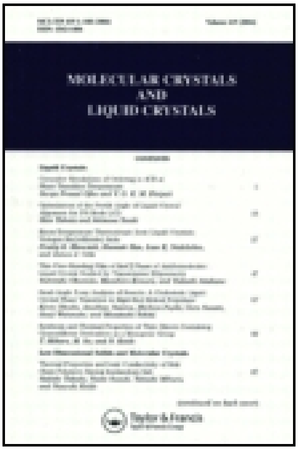

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Selective Patterning of Quantum Dots on Functionalized Surface Using Polyelectrolyte Transfer

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We reported a simple method to pattern quantum dots, CdSe/ZnS, on selectively functionalized surface. This selective patterning of the quantum dots solution can be understood by considering the difference in affinity owing to different chemical functionality between the surface charge of quantum dots and transferred polyelectrolyte. Thus the quantum dots can be easily deposited on desired surface by simple dipping method. And the patterned shape and size can be freely controlled by polymer transfer technique according to the variation of used micromold.

Keywords: patterning; polyelectolytes; polymer transfer; quantum dots; surface modification

1. INTRODUCTION

Nanoparticles with a size range of a few nanometer show unprecedented chemical and physical properties [1,2]. Especially, quantum dots, nanoparticles of inorganic semiconductor, have attracted considerable interests due to their unique optical properties from quantum sized effects [1,2]. They have been extensively applied to various potential

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applications including fluorescent biological label, photovoltaic cells, organic light emitting diodes (OLEDs), field emission display, single electron transistors, data storage devices, and optical sensors [3–5]. Before those applications can be realized, the quantum devices requires precise and accurate pattern of nanoparticles on desired area. Thus, the ability to selectively immobilize nanoparticles with ordered structure onto solid substrate is of a great importance [3–5].

Recently, several approaches have been proposed to provide lateral patterning method including holographic lithography [6], lift-off lithography [7] and microcontact printing [8]. However, these methods require templates being prepared as the first step by lithography. The following processes are complicated, expensive, and demanding strict control of the processing parameters as well as many preparing steps. Therefore, these methods are difficult to realize the industrial application because the most important requirement is rapid, simple, and reliable process and patterning method can be applied to large area processing with the formation of large scale periodic patterns of nanoparticles.

One of the attractive methods in patterning techniques of nanoparticles relies on the engineered surfaces with long and short range order [9,10]. The fabrication of engineered surfaces is interesting in many areas of science and technology due to its attractive characteristic feature such as high specificity, controlled affinity, and reversibility. The critical issues in selective immobilization of nanoparticles onto desired surface are (1) the control of the chemical and physical property of the surface, (2) the structure of nanoparticles with bound chemical groups, and (3) the precise control of the molecular interactions including hydrogen bonding, electrostatics, metal coordination, and van der Waals force between nanoparticle and the engineered surface [11,12].

In this study, we reported a simple method to pattern quantum dots (CdSe/ZnS) on selectively functionalized surface by polyelectrolyte transfer, where a strong electrostatic interaction has been occurred between selectively patterned surface of polyelectrolyte polymer and modified CdSe/ZnS. Selective immobilization of nanoparticles onto engineered surface prepared by the polymer transfer technique is achieved. This method introduces some advantages. First, quantum dots can be easily deposited on desired region by simple dipping method. And quantum dots having different functional chemical groups can also be used for patterning because the functionalized surface with polyelectrolyte multilayers (PEL) has an ability to selectively adsorption of CdSe/ZnS. Secondly, the patterned shape and size can be freely controlled by simple polymer transfer technique according to the variation of used micromold. Third, the roughness and topography of the functionalized surface can be modulated by the different thickness of PEL from variation of stacked polyelectrolyte layers. Furthermore, several kinds of particles made of various materials such as polystyrene, silica, metal/metal oxides, and fluorescent dyes may be used for patterning on designed area.

