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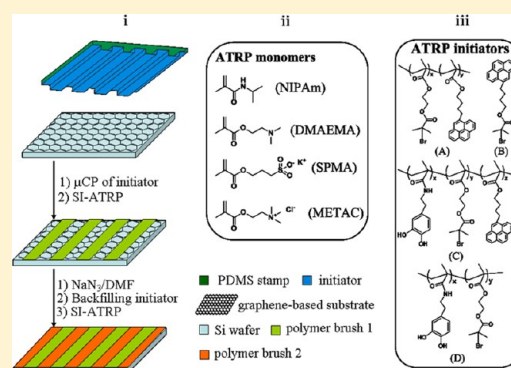
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Noncovalent Microcontact Printing for Grafting Patterned Polymer Brushes on Graphene Films

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Supporting Information

ABSTRACT: This article describes a simple and universal approach to prepare patterned polymer brushes on graphene-based substrate surfaces by microcontact printing (μ CP) of initiator molecules and subsequent surface initiated atom transfer radical polymerization (SI-ATRP) method. Four different initiators are designed and have strong adhesion with graphene-based substrates through noncovalent interaction. Optical and fluorescence microscopy, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS) were used to characterize the successful polymerization of vinyl monomers on substrate surfaces. To demonstrate the broad applicability of this strategy, polymer brushes with different functionalities including cationic and anionic polyelectrolyte, thermally and pH responsive polymers, as well as polymer patterns on different graphene-based surfaces are fabricated. Binary polymer brushes can also be easily prepared by further initiating the initiator backfilled in the bare areas.



INTRODUCTION

Graphene, a two-dimensional network formed by a monolayer of sp^2 hybridized carbon atoms,¹ has attracted extensive research due to its excellent mechanical, thermal, optical, and electrical properties.^{2–5} Important applications of using graphene and graphene-based materials have been exploited for single molecule detection,⁶ field effect transistors (FET),⁷ batteries,⁸ and sensors.⁹ However, a more universal method is extremely desired for controllable modification of the graphene film with specific structure and chemical composition for further improving properties and extending its applications.

Polymer brushes with various functional groups have been demonstrated as a robust method for manipulating surfaces with a wide range of physical and chemical properties, including fabrication of the “smart”/functionalized surface,^{10–12} organic/inorganic composite materials,¹³ and so forth. And polymer brushes on surfaces with periodic micro/nanostructures are expected to have an advantage in more precisely controlling the surface properties; they have been successfully used in the fields of microfluidic devices,¹⁴ cell selective adhesion,¹⁵ and organic solar cells.¹⁶ Though many strategies such as photolithography,¹⁷ electron-beam lithographic (EBL),¹⁸ and dip-pen nanolithography,¹⁹ techniques with expensive and complex instruments or tedious steps have been applied to prepare patterned polymer brushes with controlled shape, feature dimension, spacing, and chemical functionality. Microcontact printing (μ CP), a versatile method to print patterned self-assembled monolayers (SAMs) by using a poly-(dimethylsiloxane) (PDMS) stamp on substrate surfaces, is

relatively a more simple, effective, and inexpensive patterning approach for fabricating shaped micro/nanostructures on substrate surfaces.²⁰ Surface-initiated controlled radical polymerization (SI-CRP) technique^{21–24} is a widely used method to prepare polymer brushes with controlled grafting densities, functionality, and thicknesses, while surface-initiated atom transfer radical polymerization (SI-ATRP) is one of the most popular SI-CRP methods toward the polymerization of different vinyl monomers with different functional groups for inexpensive initiation systems and mild controllable polymerization conditions.^{25,26} Therefore, SI-ATRP is no doubt the best partner of μ CP to prepare patterned polymer brushes on substrate surfaces.

