Micro-patterning of C–C covalently-bound grafts by mecha-nochemical imprint lithography†

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A simple, inexpensive and versatile patterned removal of C–C grafts has been realized for scalable multicomponent micropatterned functionalization.

The family of sp²-carbon materials includes, among others, different forms of graphite, graphene, graphene oxide, graphene quantum dots and carbon nanotubes. Covering a broad range of often exceptional, mechanical, optical, electronic and chemical properties, these materials either already have well-established industrial applications (e.g., as lubricants, adsorbents, electrochemical/battery electrodes, supercapacitors, catalyst supports, etc.) or have shown great potential during tests in research laboratories (e.g., as various sensors, electronic and biomedical devices, opto-electronic components, etc.).

The performance and applications of the carbon-based materials can be further enhanced through the covalent functionalization of existing functional groups (e.g., –COOH in graphene oxide, carbon dots, oxidized carbon nanotubes) or by the addition of suitably functionalized reactive species (dienes, carbene, radicals, etc.) to C–C double bonds in pristine materials. For the latter approach, in situ electrochemically (EC) generated aryl radicals are particularly convenient since (1) a wide variety of functionalized aniline precursors are commercially available, (2) the formed C–C covalent grafts are thermally and chemically stable, and furthermore, (3) the EC activation allows short reaction times and superior control over the grafting process (e.g. in comparison, the success and quality of thermal grafting is substrate-dependent and is harder to control). Such functionalization has already enabled the custom design of highly sensitive plasmonic biosensors, electrochemical transistors, improved solar cells and energy storage materials.

Currently, the research is focused on the approaches to control not only the chemistry and surface density of functional grafts, but also their spatial order. Bottom-up strategies for patterned covalent functionalization rely on the design of special radical precursors, molecular building blocks or larger aggregates capable of on-surface self-assembly. Upon activation of aryl radicals, such on-surface adsorbates lead to patterned grafting that matches the symmetry and dimensions of the initial self-assembly, albeit with limitations that arbitrary shapes are not possible, and that for each new pattern one has to design and optimize another new ‘molecular assembly-grafting’ system. Using diazonium salts as reactive inks has been demonstrated in direct writing and micro-contact printing technologies, though coupling together lithography and covalent functionalization in the same step can limit the general applicability and control over the patterning processes. In this regard, subtractive SPM lithography, based on local mecha-nochemical degrafting of previously functionalized substrates by the scanning AFM tip, allows direct and clean “nanoshaving” of custom patterns. The natural limitations of this method for large-scale patterning include the small SPM scan size (typically < 100 µm) and prolonged processing times. Finally, important milestones are the successful integration of (electro)chemical grafting and industrial-grade lithography in a complex multi-step procedure allowing multi-component micropatterned functionalization of graphene surfaces.

Here, we discovered that C–C covalently-bound aryls can be spatio-selectively degrafted upon physical contact with soft PDMS stamps. The patterning procedure does not require any pre-treatment of contacting surfaces, does not use solvents, inks or resists, and can be conveniently conducted at room temperature using inexpensive equipment.

Fig. 1 illustrates the electrochemical arylation reaction and standard characterization of the covalently functionalized substrates. In this study, we focus exclusively on highly oriented...
imprinting, but so far, all such attempts were unsuccessful, as evidenced by the absence of patterned degrafting (Fig. S1, ESI†). Presumably, this is due to difficulties in ensuring perfect alignment/full contact between all micropatterned features of the hard imprint and the rigid HOPG substrate. That is why we switched to highly elastic PDMS – the material of choice for various soft lithographies (e.g., chemical lift-off lithography, microcontact printing, nanoimprint lithography, etc.).

When a 1.5 μm linear grating made of PDMS was brought into contact with the TMP-grafted HOPG surface (Fig. 2) on a high-precision two-dimensional transfer platform, the alignment and contact were easily monitored using a built-in optical microscope. After detachment of the stamp, AFM analysis revealed that the created linear pattern on the HOPG surface matches the 1.5 μm periodicity of the PDMS (Fig. 2c). The depth of the linear trenches on the patterned TMP-grafted layer was 0.8 ± 0.2 nm, thus implying successful degrafting, as also evident from the decreased \(I_D/I_G\) ratio of TMP after imprinting (Fig. S2, ESI†). Finally, large-scale scanning electron microscopy (SEM) imaging, overcoming the limited scanning range of our AFM (30 μm), confirms the presence of the graft pattern throughout the imprinting contact area (Fig. S3, ESI†).