2. EXPRIMANTALS

2.1. Preparation of Quantum Dots

Quantum dots (CdSe/ZnS; core-shell nanoparticles) used in this work were synthesized according to the previously published procedure in a three-component coordinating solvent mixture of hexadecylamine, trioctylphosphine (TOP), and trioctylphosphine oxide (TOPO) [1,2,13]. An amount of ZnS precursor {diethylzinc $(CH_2CH_3)_2$: hexamethyl(disilanthaine)($(TMS)_2S$) = 1:1 in TOP} were added in TOPO-functionalized CdSe solution at elevated temperature. Finally, solution was sequentially washed with methanol and chloroform and stored in chloroform at 4°C.

2.2. Ligand Exchange for Water Soluble Quantum Dots

The resulting organic soluble CdSe/ZnS were converted into water soluble nanoparticles through ligand exchange method with mercaptoacetic acid according to previous procedures [14,15]. In brief, the TOPO-capped CdSe/ZnS quantum dots (2 ml; 3.5 mg/ml) were mixed with 1 M solution of mercaptoacetic acid (MAA). The mixed transparent solution was sonicated for 200 min at 60°C. To discard the excess of MAA, aqueous solution of quantum dots was centrifugated after the addition of the PBS buffer (pH 7.4, 20 mM). Finally obtained water soluble quantum dots were stored in PBS buffer at 4°C.

2.3. Fabrication of Polyelectrolyte Patterned Substrate Using Polymer Transfer

Glass was cleaned with a piranha solution consisting of a 4:1 mixture of 50% aqueous solution of H_2SO_4 and 30% aqueous solution of H_2O_2, rinsed sequentially with deionized water, ethanol, acetone, and finally dried with nitrogen. Activated glass was spin-coated with polyallylamine hydrochloride (PAH) at 4000 rpm for 15 sec [16]. To remove the unbound PAH, the substrate is washed with distilled water for three times and then spin-coated with a solution of polyacrylic acid (PAA) (20 mM; pH 9.0) at 4000 rpm for 15 sec. This procedure was repeated until the desired number of PEL layers was assembled on the slide.

For the transfer of PEL polymer, PDMS micromold was sequentially immersed in positively charged PAH and negatively charged PAA polymer. In this study, PAH/PAA/PAH, three-layer, were deposited onto the PDMS micromold. The PDMS was carefully attached on PEL multilayer substrate having PAA as a top layer for 30 min. And then, PAH polymers on the PDMS micromold could be transferred onto the PEL multilayer coated surface. The transferred polymer substrate was confirmed by the analysis of contact angle and AFM.

2.4. Deposition of Water Soluble Quantum Dots onto the Modified Substrate

The finally prepared substrate was immersed in anionic MAA-QDs (5 ug/ml) for 20 min. After deposition of MAA-QDs, the substrate was washed with PBS buffer to remove non-specifically bound nanoparticles. The overall schematic diagram of patterning was shown in Figure 1.

2.5. Analytical Instruments

Absorption spectra of synthesized QDs and modified MAA-QDs were performed at UV-Vis spectroscopy (AGILENT, 8453) and property of surface charge was obtained with zeta-potential analyzer (OTSUKA, ELS-8000). Contact angles of the substrates were determined with Krüss G10 contact angle analyzer (Krüss GmbH, Hamburg, Germany) to investigate wettability and surface tension of surface. All the measurements were carried out at room temperature and ambient humidity. Each reported value was the average of contact angles measured for five times. Fluorescence images were performed with fluorescence microscopy (NIKON, TE-2000U, Japan). Surface morphology of the fabricated substrate was analyzed with atomic force microscopy (PSIA, XE-100) using XEI analysis program.

3. RESULTS AND DISCUSSIONS

3.1. Properties of Water Soluble QDs

For the preparation of water soluble QDs, ZnS-capped CdSe QDs was reacted with mercaptoacetic acid (MAA) and purified three times by

