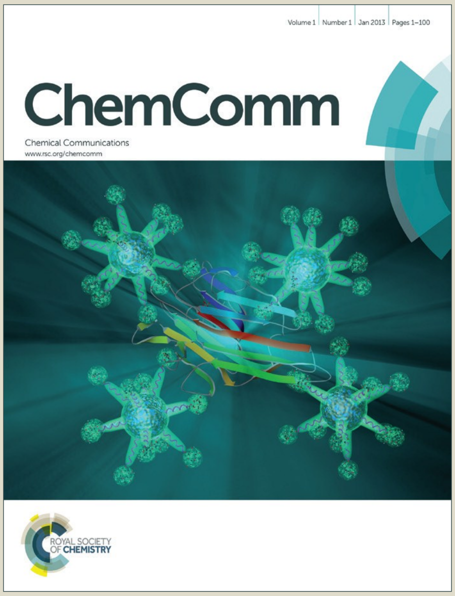
ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Please do not adjust margins

Journal Name

COMMUNICATION

Electrically Charged Selectivity of Poly-*para*-xylylene Deposition

Chih-Yu Wu†, Ho-Yi Sun†, Wei-Chieh Liang, Hung-Lun Hsu, Hsin-Ying Ho, Yu-Ming Chen, and Hsien-Yeh Chen*

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

The bottom-up patterning approach provides intrinsic advantages associated with unlimited resolution but is limited by the materials available for selection. A general and simple approach towards the selective deposition of poly-para-xylylenes is introduced in this communication. The chemical vapour deposition (CVD) of poly-para-xylylenes is inhibited on the high-energy surfaces of electrically charged conducting substrates. This technology provides an approach to selectively deposit poly-para-xylylenes irrespective of the substituted functionality and to pattern these polymer thin films from the bottom up.

The emerging concept of imparting chemical or biological functionalities to the surfaces of materials has shown potential.[1-3] Precise positioning of these functionalities in regions of interest on the surfaces of materials can be achieved by (i) surface patterning, (ii) surface compositional gradients or a multifunctional combination of (i) and (ii). Patterning approaches are collectively classified as top-down or bottom-up techniques.[4] The former, although widely exploited owing to their well-established processes and availability, are limited by the resolution and dimensional characteristics of substrates.[5] The latter approaches using bottom-up techniques, in contrast, provide precise resolution but require substantial knowledge of how to perform the modification processes and are usually applied in solution-based methods that are applicable only to selected materials.[6, 7] The important interface materials poly-*para*-xylylenes have been demonstrated to be a robust tool for modifying the surfaces of materials to impart precise surface properties.[8] Approaches using poly-*para*-xylylenes to enable top-down modification of selected regions have been achieved by microcontact printing (μCP),[9, 10] vapour-assisted micropatterning in replica structures (VAMPIR)[11] and mask-assisted[12, 13] or maskless photopatterning.[14, 15] Bottom-up approaches using poly-*para*-xylylenes rely on material-dependent selectivity during the vapour deposition process and have been reported using transition metal substrates for non-functionalised poly-*para*-xylylenes[16-18] and vinyl-functionalised poly-*para*-xylylene.[19] However, the quest for a general method of performing the selective deposition of poly-*para*-xylylenes remains unresolved. A more general concept of the selective deposition of poly-*para*-xylylenes offers advantages in not only feature resolution but also a simpler and more straightforward formation of the patterned layer compared with top-down approaches. For instance, nonfunctional poly-*para*-xylylenes will provide a protective coating in the region where protection is needed and functionalised poly-*para*-xylylenes additionally enable the immobilisation of specific biomolecules and create a functional material interface in the same region-specific manner.

However, although the mechanism is not fully understood, several transition metals, such as iron, copper, silver, and platinum, have been shown in previous reports to provide high surface energy for the neutralization of quinodimethanes on the substrate surface and prevent further initiation and propagation of the polymerization reaction from forming poly-*para*-xylylenes.[18] Limitations of the selective deposition were found only for nonfunctional poly-*para*-xylylenes and vinyl-functionalized poly-*para*-xylylenes on a small group of metal surfaces. Other functionalized poly-*para*-xylylenes showed a higher interaction with the underlying substrates and demonstrated no inhibition regardless of the high surface energy of certain transition metals.[19] In light of these outcomes and considering that the high surface energy of these substrates may account for the neutralization of quinodimethanes, we herein hypothesized that supplying electrical energy to the substrate surface can enhance deposition selectivity by increasing the transition of the surface energy instead of relying on the innate and native surface energy of the substrates. The approach of charging the substrate surface is (i) universally applicable to other

