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Short communication

Reborn water-soluble CdTe quantum dots

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ABSTRACT

Recovery of fully aggregated water-soluble CdTe quantum dots was achieved by simple treatment with a strong base. A deprotonation-triggered disaggregation is postulated to be the main mechanism involved in the quantum dots "reborn" process.

1. Introduction

Colloidal quantum dots (QDs) are a class of highly photoluminescent semiconductor nanocrystals. This type of inorganic nanoparticles, with diameters in the range of ca. 1–10 nm, can be synthesised using different core and core–shell semiconductor compositions (e.g. Cd, Te, Se and Zn). Over the last few years a great effort has been made in the engineering of QDs, thus leading to an extended library of materials with emission wavelengths ranging from visible to near UV [1].

QDs attracted considerable attention as sensing and recognising elements when used as fluorescent labels, due to their good photodegradation stability, high luminescence efficiency, continuous absorption spectra, narrow emission, and ability to form complexes with important biomolecules. Also, their unique and adaptable optical and electronic properties, achieved by changing their size, structure and surface functional groups [2], lead to an excellent performance in electro-optics [3], chemosensing [4], and biological imaging applications [5,6].

In particular, water-soluble QDs are of special importance due to the opportunity of studying biological environments such as living tissue [7,8]. However, these QDs are reported to be chemically unstable, being the loss of their optoelectronic properties mainly due to aggregation events [9]. This behaviour is a major problem since the limited lifetime of this type of QDs (ca. 9 days) shutdown practical applications. Recently, cysteamine-capped QDs aggregates shown to be disassembled to highly stable colloids by the addition of fluoride ions at low concentration (0.1 μM to 1 mM) [10].

In the sequence of our studies on water-soluble mercaptoethanol-capped QDs we found that pH plays a key role on the "reborn" of their optical properties and stability. Surprisingly, we found that aged solutions of water-soluble thiol-capped QDs showing non-fluorescent grey QDs clusters can be totally recovered (Fig. 1). After addition of a NaOH 1 M solution, bright, yellow fluorescent, clear solutions are obtained (Fig. 2). In the presence of weaker bases, such as triethylamine and sodium hydrogen carbonate, nothing happened. This probably means that a stronger base is needed to and that a deprotonation of the hydroxyl from the ligand may trigger the disaggregation process.

A zeta potential study was carried out to support our findings. Freshly prepared mercaptoethanol-capped CdTe quantum dots show a near neutral zeta potential ($\zeta = -6$ mV). However, after base addition (pH 10.1) a negative value was observed ($\zeta = -20$ mV), thus meaning that the quantum dots surface turned more negative due to hydroxyl ion formation. This result is in agreement with reported data for water-soluble thioglycolic acid-capped CdTe QDs (pH 10, $\zeta = -50$ mV) [11].

Based on the zeta potential data we postulate that the mechanism involved comprises a two-steps cascade event: deprotonation of the hydroxyl outer-shell followed by an electrostatically-driven disaggregation, initiated by the formation of highly charged QD surfaces.

The QDs particle size was accessed by DLS (Dynamic Light Scattering), 24 h after the synthesis. At this time, QDs already show some aggregation ($d = 152$ nm). After 7 days the particles fully aggregate and deposit. Treatment of the aged solutions with a

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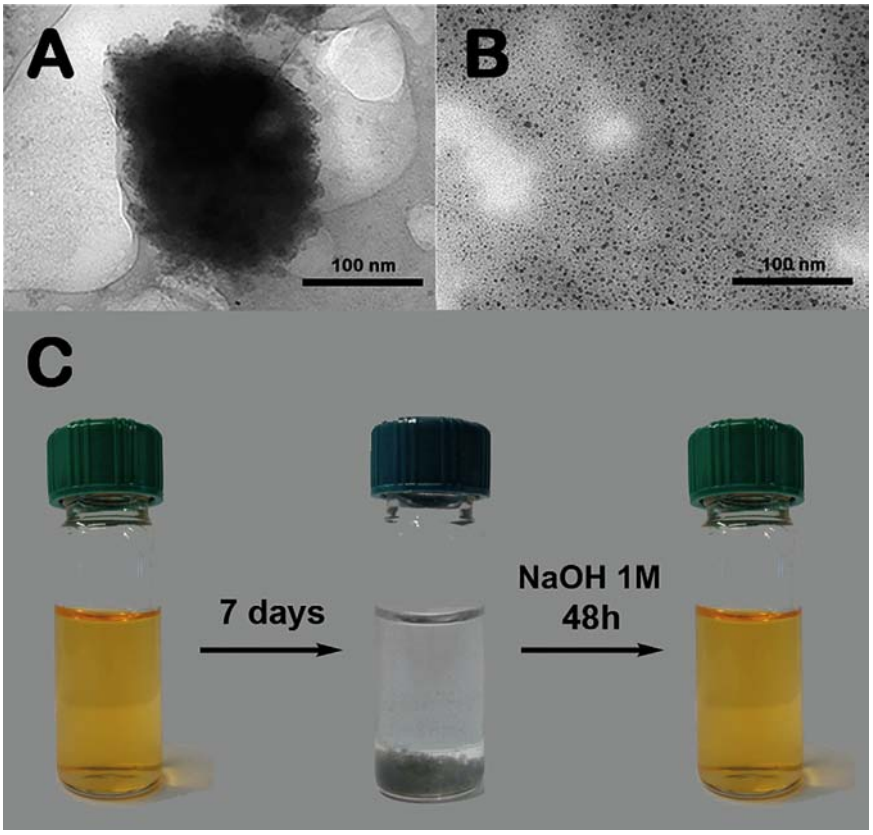

Fig. 1. Recovery of water-soluble mercaptoethanol-capped CdTe quantum dots after 48 h. SEM images show (A) aggregated (after aging and before treatment) and (B) non-aggregated quantum dots (after treatment). The picture (C) shows quantum dots before aging (left), after aging (center) and after recovery (right).

