Electrochemically-deposited benzophenone moieties: precursors for dual mode patterning of polymer brushes on conducting surfaces[†]

Maria Celeste Tria, Jin Young Park and Rigoberto Advincula*

Received 24th September 2010, Accepted 14th November 2010 DOI: 10.1039/c0cc04046k

A new method for patterning polymer brushes on conducting surfaces *via* electro-deposited benzophenone moieties is reported. The dual patterning capability of the technique was demonstrated and characterized *via* the AFM and for the first time, an IR-imaging technique for a patterned brush.

Patterning of surfaces with polymeric materials has been of high interest because of its vast applications in different areas such as biomaterials, micro/nanofluidic systems, microelectromechanical devices (MEMS), and photonic crystal materials.¹ Over the past decade, research efforts were geared toward developing strategies of fabricating patterns on surfaces, which includes microcontact printing,² photolithography,³ and electron beam lithography.⁴ Conventionally, patterned polymer brushes are produced from polymers grown from patterned initiators that are lithographically printed on surfaces. Several non-conventional methods have also been presented to provide an alternative way to the traditional technique such as capillary force lithography,⁵ photoetching,⁶ and electro-oxidation method.⁷ Despite the success of these approaches in producing patterned surfaces, most of these techniques either necessitate lengthy or complex steps or could only be applicable to specific surfaces by self-assembled monolayers (SAM), which require synthesis of several types of initiators (e.g. thiol or silane initiators) depending on the substrate being employed.

To address these issues, we present a simple yet versatile route of patterning polymer brushes by using electrochemically-deposited benzophenone moieties that could either be electrochemically or photochemically patterned on the surface. The dual patterning capability of the method relies on the presence of both an electro-active and photoactive functional group in the molecule of interest. Benzophenone is well known for its photo reactivity and its ability to attach C–H bonds in a wide range of chemical environments.⁸ Carbazole, on the other hand, is known to be electrochemically active and can be electrodeposited on a wide range of conducting surfaces by either potentiodynamic or potentiostatic methods.⁹ This approach offers an advantage over other techniques for patterning surfaces because of its applicability on any conducting surfaces by using only a single photocrosslinker, which would avoid extensive synthetic efforts of various initiators or anchoring groups specific for different electrodes.

Scheme 1 depicts the dual patterning routes of the method presented. The process was used on a patterned conducting surface, in this case a patterned ITO (see ESI[†] for the detailed preparation procedure), where 4-benzoylphenyl-3,5-bis(4-(9*H*-carbazol-9-yl)butoxy)benzoate (CbzBP) was first selectively electro-patterned on the conducting regions of the surface. A polymer thin film was spin-coated and irradiated with UV light after which it was rinsed with an appropriate solvent to remove the unbound polymer, creating the patterns on the conducting surface. On the other hand, a polymer thin film was also spin-coated on a plain conducting substrate with electrodeposited CbzBP. A photo mask was employed upon UV irradiation of the film to selectively graft the polymer only on the exposed areas. The unadsorbed polymers were rinsed off to form the patterns on the surface.

The electro-active benzophenone molecule (CbzBP) was synthesized *via* coupling of 4-hydroxybenzophenone with the



Scheme 1 The preparation of patterned polymer brushes using the electrochemically-active benzophenone moiety *via* electropatterning (Route 1) and photopatterning (Route 2).

Department of Chemistry and Department of Chemical and Biomolecular Engineering, University of Houston, TX 77204-5003, USA. E-mail: radvincula@uh.edu; Fax: +1 713-743-1755; Tel: +1 713-743-1760

 $[\]dagger$ Electronic supplementary information (ESI) available: Materials and surface characterizations, synthesis of the electro-active photocrosslinker, cyclic voltammograms of the CbzBP and benzophenone, UV-vis data for the uncrosslinked and crosslinked CBz-BP, XPS survey spectra of the films and IR-imaging of the pattern focused at the C==O region. See DOI: 10.1039/c0cc04046k