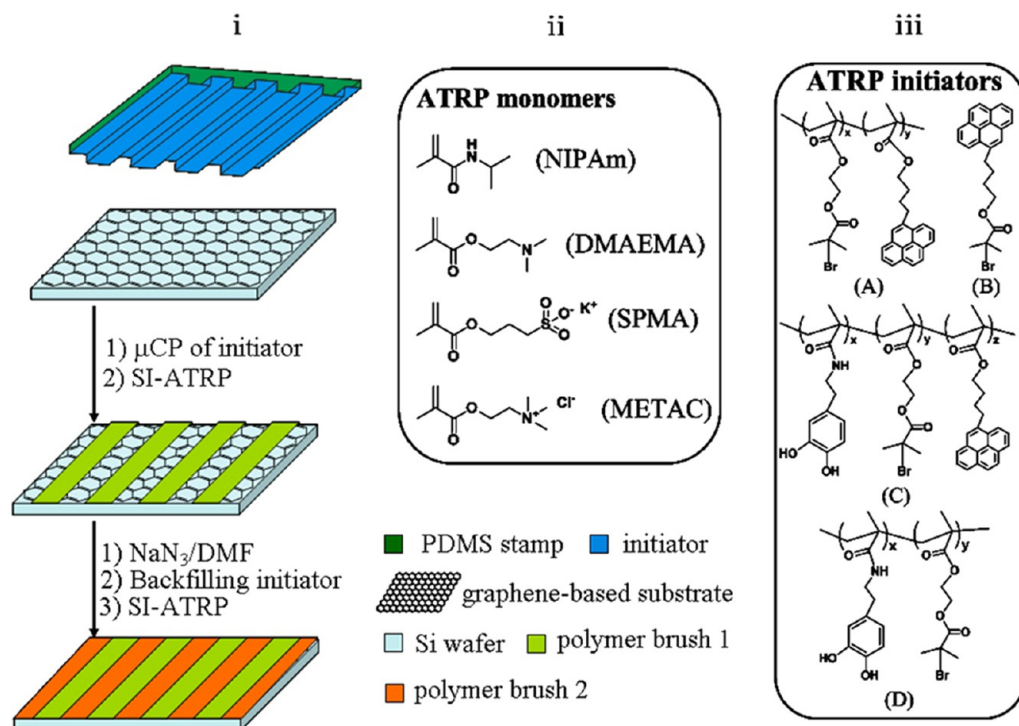
Recently, a lot of studies have focused on fabricating patterns of graphene, reduced graphene oxide (RGO) and graphene oxide (GO) film for the use of high performance OFETs,²⁷ sensors^{28,29} by mask lithography, transfer printing, μ CP, and direct-write process. Whereas polymer patterns on surface of graphene or GO films are less reported, especially for polymer brush fabricated by a combined μ CP and followed SI-ATRP method. Byun et al.³⁰ fabricated the conducting Ppy patterns doped with adenosine triphosphate (ATP) on the graphene surface by patterned photoresist assisted electrochemical deposition method, and used for controlling the release of biomotor fuel, ATP, by electrical stimuli through the graphene.

Received: November 5, 2012

Revised: December 24, 2012

Published: January 7, 2013

Scheme 1. Procedures for Fabricating Patterned and Binary Polymer Brushes on Graphene-Based Substrates with the Chemical Structures of Used ATRP Initiators and Monomers^a



^aStructures of the used initiators: the pyrene-terminated macroinitiator (A), the catecholic-terminated macroinitiator (B), the catechol-co-pyrene-terminated macroinitiator (C), and the pyrene-terminated small-molecule initiator (D).

Steenackers et al.³¹ directly prepared polystyrene patterns on graphene-based surface by surface photopolymerization without causing any detectable disruption of the basal plane conjugation of graphene. However, just specific polystyrene brushes can be formed on graphene surface; other vinyl monomers display no reactivity with graphene. Therefore, a more simple, universal, controllable method was urged to prepare patterned polymer brushes on graphene-based substrate surfaces, expecting to endow the graphene substrate surface with various properties.