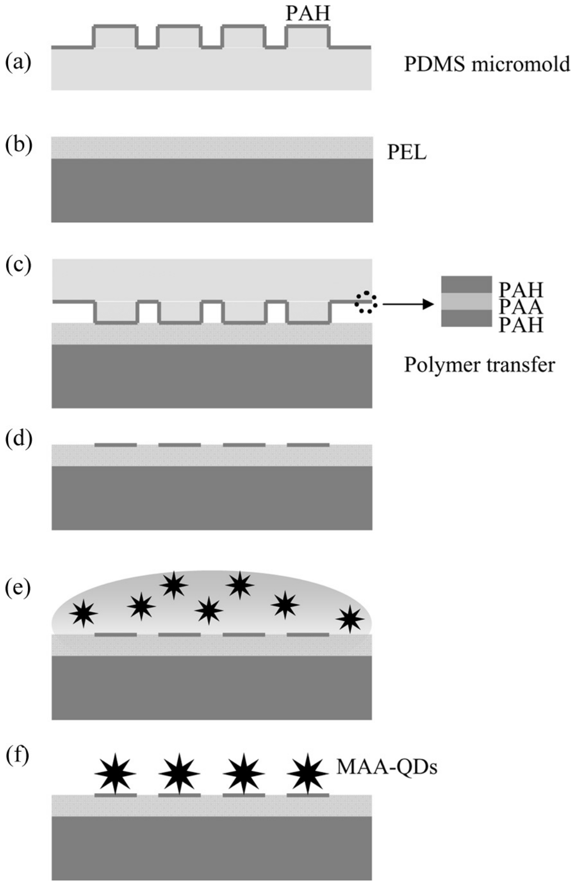


FIGURE 1 Schematic diagram of selective QDs patterning. (a) Deposition of PAH as a top layer onto PDMS micromold, (b) layer-by-layer deposition of PEL having PAA as a top layer, (c) polymer transfer from PDMS micromold to PEL coated substrate, (d) peel off PDMS micromold, (e) loading MAA-QDs, (f) detection of selective QDs patterning.

methanol/ethanol precipitation, centrifugation, and resuspension in PBS buffer. The carboxylated QDs have an ability to be easily solubilized in aqueous solution.

The absorption and luminescence spectra of unmodified QDs and MAA-QDs were obtained (Fig. 2a). The observable peak of MAA-QDs from 400 nm to 700 nm was almost identical to unmodified QDs (TOPO-capped CdSe/ZnS) although intensity of MAA-QDs was relatively reduced. In the case of analysis of photoluminescence, maximum

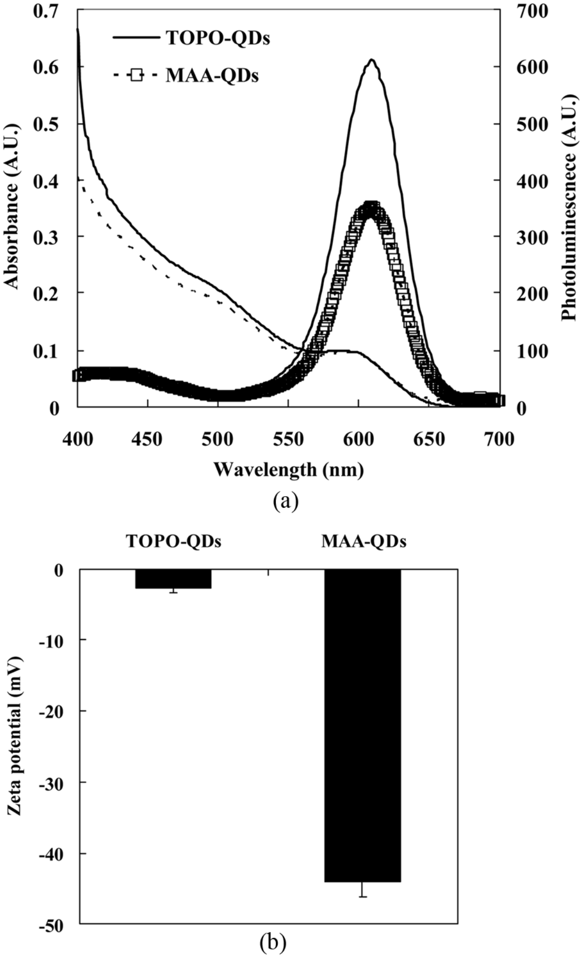


FIGURE 2 Characterization of optical and surface properties of QDs. (a) Absorption and photoluminescence spectra of unmodified QDs (TOPO-QDs) and MAA-QDs. The concentration of MAA-QDs solution (50 ug/ml) was introduced. (b) Zeta potentials of TOPO-QDs in chloroform and MAA-QDs in PBS buffer (pH 7.4, 20 mM).

positions of peaks in fluorescence emission are almost same. Thus modified MAA-QDs retained their inherent optical property although surface ligands were replaced with mercaptoacetic acid. In addition, emission bands of both samples in luminescence spectra showed relatively narrow (FWHM = 35 – 45 nm), which indicated the good size distribution was preserved. The narrow size distribution of the nanoparticles led to better resolution.

