

Positioning of Quantum Dots into Prestructured Arrays by Polymer Encapsulation

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INTRODUCTION

Controlled structuring on the length scale of a few nanometers to 1 μm of surfaces and three-dimensional objects is an attractive challenge¹⁻³. Positioning of small objects (e.g. 5 nm in size) in arrays of larger dimensions (e.g. 100 nm) in an efficient manner is of interest, for example, in the context of the addressing and optical properties of single quantum dots located in larger metal structures functioning as a nano-antenna^{4,5}. We have followed the approach of encapsulation of small inorganic particles in polymer particles^{6,7}. This size enlargement can facilitate manipulation of the particles, sensitive inorganic particles can be protected during further manipulation steps⁸, and an interaction of the organic polymer particle surface with pre-structured arrays can be utilized for positioning.

EXPERIMENTAL

General Methods and Materials. Monodisperse polystyrene (PS) particles, \varnothing 1.39 μm (CV = 2.6%) were purchased from Microparticles, Germany, as a 10% aqueous dispersion. P (BMA-co-MMA) was supplied by Aldrich. Quantum dots of CdSe ($\lambda_{\text{max}} = 610$ nm) and ZnS@CdSe ($\lambda_{\text{max}} = 640$ nm) stabilized with octylamine and dispersed in toluene were supplied by nn-labs. Deionized water was distilled under nitrogen. Styrene was distilled under reduced pressure to remove inhibitor prior to polymerization. Reactive ion etching (RIE) was performed on the self-assembled PS monolayer at a total pressure of 10 mTorr of oxygen and a power of 100 W with a controlled etching rate of ca. 200 nm min^{-1} . TEM images were obtained with a Zeiss Libra 120 instrument. AFM studies of the structures of samples on a glass substrate were performed in tapping mode on a JPK NanoWizard instrument. SEM images were observed using Zeiss cross beam 1540 XB. Fluorescence studies were carried out on a custom-made confocal microscope setup with a spatial resolution of 0.8 μm , with an Nd:YAG laser operating at 532 nm as the excitation source.

Synthesis of Polystyrene Nanoparticles by "Surfactant Free" Emulsion Polymerization. Sodium styrene sulfonate (20 mg) comonomer, sodium bicarbonate buffer (60 mg), and potassium persulfate initiator (95 mg) were dissolved in 100 mL of water. The mixture was transferred into a mechanically stirred reactor vessel, along with 10 g of styrene. Polymerization was performed under argon atmosphere at 50°C for 16 h while stirring with 300 rpm.

Preparation of Polymer Encapsulated Quantum Dots by Secondary Dispersion. 0.1 mL of the original toluene solution of quantum dots was diluted and mixed with 0.4 g of PBMA-co-PMMA to a 2mL toluene solution, which was agitated with a mechanical shaker overnight. The solution was mixed with an aqueous solution of 10 mg of SDS, and stirred for 20 min under inert atmosphere, followed by sonication for 10 min (Bandelin HD2200 with KE76 tip, operated at 55% power). The solvent was removed by stirring the miniemulsion overnight and then under vacuum for 5 hours, injecting 2mL of water during the latter step.

RESULTS AND DISCUSSION

Patterned substrates were prepared by nanosphere lithography (NSL)^{9,10}. Briefly, monodisperse polystyrene (PS) colloids, with a particle size ranging from micrometers to several hundred nanometers were spread on a water surface to prepare a highly ordered monolayer. This was transferred to the solid substrate analogous to the Langmuir-Blodgett method. The PS particles are hexagonally close packed usually. The size of the PS particles on the substrates were reduced by

an oxygen plasma in a reactive ion etch (RIE) instrument, leaving the distance between particles unchanged. A gold film was evaporated on the substrates, followed by removal of the PS by dissolving in toluene. Generally, the distance between 'holes' can be tuned by the size of the original PS particles, and the size of 'holes' can be adjusted by the diameter of the etched PS particles, via the RIE parameters (Figure 1). The depth of the 'holes' can be controlled directly by the gold evaporation step.

The surface was modified by immersing in a 2mM 1-octadecanethiol (ODT) ethanol solution overnight, followed by thorough washing with ethanol and drying in argon, and exposure to a 4mM ethanol solution of 3-amino-propyl triethoxy silane (APTES) for 3 h. The glass 'bottom' of the 'holes' is rendered positively charged by the amine, while the continuous gold surface is rendered hydrophobic by a thiol monolayer.

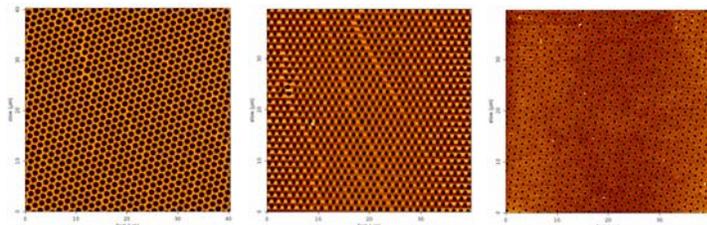


Figure 1. AFM images of structured surfaces with different 'hole' diameters (left: 1.2 μm , center: 0.8 μm , left: 0.4 μm).

