

Quantum Dot/Stimuli Responsive Polymer Hybrid Platforms

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INTRODUCTION

Quantum dots (QDs) have gained much attention as fluorescent probes due to their unique composition and size-tunable optical properties, broad excitation and narrow emission spectra (Figure 1), and high chemical and photochemical stability [1,2]. Applications include areas such as biolabelling [3] and sensing [4]. Before considering these applications, several requirements must be fulfilled regarding the dispersability of the QDs in the surrounding medium. In addition, luminescence quantum yields (QY), and chemical and photochemical stability of the QDs in the surrounding medium must be considered. These requirements can be met by tailoring the ligands at the semiconductor nanoparticle surface [5].

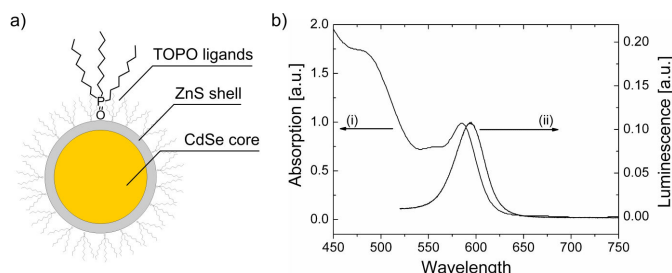


Figure 1. a) Schematic representation of a CdSe-ZnS core shell QD with surface bound TOPO ligands. b) The unique feature of QDs is a combination of a broad absorption spectrum (i) with narrow emission lines (ii). The spectral position of the absorption and emission peaks can be tuned by controlling the size of the QDs.

Poly(N-isopropylacrylamide) (PNIPAM) is a temperature-responsive polymer that undergoes a reversible phase transition in water when crossing the polymer lower critical solution temperature (LCST, $\sim 32^\circ\text{C}$) [6,7]. Above the LCST, the PNIPAM chains are hydrophobic and are in a collapsed state, while below the LCST the PNIPAM chains are hydrophilic, and extend into water.

The combination of the unique optical properties of QDs with stimulus responsive polymers, like PNIPAM, allows one to design hybrid platforms for sensing and signal transduction. Optical transduction of the temperature modulated PNIPAM phase transition could be realized by combining nanoparticles with polymer chains and monitoring their optical properties as a function of temperature. In this context the proper choice of the polymer, and the QD surface functionalization methods are crucial. Additionally, one must ensure that a hybrid material capable of optically transducing the stimulus is indeed achieved.

In this contribution we present two different approaches towards fabrication of temperature responsive QD/PNIPAM hybrid platforms.

The first approach relies on PNIPAM brushes grafted from a gold surface by iniferter-type controlled radical polymerization. The QDs are covalently coupled to the chain ends of the brushes. In the second approach we introduce PNIPAM chains of various chain lengths directly onto the surface of the QDs by using a novel amphiphilic polymeric coating. Luminescence imaging, absorption, and emission spectroscopy confirm that the hybrid materials display temperature modulated properties with the QDs serving as signal transducers.

RESULTS and DISCUSSION

i) Temperature Modulated Quenching of QDs Covalently Coupled to Chain Ends of PNIPAM Brushes on Gold

A thermo-responsive polymer/quantum dot platform based on PNIPAM brushes grafted from a gold substrate and quantum dots (QDs) covalently attached to the PNIPAM layer is presented. The grafting was achieved by using an iniferter-type controlled radical polymerization (Figure 2). The PNIPAM chain-ends are functionalized with amine groups for coupling to water-dispersible COOH-functionalized QDs. [8]

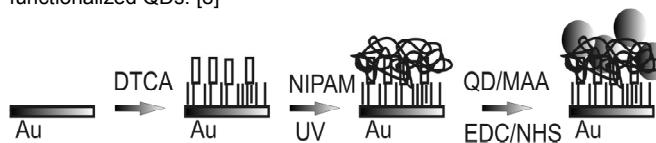


Figure 2. Scheme of the gold surface functionalization with PNIPAM and QDs.

