

Patterned Assembly of Quantum Dots onto Surfaces Modified with Click Microcontact Printing

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Semiconductor quantum dots (QDs) are a unique class of materials possessing extraordinary properties^[1] as a result of quantum confinement. QDs have been attracting attention for applications in light emitting diodes,^[2] nanoelectronic devices,^[3] solar cells,^[4] quantum computing^[5] and highly sensitive biometric diagnostics,^[6] largely owing to their unique electronic capabilities.^[7] In order to exploit these unique properties of QDs in applications and devices, finding ways to pattern very large surfaces—multiple square centimeter areas—homogeneously has become an active area of research. Although examples of patterning on smaller scales through X-ray,^[8,9] electron beam^[10] and scanning probe^[10] lithographic techniques have been reported, the fact remains that they do not lend themselves to economical scale-up. By contrast, soft lithography allows the rapid patterning of surfaces with multiple components, a process not currently attainable by standard lithographic procedures. The most promising and facile method reported^[12] for the patterning of QDs over large areas is microcontact printing which either (i) involves the modification of the QDs with functional groups so as to bind them chemically to surfaces pre-patterned by microcontact printing^[13,14] or (ii) the direct microcontact printing of QDs by inking a modified stamp with a solution containing QDs.^[14] There are a few reports^[15,16] in which unfunctionalized QDs are assembled onto modified surfaces pre-patterned by microcontact printing. They include a number of methods making use of self-assembled monolayers (SAMs) of organo-thiols on gold surfaces to create specific architectures.^[15] With this background in mind, we sought to apply a more versatile strategy that would allow for (i) “post-synthetic modifications” before or after surface-patterning with QDs had occurred, (ii) perform the surface self-assembly from freshly synthesized QDs and (iii) using a SAM

which is bound covalently to the substrate and does not suffer from the oxidative,^[17] thermal^[18] or diffusion^[19] related shortcomings of gold-thiol platforms.

In order to accomplish our goal of robust and extensible QD pattern formation, we decided to investigate alkyl-azide modified monolayers on silica surfaces because, a priori, there seemed to be little chance of strong interactions between QDs and surface-bound alkyl azides. Using the well-known copper-catalyzed azide-alkyne cyclization^[20–22] (CuAAC) chemistry, it is possible to transform the azides into functional groups which are known to coordinate strongly to the surface of QDs. Furthermore, this chemistry has been shown^[23,24] to work well when using stamping techniques and yields well-defined patterns over substrates that are not atomically smooth. By pre-inking a poly(dimethylsiloxane) (PDMS) patterned surface with pentynoic acid and Cu(I), we were able to obtain surfaces containing regularly alternating regions of terminal azides and carboxylic acids. Exposing the surfaces to organic solutions of freshly prepared QDs resulted in their surface adhesion, all but selectively, to the areas functionalized with terminal carboxylic acids with minimal residual deposition on the azides after washing, indicating that azides are indeed very poorly coordinating groups for CdSe QD. Subsequently, we were able to functionalize the remaining surface bound azides with hexyne using a second CuAAC reaction without perturbing the existing QD pattern. This proof-of-concept shows the capacity to form discrete interdigitated patterns of QDs by means of a simple, yet robust protocol.

Click microcontact printing is a convenient bench-top method to pattern substrates^[25,26] using a “click” reaction—a reaction which is atom economical and can be carried out with the intent of minimizing the environmental impact of the chemistry. In this case, the use of the CuAAC procedure affords a triazole ring from the reaction of terminal alkynes and terminal azides. Because these functional groups—in particular the azide—are orthogonal to most chemical reactions, click chemistry affords an ideal platform for the formation of patterns useful in the nucleation of microcrystalline materials. For the selective patterning of a silica surface, we employed a three-step process (**Scheme 1**) which begins with a SAM of alkyl azide either on quartz or on a layer of silica oxide created on a surface of silicon. A patterned elastomeric gel (PDMS), inked with pentynoic acid and Cu(I) is placed on the surface overnight and the resulting substrate is washed to remove residual copper and unreacted pentynoic acid. We have previously demonstrated^[23,24] that after approximately 7 h, the yield of the reaction is 95% and provides even and uniformly patterned surfaces. This reactivity could be verified using AFM which

