

Fabrication and responsive behaviour of Quantum Dot/PNIPAM micropatterns obtained by template copolymerization in water

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A facile method for the fabrication of Quantum Dot/poly(N-isopropyl acrylamide) (QD/PNIPAM) micropatterns on glass is presented. Water-soluble QDs functionalized with polymerizable methacrylic groups effectively copolymerize with N-isopropyl acrylamide monomer resulting in stable hybrid organic-inorganic networks. The patterns display temperature and pH responsive luminescence behaviour.

Size- and shape-dependent optical and electronic properties of semiconductor nanocrystals (Quantum Dots, QDs) make them attractive materials in optoelectronics and photonic applications. Integrating QDs with polymers has been often explored and a variety of such novel hybrid materials has been prepared.¹ A functional polymeric matrix, i.e., one that does not only provide a mechanical support for the QDs, may be used, adding new interesting features to the hybrid material, e.g., electroactive polymers are widely used in the fabrication of photovoltaic devices.² The use of responsive polymer, which exhibits large changes in its structure and properties in response to small variations in some environmental stimulus, adds an interesting feature to the matrix. The photonic properties of such materials can be controlled by transducing the matrix response to external stimulus down to a light emitting entity, like QD. Such hybrid QD/responsive polymer materials, like poly (*N*-isopropyl acrylamide)³ (PNIPAM) and water-soluble QDs have received particular attention.^{4,5} PNIPAM is a well-studied stimulus responsive, water-soluble polymer, which displays a lower critical solution temperature (LCST) around physiologically relevant temperature of 32 °C. When crossing the LCST by increasing the temperature, PNIPAM displays abrupt changes in morphology due to the rupture of intra-, and inter-chain hydrogen bonds mediated by water. Below the LCST, PNIPAM is hydrophilic and soluble in water, while above the LCST it becomes hydrophobic and aggregates. For crosslinked PNIPAM networks the LCST transition is marked by substantial and abrupt volume changes as the network swells and de-swells in water. The volume transitions combined with changes in hydrophilicity makes PNIPAM attractive for many applications covering drug release systems,⁶ bioanalytics,⁷ tissue engineering,⁸ and smart polymeric patterns.⁹ PNIPAM can be used as an active matrix transducing environmental changes to embedded QDs. The primary challenge in the fabrication of QD/PNIPAM materials lies in obtaining thermally stable structures with homogeneously dispersed, non-aggregated QDs, which would maintain their optical properties, and would be effectively entrapped by the PNIPAM matrix. Recently, we have reported on a robust fabrication method based on copolymerization of QDs with NIPAM, which results in luminescent hybrid materials with thermoresponsive properties.^{4,5} Water-based fabrication of such structures reduces costs and makes the related protocols more environmental friendly.

Development of functional micro patterns made of polymers and QDs is relevant in microelectronics and optoelectronics.¹⁰ Different fabrication approaches were employed, with various degrees of success, to obtain such patterns including co-polymerization,¹¹ layer-by-layer fabrication,¹² encapsulation in pre-polymerized solution,¹³ in-situ nanoparticle synthesis,¹⁴ and direct stabilization of QDs by the polymer matrix.¹⁵ However, each of these methods has some particular drawback: 1) it may not provide large, micrometer sized structures; 2) the assembly is based on weak interactions between the polymer and the QDs; 3) it may not include highly luminescent materials; or 4) finally it may not address the functionality of the polymeric matrix. It would be desirable therefore to design a new fabrication method, which does address all these drawbacks.

In this study we show that QDs encapsulated in amphiphilic polymeric coatings bearing chemical functionalities with carbon-carbon double bonds can be copolymerized with NIPAM. To obtain three-dimensional structures the polymerization proceeds in a template consisting of microgrooves in a rubber stamp made of poly(dimethyl siloxane) (PDMS). The grooves are covered tightly with a glass slide, which is functionalized with copolymerizable methacrylate groups via silanization. After the polymerization reaction, and peeling off the PDMS, a luminescent, micro-patterned polymeric network covalently attached to glass is obtained. The luminescent, thermoresponsive and pH responsive properties of the patterns are investigated.