Upon increasing the temperature above the lower critical solution temperature (LCST) of PNIPAM the QD luminescence is quenched. The luminescence was observed to recover upon decreasing the temperature below the LCST (Figure 3). The data obtained are consistent with temperature-modulated thickness changes of the PNIPAM layer and quenching of the QDs by the gold surface via nonradiative energy transfer.

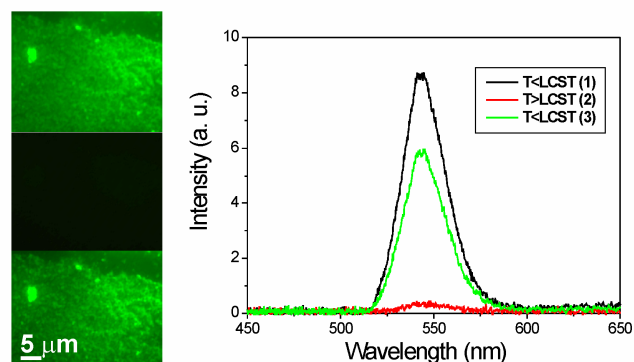


Figure 3. Left: Luminescence images of Au/PNIPAM/QD assembly obtained at 25°C (top), after heating to 50°C (middle), and after cooling back to 25°C (bottom). Right: Spectra measured at below the LCST (1,3) and above the LCST (2), showing the quenching and recovery behavior.

ii) PNIPAM Functionalized QDs by Using Thermoresponsive Amphiphilic Polymers

PNIPAM of three different molar masses (Table 1) and *n*-octylamine were grafted to poly(isobutylene-*alt*-maleic anhydride) backbone (38 monomer units) (Figure 4). Such amphiphilic polymer serves as a coating for QDs without exchanging the hydrophobic stabilizing ligand layer [9]. The hydrophobic octyl functionality of the amphiphilic polymer interacts with the organic ligands on the QD surface, while the hydrophilic parts induce water dispersability and colloidal stability [10,11].

Table 1. Amphiphilic Polymers Used for Coating of the QDs

| Sample | PNIPAM Chains (Mn X 10 ³ g/mol) | Number of PNIPAM Chains/backbone |
|--------|--|----------------------------------|
| R1 | 1 | 13 |
| R10 | 10.8 | 3 |
| R25 | 25.4 | 1 |

The QDs were successfully transferred to water upon polymer coating. No aggregation or precipitation was observed and the polymer coated QDs were stable for several months during storage in water.

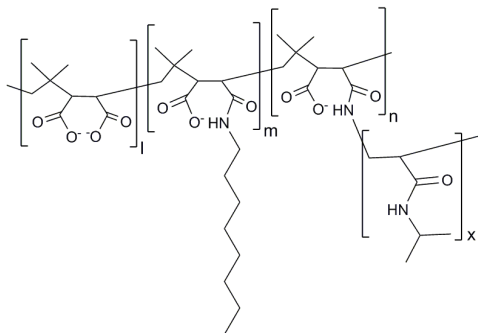


Figure 4. Poly(isobutylene-*alt*-maleic anhydride) backbone after grafting of NH₂-terminated PNIPAM and *n*-octylamine. (I + m + n = 38).

The absorption and emission of polymer coated QDs display essentially the same features as the original QDs in chloroform. Different absorption at higher energies may be related to different amounts of the polymers on the QDs surface (Figure 5). A decrease in the luminescence intensity was observed for sample R10; the reasons for the decrease still should be explained.