For the confirmation of modified QDs, surface charges of unmodified QDs (TOPO-QDs) and MAA-QDs suspend in PBS buffer (pH 7.4, 50 mM) were estimated using the smoluchowski method (OTSUKA, ELS-8000). The zeta potential values of unmodified QDs and MAA-QDs were measured to −2.26 mV and −45.66 mV, respectively (Fig. 2b), which proved that the modification of QDs with MAA was correctly performed because the presence of anionic MAA renders strong negatively charged surface.

3.2. Wettability of modified surfaces

Micropatterned substrates with selective binding ability for QDs were fabricated by way of self-assembled polyelectrolyte deposition and polymer transfer technique (Fig. 1). Spatial binding of QDs to oppositely charged surface formed by polymer transfer was demonstrated. For the confirmation of modified surfaces, the wettability of various modified surfaces with water contact angles is determined (Fig. 3). This fact suggests that deposited polyelectrolyte layers can modulate the wettability of substrates by simple adsorption of polymers onto desired surface and area. As a control experiment, bare and plasma treated glass were also examined. The decrease of contact angle at the plasma

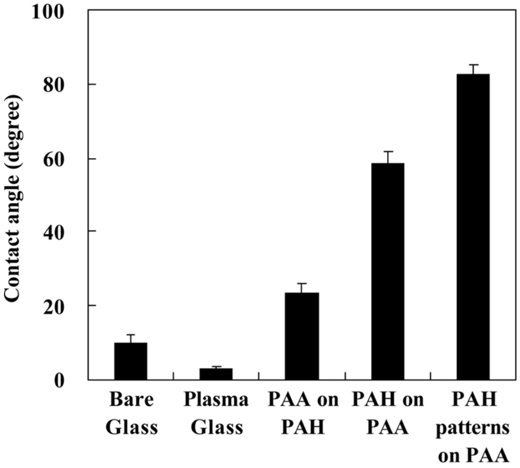


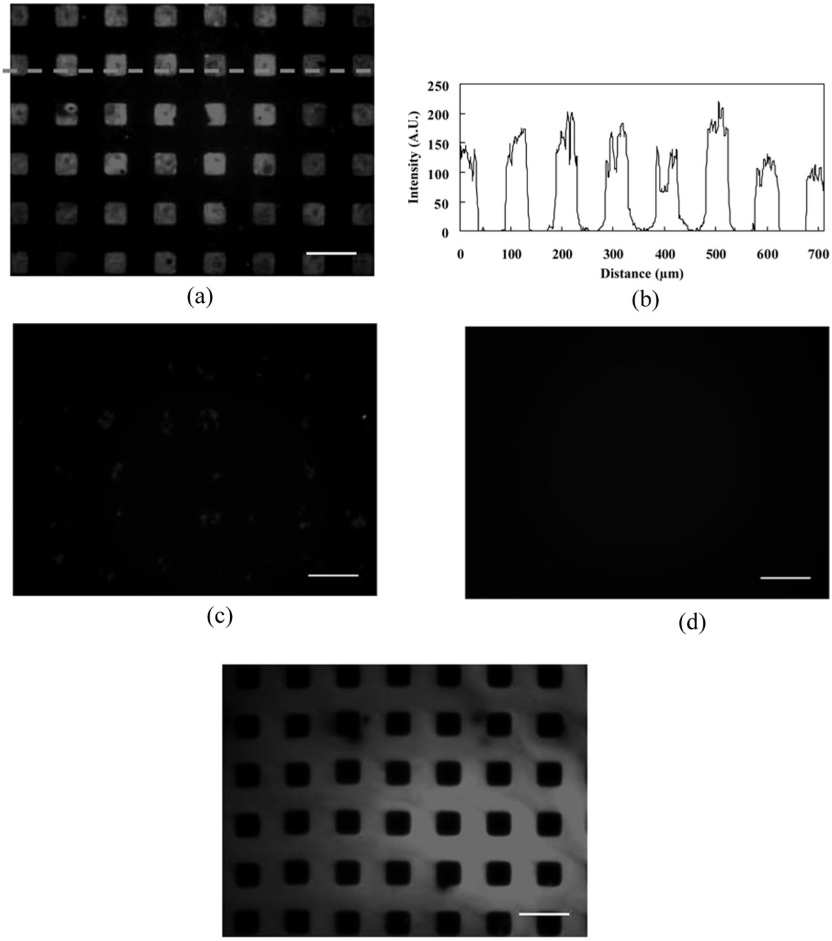
FIGURE 3 Water contact angle of various substrates. (a) Bare glass, (b) plasma treated glass, (c) PAA coated onto PAH (PAH/PAA; bilayer), (d) PAH coated onto PAA (PAH/PAA/PAH; triple layer), (e) patterned PAH on PAA (PAH/PAA/patterned PAH).