---

Department of Chemical Engineering, National Taiwan University, Taipei, 10617, Taiwan.
† C.-Y. Wu and H.-Y. Sun contributed equally to this work.
* To whom correspondence should be addressed: hsychen@ntu.edu.tw

Electronic Supplementary Information (ESI) available: experimental details and spectroscopic data. See DOI: 10.1039/x0xx00000x

Please do not adjust margins

ChemComm Accepted Manuscript

conducting substrates and (ii) demonstrates effective selectivity for the deposition of both nonfunctional poly-*para*-xylylenes and the family of functionalized poly-*para*-xylylenes. The evidence for deposition selectivity was first verified by using Fourier transform infrared reflection absorption spectroscopy (IRRAS). The spectra were recorded and compared with the surfaces after the CVD deposition of polydichloro-*para*-xylylene (PPX-C or commercially named parylene C) or aldehyde-functionalized poly-*para*-xylylene (PPX-aldehyde) on titanium (Ti), copper (Cu), silver (Ag), gold (Au), zinc (Zn), aluminium (Al), and conducting glasses with fluorine-doped SnO$_2$ (FTO), where electrical charges were applied to the substrates. Control substrates without applied charges were also tested in parallel for comparison. As indicated in **Fig. 1 a-b**, the spectra were dominated by characteristic –C–Cl stretching at 1030-1100 cm^{-1} for polydichloro-*para*-xylylene (**Fig. 1a)**, at 2860-3040 cm^{-1} for the symmetric and asymmetric stretching corresponding to –C–H absorptions, and at approximately 1662 and 1603 cm^{-1} attributed to unsaturated –C=O stretching for aldehyde-functionalized poly-*para*-xylylene, as demonstrated in (**Fig. 1b)**. These characteristic bands were present on the pure substrate surfaces and showed consistent selectivity compared with previous reported results.[18, 19] In contrast, all these bands could not be observed on the same metals or FTO substrates with the addition of applied electrical charges (**Fig. 1 c-d**). These results revealed that a universal selectivity was found for conducting substrates and that the selectivity was equally applicable for both nonfunctional and functionalized poly-*para*-xylylenes. The same approach described for PPX-C and PPX-aldehydes was then applied to other poly-*para*-xylylenes, including trifluoroacetic-functionalized poly-*para*-xylylene (PPX-TFA) and aminomethyl-functionalized poly-*para*-xylylene (PPX-amine), on the same selection of conducting substrates, and the results are recorded in the electronic supplementary information (ESI).

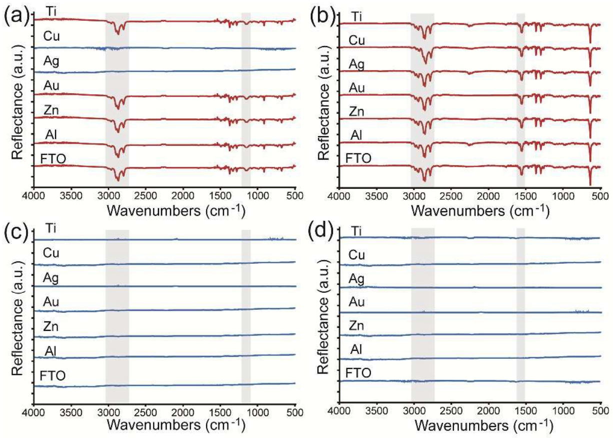


Fig. 1 IRRAS characterizations of selectively deposited PPX-C or PPX-aldehyde on different conducting substrates (Ti, Cu, Ag, Au, Zn, Al, and FTO) with deposition rate of 30 Å/s. (a) The deposition of PPX-C was inhibited only by Cu and Ag before applying charges to the substrates. (b) The deposition of PPX-aldehyde showed no inhibition on the surfaces before applying charges to the substrates. (c) The deposition of PPX-C was inhibited on all surfaces after applying charges to the substrates. (d) The deposition of PPX-aldehyde was inhibited on all surfaces after applying charges to the substrates. Film thickness of approximately 150 nm PPX-C or PPX-aldehyde was measured for non-inhibitory surfaces.