To make QDs compatible with aqueous polymerization protocols, the QDs must be dispersible in water and display functional groups that would allow them to copolymerize with water-soluble monomers. Hydrophobic, TOPO-coated CdSe/ZnS QDs with emission at 600 nm were functionalized with an amphiphilic polymer and transferred into water following previously published protocols.^{5,16} The copolymer used was synthesised by modification of poly(isobutylene-*alt*-maleic anhydride) ($M_w = 6000$ g/mol) with *n*-octylamine, and 2-aminoethyl methacrylate (Fig. 1a). The amphiphilic coating exhibits hydrophobic *n*-octyl side chains to interact with the TOPO-capped QDs via hydrophobic/hydrophobic interactions. In addition, it features hydrophilic carboxylic groups in the form of a sodium salt for water dispersability, and methacrylic ester units for copolymerization. The ratio of these functional units, which influences the stability and performance of the QD assemblies, can be controlled. The polymerizable groups convert the QDs into water-soluble polymerizable assemblies. Our approach eliminates the ligand exchange step and usually results in good optical properties of the QDs after the water-transfer.

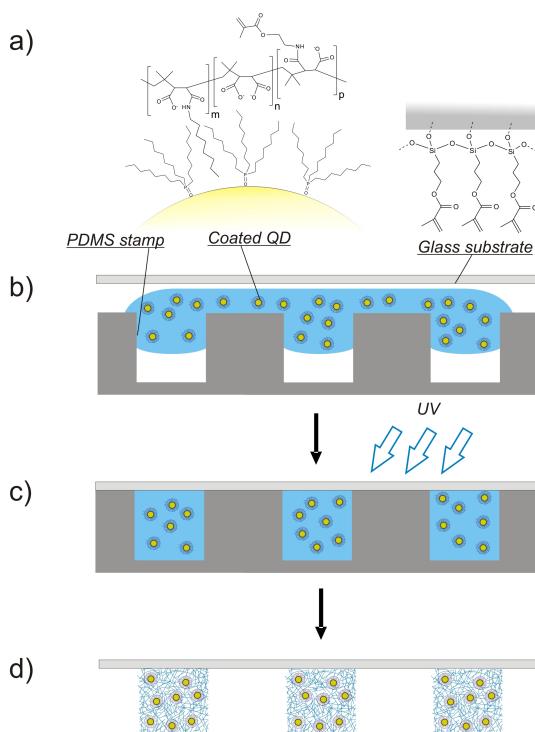


Fig. 1 General scheme of the micro-patterning procedure. a) Coated QD and functionalized glass used for patterning experiments. b) A drop of an aqueous solution of QDs and NIPAM is placed onto the PDMS stamp with prefabricated grooves pattern (2 μm wide, 2 μm high, 2 μm edge to edge distance between the stripes). c) A glass substrate, functionalized with polymerizable methacrylate groups, is then pressed onto the stamp and the polymerization in the channels is initiated by UV irradiation. d) After removing the PDMS stamp, QD/PNIPAM hybrid structures, covalently attached to glass, are obtained.

For the copolymerization reaction, the aqueous solutions of QDs were mixed with NIPAM. Such copolymerization mixtures were tested for different compositions and although no significant effects of the QD concentration was observed, NIPAM concentrations between 20 to 60 mg/mL were necessary to obtain the patterns. Lower concentrations of NIPAM resulted in discontinuous patterns, while higher concentrations yielded patterns damaged by monomer crystallization. The patterning mould was formed by trapping the copolymerization mixture in hydrophobic micro-grooves created between a glass slide and a PDMS stamp (Fig. 1). The glass substrate was pretreated with 3-(trichlorosilyl) propylmethacrylate to obtain a surface functionalized with methacrylic groups. The resulting patterns were therefore expected to form strong covalent bonds with the substrate but should be weakly bound to PDMS allowing peeling under low stress. Initially we also explored the use of the micromolding in capillaries (MIMIC)¹⁷ technique. However, it yielded only incomplete patterns, probably due to the relatively high viscosity of the copolymerization mixtures. Other methods were also explored but the most effective approach appeared to be dispensing of several drops of the copolymerization solution directly on the grooves in the PDMS stamp and then pressing the glass substrate onto PDMS, forcing the liquid into the hydrophobic channels in the stamp (Fig. 1). The polymerization reaction was initiated directly by UV irradiation, and no additional initiators were needed.⁵ As a result, patterns of PNIPAM covalently attached to the functionalized glass substrate with covalently entrapped QDs were obtained.