In this paper, the patterned initiator molecules were first printed on GO substrate surface by direct μ CP, then polymer patterns with controlled thicknesses, shapes, and functionalities were successfully fabricated by a simple, commonly used SI-ATRP of vinyl monomers. Results suggest that not only this method can make polymer patterns on different graphene-based films, including GO film, RGO films and CVD (chemical vapor deposition) graphene films, but also different vinyl monomers with different functional groups can be successfully polymerized, and even the binary polymer brushes on GO surface can be easily achieved by SI-ATRP of the initiator backfilled in the bare substrate area. Besides, the patterned POEGMA-OH (poly[monohydroxyoligo(ethylene glycol) methacrylate]) separator provides a new bridge for the fluorescein isothiocyanate (FITC)-streptavidin and graphene substrate. We believe that the patterning strategy can be extended to all the other monomers and other types of polymerization, and the polymer brushes with different functionalities and specific micro/nanostructures on graphene-based substrate may find great use in sensors, supercapacitors, microfluids, and so forth.

EXPERIMENTAL SECTION

Materials. *N*-Isopropylacrylamide (NIPAm), 3-sulfopropyl methacrylate potassium salt (SPMA), methacryloylcholine chloride (METAC), *N,N'*-dimethylamino ethylmethacrylate (DMAEMA), pentamethyldiethylenetriamine (PMDETA), and monohydroxyoligo(ethylene glycol) methacrylate (OEGMA-OH, MW 526) were all obtained from Aldrich. Graphite (powered flake graphite), biotin, and FITC conjugated streptavidin were obtained from Alfa-Aesar. Ultrapure water used throughout the experiments was obtained from a NANOpure Infinity system from Barnstead/Thermolyne Corp. Copper(I) bromide was purified by reflux in acetic acid, and other chemicals were used as received. Silicon wafers (100) were used as the substrate to deposit GO films.

Characterization. Atomic force microscopy (AFM) images were taken by using a multimode AFM (Nanoscope IIIa, Veeco Instrument, Santa Barbara, CA) operating in the tapping mode. Optical and fluorescent images were taken with a fluorescence microscope (Olympus BX51). The Raman scattering measurements were performed at room temperature on a Raman system (JY-HR800) with confocal microscopy. The solid-state diode laser (633 nm) was used as an excitation source. Chemical composition information of the samples was obtained by X-ray photoelectron spectroscopy (XPS), carried out on a PHI-5702 multifunctional spectrometer using Al $K\alpha$ radiation, and the binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

Film Preparation. GO was prepared by oxidation of flake graphite using $\text{KMnO}_4/\text{H}_2\text{SO}_4/\text{NaNO}_3$ according to a modified Hummers' method.³² The GO sheet assembled on Si with the water volatilized to afford the GO film, and the RGO film was prepared by reducing the GO film using HI.

Surface-Initiated Polymerizations. For μ CP, 1 mM initiator solution was spread onto the PDMS stamp, blow dried, and made contact with surface for more than 1 min to fabricate the patterned initiator on graphene-based substrates. The surface-initiated polymerization of the initiator-patterned surface was performed in Schlenk

