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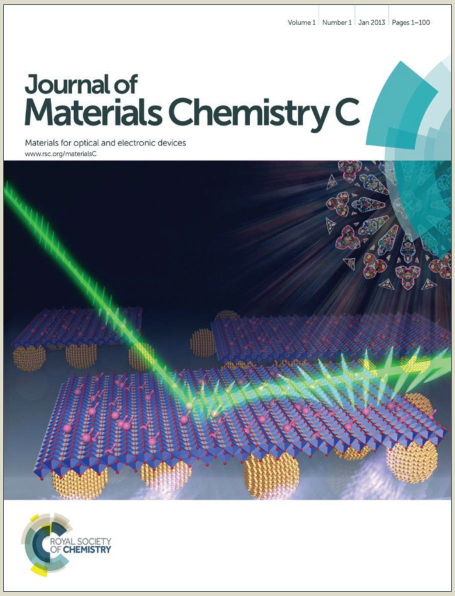

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Journal Name

ARTICLE

Direct Microcontact Printing Induced Supramolecular Interaction for Creating Shape-tunable Patterned Polymer Surfaces

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Multifunctional polymeric patterning surfaces are of significant importance for numerous surface-based researches. We demonstrated that commerical polymer of polyethylenimine (PEI) with rich amino groupscan be used as a versatile ink for the direct fabrication of PEI patterning surfaces viasupramolecular interaction between amino in PEI and -OH on silicon wafer induced by microcontact printing (μCP). The thickness and shapes of the formed PEI surfaces can be finely tuned by changing the molecular weight and/or concentration of PEI. The obtained polymeric patterning surfaces could be amplified further to grow other polymersas brushes, or be explored as novel surface-enhanced Raman scattering (SERS) active material by electrostatic adsorption with negative charged gold nanoparticles (AuNPs).

Introduction

Patterning surfaces with functional polymers have attracted tremendous interest because of the abundance functionalities of polymers and a wide range of applications including cell biology, tissue engineering, medicinal science, optics and electronics.[1-3] These patterned polymer surfaces could be created via various strategies such as photolithography (PL),[4-6] nanoimprint lithography (NIL),[7,8] soft lithography,[9,10] and Dip-pen nanolithography (DPN), [11,12] etc. Among these methods, as one important strategy of the soft lithography, microcontact printing (μCP) is a powerful and widely-used approach to achieve the polymeric patterning surfaces with high versatility in sub-micrometer accuracy.[13-15] Husemann and co-workers[16] reported the first example of the fabricating polymeric patterned surface by polymerization amplification from self-assembled monolayers (SAMs) of initiator patterns created through μCP. There is considerable demand to pattern complex polymer microstructures because the properties of materials are highly dependent on the complexity of the structures. Using a muti-step μCP of initiator, in the combination with deactivation of the dormant polymer chain end and atom-transfer radical polymerization (ATRP), Zhou and co-workers[17] could achieve patterned multi-component polymer brushes of high complexity. We have developed this μCP technique to fabricate various new complex polymer brush microstructures that do not exist on the original stamp via the "dynamic μCP"[18] or other parameter adjustment during μCP process.[19,20] Through covalent attachment, polymeric patterning surfaces could be fabricated also by direct μCPof polymer ink such as polyethylenimine (PEI) or various polyelectrolytes on the functional target substrates via chemical reaction without further polymerization.[21,22] However, this strategy lack the possibility to achieve the complex polymeric surface. Recently, this μCP technology has been further developed by our group [23-25]to induce the supramolecular interaction between ink molecules and OH-functionalized substrates during μCP process.

In this article, we reported an alternative simple approach that highly branched and commercial available polymer ofpolyethylenimine (PEI) with rich primary and secondary amino group could be used as the ink to fabricate the polymeric patterning surfaces directly via supramolecular interaction of hydrogen bonds between amino groups with hydroxylated functionalized silicon wafer during μCP. Due to the inherent molecular properties of polymer such as long molecule chain, high viscosity, big chain entanglement and suppressed low diffusion,[26] remarkable feature of the created PEI patterned surfaces can be easily tuned into various morphologies such as necklace grid, stripe grid, rings array and cubes array with the use of the same stamp. The obtained polymeric patterning surfaces could be amplified to grow other polymers as brushes, or be explored as novel surface-enhanced Raman scattering (SERS) active material by

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‡ Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

electrostatic adsorption with negative charged gold nanoparticles (AuNPs).