The existence of an upper limit, i.e., a maximum deposition thickness of poly-*para*-xylylene, at which deposition will commence and the relative selectivity of the charged surface will be lost, was examined on Al substrates, which previously showed no inhibitory effect for poly-*para*-xylylenes.[18] As indicated in **Fig. 2a**, a selectivity loss eventually occurred after the deposition of thick PPX-C or PPX-aldehyde (by comparison with a reference surface without applied electrical charges), and a tendency of increased electrical energy was found to be correlated to a greater inhibitor surface (thicker maximum deposition thickness). This trend was also anticipated for all the poly-*para*-xylylenes studied, irrespective of their substituted functionalities. The results of varying the monomer delivery rate as a function of the maximum deposition thickness on such charged surfaces supported the previously found deactivation theory.[18] In addition, the reported rate equation was found to correlate well with the deposition of the studied PPX-C or PPX-aldehyde on the charged surfaces (**Fig. 2b**). Furthermore, compared with the native activity of transition metals (literature data shown in **Fig. 2b**), the higher activity provided by the charged surfaces resulted in a shift in the required selective deposition conditions in the low monomer delivery rate regime. Thus, a high maximum deposition thickness can be achieved at a very low delivery rate of 0.3 Å/s; such control was previously thought to be

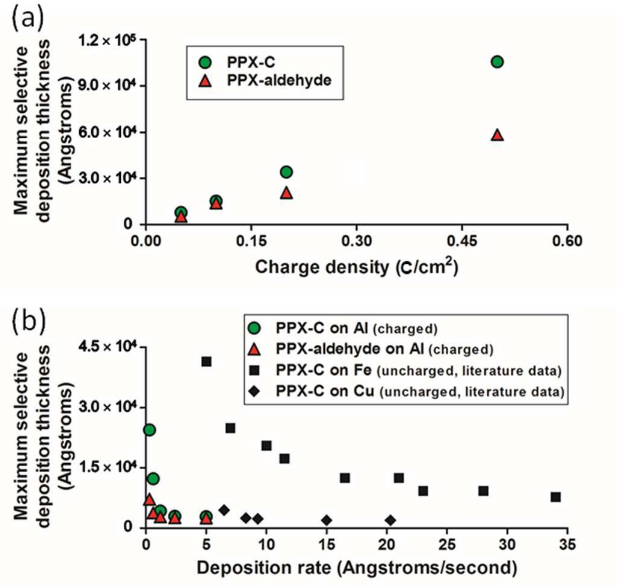


Fig. 2 Maximum selective deposition thickness of PPX-C (data points presented as green circles) and PPX-aldehyde (data points presented as red triangles) on charged Al substrates. (a) Selective deposition was performed with varying charging intensities. (b) Selective deposition was performed by varying the deposition rate; the results were compared with the literature data (Ref. 23) for selectively deposited PPX-C on Fe and Cu surfaces (literature data points presented as black squares and diamonds, respectively).

ChemComm Accepted Manuscript

Please do not adjust margins

impossible.[18] The mechanism of growth inhibition can possibly involve deactivation of the high-energy triplet state of quinodimethanes to a low-energy singlet state[16, 18] when adsorbed on the charged surface. In addition, the sticking coefficient (S)[20] that was calculated for such a charged surface was reduced by one order of magnitude compared with an inhibitory surface of Fe ($S = 1.94 \times 10^{-6}$ compared with 1.94×10^{-5} for Fe; a detailed calculation is shown in the ESI), which was previously found to be the best inhibitory metal surface for some poly-*para*-xylylenes.[17, 18] These results unambiguously support our hypothesis of an increased transfer of surface energy to the substrates, which thereby serve as a better inhibitor of the deposition of poly-*para*-xylylene. This active pathway is anticipated to be applicable to other conducting substrates.

Finally, patterned substrates were prepared by placing conducting Al metal channels on a nonconductive glass surface and allowing for the selective deposition of PPX-TFA, PPX-amine, and PPX-aldehyde. The scanning electron microscope (SEM) image in **Fig. 3a** shows the deposition footprint of the selectively deposited PPX-aldehyde on the anticipated areas of glass background, where no charged was applied. Furthermore, energy dispersive X-ray spectroscopy (EDS) elemental mapping analysis revealed the selective growth of these poly-*para*-xylylene films by showing a spatially confined distribution of fluorine signals for PPX-TFA, nitrogen signals for PPX-amine, oxygen signals for PPX-aldehyde, and chlorine signals for PPX-C (**Fig. 3b-e**). These fluorine-, nitrogen-, oxygen- and chlorine-containing areas unambiguously correspond to the negative areas of patterned Al (verified Al elemental map shown in **Fig. 3f**), providing direct evidence that these poly-*para*-xylylenes were inhibited by the electrically charged Al surfaces during CVD polymerization. The resulting patterned polymer film of PPX-aldehyde also showed reactive characteristics to support nucleophilic addition with a hydrazine or hydrazide to yield hydrazones.[21] Fluorescently labelled Alexa Fluor® 568 hydrazide molecules were allowed to react with the aldehyde side groups on PPX-aldehyde, and the fluorescence signals were only detected on those areas in which the Al/electrically charged characteristics were absent, as indicated in **Fig. 3g**. These results unambiguously verify that the growth of the functional PPX-aldehyde was inhibited by such a charged surface.