synthesized carboxylic acid carbazole moiety that was developed in our lab and is published elsewhere.¹⁰ The CbzBP was initially deposited through potentiodynamic method on a plain ITO substrate, which was done with a scan rate of 50 mV s⁻¹ at the potential range between 0 to 1.3 V (Fig. S1, ESI[†]). The stability of the benzophenone group during electro-deposition is one of the main concerns for the succeeding photo-grafting step. To verify this, a CV run was made for pure benzophenone within this potential window. The cyclic voltammogram showed no redox peaks between 0 to 1.3 V, signifying that the benzophenone is unaffected at this potential region (Fig. S2, ESI⁺). This also indicated that the redox peaks found in the CV diagram of CbzBP is solely attributed to the carbazole moieties that are being cross-linked during the electrodeposition process. The electrochemical cross-linking of the carbazole moieties was further supported by the UV-vis analysis before and after the electrodeposition of the CbzBP on the ITO substrate (Fig. S3, ESI[†]). The presence of the broad maxima at around 400 nm and 800 nm for the electro-generated CbzBP which are assigned to the dicarbazyl radical cation and dicarbazyl dication, respectively,¹¹ signifies the successful cross-linking of the carbazole moieties. On the other hand, these peaks are not observed in the control system where CbzBP was just spin-coated on the ITO surface.

A thick film of polystyrene (PS) (MW 250K) was spin-coated on the electro-generated CzBP film and was subsequently irradiated with UV for an hour to photo-graft the polymer on the surface. One hour of irradiation time was necessary to reach the maximum thickness based on prior kinetic measurements made by plotting the irradiation time *versus* thickness (Fig. S4, ESI†). This result was also in corroboration with the one reported by Frank and co-workers for PS (MW 233K).^{8a} The surface modification was monitored and verified by X-ray photoelectron spectroscopy (XPS) and attenuated total reflection-infrared (ATR-IR) spectroscopy as shown in Fig. 1. XPS survey scans of the films before and

after photo-grafting of the polymer showed the presence of all the expected elements in the CbzBP and the PS (Fig. S5, ESI[†]). High-resolution scans of the films before and after photocrosslinking of PS showed an increase in the peak intensity of C 1s attributed to the grafting of the carbon-rich polymeric chain (Fig. 1a) and a decrease in the N 1s intensity due to the coverage of the CbzBP layer by the grafted PS on the surface (Fig. 1b). ATR-IR spectrum of the grafted polystyrene showed the expected peaks at 3034 cm⁻¹, 2932 cm⁻¹, 1600 cm⁻¹, 1500 cm^{-1} , 1456 cm^{-1} , and 850 cm^{-1} corresponding to the aromatic C-H stretch, aliphatic C-H stretch of the polymer backbone, 2 bands for C=C (in ring) stretches, C-C aromatic stretch (in ring), and C-H bending and ring puckering, respectively. All these steps were also done on Au substrate to monitor the thicknesses of the electrodeposited CbzBP and the final photografted polymer, which was found to be 2.93 nm and ~ 6.5 nm, respectively.

After the confirmation of the technique on unpatterned surfaces, the whole process was then applied to patterning the polymer brush on conducting substrates. Fig. 2 shows the atomic force microscopy (AFM) images of the patterned polymer brushes fabricated using the two routes shown in Scheme 1. As expected, the polymer only selectively attached to the regions where the CbzBP is electropatterned for the first route (Fig. 2a) and to the exposed areas under UV light in the case of the second route (Fig. 2c). This selective polymer grafting is even emphasized on the 3D image of the AFM scans where the height is higher on areas where the PS is expected to be grafted (Fig. 2b and d).

FT-IR imaging (Varian) with a focal plane array (FPA) detector of the grafted PS brush was also conducted to give information about the chemical composition of the patterns produced. This method serves as a powerful tool for patterned surfaces that could not be chemically characterized by AFM, optical microscope or SEM, which are the traditional methods for imaging patterned materials on surfaces. To our knowledge, this is the first report for the use of this technique to chemically



Fig. 1 XPS spectra of the film before and after photo-crosslinking of the PS for (a) C 1s and (b) N 1s. (c) ATR-IR spectrum of the photo-grafted PS film.



Fig. 2 2D and 3D AFM images of (a, b) electropatterning route and (c, d) photopatterning route of the grafted PS brush.



Fig. 3 2D and 3D IR-imaging frames for the (a, b) electropatterned and (c, d) photopatterned PS brush. Scale bar is equivalent to $30 \ \mu m$.

map out patterned brushes on surfaces. Fig. 3 shows the IR image of the patterned films on the surface using the two routes presented. The images are focused at the aromatic C–H stretch frequency of the film (3034 cm⁻¹), which is the signature functional group of the PS. The green color intensity is where the high concentration of this frequency is present, signifying the selective grafting of PS on that region, depending on the patterning method employed (*i.e.* on the boundaries for the electropatterned surface and on the squares for the photopatterned area). These patterns were not observed upon scanning on other frequencies for functionalities that are not present in the PS brush (*e.g.* 1680–1800 cm⁻¹ for C=O stretch, see Fig. S6 (ESI†)), which further proved the power of IR-imaging to chemically map the functionalities of the grafted brush on the surface.

