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Photoluminescent quantum dot–cucurbituril nanocomposites†

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The preparation of entrapped CdSe–ZnS fluorescent quantum dots (QDs) in cucurbituril (CB) polymer capsules is reported.

Colloidal photoluminescent (PL) quantum dots (QDs) such as core–shell CdSe–ZnS are receiving increasing attention due to their excellent optical properties including broad absorption and narrow emission, size-tunable bandgap and excellent photostability. As a consequence, they appeared to be of practical interest for biological imaging¹ and are promising candidates for a variety of other applications.² Yet, one important drawback for bioimaging lies in the surface ligands of the QDs that are highly accessible to a variety of biological species that lead to their degradation thus decreasing their efficacy and increasing their cytotoxicity.³ Although a number of different approaches have been successfully demonstrated to address this problem,⁴ such as for example, polymer spheres (that have been used to entrap QDs in their fully occupied interior),⁵ the introduction of an easy and tunable method for surface functionalization, while protecting the nanoparticles, would add a new dimension to these architectures and constitute a significant advance to that burgeoning field. To reach this aim, the encapsulation of semiconductor PL QDs in hollow polymeric-type capsules⁶ may provide an appealing route to multifunctional and tailorable nano toolbags using a molecular toolkit in which all the components are assembled in a final step.

Very recently, we focused our efforts on interfacing light-emitting semiconductor QDs with supramolecular gels⁷ prepared by ultrasound.⁸ The resulting QD@dipeptide nanocomposites showed bright luminescence under UV light that was used to probe nitroxide recognition on the QD surfaces and monitor free radical recombination reactions. In our

current investigation to interface QDs with promising new materials, we turned our attention onto cucurbiturils (CBs).^{9,10} Indeed, as QDs and CBs are the subject of growing interest separately, it is surprising that there have been no studies reported at the QD/CB interface. Recently, Kim and co-workers reported the direct functionalization of CBs,¹¹ opening the way to a variety of new derivatives and applications.¹² Among them, the allyloxy-type dodecafunctionalized cucurbit[6]uril, CB[6]-(Oallyl)₁₂, was shown to readily polymerize under UV in the presence of dithiols producing spherical hollow nanocapsules whose surfaces are composed of the cucurbituril macrocycles.¹³ We reasoned that QDs entrapped inside such capsules would produce a fluorescent architecture allowing (i) protection of the QDs from their environment and (ii) keeping the surface available (the fluorophore is inside the capsule and not bound to the CB[6] cavities) for further easy (non-covalent) functionalization. Here we report the preparation of cucurbituril (CB) hollow capsules containing QDs in their cores and the fluorescence study of the nanoengineered composites.

The dispersity of the QDs in methanol was found to be critical since insufficient solubility resulted in empty capsules. Trioctylphosphine oxide–trioctylphosphine (TOPO–TOP)-capped core–shell CdSe–ZnS QDs were first prepared and subsequently ligand exchanged using mercaptoundecanoic acid (MUA) or 2-mercaptoethanol (ME) as methanol soluble molecules (Fig. 1).

The PL intensity was found to significantly decrease after ligand exchange presumably due to internal quenching because of the QDs aggregation as observed by TEM.¹⁴ This likely arises because of the high amount of carboxylic acid and

Fig. 1 PL spectra and TEM images of the ME-capped QDs ($\lambda_{\text{exc}} = 500$ nm). Red line: QDs in hexanes where surface ligands are TOPO–TOP. Blue line: QDs in methanol, after ligand exchange using 2-mercaptoethanol (ME). The TEM picture (inset, left) shows the tendency of the ME-capped QDs to aggregate slowly in methanol within the time. The high resolution (HR)-TEM image (right) shows the size of the ME-capped QDs.

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Fig. 2 SEM (a–c) and TEM (d–i) images of QD-entrapped CB capsules. (a) to (c) Capsules formed using MUA-capped QDs; (d) MUA-capped QDs inside CB capsules after 10 hours of UV exposure at 350 nm; (e) and (f) show the obtained capsules after 10 hours more exposure under UV at 300 nm. The decreased degree of aggregation of the QDs inside the capsules is clearly seen. After simultaneous UV exposure under 300 nm and 250 nm (4 lamps each), TEM images show the CB polymer containing ME-capped QDs in its matrix (g, 10 hours) and the development of bunches of capsules (h, 10 hours) prior to the release of QD-included polymer hollow capsules (i, 20 hours).

hydroxy functions covering the surface of MUA- and ME-capped QDs, respectively.

CB[6]-(Oallyl)₁₂ (typically 3.12 mg) and 3,6-dioxa-octane-1,8-dithiol (13.84 mg) were added to a preliminary prepared 3 mL MUA or ME functionalized QDs methanolic solution in a 15 mL quartz tube just prior to photopolymerization at room temperature (Scheme 1). After completion of the reaction, the MUA-capped and ME-capped QDs are encapsulated inside the CB capsules as evidenced by SEM and TEM (Fig. 2a–c and Fig. 2f and i, respectively). In the case of MUA-capped QDs, we observed the presence of large QD aggregates after the first 10 hours exposure to 350 nm wavelength UV light (Fig. 2d).