treated glass was attributed from the introduction of hydrophilic polar group by a way of strong irradiation of high radical energy [16]. The sequential deposition of positively charged polymer (PAH) and negatively charged polymer (PAA) provides the change of contact angle because the wettability of fabricated films strongly depends on the outermost polymer layer. The contact angles of PAH and PAA indicated $55^\circ \pm 2^\circ$ and $25^\circ \pm 2^\circ$, respectively, which is well matched with previous results [17,18]. As the increase of deposited layers, the regular osciallation is obtained (data not shown). However, micropatterned surface by polymer transfer technique showed the higher increase of contact angle ($84^\circ \pm 2^\circ$) because the increase of surface roughness governing wettability enhances its hydrophobicity [19,20].

3.3. Patterning of QDs onto Functionalized Surface

Patterning of carboxylated CdSe/ZnS core-shell nanoparticles (QDs) are employed to demonstrate that the functionalized surface can be applied to selectively immobilize them due to the electrostatic interaction. The carboxylated QDs at pH 7.0 were loaded onto the micropatterned surface. At the condition, all the carboxylate ions have negatively charges and provide the electrostatic interactions with positively charged surface region. To confirm regions of positive and negative charge, the modified surface were reacted with a negatively charged MAA-QDs.

Figure 4a clearly confirmed that negatively charged QDs were selectively deposited onto the PAH transferred square region. The fluorescence areas are where MAA-QDs binding has occurred and dark background indicates the nonadhesive surface for MAA-QDs due to the strong repulsion between negatively charged PAA and anionic QDs. The line profile of fluorescence image clearly showed the patterning of QDs was successfully performed onto only defined PAH regions (Fig. 4b). However, fluorescence image could not be obtained when solution of carboxylated QDs at pH 4 was applied (Fig. 4c). In the case of acidic condition (pH 4), carboxylated ions on QDs can be easily protonated and lose their electrostatic interaction force. In addition, negatively charged layer as a top layer provides repulsion of negatively charged QDs when the surface having PAA polymer lastly deposited was used for control experiment (Fig. 4d). Finally, reverse patterning of QDs could be obtained when the PAH was coated on background and the region of patterns was PAA (Fig. 4e). Thus, polymeric layer including strongly indentical charges can act as prevention of non-specific binding when electrostatic interaction as main driving force is applied.