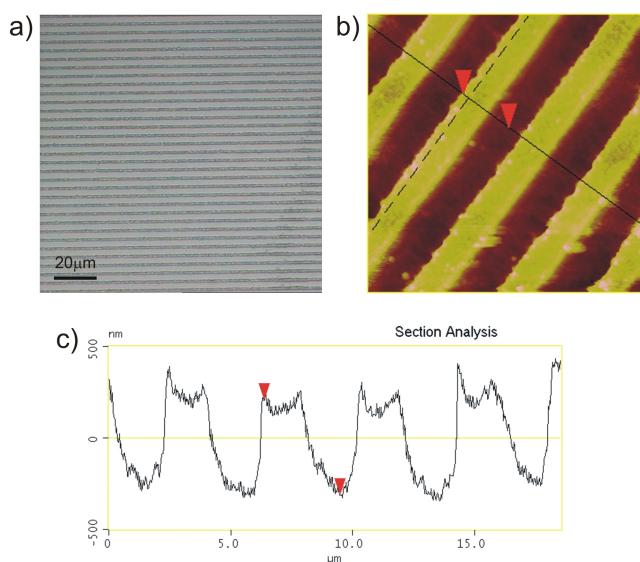


Fig. 2 a) Optical image of the QD/PNIPAM patterns attached to a glass substrate. b) AFM height image of the patterns (scan size: 15 μm x 15 μm). The black solid line and the red cursors mark the height cross-section shown in c). All images were obtained for dry patterns in air.

Several parameters were fine-tuned to optimize the process. Best quality patterns were obtained for reactions carried out at 40 °C in a nitrogen environment. The optimal time for the co-polymerization was 3 hours. When observed under optical microscope, the substrate shows well-defined and continuous stripes attached onto its surface (Fig. 2a), thus showing a successful transfer of the grating patterns of the PDMS mould to the substrate.

A representative AFM height image and a height cross section of the patterns are shown in Fig. 2b. Although the width of the patterns corresponds to the widths of the PDMS grooves, the height of the patterns (taken between the two cursors in Fig. 2a and 2c) is smaller than the depth of the PDMS grooves. The height of the dry patterns is ~ 4 times smaller than that of the wet patterns. This is due to drying of the PNIPAM matrix in air and indicates a rather low crosslink density and a hydrogel-like behaviour of the network. The QDs embedded in the PNIPAM patterns retained their luminescence. In Fig. 3a a confocal fluorescence image of a well-defined luminescent stripe-pattern corresponding to the QD/PNIPAM patterns is shown. Most of the QDs are confined within the patterns. Luminescence imaging revealed also areas of lower and higher than average luminescence. Because the AFM images show that the surface of the patterns is smooth, i.e., no holes or large protrusion are present, the confocal imaging results indicate that

some minor aggregation of the QDs inside the patterns may occur on the sub 1 μm scale. To test whether the a) PNIPAM retained its thermoresponsive properties, and b) the morphological changes of PNIPAM when crossing the LCST can influence the emission of the QDs in the grooves and c) the patterns are responsive to changes in the pH, we imaged the patterns in water at different temperatures and pH values. For temperature tests, a patterned glass slide was placed into a sealed sample holder and immersed into hot water. The measurements were first performed at high temperature and the sample was cooled down prior to performing the measurements at RT. Fig. 3a and 3b shows the same area of the pattern scanned at below the LCST, and at above the LCST of PNIPAM, respectively. The luminescence images and luminescence intensity cross sections (Fig. 3c) show that the luminescence of the QDs in the patterns depends to some extent on the imaging conditions. Notably, the patterns show slightly increased luminescence at above the LCST (Fig. 3b). Upon decreasing the temperature to below the LCST there is also some reorganization of the network and leaching of loose QDs out of the PNIPAM network. The leaching effects render quantitative analysis of the data difficult, but a general trend of lower emission at $T < T_{\text{LCST}}$ is clearly observed. It should be noted that the vertical size of the structures is comparable to the depth of focus and higher intensities observed at $T > T_{\text{LCST}}$ may simply be due to network collapse and increased density of QDs in the excitation volume during confocal imaging.

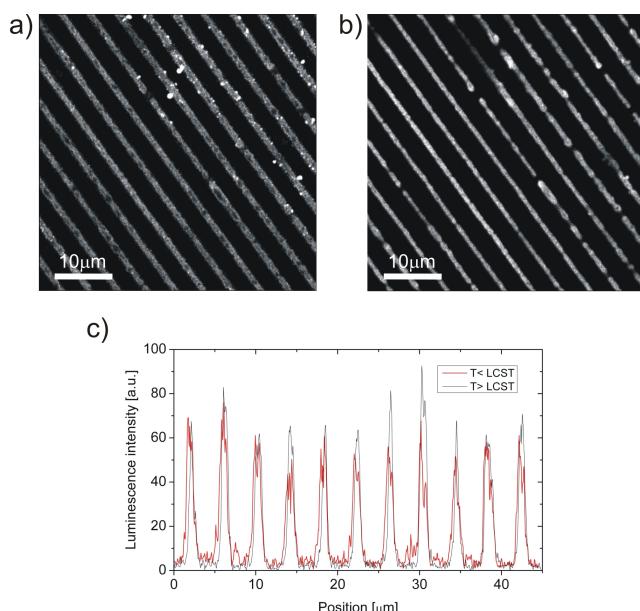


Fig. 3 Luminescence of the same areas of the QD/PNIPAM patterns imaged in water. a) Intensity image at RT; b) intensity image at $T > \text{LCST}$; c) Luminescence intensity cross section obtained from the same regions of (a) and (b).