Interestingly, we observed the presence of a higher number of aggregates of generally smaller size inside the capsules after 10 hours more exposure to 300 nm wavelength UV light (Fig. 2e and f). The higher energy reaction might have caused the ligands to release from the surface of the QDs (including the 3,6-dioxa-octane-1,8-dithiol cross-linking agent) resulting

Scheme 1 Preparation of fluorescent capsules in methanol.

in a dissemination inside the capsules. Nevertheless the average value of the particles' diameter is not consistent with single isolated QDs and so smaller aggregates are observed inside the capsules. Another striking result was the presence of QDs inside the capsules only (*i.e.* not on the surface). This likely arises from (i) the utilization of the dithiol rendering the QDs compatible with the polymer matrix and (ii) the mechanism of capsule growth and separation from the CB polymer.¹³ This is further supported by TEM experiments of the reaction using ME-decorated QDs (Fig. 2g–i). When ME-capped QDs were used for the reaction, similar results were obtained when 250 and 300 nm wavelengths were used simultaneously. After 10 hours of UV exposure, the amorphous CB polymer reached the level necessary to observe the growth of bunches of capsules forming on its surface, some areas presenting a dense network of QDs in the matrix and capsules having entrapped a set of QDs prior to polymer separation (Fig. 2g and h and Fig. S1 and S2, ESI†). Stirring (even gently) affected the shape of the objects obtained since clear spherical capsules could not be observed in this case. When ME–QDs were used under the conditions of the first reaction (successive UV wavelength at 350, 300 and 250 nm), the capsules containing QDs also formed. Significantly, we also observed rice-shaped (50 × 100 nm) and rod-like tubes (50 × 400 or longer nm) with additional very long fibers on the μm scale. The presence of QDs inside such structures was again ascertained by HR-TEM (see Fig. S3, ESI†). The proportion of the cucurbituril capsules having ME-capped QDs entrapped in their core greatly increased (up to approximately 90%) by using a concentrated solution of the QDs with 100 μL of ME added to enhance the QDs solubility. However, we also observed very slight capsule deformation in regard to the ideal spherical shape, this likely coming from the additional amount of ME with its thiol group probably competing during the polymerization reaction. Thus the present system seems highly dynamic and dependant on several parameters, the importance of which is not yet clear. However, the system clearly shows a high tendency to afford the targeted capsules.

We then focused on characterizing the PL properties of the newly prepared QD@CB capsule composites. The QD-imparted luminescence was found to increase significantly as a function of either (i) the reaction time or (ii) the decrease of the selected UV wavelength (Fig. 3), irrespective of the QD used.

In the case of ME functionalized QDs, a regular increase in the photoluminescent (PL) intensity was recorded as a

Fig. 3 UV light effect on the photoluminescent spectra of the reaction mixture during the course of the reaction of the CB polymerization containing CB[6]-(Oallyl)₁₂, the dithiol and (a) MUA-QDs or (b) ME-QDs. (The + symbol is for a simultaneous use of the two wavelengths.)

Fig. 4 PL spectra illustrating the effect of the dithiol on the ME-capped QDs in the absence of CB[6]-(Oallyl)₁₂. Orange line: ME-capped QDs in methanol. Blue line: ME-capped QDs with dithiol in methanol after 20 hours stirring at room temperature. Brown line: ME-capped QDs with dithiol in methanol after 20 hours exposure of UV light (4 lamps at 250 nm and 4 lamps at 300 nm) thus highlighting the protective effect of the capsules on the PL properties of the QDs ($\lambda_{\text{exc}} = 500 \text{ nm}$).

function of the reaction time, presumably due to light scattering of the spheres. The persistence of the QDs PL under such harsh conditions is highly interesting since without CB[6]-(Oallyl)₁₂ the PL was observed to decrease dramatically as a function of the reaction time (Fig. 4). This directly proves the protective effect of the capsules regarding the QD optical properties.

Thus the formation of CB capsules embedding QDs is unique and can be summarized as follows: (i) growing of the CB polymer sheets with incorporation of the QDs as either aggregates or isolated nanocrystals, (ii) evolution of the growing polymer around the QDs in bunches of capsules and separation from the polymer matrix, (iii) 3D closure of the polymer surface and (iv) termination of the reaction by final cross-linking between the CBs and spreading of the QDs inside the capsules. The ability of this polymer to readily include QDs while preserving their function from extinction (PL loss) is remarkable and bodes well for further developments.

In conclusion, this is the first report to our knowledge at the cucurbituril–quantum dot interface, two independent research fields that are rapidly and separately developing. It is demonstrated that the resulting QD@CB nanocomposites have the QDs entrapped inside hollow capsules built from the CB macrocycles that define the polymer surface. The dithiol cross-linker used during the synthesis is of prime importance in providing compatibility between the growing polymer and the QDs for their successful encapsulation. It may also play a significant role in preserving the imparted fluorescence^{7,15} in the course of the reaction while keeping the capsule surface available for further possible non-covalent functionalization using the cucurbituril cavities (the fluorophore is inside the capsule and not bound to the CB[6] cavities). Interestingly, this general approach represents a new entry into multifunctional fluorescent hollow polymer spheres with a potential for an easy and tunable surface functionalization as demonstrated in the seminal report¹³ (the fluorophore was bound to the surface of the spheres by means of the CB[6] cavities). We believe that this approach can be easily extended to a variety of other nanoparticles, especially magnetic nanoparticles or for a joint

use to multifunctional magnetic, luminescent and surface tailorable nano toolbags.

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