Experimental

Materials and Sample Preparation

PEI(average molecular weight, M*w* = 600, 1800, 10000) was provided by aladdin-reagent China (Shanghai) Co., Ltd., PDMS stamp with grid configuration were fabricated from Sylgard 184 (the ratio between component A and B was 1:10) on a silicon master. The silicon wafer was cleaned in the mixture of H_2O_2/H_2SO_4, 1:3 (v/v, "piranha solution") at 80 °C for 2h. Subsequently, they were rinsed with deionized water abundantly and blow-dried with N_2.

Micro-contact Printing (μCP)

The PDMS stamp was inked by exposing the stamp features to an ethanol solution of PEI for 3 min and drying with nitrogen, subsequently, the stamp was brought into contact with substrates surface for 1 min to fabricate patterned PEI films on Si substrates.

Self-initiated Photografting and Photopolymerization (SIPGP)

The patterned polymer brushes were synthesized following a literature procedure.[23-25] The patterned substrate surface was submerged in ~2 mL of distilled and degassed bulk monomer(for example, styrene) and irradiated with an UV fluorescent lamp with a spectral distribution between 300 and 400 nm (intensity maximum at λ = 365 nm with a total power of ~240 mW/cm$_2$) for required time. Then, the substrates was extensively rinsed by different solvents (toluene, ethyl acetate, and ethanol) to remove physisorbed styrene (PS) as much as possible.

Gold Nanoparticles (Au NPs) Deposition

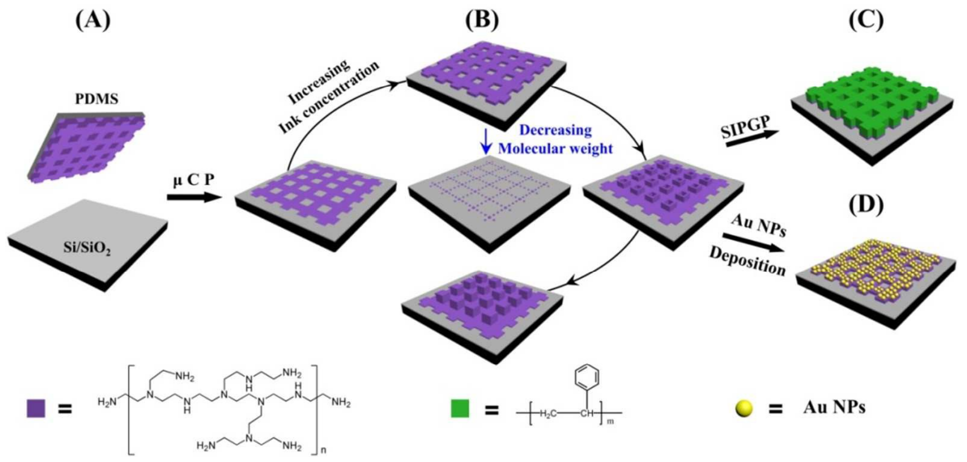
The Au NPs were prepared according to our previous reports.[27,28] Briefly, 100 mL of 2.5×10^{-4} M $HAuCl_4$ solution was heated to 120 °C in oil bath under vigorous stirring for 30 min. Subsequently, 1% sodium citrate solution (5 ml for 20 nm particles) was added into above solution with continuous boiling. After 20 min, the color of the boiled solution changed into ruby red, indicating the formation of AuNPs in the solution. The patterned substrate surface was submerged in ~ 10 mL Au NPs aqueous solution for 5 min and rinsing with deionized water twice, then drying with nitrogen.

Characterizations

Atomic force microscopy (AFM) images were taken by a multimode AFM (Being Nano-Instruments, Ltd) operating in the contact and/or tapping mode using silicon cantilevers (spring constant: 0.15Nm-1, resonant frequency: 12KHz for cantilever of contact mode, spring constant: 3~40 Nm-1, resonant frequency: 75~300 KHz for cantilever of tapping mode). The SERS measurement is conducted on the RenishawinVia-Reflex micro-Raman spectrometer equipped with 633 nm laser. The Raman spectrum is calibrated using silicon substrate. The sample is exposed by the laser for 2 s every time and is scanned for 5 times under 1% total laser power.