As a model for studying the positioning of polymer particles in the aforementioned substrates, negatively charged PS nanoparticles were synthesized by emulsion copolymerization of styrene and sodium styrene sulfonate. This 'surfactant-free' polymerization affords particles electrostatically stabilized by covalently attached charged groups^{11,12}, such that by contrast to surfactant (e.g. SDS) stabilized particles desorption and distribution on the substrate is a minor issue. Monodisperse particles are obtained, with e.g. 260 nm size (Figure 2).

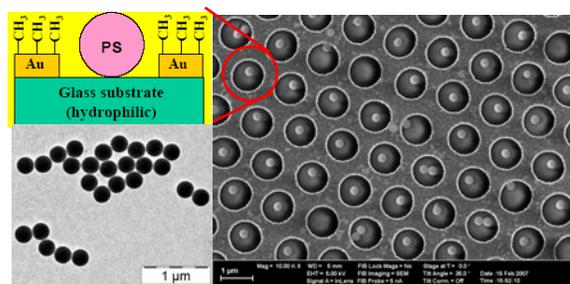


Figure 2. TEM image of PS particles from 'surfactant free' emulsion polymerization (lower left); SEM image of PS particles arranged in 'holes' (1.2 μm) of a substrate (right); and schematic cartoon of the latter (upper left).

To adsorb the PS particles on the aforementioned patterned and surface-modified substrates, the latter were floated onto the aqueous particle dispersion, resulting in selective adsorption of the particles in the 'holes' (Figure 2).

Quantum dots encapsulated in polymer particles were prepared by secondary dispersion of poly (butyl methacrylate-co-methyl methacrylate) (Poly(BMA-co-MMA))¹³ and lipophilically modified CdSe (optionally with a ZnS shell) nanoparticles in water. As polymer particles containing no more than a single quantum dot are desired for the studies of optical properties of isolated quantum dots, conditions were chosen such that the number of polymer particles prepared exceeds the number of quantum dots. This statistical approach was successful indeed: ca. 13 % of the polymer particles contain a single quantum dot, while the rest is empty (Figure 3).

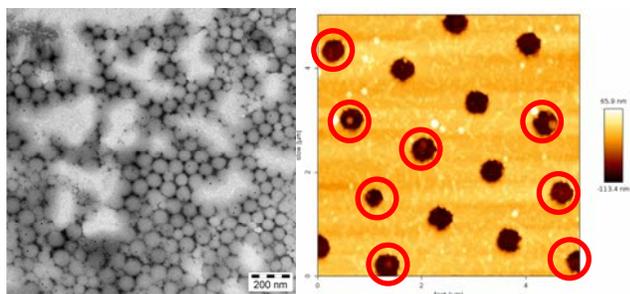


Figure 3. TEM image of Poly (BMA-co-MMA)-encapsulated quantum dots (left). AFM image of polymer-encapsulated quantum dots in gold holes array surface (right), circles designated particles in 'holes'

Studies with the quantum dot-containing polymer particle dispersions resulted in adsorption to the substrate upon floating the latter on the dispersion, analogous to the PS particles (Figure 3). In these preliminary studies, arrangement was not as selective as with the PS particles.

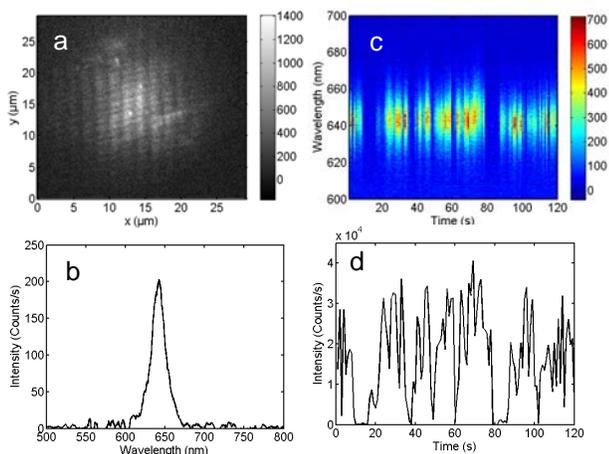


Figure 4. (a) Fluorescence confocal microscopy image of polymer particle-encapsulated quantum dots on substrate. (b) Fluorescence spectrum of single ZnS@CdSe quantum dots, (c) Spectrally resolved photoluminescence time trajectory of single polymer encapsulated quantum dot. (d) Spectrally integrated photoluminescence time trajectory for the same particle. All measurements at room temperature.

Microphotoluminescence studies were carried out employing confocal microscopy. Bright photo emission from single polymer encapsulated quantum dots could be detected (Figure 4 a and b, small bright dots in a). In time-resolved observations blinking of the photoluminescence emission is observed (Figure 4 c and d), which is indicative of the individual emitters indeed being single isolated quantum dots^{14,15}.

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