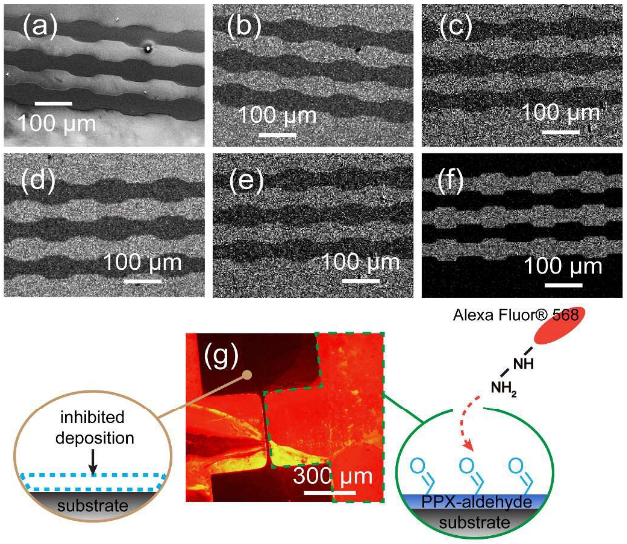


Fig. 3 Selective deposition of PPX-TFA, PPX-amine, PPX-aldehyde, and PPX-C on patterned substrates of Al. (a) SEM image showing the footprint of selectively deposited films of PPX-aldehyde on the corresponding areas of Al-free background. EDS elemental mapping analysis shows the confined elemental map of (b) fluorine for PPX-TFA, (c) nitrogen for PPX-amine, (d) oxygen for PPX-aldehyde, and (e) chlorine for PPX-aldehyde on the corresponding areas where the charged Al inhibitor was absent. (f) An elemental map of Al was also recorded, showing charged regions for comparison. (g) Fluorescence micrograph showing the immobilized Alexa Fluor® 568 hydrazide molecules on confined areas corresponding to the selectively deposited PPX-aldehyde.

As prospective materials require more delicate and sophisticated functions on their surfaces, together with the fabrication of miniature-sized devices with complicated geometries, control over the surface properties requires precision in both the chemical and topological definitions with respect to the spatial resolution and chemical functionalities. The introduced selective deposition technology is not constrained to nonfunctional poly-*para*-xylylenes (parylene N or parylene C) or to vinyl-functionalized poly-*para*-xylylenes, which were found to selectively deposit only on transition metals. In addition, this technology provides a simple and robust tool to modify material surfaces from the bottom up without the need of post-modification. The vapour-based deposition characteristics also feature a general method through which the coating can be prepared conformally with respect to substrate topology, curvature, and geometry, and the deposition and immobilization technologies of poly-*para*-xylylenes are well-transferred from one substrate to another.[8, 22] Future research should be dedicated to the manipulation of the electrical parameters, the determination of the critical thickness on different conducting materials (including metals, indium tin oxide and their derivatives and wide selections of conducting polymers and graphene), and the multifunctional presentation of selectively deposited poly-*para*-xylylenes with distinct functionalities. The extension of the selective deposition technology can transfer well from the reported functionalities to other existing libraries of functional poly-*para*-xylylenes.[23-25] We foresee applications in semiconductors, bioelectronics, sensors, and conducting polymers to take advantage of this selective coating technology.

Acknowledgements

H.-Y. Chen gratefully acknowledges support from the Ministry of Science and Technology of Taiwan (MOST 104-2628-E-002-010-MY3 and MOST 101-2628-E-002-034-MY3) and National Taiwan University (102R7745 and 103R7745).

Notes and references

1. T. Sun, G. Qing, B. Su and L. Jiang, *Chem. Soc. Rev.*, 2011, **40**, 2909-2921.
2. M. M. Stevens and J. H. George, *Science*, 2005, **310**, 1135-1138.
3. M. A. Cole, N. H. Voelcker, H. Thissen and H. J. Griesser, *Biomaterials*, 2009, **30**, 1827-1850.