Results and discussion

The procedure of fabricating polymeric patterned surfaces via direct μCP by using PEI as ink molecules and their two potential applications such as further amplification of the pattern by SIPGP and interacting with AuNPs for the construction of a novel SERS active substrate is schematically shown in **Scheme 1**. In our present study, the silicon substrate



Scheme 1 Schematic procedure of fabricating polymeric patterned surfaces on silicon substrate via direct μCP by using PEI as ink molecules (A), the microstructures of patterned PEI film are tunable by varying ink concentration and molecular weight (B), subsequent amplification of the patterns to grow other polymer brushes through SIPGP (C), and used as the template for the deposition of negative charged Au NPs(D).

was pre-treated by "piranha solution", which endows the surface with rich -OH groups. A PDMS stamp with grid pattern (grid size of 11 μm) was used to transfer the ink molecules onto the silicon substrate. PEI, a highly branched polymer with rich amino groups, was selected as a special ink molecule to directly fabricate the polymeric patterning surfaces via supramolecular interaction with silicon surfaces. An ethanol solution of PEI inked PDMS stamp, was dried first with nitrogen, and then contacted with the OH-terminated silicon substrate with a gentle force (**Scheme1A**). Because the interaction of hydrogen bonds between PEI and silicon substrate interfaces is stronger than that between PDMS and PEI, micro-patterned PEI is easily transferred from the PDMS stamp onto the Si wafer once the stamp is removed after μCP. Using the same stamp, through varying the molecular weight and concentration of PEI, various polymeric patterns such as necklace grid, stripe grid, rings array and cubes array can be easily obtained (**Scheme1B**). Due to the rich amino groups of PEI, the resultant patterns can provide plenty of photoactive sites for the further growth of polymer brushes via SIPGP (**Scheme1C**). In addition, the obtained patterns can be used to fabricate novel SERS substrate by interacting with negative charged Au NPs through electrostatic absorption (**Scheme1D**).

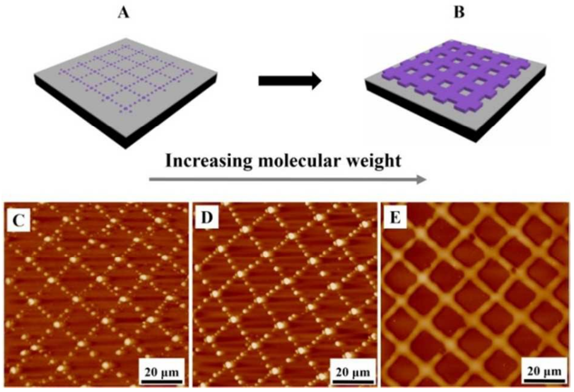


Fig. 1 Schematic illustration showing the morphology transition from necklace grid (A) to smooth and compact grid (B). Tapping mode AFM height images (90 μm × 90 μm) of the PEI patterns with average M*w* of (C) 600, (D) 1800 and (E) 10000. The concentration of the PEI ink is 10 mg/mL. All the printing used the same grid PDMS stamp.

In order to investigate the morphology of polymeric patterning surfaces, the effect of the molecular weight and concentration of PEI were studied. **Fig. 1** shows the effect of the molecular weight of PEI on the morphology. It is obvious to see that the ink of PEI with low molecular weight (M*w* = 600 or 1800) tends to form the necklace grid (**Fig.1C, D**), consisting of PEI dots array. Particularly, the size of PEI dots at each cross-point of grid is larger than other dots, which lead to the formation of hetero-patterning. AFM images (**Fig. S1A, B** in **ESI ‡**) show PEI dots were formed on stamp before microcontact printing because of PEI inked stamp was dewetted after drying with nitrogen.[29] Necklace grid pattern was fabricated by transferring the PEI dots on grid stamp to silicon wafer via μCP. As the dots at cross-point of the grid stamp are bigger than the dots on stripe after dewetting of polymer films, hetero-pattern was formed. The necklace grid is promising for the applications such as creating large band gap photonic crystal and flitting light.[30,31] While, under identical experimental conditions (i.e., stamp, temperature, force, and reagent concentrations) except for the use of PEI with high molecular weight (M*w* = 10000), the ink of PEI likes to form the smooth and compact stripe grid polymer film on stamp (**Fig. S1C** in **ESI‡**). After transferring to Si substrate by μCP, grid PEI film with thickness over 100 nm was fabricated (**Fig. 1E**).