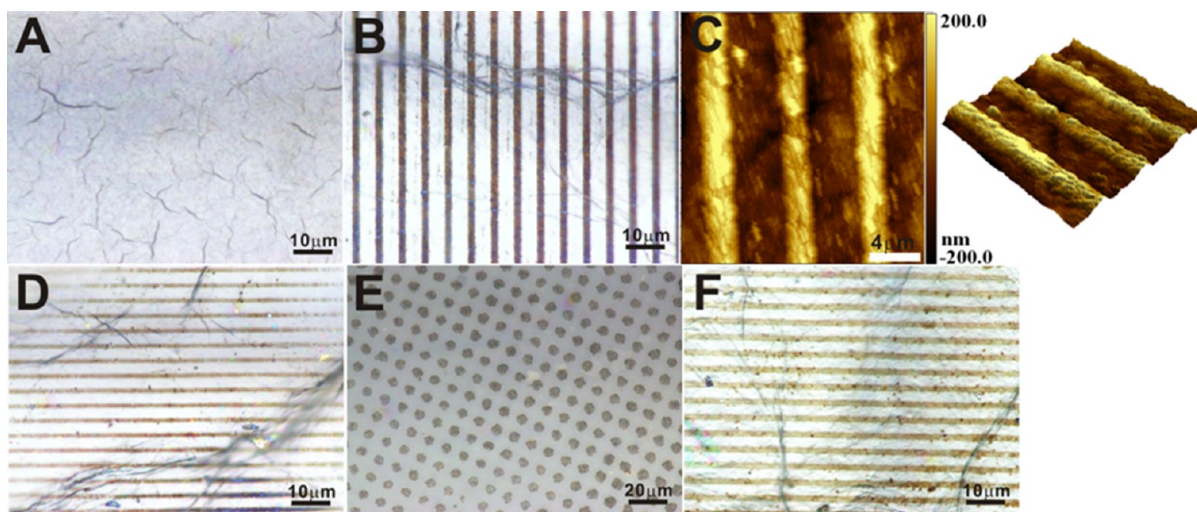


Figure 1. Optical microscope images of self-assembled GO film on Si wafer (A), and patterned PNIPAm polymer brushes on GO films by using different initiators as the anchoring ink, the pyrene-functionalized macroinitiator (B). (C) Corresponding AFM topographic image and surface plot of (B), the pyrene-terminated small-molecule initiator (D), the catechol and pyrene functionalized macroinitiator (E), and the catecholic-functionalized macroinitiator (F).

tubes. The general polymerization procedures, polymerization conditions of NIPAm, DMAEMA, and passivation of the polymer brushes were programmed according to the literature.³³ Polymerization recipes for monomers SPMA, METAC, and OEGMA-OH are as follows: SPMA 12 g, CuBr 0.2 g, bipy 0.6 g, water/methanol (30 mL, 2/1 v/v) 30 min; METAC 16 g, methanol 35 mL, and bipy 0.2 g, CuBr 0.1 g, 30 min; OEGMA-OH 11 g, CuBr 0.04 g, bipy 0.16 g, water/methanol (25 mL, 4/1 v/v) 30 min.

RESULTS AND DISCUSSION

In this paper, the traditional microcontact printing (μ CP) combined with surface initiated polymerization (SIP) was used to prepare patterned polymer brushes on GO film substrate. Scheme 1 clearly illustrates the procedures to fabricate patterned polymer brushes on GO substrate with the chemical structures of used ATRP initiator inks and polymerized ATRP monomers. First, the initiator monolayer was printed on a substrate surface by a μ CP procedure, which was followed by SIP of different monomers with different functional groups to afford different polymer brushes modified GO films. In order to maintain the properties of the substrate surface, noncovalent interaction is more favorable than covalent binding. Though oxygen-containing groups on GO surface severely destroy the conjugate structure of the basal plane, areas that are not oxidized still exist on GO surface. And previous studies³⁴ indicate that the pyrene-terminated compounds can be successfully used to functionalize the graphene and GO via π - π stacking interactions. Macroinitiators, which have several anchoring sites on the high-molecular-weight polymer chains, are expected to be more superior in improving the anchoring stability by multiple bonding interactions, especially for the weaker noncovalent binding such as hydrophobic, hydrogen bonding or electrostatic interactions.³⁵ We designed the pyrene-terminated macroinitiator and tried to use it as the anchoring ink to functionalize the GO substrate by multi- π - π stacking interactions. Other initiators that can be selectively transferred onto graphene films are also listed in Scheme 1, and they will be mentioned later.

Figure 1A shows the optical microscopic image of self-assembled GO film with some unavoidable wrinkles on the surface. After μ CP of the initiator and SIP, regular poly[N-