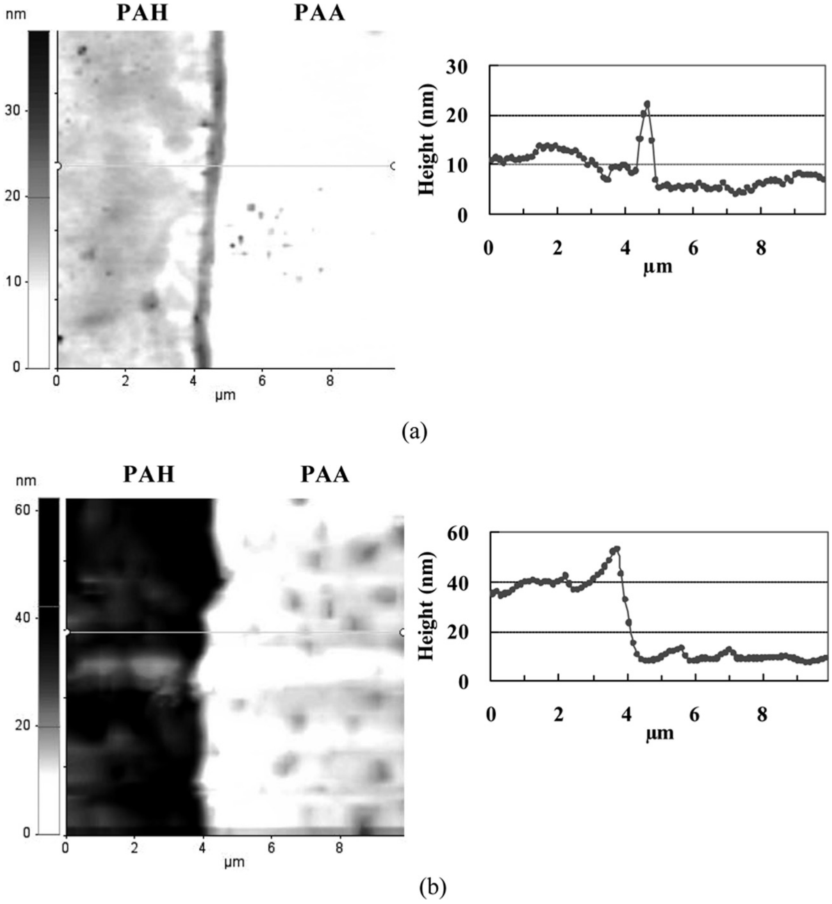
(a) (b)

(c) (d)

(e)

FIGURE 4 Fluorescence image of patterning on three types of substrates. (a) The image of patterned MAA-QDs onto surface selectively modified with PAH, (b) line profile of fluorescence intensity, (c) image after the loading of MAA-QDs in pH 4.0 solution; At this condition, most of carboxylated ions on MAA-QDs were protonated, (d) fluorescence image when the MAA-QDs was introduced onto PAA coated layer as a control experiment, (e) the image of background patterning in the case of background modified with PAH while patterns were coated with PAA. The scale bar of image indicates 100 μm.

In Figure 4 selective patterning of QDs were successfully demonstrated because positive charged PAH polymer was directly transferred onto an outermost PAA layer of PAH/PAA multilayer. The patterned



(a)

(b)

FIGURE 5 AFM image of border line between pattern and background. (a) AFM image of patterned surface with PAH and PAA; Line profile means the height of surface, (b) AFM image of selectively deposited MAA-QDs; dark and bright color indicate PAH region and PAA region as a background, respectively. After the loading of MAA-QDs onto the prepared surface, the height of PAH region was increased and flatten, which suggested the selective immobilization of nanoparticles due to the strong electrostatic interaction between PAH and MAA-QDs. The images were performed by tapping mode and scanning area is $10\,\mu m \times 10\,\mu m$.

region was characterized using atomic force microscopy (AFM). Figure 5 showed AFM topographic images and line profile of boundary region between PAH micropattern and PAA background at both before and after deposition of MAA-QDs. For comparison, the morphological analysis was also investigated after the selective deposition of carboxylated QDs. The two images obviously exhibited difference morphologies as evidenced by line profiles. Figure 5a showed transferred PAH region has edge profile after the detachment of PDMS micromold, which indicated that relatively large amount of PAH polymer on the edge of PDMS micromold was transferred. The polymer that is transferred at edge during the transfer of polymer from PDMS micromold is relatively thick due to the large cohesive interaction between previously coated PEL on substrate and the viscous property of the inked polymer on the edge region of PDMS micromold.