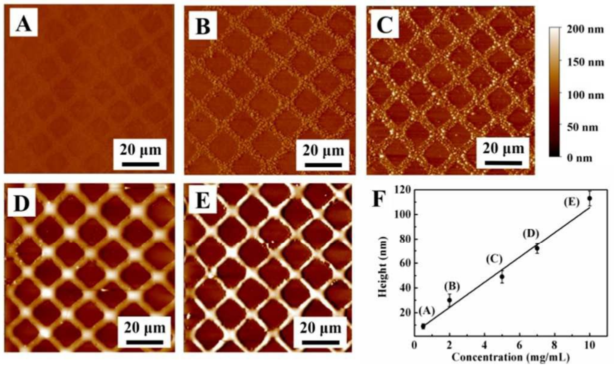


Fig. 2 Tapping mode AFM height images (90 μm × 90 μm) of PEI pattern with the ink concentration of (A) 0.5 mg/mL, (B) 2 mg/mL, (C) 5 mg/mL, (D) 7 mg/mL, (E) 10 mg/mL. (F) Height of PEI films versusink concentration accompanied with linear fitting. The M*w* of the PEI is 10000.

Beside molecular weight, concentration of the ink is another critical factor to affect the morphology and thickness of the pattern during μCP. Thin PEI pattern was achieved with the thickness below 10 nm by using PEI ethanol solution with concentration of 0.5 mg/mL as the ink (**Fig. 2A**). The thickness of the PEI patterns can be precisely controlled by varying the ink concentration. When the ink concentration increases to 2, 5, 7 and 10 mg/mL, the height of the patterns rise to 35, 52, 73 and 112 nm, respectively (**Fig. 2B, C, D, E**). Height of PEI films versus ink concentration accompanied with linear fitting (**Fig. 2F**). The AFM images of **Fig. 2C** and **Fig. 2D** show that, with the increase of ink concentration, the grid pattern transform from granular into smooth structure. The patterned polymer films with various thickness and surface roughness are very potential in many surface-based technologies such as protein-resistant coatings, sensors, and substrates for cell-growth control.

There is considerable demand to pattern complex polymer microstructures because the properties of materials are highly dependent on the complexity of the structures. Our previous work reported series of patterning strategies to obtain new complex polymer brush microstructures that do not exist on the original stamp by various µCP condition including physical deformation, UV-Ozone treatment induced chemical modification of PDMS stamp feature,[19] or dynamic printing by moving or jumping the stamp during µCP,[18] in combination with surface-initiated atom-transfer radical polymerization (SI-ATRP) of N-isopropylacrylamide (NIPAAM). The "one stamp for shape-tunable patterns" concept is developed in direct µCP. Using the same stamp, through increasing the concentration of PEIwith high molecular weight, new complex patterning polymer microstructures were achieved via normal µCP (**Fig. 3**). Stripe grid (**Fig. 3A**), rings array (**Fig. 3B**) and cubes array (**Fig. 3C**) PEI patterns with the same size of ~11 µm and enhancement of height were obtained *via*µCP by increasing the ink PEI concentration. **Fig. 3D** shows an AFM height image of smooth grid pattern with ~112 nm height and ~11 µm distance between the stripes of grid at the ink concentration of 10 mg/mL. That's a normal result as the size of the pattern is consistent with the feature on stamp. As increasing the ink concentration to 20 mg/mL, PEI rings array with size of ~11 µm and height of ~388 nm were fabricated, which don't exist on the original stamp (**Fig. 3E**). The size of the rings is ~11 µm, corresponding to the distance between the grid. It's worth noting that the ring marked with white pane is close to cube structure due to local high concentration. **Fig. 3F** shows cubes array with size of ~11 µm and height of ~503 nm at the ink concentration of 30 mg/mL. Because of the high ink concentration, inked PEI on grid and groove of the stamp is demolded easily from the stamp, forming inverted PEI cubes array pattern. Due to the inherent molecular properties of polymer such as long molecule chain, big chain entanglement, compact polymer bulks can easily formed on the grid and groove of PDMS stamp. When the polymer bulks on groove are small and can't contact the substrate, the smooth and compact grid was fabricated after µCP. As increasing ink concentration, polymer bulks on groove wall were contacted and transferred to substrate to form rings array. The centre area and the naked silicon wafer have the same height (**Fig. S2, ESI‡**), indicating there are no polymer films in the center of rings. Cubes array were formed when the polymer bulks on grid and groove of the stamp transferred together to substrates at a higher ink concentration. The patterns on substrates are regular as the high viscosity, and suppressed low diffusion of polymer. This approach provides a new way to fabricate complex patterned functional polymer surfaces that only needs one step printing by adjusting the concentration of polymer ink.