In conclusion, a new, simple and versatile method of patterning brushes on conducting surfaces *via* the use of electro-deposited photoactive moiety was demonstrated. The patterning was made suitable for conducting surfaces such as ITO and Au with the use of only one electro-active photocrosslinker, which avoids synthesis of different photocrosslinkers with functionalities specific for each substrate. The bifunctionality of the CbzBP also made it possible

to pattern PS brushes using two different routes, namely electropatterning and photopatterning as observed in the AFM and IR-imaging analysis. The presented method is promising in that it could extend the scope on other conducting electrodes that are viable for semiconductor processing set-ups and the biomedical device field.

The authors acknowledge funding from NSF DMR-10-06776, ARRA-CBET-0854979, CHE-10-41300, Texas NHARP 01846, and Robert A. Welch Foundation, E-1551. Technical support from Agilent Technologies and Optrel is also acknowledged. The authors also thank Ms Hanae Ohtsuka of Tokyo University of Agriculture and Technology for help in the preparation of some films.

Notes and references

- (a) F. J. Xu, K. G. Neoh and E. T. Kang, *Prog. Polym. Sci.*, 2009, 34, 719–761; (b) Z. Nie and E. Kumacheva, *Nat. Mater.*, 2008, 7, 277–290; (c) M. Geissler and Y. Xia, *Adv. Mater.*, 2004, 16, 1249–1269.
- 2 (a) T. Chen, D. P. Chang and S. Zauscher, Small, 2010, 6, 1504–1508; (b) D. M. Jones, J. R. Smith, W. T. S. Huck and C. Alexander, Adv. Mater., 2002, 14, 1130–1134.
- 3 (a) R. Konradi and J. Ruhe, *Langmuir*, 2006, 22, 8571–8575; (b) O. Prucker, M. Schimmel, G. Tovar, W. Knoll and J. Ruhe, *Adv. Mater.*, 1998, 10, 1073–1077; (c) F. Zhou, L. Jiang, W. Liu and Q. Xue, *Macromol. Rapid Commun.*, 2004, 25, 1979–1983.
- 4 (a) A. Rastogi, M. Paik, M. Tanaka and C. Ober, ACS Nano, 2010,
 4, 771–780; (b) S. J. Ahn, M. Kaholek, W. Lee, B. LaMattina,
 T. LaBean and S. Zauscher, Adv. Mater., 2004, 16, 2141–2145;
 (c) B. Brough, K. L. Christman, T. S. Wong, C. M. Kolodziej,
 J. G. Forbes, K. Wang, H. D. Maynard and C. M. Ho, Soft Matter, 2007, 3, 541–546.
- 5 (a) Y. Liu, V. Klep and I. Luzinov, J. Am. Chem. Soc., 2006, 128, 8106–8107; (b) K. Y. Suh, M. C. Park and P. Kim, Adv. Funct. Mater., 2009, 19, 2699–2712.
- 6 M. Husemann, M. Morrison, D. Benoit, J. Frommer, C. M. Mate, W. Hinsberg, J. L. Hedrick and C. J. Hawker, J. Am. Chem. Soc., 2000, 122, 1844–1845.
- 7 C. R. Becer, C. Haensch, S. Hoeppener and U. S. Schubert, *Small*, 2007, 3, 220–225.
- 8 (a) O. Prucker, C. Naumann, J. Ruhe, W. Knoll and C. Frank, J. Am. Chem. Soc., 1999, **121**, 8766–8770; (b) K. Horie, H. Ando and I. Mita, Macromolecules, 1987, **20**, 54–58.
- 9 (a) P. Taranekar, A. Baba, T. Fulghum and R. Advincula, *Macromolecules*, 2005, **38**, 3679–3687; (b) A. S. Sarac, M. Ates, E. A. Parlak and E. F. Turcu, *J. Electrochem. Soc.*, 2007, **154**, D283–D291; (c) C. Xia, R. Advincula, A. Baba and W. Knoll, *Chem. Mater.*, 2004, **16**, 2852–2856.
- 10 C. Kaewtong, G. Jiang, M. J. Felipe, B. Pulpoka and R. Advincula, ACS Nano, 2008, 2, 1533–1542.
- 11 J. F. Ambrose and R. F. Nelson, J. Electrochem. Soc., 1968, 115, 1159–1164.