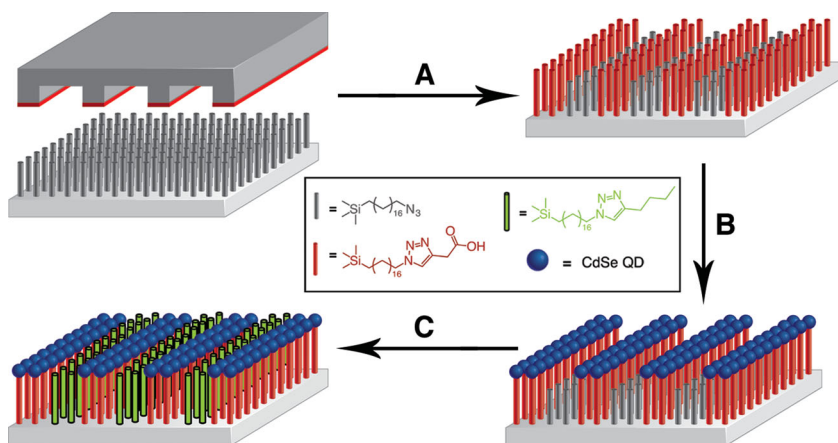
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Scheme 1. Route to obtaining the QD-patterned surfaces begins by reacting pentynoic acid and Cu(I) in an inked elastomeric stamp with a surface area monolayer of alkyl azides to form (a) interdigitated rows of alkyl carboxylic acids and alkyl azides. Submersion in a (b) 10^{-7} M organic solution of CdSe QDs results in the preferential deposition of QDs over the acid-terminated surfaces, leaving the azides free. Finally, the QD patterned wafer is (c) immersed in a CH_2Cl_2 solution of 0.1 M Cu(I)TBTA and 0.1 M hexyne to convert the remaining azides to alkyltriazoles.

identified (Figure 1a) a 1 nm differential between the carboxyl-terminated surface and the azide surface—in agreement with previously reported^[23] values. The surfaces modified by click microcontact printing with alternating carboxylic acid- and azide-terminated features were used subsequently to assemble CdSe QDs from solution by simple submersion in a CH_2Cl_2 solution of freshly prepared QDs. The substrate was then removed from the solution and washed vigorously with solvent before analysis. The surfaces were characterized extensively with a large variety of analytic techniques in order to ensure the successful adsorption of the CdSe QDs. AFM shows (Figure 1a) the height of the adsorbed features is approximately 4–7 nm, corresponding well to the size of the QDs that were used. It is noteworthy that in all cases, the QDs assembled in aggregates on the carboxyl-terminated patterned surfaces, occasionally leaving voids (Figure 1b) which contain no QDs. This is likely due to the presence of equally strongly coordinating surface ligands of steric acid formed from the synthesis of the QDs and not, as recent literature^[27] suggests, more weakly bound phosphine oxides. Little of such aggregation (Figure S5, Supporting Information) was found on the azide surfaces, however, even when relatively large areas were scanned.

The fluorescence of the QDs was investigated both by optical fluorescence spectroscopy and by microscopy, after performing the reaction on optically transparent

quartz. The emission spectra (Figure 2) of the QDs in solution, and on a patterned surface, show a λ_{max} of 580 nm in solution and a broadened peak with a λ_{max} at 570 nm when adsorbed on the surface. The hypsochromic shift and broadening is indicative of photobrightening of the surface QDs.^[28] Fluorescence optical microscopy (Figure 3a) characterization indicated very clear patterns as well as the periodic aggregate formation of QDs. Using ImageJ, we found that the carboxylic acid terminated areas showed a fluorescence increase of 86% as compared with the azide-covered areas, indicating a substantial preference for chelation to the acid sites, once again consistent with literature observations.^[24] When carried out on a surface not functionalized with pentynoic acid, only sparsely grouped aggregate formation (Figure 3b) was observed lending evidence to the fact that the QDs do not show a strong affinity for the azide surfaces. Since EDS spectroscopy was not sufficiently sensitive to detect the signature traces of Cd against the background of