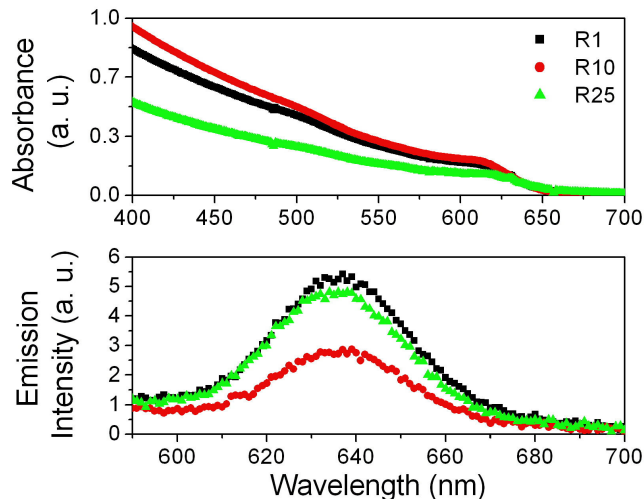


Figure 5. Absorption and emission spectra of R1, R10 and R25.

In order to characterize the temperature responsiveness of the QDs coated with PNIPAM, a series of temperature-dependent absorption measurements were performed. Figure 6 shows the fluctuations of the absorbance upon varying the solution temperature above and below the LCST of PNIPAM.

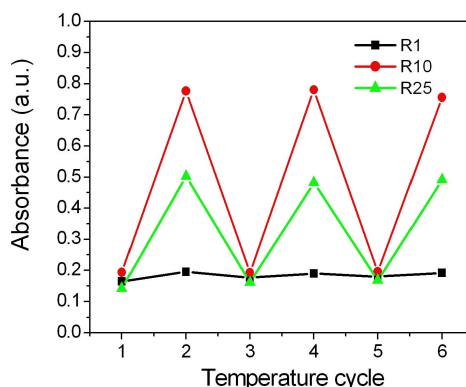


Figure 6. Absorbance recorded at 500 nm as a function of temperature (recorded values at 25 °C (odd numbers) and at 50 °C (even numbers)).

Upon reaching temperatures above the LCST, the absorbance of all three samples increases. The transition is reversible and by cooling the solutions down below the LCST the original absorbance values are obtained. These transitions can be clearly followed by looking at turbidity changes of the solutions (Figure 7).

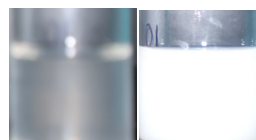


Figure 7. R10 solution at T < LCST (left) and T > LCST (right).

Upon increasing the temperature the solutions become turbid and opaque. This indicates a phase separation process combined with aggregation to occur in the sample. In general, changes in molecular conformation of PNIPAM chains grafted onto surfaces has been found to depend on the grafting density and molar mass [12]. In our study the structure of the amphiphilic polymers defined by grafting density of the PNIPAM side chains may also influence the total number of polymer chains on the QD surface. Sample R10 may therefore display a most favorable combination of the number of PNIPAM chains on the amphiphilic polymer making the coating process efficient and in consequence resulting in the largest number of PNIPAM chains on the QD surface. In contrast, when using R25 steric effects may result in poorer coating quality (low number of amphiphiles on the surface of QDs) even at low grafting density of the PNIPAM on the polymer backbone. Conversely, when using R1 the coating quality may be better but the low molar mass of the polymer results in poor LCST behavior, independently on the number of PNIPAM chains on the QD surface.

CONCLUSIONS

We have demonstrated two types of stimulus responsive QD/PNIPAM platforms. We discussed a thermo-responsive Au/polymer/quantum dot system based on PNIPAM brushes grafted from Au substrate using an iniferter-type polymerization, and QDs covalently attached to the PNIPAM chain ends. Luminescence imaging and luminescence spectra measurements showed that upon increasing the temperature above the LCST of PNIPAM the QD emission is quenched. The Au/PNIPAM/QD system reported here may be explored in sensing and surface thermometry. An efficient method towards fabrication of water soluble, temperature-responsive QD/amphiphilic polymer hybrid nanoparticles was described in the second part. Maleic anhydride-based polymer was used as the backbone for grafting PNIPAM chains of three different molar masses. The QDs coated with this polymer were successfully transferred to

water and displayed high stability without any aggregation. The hybrid nanoparticles exhibited an LCST behavior. These nano-sized, temperature responsive hybrid particles hold a great promise towards realization of sensor devices with a broad range of applications.

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