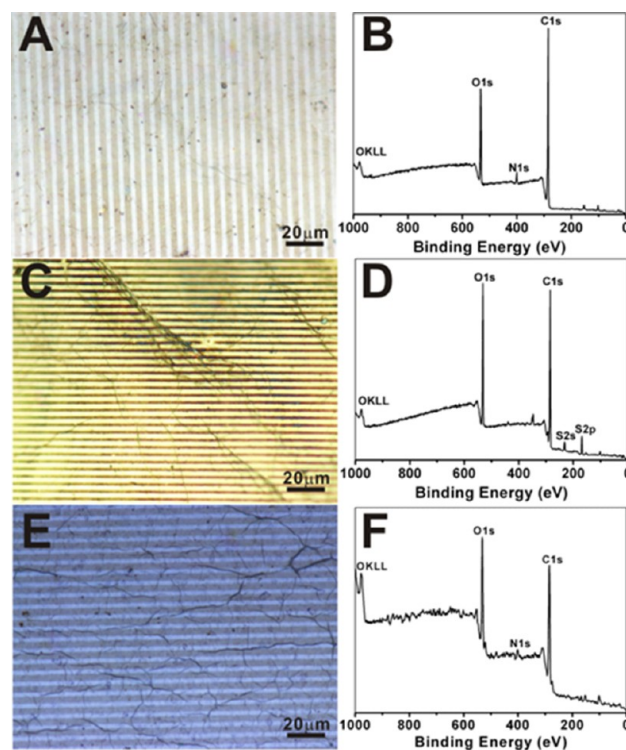


Figure 2. Optical microscope images and XPS spectrum of different polymer brushes on GO film: PDMAEMA brush (A and B), PSPMA brush (C and D), and PMETAC brush (E and F).

isopropylacrylamide] (PNIPAm) patterns with line width 2 μ m are clearly seen from Figure 1B. Figure 1C presents the corresponding AFM topographic image and surface plot of Figure 1B for further characterizing the structures of GO surface and patterned polymer brushes obtained by SI-ATRP. It can be seen that the pattern is regular with high resolution, though the surface of the GO film is a bit rough. With the exception of the pyrene-terminated macroinitiator, pyrene-terminated small-molecule initiators (Scheme 1B) can also be used to prepare patterned polymer brush functionalized GO

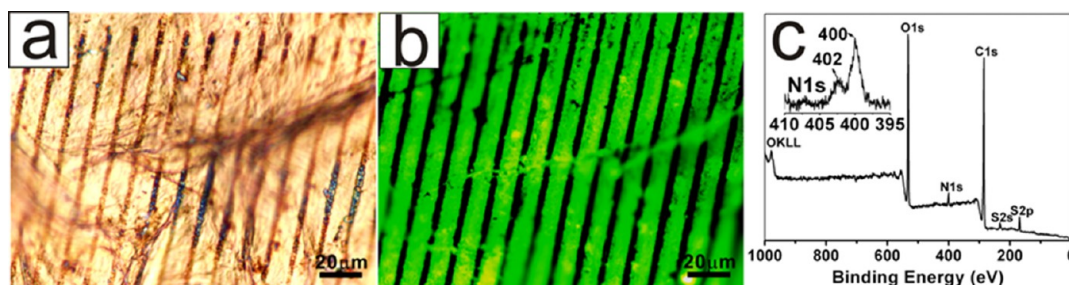


Figure 3. Binary PNIPAm/PSPMA pattern on GO film: (a) the optical microscope image, (b) the corresponding fluorescence image (the bright green area is PSPMA), and (c) the XPS analysis of the polymer brushes.