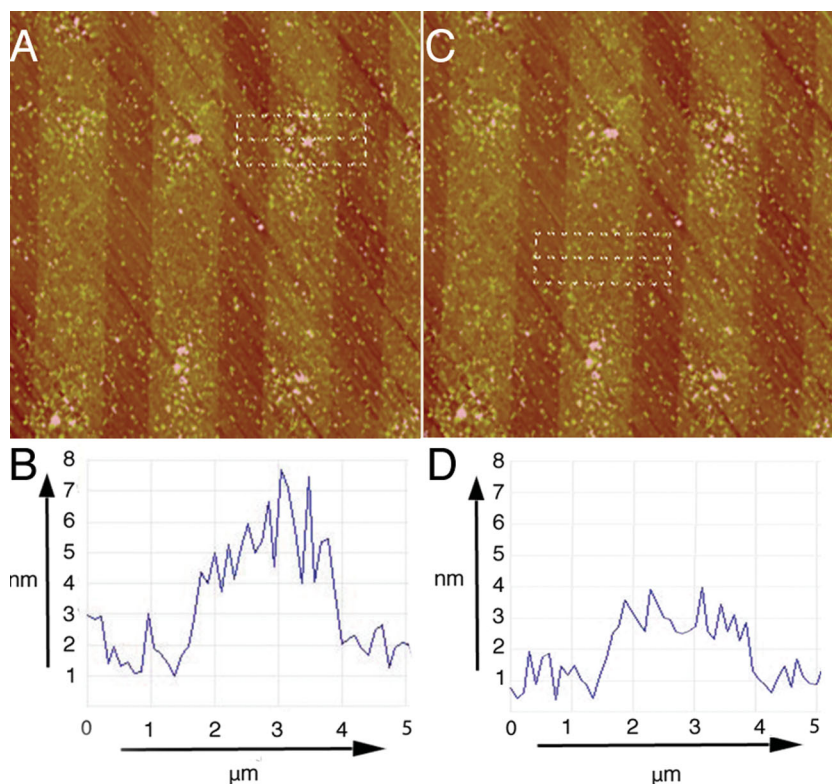


Figure 1. a) Tapping mode AFM image of a local cluster of QDs on the surface after submersion and rinsing in a 10^{-7} M solution of CdSe QDs. The cluster is largely confined to the terminal carboxylic acid pattern. b) Profile showing the height difference of 1 nm between the higher carboxylic acid and lower azide terminated features plus the adsorbed QDs (average diameter of 5 nm). c) Tapping mode AFM image of an area of the surface just below QD cluster where very little adsorption occurs. d) Profile showing a height difference of 1 nm corresponding only to the carboxylic acid-terminated features above the azide surface suggesting not all of the acid terminated sites end up saturated with QDs.

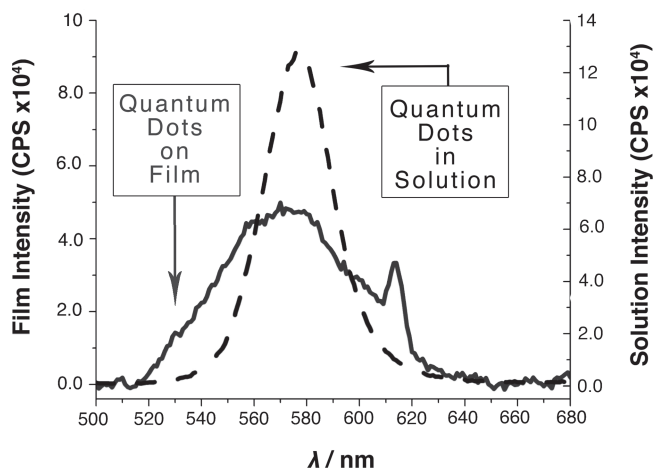


Figure 2. Emission spectra of the QDs in solution (black dotted line) and adsorbed onto a quartz surface modified by click microcontact printing (red solid line) ($\lambda_{\text{ex}} = 460$). The peak at 615 nm likely corresponds to a Raman overtone from the hydrocarbons on the surface.

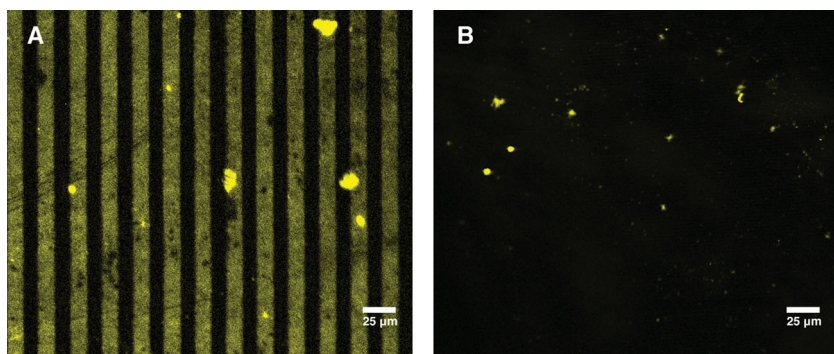


Figure 3. Fluorescence microscopy ($\lambda_{\text{ex}} = 488$ nm) of a) patterned surfaces coated with CdSe QDs; small amounts of aggregated QDs were observed. b) A surface which contains only azides. Note that the QD aggregates are visible on this surface as well.