After the transfer of polymer (PAH/PAA/PAH) onto an outermost PAA layer of PAH/PAA multilayer, the increase of height of patterned region was about 6 nm (Fig. 5a). Because the statistical average thickness of monolayer is 2 nm in the layer-by-layer deposition [21], the transferred three layers (PAH/PAA/PAH) was nicely deposited onto the substrate under our experimental process. The introduction of MAA-QDs resulted in the increase of thickness of the QDs onto deposited area (about 30 nm) (Fig. 5b). When considered the size of applied QDs (5 nm), the immobilized QDs formed multi-stacking. The edge profile was also reduced after the deposition of QDs onto the PAH region. This difference of the surface geometry directly proved that our proposed method can be successfully performed.

4. CONCLUSION

Simple approach to patterning of nanoparticles using self-assemble PEL and polymer transfer technique was presented by a way of strong electrostatic interaction. Our proposed method involves the simple polymer transfer from micromold to wide range of substrates and easily controls the size and shape of micropatterns. In addition, the top layer of polymeric thin film was controlled by the direct stamping of desired polymers. Therefore, the approach will be useful for the manipulation of quantum dots with surface chemistry and solve the demand for strict control over the positioning in many applications such as microdevices, biosensors, and molecular probes.

REFERENCES

[1] Beverly, K. C., Sample, J. L., Sampaio, J. F., Remacle, F., Heath, J. R., & Levine, R. D. (2002). *Proc. Natl. Acad. Sci. USA*, *2*, 6456.
[2] Vanmaekelbergh, D. & Liljeroth, P. (2005). *Chem. Soc. Rev.*, *34*, 299.
[3] Maier, J. (2005). *Nat. Mater.*, *4*, 805.
[4] Psaltis, D., Quake, S. R., & Yang, C. (2006). *Nature*, *442*, 381.

[5] Hotz, C. Z. (2005). *Methods Mol. Biol.*, *303*, 1.
[6] Tomita, Y., Suzuki, N., & Chikama, K. (2005). *Opt. Lett.*, *30*, 839.
[7] Hua, F., Lvov, Y., & Cui, T. (2002). *J. Nanosci. Nanotechnol.*, *2*, 357.
[8] Wu, X., Lenhert, S., Chi, L., & Fuchs, H. (2006). *Langmuir*, *22*, 7807.
[9] Dibbell, R. S., Soja, G. R., Hoth, R. M., & Watson, D. F. (2007). *Langmuir*, *23*, 3432.
[10] Xu, H., Hong, R., Lu, T., Uzun, O., & Rotello, V. M. (2006). *J. Am. Chem. Soc.*, *128*, 3162.
[11] Binder, W. H., Kluger, C., Straif, C. J., & Friedbacher, G. (2005). *Macromolecules.*, *38*, 9405.
[12] Nolte, M. & Fery, A. (2006). *IEEE Proc. Nanobiotechnol.*, *153*, 112.
[13] Potapova, I., Mruk, R., Hubner, C., Zentel, R., Basche, T., & Mews, A. (2005). *Angew. Chem. Int. Ed. Engl.*, *44*, 2437.
[14] Kloepfer, J. A., Bradforth, S. E., Nadeau, J. L. (2005). *J. Phys. Chem. B. 109*, 9996.
[15] Algar, W. R. & Krull, U. J. (2006). *Langmuir*, *22*, 11346.
[16] Sadhu, V. B., Perl, A., Peter, M., Rozkiewicz, D. I., Engbers, G., Ravoo, B. J., Reinhoudt, D. N., & Huskens, J. (2007). *Langmuir*, *23*, 6850.
[17] Shi, Z., Neoh, K. G., Zhong, S. P., Yung, L. Y., Kang, E. T., & Wang, W. (2006). *J. Biomed. Mater. Res. A*, *76*, 826.
[18] Kolasinska, M. & Warszynski, P. (2005). *Bioelectrochemistry*, *66*, 65.
[19] Li, X. M., Reinhoudt, D., & Crego-Calama, M. (2007). *Chem. Soc. Rev.*, *36*, 1350.
[20] McHale, G., Shirtcliffe, N. J., Aqil, S., Perry, C. C., & Newton, M. I. (2004). *Phys. Rev. Lett.*, *93*, 036102.
[21] Jiang, X., Zeng, H., Gourdin, S., & Hammond, P. T. (2002). *Langmuir*, *18*, 2607.