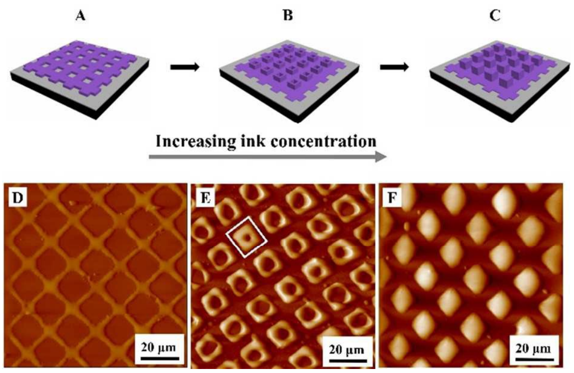


Fig. 3 Schematic illustration and corresponding tapping mode AFM height images (90 µm × 90 µm) of three different microstructures of patterned PEI film fabricated viaµCP by varying the ink PEI concentration. (A, D) Grid PEI pattern on Si wafer replicated the inked grid feature on PDMS stamp with ink concentration of 10 mg/mL. (B, E) When the ink concentration rising to 20mg/mL, rings array appeared on the grid center as the PEI adhered on wall of the groove of inked PDMS stamp transferred to the Si substrate. (C, F) Inverted PEI cubes array formed due to transferring together of inked PEI on grid and groove of the PDMS stamp with ink concentration of 30 mg/mL. The M*w* of the PEI is 10000.

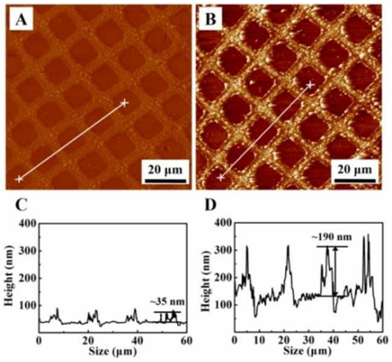


Fig. 4 Tapping mode AFM height images (90µm × 90 µm) and corresponding cross-sectional profiles of before (A, C) and after (B, D) SIPGP of grid PEI pattern.

With the development of UV polymerization, SIPGP provided us with a convenient strategy to prepare polymer brushes even without a surface bound initiator on patterned self-assembled monolayers (SAMs).[25,32] The photoactive group of primary and secondary amine groups on patterned PEI could be initiated to grow polymer brushes by SIPGP upon being immersed in various monomer solutions and irradiated with an UV lamp. Height variation of the patterned substrate surface before and after irradiation for two hours was investigated by AFM. The height of PEI grid generated from 2 mg/mL PEI ethanol solution was about 35 nm (**Fig. 4A, C**). Upon employing the SIPGP, patterned PEI-g-PS polymer brush with the height of ~ 190 nm was formed (**Fig. 4B, D**).