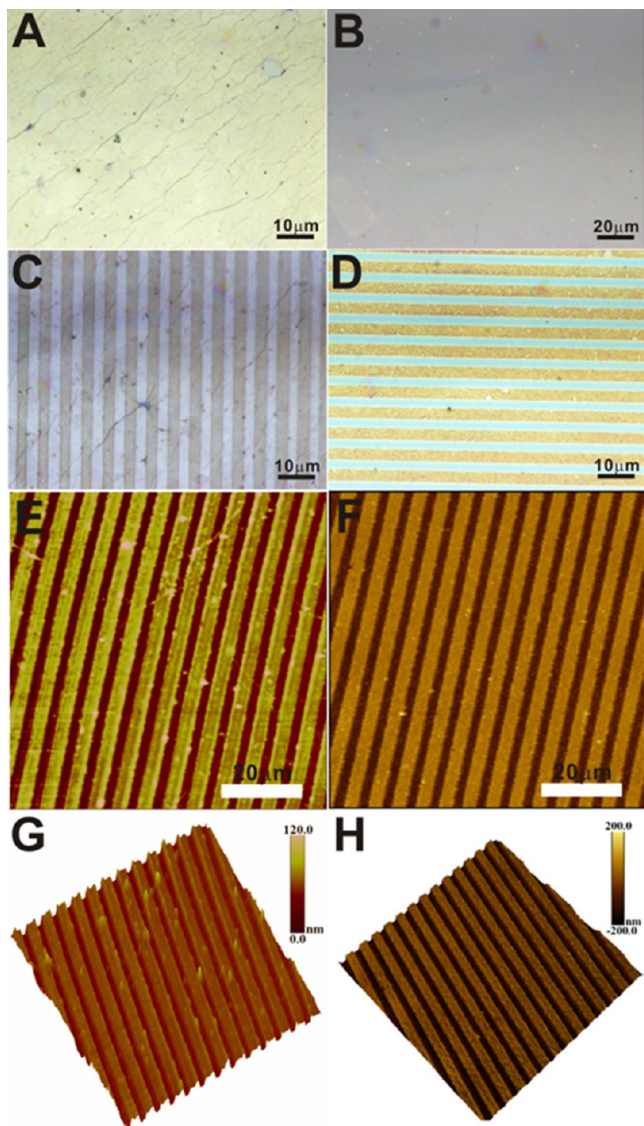


Figure 4. Optical microscope images of RGO (A) and CVD graphene film (B), and patterned polymer brushes on these surfaces. Panels (C), (E), and (G) are, respectively, the optical microscope image, the corresponding AFM topographic image, and the surface plot of patterned PMETAC on RGO film, while panels (D), (F), and (H) are images of PNIPAm on CVD graphene film.

surface. Figure 1D shows the PNIPAm brush on the GO surface when using the pyrene-terminated small-molecule initiator as the anchoring ink.

Taking consideration from the special structure of GO, it consists not only of the intrinsic sp^2 networks, but also abundant oxygen-containing groups³⁶ on its platelet and edge. Despite chemical reactions with the oxygen-containing groups, other noncovalent interactions such as π - π stacking,³⁴ the hydrogen bond,³⁷ electrostatic interactions,³⁸ and van der Waals³⁹ interactions can also be effectively used to functionalize the GO sheet to further improve the performance of GO. The biomimetic catecholic dopamine molecules have been proven to be a powerful and versatile adhesive compound to a variety of organic and inorganic surfaces including metal, metal oxide and polymer surfaces and so on.^{40–42} Previous studies have successfully prepared PDA-capped RGO nanosheets by using the self-polymerization of dopamine and chemical reaction with the surface oxygen groups of GO sheet.⁴³ Here, the biomimetic catecholic-terminated macroinitiator was synthesized and used as the anchoring ink by using the excellent affinity of dopamine and the oxide surface. The patterned PNIPAm brush on GO surface shown in Figure 1F provides visual proof for the successful modification of GO film. In order to further enhance the interaction between the initiator and the GO surface, the catechol and pyrene copolymerized macroinitiator which simultaneously contains the two functional groups on the polymer chains was designed to synthesize and used as the anchoring initiator. The circle dot patterns of the PNIPAm brush shown in Figure 1E offer powerful evidence for the successful modification of the copolymerized macroinitiator on the GO surface. From the above analysis, it can be concluded that all four kinds of initiator can be used to prepare robust polymer brushes on GO surfaces via the sample μ CP procedures.

In addition to the NIPAm, our experiments reveal that other ATRP monomers with different functional groups can also form regular patterns on the GO surface with expectation to render the GO films with different properties. Figure 2A, C and E shows the optical images of three different polymer brushes, nonionic PDMAEMA, anionic PSPMA, and cationic PMETAC, that regularly grew from the GO surface. The N1s, S2p, and N1s peaks seen from Figure 2B, D and F are the corresponding characteristic element of these three polymer brushes, which reveals the successful polymerization of ATRP monomers and feasibility of this μ CP method.

