

Fig. 3 Normalized absorption (a) and emission (b) spectra of CdTe QR in aqueous solutions. Please note that the numbers in the legend (*i.e.*, 1 through 37) correspond to the reaction time in hours. All CdTe QR aqueous solutions were photoexcited at 420 nm, exhibiting an optical density of 0.1.

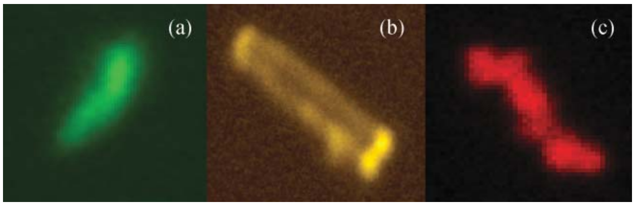

Fig. 4 Confocal microscopic image of an individual CdTe nanorod after 3 (a), 14 (b) and 30 (c) hours reaction time respectively emitting in the green part of the visible spectrum. The size of the abscissa is 2.53 (a), 4.61 (b), 5.12 μm. Strong light scattering (*i.e.*, excitation and emission) limits the spatial resolution and, thereby, hampers establishing accurate dimensions.

typical SAED pattern for CdTe QR, both the typical 220 and the 311 lattice planes were identified. Decisive evidence for the CdTe QR crystallinity was obtained by performing powder X-ray diffraction. The standard diffraction peak and relative intensities of bulk zinc blende CdTe are indicated in Fig. S2 (ESI).† Importantly, this measured diffraction pattern matches quantitatively the 2θ values found in the International Centre for Diffraction Data (ICCD®) (Powder Diffraction File 015-0770), namely, 23.759° (111), 39.312° (220) and 46.434° (311).

UV–Vis absorption and steady-state emission features of as-prepared colloidal CdTe QR are depicted in Fig. 3. Both figures reveal the continuous red-shift of the characteristic long-wavelength absorption peak and the photoluminescence (PL) maxima with a rate of ~2 nm per hour reaction time. Importantly, we reach PL quantum yield of up to a remarkable 25%. The maximum is seen after a reaction time of 11 hours. In contrast, after 37 hours reaction time the quantum yields drop to 6%, before decomposition of the QR sets in.

In summary, this paper exemplifies a simple, mild and cheap methodology for preparing highly fluorescent CdTe nanowires with narrow emission spectra and long emission lifetimes ($\tau_{1/e}$ up to 14 ns)[10] that show PL quantum yields of up to 25%. Such a remarkable value is comparable with those reported for negatively charged CdTe QR (2–29%)[7a] and for positively charged CdTe QD (30%).[8] Due to this intense PL, the emission of a single QR was readily observable in a standard laser scanning confocal microscope (see Fig. 4).[11] The positive charge that these water soluble rods possess emerges as a useful feature for electrostatic assembly of biomolecules. Moreover, these multifunctional nanomaterials hold great promise as integrative components for the construction of photovoltaic devices in combination, for example, with carbon nanostructures.

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Notes and references

‡ *Preparation of NaHTe*: In a three-necked flask (25 ml), sealed with septa and valves, 1.5 ml water was deaerated with argon for 20 min. Next, $NaBH_4$ (127.6 mg, 3.384 mmol) was added and the resulting suspension was stirred under argon until $NaBH_4$ was completely dissolved. Then, the solution was mixed with metallic Te powder (78.2 mg, 0.612 mmol). The resulting suspension was stirred at room temperature for 2 hours.

Preparation of CdTe QR: In a three-necked flask (250 ml), equipped with a reflux condenser, septa and valves, $Cd(ClO_4)_2 \cdot 6H_2O$ (547.5 mg, 1.305 mmol) was dissolved in 98.5 ml phosphate buffered aqueous solution. 2-(Dimethylamino)ethanethiol hydrochloride (462.2 mg, 3.263 mmol) and L-cysteine (79.1 mg, 0.653 mmol) were added and the solution was adjusted to pH 5 with aqueous NaOH (1 M) and stirred under argon at room temperature for 30 minutes. Then, the supernatant NaHTe solution was added under argon and the molar ratio of $Cd(ClO_4)_2 \cdot 6H_2O$/2-(dimethylamino)ethanethiol hydrochloride/L-cysteine/NaHTe was set to 1 : 2.5 : 0.5 : 0.46 with an effective Cd^{2+} concentration of 13.05 mM. The mixture of the precursors turned from colorless to orange and was then refluxed. At particular times, samples of 5 ml were separated and stored in the dark under argon atmosphere at 4 °C.

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