QDs coated with carboxylic groups can be suspended in water at high pH values. To study the influence of pH on the luminescence emission in solution is however problematic as reducing the pH results in a loss of the colloidal stability due to protonation of the carboxylic groups.¹⁸ This leads to aggregation and precipitation, which masks the effect of pH on the emission of the QDs. Encapsulating QDs into hydrophilic polymeric patterns, however, may provide a good platform to study the pH effects since the QDs will be covalently immobilized in the polymeric network preventing aggregation. The QD/PNIPAM patterns were imaged using a fluorescence microscope after exposing the sample to solutions of different pH by depositing drops of phosphate buffers of pH 3 and pH 8 at RT. Fluorescence images (Fig. 4) clearly show changes in the luminescence of the patterns induced by the variation of pH. Upon changing the pH from pH 8 to pH 3 the contrast between the grooves and stripes of the pattern increased by 6 to 10 times. To test the reversibility of this effect, we performed several cycles of changing the solution pH (Fig. 4c). The luminescence changes are reversible and after the 4th cycle we recover 95 % of the initial QD luminescence.

The mechanism for the pH-responsive luminescence is subject of future studies. We tentatively associate the observed behaviour with interactions between the carboxylic polymer coating and the QD surface since in the investigated pH range the carboxylic group is undergoing reversible protonation and deprotonation.

This may result in changes of the charge density of the QD shell (upon deprotonation in high pH) and in different dielectric environment, or in direct reversible interaction of carboxylic groups with the QD surface.

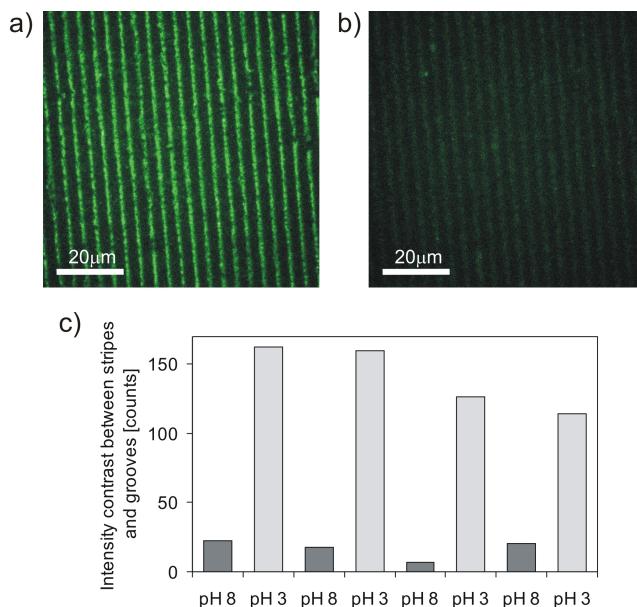


Fig. 4 Luminescence of the same area of QD/PNIPAM patterns imaged in water. a) Intensity image at pH = 3; b) intensity image at pH = 8; c) average intensity contrast value, i.e., difference in intensities between stripes and grooves (bright area minus dark area) of the pattern exposed to changes of pH. Four cycles of changes for the same area are presented. (For absolute changes in fluorescence see ESI.)

Conclusions

In summary, we present an easy and robust method for the preparation of surface-attached micropatterns of QD/PNIPAM on glass. The QDs and the glass slide used were functionalized with polymerizable groups and the copolymerization was initiated directly by UV irradiation. Thus, a hydrogel covalently attached to the substrate was obtained. The QDs exhibited stable luminescence in the patterns. The patterns displayed temperature dependent luminescence behaviour when crossing the LCST, which is attributed to the responsive behaviour of the PNIPAM matrix. In addition, pH dependent luminescence emission was also observed in the range between pH=3 and pH=8, which is attributed to reversible protonation and deprotonation of the carboxylic groups in the QD coating. The microfabrication method presented here is not limited to PNIPAM, but in principle can be applied to other types of nanoparticles and water-soluble monomers.

Acknowledgments

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