Hammond and co-workers[33] obtained 2D arrays of particles on patterned polyelectrolyte surfaces as functional templates. Our previous work[34] achieved stimulus-responsive, "egg-cup" shaped polymer brush microstructures on thiol initiator modified gold surfaces by μCP, which can be used as motor arrays to manipulate the movement of gold NP aggregates. As patterned polyelectrolyte surface, the PEI surfaces were further used to patterning Au NPs by electrostatic interaction between PEI and negative charged Au NPs with diameter in 20nm. The morphology and height change was investigated with AFM (**Fig. 5A, B**). After submerging in 10 mL Au NPs aqueous solution for 5 min, the height of PEI pattern increased from 7 nm to 22 nm, indicating a monolayer of Au NPs absorbed on the patterned PEI surface(**Fig. 5D**). The SERS spectra of R6G based on Si substrate exhibit relative weaker Raman signal. Using patterning Au NPs surface as SERS substrate, dramatic increase in Raman signals can be observed (**Fig. 5E**). Bands at 614 and 774 cm^{-1} are aroused by the C-C-C ring in-plane and out of-plane bending vibration, respectively. Band at 1127 and 1185 cm^{-1} is assigned to the C-H in-plane bending and the band at 1310 cm^{-1} was assigned to C-O-C stretching. Bands at 1361, 1511, 1572 and 1650 cm^{-1} were attributed to C-C stretching of aromatic rings.[35] Quantitative SERS data can be estimated according to our previous work.[36] The absolute value of the enhancement factor (EF) was calculated by using the formula: EF=ISERS/IO×NO/ NSERS, where ISERS and NSERS are the intensity of the band and number of the adsorbed molecules for SERS, respectively. IO and NO are the intensity of the band and number of molecules for free R6G molecules. The intensity of Raman peaks were enhanced by an EF of approximately 6.4×10^4 for AuNPs/PEI pattern. Such a high enhancement factor is considered to be due to the hotspot in AuNPs/PEI pattern.

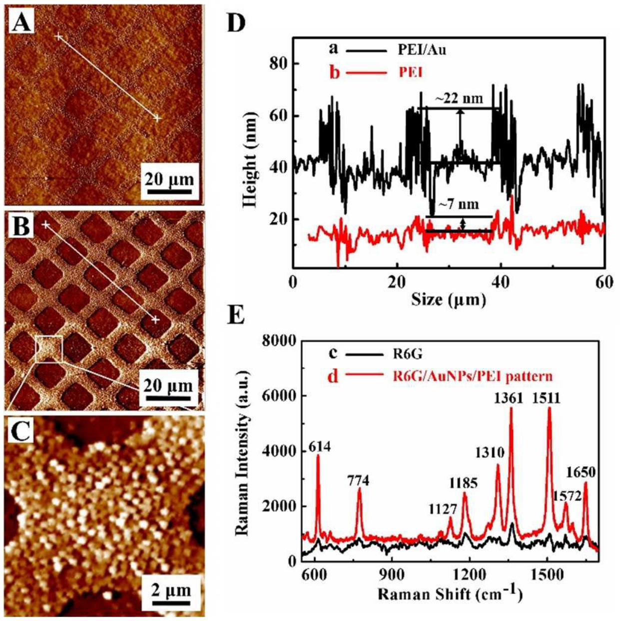


Fig. 5 Tapping mode AFM height images and corresponding cross-sectional profiles of PEI pattern before (A, b) and after (B, C, a) deposition of Au NPs. (E) SERS spectra of R6G molecules (10-^{6} M) collected on Si substrate (c) and patterning PEI-Au NPs substrate (d).

Conclusions

Based on the considerable demand to fabricate pattern complex polymer microstructures simply, we developed the microcontact printing technology to achieve this goal using commercial available polymer of PEI as the Ink. Rich amino groups inside branched PEI ink, allows the supramolecular interaction of hydrogen bonding between PEI and OH-functionalized silica substrate during μCP process. Differing from the conventional “one stamp for one shaped pattern” in direct μCP, complex PEI morphology could be achieved to demonstrate the concept of “one stamp for shape-tunable patterns”. The thickness and shapes of the formed PEI surfaces can be finely tuned by changing the molecular weight and concentration of PEI. The obtained polymeric patterning surfaces could be amplified to grow other functionalized polymer brushes, or be explored as novel surface-enhanced Raman scattering (SERS) active material by electrostatic adsorption with negative charged gold nanoparticles (AuNPs).

Acknowledgments

We thank the Natural Science Foundation of Hubei (2011CDC068), the State Key Laboratory of Agricultural Microbiology (AMLKF201205), the Fundamental Research Funds for the Central Universities (52902-0900202265), Chinese Central Government for Thousand Young Talents Program, the Natural Science Foundation of China (21404110, 51473179, 21304105, 51303195), Excellent Youth Foundation of Zhejiang Province of China (LR14B040001), and Ningbo Science and Technology Bureau (Grant 2014B82010).

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TOC

Morphology adjustable PEI pattern could be achieved by microcontact printing induced supramolecular interaction directly and serve further as the template for constructing highly active SERS substrate by the deposition of Au NPs.