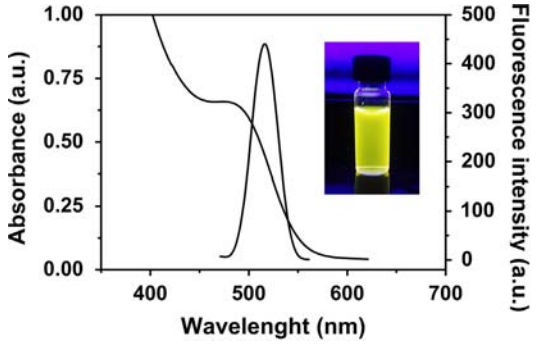

Fig. 2. Absorption and fluorescence spectra of recovered mercaptoethanol-capped CdTe quantum dots. The inset shows an aqueous solution under a UV lamp (λ_{ex}=366 nm).

base led to the recovery of the original particle size (d=10 nm) (see Fig. 3).

Interestingly, we also found that after recovery no more precipitation was observed in the next months. The lifetime enhancement of water-soluble QDs is of special importance for undergoing studies and will expand its potential in future applications.

2. Conclusions

The optical properties of aged, fully aggregated, water-soluble mercaptoethanol-capped CdTe QDs can be fully recovered by simple treatment with a strong base. The mechanism is apparently irreversible and involves a deprotonation-triggered disaggregation process.

3. Notes and references

3.1. Synthesis of water-soluble CdTe QDs

The QDs were synthesised following a reported procedure [12,13]. Tipically, β-mercaptoethanol (50 μl) was added to a solution of cadmium chloride hemi(pentahydrate) (0.057 g) in water (180 ml), and mixed in a two-neck flask to form the cadmium precursor. Then, 1.5 ml of freshly prepared NaHTe aqueous solution from $NaBH_4$ (0.363 g) and Te (0.0636 g) powder was injected into the reaction system under stirring, and the solution was heated up until boiling with reflux for 6.5 h.

3.2. Quantum dots disaggregation

After one week of ageing QDs become fully aggregated and deposit in the bottom of the flask as a grey precipitate. The aqueous solution, initially with an orange colour, becomes clear and the characteristic yellow fluorescence is lost. At this stage a NaOH 1 M solution was added and after 48 h the QDs fully disaggregated and the fluorescence of the solution was recovered.

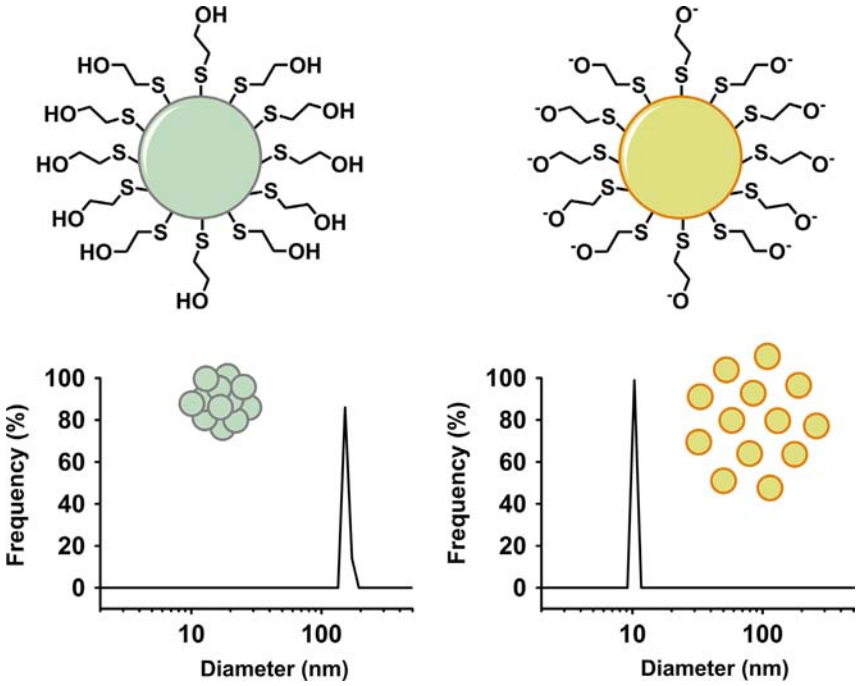

Fig. 3. Schematic representation of mercaptoethanol-capped CdTe quantum dots before (left) and after (right) the treatment with base. The graphs show the corresponding particle size measured by DLS.

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