Previous studies¹³ demonstrate that it is easy to construct binary polymer brushes on substrate surfaces by a two-step SI-ATRP procedure. The binary brushes can be different, or identical but with different thicknesses. The general procedures to prepare binary polymer brushes on GO surface are described in Scheme 1, specifically, backfilling the initiator after the first polymerization and then proceeding with the secondary polymerization. Before backfilling the initiator, the remaining

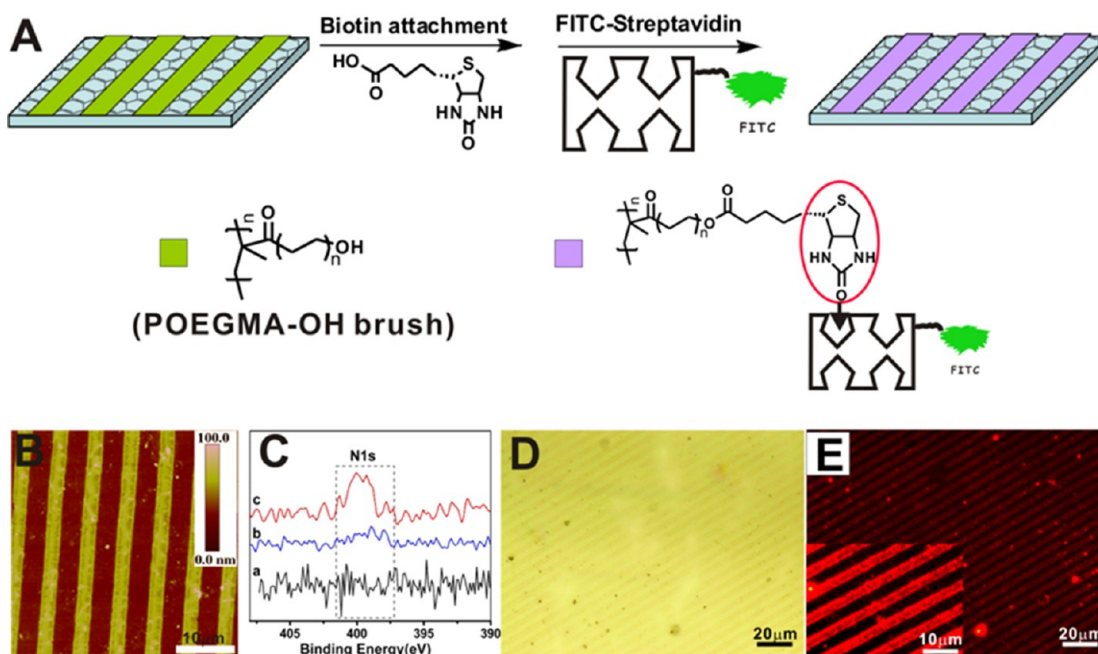


Figure 5. (A) A schematic representation of the procedures for immobilizing patterned fluorescent streptavidin on RGO film by using a POEGMA-OH brush scaffold. (B) AFM topographic image of the POEGMA-OH brush on RGO film. (C) Variation of XPS spectra of N1s during reaction: (a) RGO-POEGMA-OH brush, (b) RGO-POEGMA-OH brush-biotin, and (c) RGO-POEGMA-OH brush-biotin-streptavidin. (D) An optical microscopic image of the area of specific biotin-streptavidin recognition and (E) the corresponding fluorescence image in the same area. The inset shows a zoomed-in image.

initiator moieties are deactivated by NaN_3 to avoid reinitiation on existing brushes. Figure 3a shows the optical image of the binary PNIPAm/PSPMA patterns on GO surface. The anionic PSPMA polymer brush was stained with a cationic fluorescent dye, Rh6G, which is a commonly used fluorometric reagent.³³ The fluorescence image (Figure 3b) displays that the black lines with no fluorescence represent the PNIPAm brushes, and the green lines with strong fluorescence emission represent PSPMA brushes. The N1s and S2p peaks appeared in the XPS spectrum (Figure 3c) prove that both the PNIPAm and PSPMA brushes were successfully prepared on GO surface. And the inserted N1s peaks at 400 and 402 eV are attributed to the two different N atoms in PNIPAm brushes and the azide group, respectively.