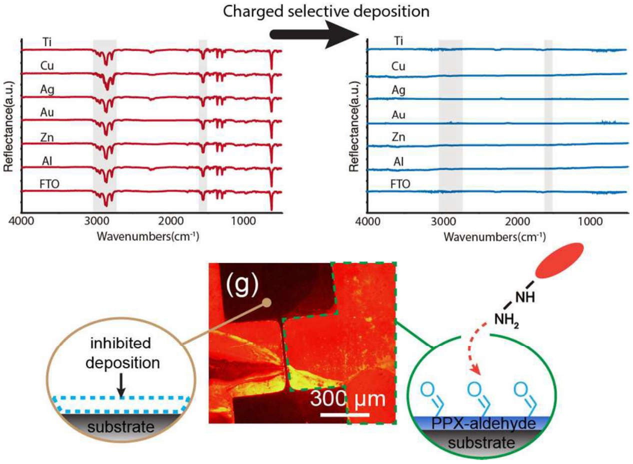
ChemComm Accepted Manuscript

Please do not adjust margins

4. Z. Nie and E. Kumacheva, *Nat. Mater.*, 2008, **7**, 277-290.
5. A. Biswas, I. S. Bayer, A. S. Biris, T. Wang, E. Dervishi and F. Faupel, *Adv. Coll. Inter. Sci.*, 2012, **170**, 2-27.
6. W. Lu and C. M. Lieber, *Nat. Mater.*, 2007, **6**, 841-850.
7. C. A. E. Hauser and S. Zhang, *Chem. Soc. Rev.*, 2010, **39**, 2780-2790.
8. H.-Y. Chen, M. Hirtz, X. Deng, T. Laue, H. Fuchs and J. Lahann, *J. Am. Chem. Soc.*, 2010, **132**, 18023-18025.
9. J. Lahann, M. Balcells, H. Lu, T. Rodon, K. F. Jensen and R. Langer, *Anal. Chem.*, 2003, **75**, 2117-2122.
10. J. Lahann, I. S. Choi, J. Lee, K. F. Jensen and R. Langer, *Angewandte Chemie International Edition*, 2001, **40**, 3166-3169.
11. H.-Y. Chen and J. Lahann, *Adv. Mater.*, 2007, **19**, 3801-3808.
12. H.-Y. Chen and J. Lahann, *Anal. Chem.*, 2005, **77**, 6909-6914.
13. H.-Y. Sun, C.-Y. Fang, T.-J. Lin, Y.-C. Chen, C.-Y. Lin, H.-Y. Ho, M. H. C. Chen, J. Yu, D.-J. Lee, C.-H. Chang and H.-Y. Chen, *Adv. Mater. Inter.*, 2014, **1**, 1400093.
14. H.-Y. Chen, J.-M. Rouillard, E. Gulari and J. Lahann, *Proc. Natl. Acad. Sci.*, 2007, **104**, 11173-11178.
15. M.-G. Wu, H.-L. Hsu, K.-W. Hsiao, C.-C. Hsieh and H.-Y. Chen, *Langmuir*, 2012, **28**, 14313-14322.
16. J. J. Senkevich, C. J. Wiegand, G. R. Yang and T. M. Lu, *Chemical Vapor Deposition*, 2004, **10**, 247-+.
17. K. M. Vaeth and K. F. Jensen, *Advanced Materials*, 1999, **11**, 814-820.
18. K. M. Vaeth and K. F. Jensen, *Chemistry of Materials*, 2000, **12**, 1305-1313.
19. H.-Y. Chen, J. H. Lai, X. Jiang and J. Lahann, *Advanced Materials*, 2008, **20**, 3474-3480.
20. J. B. Fortin and T. M. Lu, *Chemistry of Materials*, 2002, **14**, 1945-1949.
21. H. Nandivada, H.-Y. Chen and J. Lahann, *Macromole. Rapid Comm.*, 2005, **26**, 1794-1799.
22. J.-T. Wu, C.-H. Huang, W.-C. Liang, Y.-L. Wu, J. Yu and H.-Y. Chen, *Macromole. Rapid Comm.*, 2012, **33**, 922-927.
23. H.-Y. Chen and J. Lahann, *Langmuir*, 2010, **27**, 34-48.
24. J. Lahann and R. Langer, *Macromolecules*, 2002, **35**, 4380-4386.
25. B. Lu, S. Zheng, B. Q. Quach and Y.-C. Tai, *Lab Chip*, 2010, **10**, 1826-1834.

ChemComm Accepted Manuscript

For Table of Contents Only



Electrically charged surfaces show inhibited selectivity for the deposition of poly-*para*-xylylenes, irrespective of their substituted functionalities.

ChemComm Accepted Manuscript