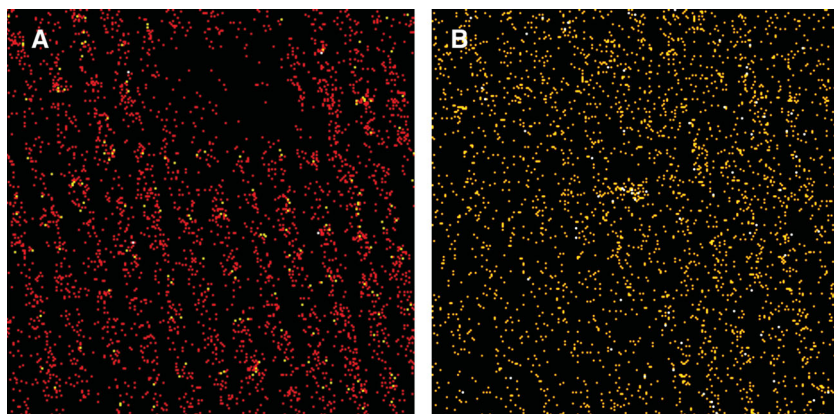


Figure 4. Mapping TOF SIMS images of the surface with assembled CdSe QDs. a) The pattern of Cd⁺ on the surface corresponding to the pattern created with click microcontact printing and the subsequent QD assembly is shown. b) The images of PDMS reveal the largely obscured pattern as a result of the repeated rinsing.

Si, in order to ensure that QDs were adsorbed, the surfaces were analyzed by time-of-flight secondary ionization mass spectrometry (TOF-SIMS). The presence of QDs on the substrates was confirmed by TOF-SIMS analysis, which indicated (Figure 4a) a distribution of peaks in the range of 106 to 116 for m/z , consistent with Cd⁺. The counts in this range decreased significantly within the first few seconds of surface ionization, an observation that can be attributed to the rapid destruction of the surface layer of QDs. Because of the low number of counts at each point on the surface, the apparent isotopic distribution of cadmium deviated from the actual isotopic distribution (see the Supporting Information).

The precise positioning of the cadmium on the surface, as well as confirmation of its presence, could be accomplished simultaneously using mapping mode SIMS (Figure 4). TOF-SIMS analysis shows clearly the linear patterns of the CdSe over the surface. Additionally, the distribution of PDMS over the surface was investigated to see if residual PDMS may be complicating the AFM measurement. The PDMS was not remotely as well-defined as the cadmium distribution (Figure 4b), indicating that the multiple washing steps spread the remaining PDMS residue more or less evenly over the surface.

The remaining surface bound azides presented us with an opportunity to demonstrate the versatility of the QD self-assembly process, even in the presence of competing cationic metals. As a proof-of-concept, we took a substrate, which had been patterned with QDs interdigitated with surface bound azides, and re-exposed it to click conditions using hexyne as the alkyne reagent. In order to minimize metal adhesion to the surface, we used the strongly chelating ligand tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA) bound to Cu(I)PF₆ and allowed the substrate to sit, immersed and in the dark, for 48 h. After washing with CHCl₃, the substrates were investigated by AFM, which revealed the aforementioned aggregate QDs situated in the same, striped pattern (see Figure S7 in the Supporting Information) but with a relatively flat underlying surface.

In conclusion, we have outlined an efficient way to pattern quantum dots onto a pre-patterned surface area monolayer utilizing simple adsorption from a solution containing quantum dots. The surfaces prepared were well characterized and both linear and dot patterns were realized. The stearate ligands attached to the quantum dots were exchanged on the surface of the silica with the surface mounted carboxyl acid functions and appeared to leave the azide layer unperturbed. The azide layer, which was still capable of further modification, was backfilled by carrying out a second click reaction. This proof-of-concept lends itself to an experimental design in which—in lieu of electronically inert alkyl chains—

substrates, which complement the QDs, can be investigated. For instance, p-type organic materials, such as phthalocyanine derivatives, could interdigitate the n-type quantum dot layers to create near-perfect hetero-junctions. With improved resolution in stamping, nearly ideal interdigitated p-n junction monolayers could be produced and built upon in a layer-by-layer approach.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

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