The graphene films appear to have more excellent electrical and mechanical properties than the GO film, and can be simply prepared by chemical reduction of the GO film (named RGO film), CVD, epitaxial growth method, and so forth. Figure 4A and B reveals the optical images of the RGO film and CVD graphene film grown on Ni substrate. Without the active oxygen-containing groups, the RGO/CVD graphene surfaces can also be modified with the pyrene-containing initiator. As seen from Figure 4C and D, clear patterns are grown on RGO/graphene surfaces after μCP pyrene-functionalized macro-initiator and SI-ATRP steps. The corresponding AFM topographic images and surface plots of these patterned polymer brushes further demonstrate the micropatterns on the graphene surface more intuitively. According to the above presentation, a wide range of ATRP monomers including those which we have not used in this paper could be used to prepare patterned polymer brushes on graphene films to make the film more functional properties.

Except for the extraordinary electrical and mechanical properties of graphene, sensors made from graphene based films also display its ultrasensitive and ultrafast detection of

chem/biomolecules.^{44,45} Kodali et al.²⁹ prepared a micro-patterned proteins on graphene film for biosensor applications by using a PYR-NHS bridge. However, as the strong fluorescence quenching properties of graphene,⁴⁶ the detection sensitivity reduced in a large extent with a prolonged detection time. In order to reduce the side effect of electron transfer between the protein and graphene substrate, the polymer chains POEGMA-OH brush with tunable thickness can be used as the electron separator as well as the scaffold to attach biomolecules and is here demonstrated by preparing micro-patterned POEGMA-OH brushes. The attachment procedures are shown in Figure 5A: the POEGMA-OH brush first reacted with the biotin and then specifically absorbed fluorescent streptavidin to afford fluorescent patterned biotin-streptavidin on graphene substrate. Figure 5B shows the AFM topographic image of POEGMA-OH patterns on RGO film; after biotin attachment and specific recognition of FITC-streptavidin, no distinct differences was seen from the optical microscope image (Figure 5D), while the corresponding fluorescent microscope image and a zoomed-in image inserted in Figure 5E clearly demonstrate the regular FITC-streptavidin patterns on POEGMA-OH brushes. The appeared N1s peak in Figure 5C-b proves the successful attachment of biotin with the POEGMA-OH brush, and the element increased intensity of N1s peak in Figure 5C-c further demonstrates the specific recognition of FITC-streptavidin.

CONCLUSIONS

In conclusion, we have demonstrated a general and soft lithographic approach to prepare patterned polymer brushes with different functional groups, including cationic, anionic and neutral polymer patterns on graphene oxide (GO) film surfaces. Four different initiators ending with pyrene/catechol or both are used as the anchoring ink to modify the GO. Binary

polymer brushes with different properties are successfully prepared by backfilling the bare GO areas with initiators and followed SI-ATRP. Polymer pattern formation on RGO and CVD graphene film further proves the flexibility of this technique. Finally, specific recognition of FITC-conjugated streptavidin with biotin attached patterned POEGMA-OH polymer brush on RGO film also provides an efficient method toward graphene based biosensors. Nevertheless, the strategy provides a more powerful route to fabricate a variety of polymer brushes with different functionalities on graphene-based substrate, and these polymer/graphene composites with micro/nanostructures may find great use in sensors, supercapacitors, microfluids, and so forth.

■ ASSOCIATED CONTENT

■ Supporting Information

(1) XPS spectra and Raman spectra of the prepared GO and RGO film, (2) structures of the used initiators, (3) XPS survey spectra of patterned PNIPAm polymer brushes on GO films by using different initiators as the anchoring ink, (4) XPS survey spectra and N1s peak of patterned polymer brushes on RGO and CVD graphene film surfaces, and (5) Raman spectra of CVD graphene film after transferred to Si substrate from Ni substrate. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The work is financially supported by NSFC (21125316) and "Top Hundred Talents" Program of CAS.

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