Testing available PDMS gratings, we have successfully employed MCIL to fabricate other linear patterns with periodicities ranging between 300 nm and 400 μm (Fig. S4, ESI†). The subtractive mechaenochemical removal of C–C covalent grafts can create features < 100 nm (Fig. S4a, ESI†). The resolution in our tests appears to be limited primarily by the quality of the PDMS stamp (Fig. S5a, ESI†) and the imperfections in the original grafted film (e.g., due to nanobubbles or physisorbed by-products that blocked the HOPG surface from covalent grafting, Fig. S5, ESI†). Uniform high-quality grafting is even more important for successful MCIL of graphene substrates (Fig. S6, ESI†). Interestingly, in larger periodicity patterns (e.g., Fig. S4d, ESI†), the...
and self-collapse lithography 20 by designing shallower PDMS
(Fig. S8, ESI†) that such degrafting was observed even for 10 µm PDMS stamps. Indeed, besides elastic compression-stretching deformations exerts both vertical and lateral strain onto the stamp inside a nanoimprinting set-up (discussed below), also did not cause degrafting, even at the maximum available pressure (4.5 bar). Probably, the micropatterns of soft PDMS are more efficient at degrafting because their compressive deformation exerts both vertical and lateral strain onto the degrafted region (W) (Fig. 3a and Fig. S9, ESI†). This controlled tuning of the W indirectly validates the good stability and precision of substrate-stamp alignment within our micro-positioning set-up, and could be explained by variable deformations of PDMS. Indeed, besides elastic compression-stretching of the PDMS stamp, we observed inelastic deformation-stretching of the PDMS stamp, observed systematically widening of the degrafted region (W) (Fig. 3a and Fig. S9, ESI†). This controlled tuning of the W indirectly validates the good stability and precision of substrate-stamp alignment within our micro-positioning set-up, and could be explained by variable deformations of PDMS. Indeed, besides elastic compression-stretching of the PDMS stamp, we observed inelastic deformations, resulting in the simultaneous widening and flattening of the PDMS features that contacted the HOPG (Fig. S10, ESI†). Interestingly, complete degrafting occurred with macroscopic (∼5 × 5 mm) non-patterned flat PDMS only when full contact and vertical compression were complemented by a lateral displacement of the stamp with respect to the substrate (Fig. S11, ESI†). Better controlled vertical compression of the non-patterned flat PDMS stamp inside a nanoimprinting set-up (discussed below), also did not cause degrafting, even at the maximum available pressure (4.5 bar). Probably, the micropatterns of soft PDMS are more efficient at degrafting because their compressive deformation exerts both vertical and lateral strain onto the grafts within the micro-contact area. This behaviour differs significantly from the proposed mechanism of chemical lift-off lithography (CLL) in which strong Si(PDMS)–O–C(SAM) covalent bonds, formed during compression between functionalized PDMS and complementarily functionalized self-assembled monolayer (SAM), ensures selective degrafting of much weaker bonds (either substrate–SAM or substrate–substrate) upon lifting the PDMS from the sample.21

To have a better control over the forces during micropatterning we have also tested MCIL using a commercial nanoimprint-set-up in which a Teflon membrane and pressurized gas facilitate reproducible uniform compression of the PDMS and TMP-HOPG stack (Fig. 3b and Fig. S12–S16, ESI†). Higher compression widens the PDMS microfeatures and increases the contact area between PDMS and HOPG. In turn, this results in a larger number of grafts that got strained and degrafted by the PDMS stamp (i.e. the degrafting areas get widened). Simply varying the offset rotation of the PDMS stamp between sequential imprinting steps enabled the creation of more complex patterns using the same linear gratings. For example, a 3.3 µm linear PDMS grating was used to create a square pattern (Fig. 3c and d). Additionally, by varying the contact pressure along with the PDMS offset angle, we could easily create a diamond pattern with two distinct degrafting widths (Fig. S17, ESI†). During this study, we did not have an access to nano-precise alignment set-ups typically used for multipatterning in photolithography. If precise re-alignment is available, then creation of much more complex micropatterns should be possible by varying the MCIL parameters (different patterns of PDMS stamps, variable offset angles and x-y positions, different compression of sequential imprints, etc.).

Finally, MCIL is fully suitable for multi-component patterned C–C functionalization (Fig. 4a). Indeed, (1) mechanochemical degrafting is common for structurally different arylated graphene layers,22 and (2) MCIL does not utilize any resists or inks that could leave hard-to-remove residues causing local electrochemical passivation (similar to purposefully designed EC passivation by n-pentacontane20). That is why, in principle, one can combine any number of MCIL (multipatterning steps and electrochemical arylation). As a very basic demonstration, we have shown that nanometer-deep degrafted trenches formed by single MCIL imprint in TMP–HOPG are seamlessly grafted by NBD (Fig. 4) or TBP (Fig. S18, ESI†) grafts. Unlike monolayers of TMP and TBP, NBD is known to form branched covalent dendrimers,13 allowing very easy identification in AFM height images.

In summary, we successfully demonstrated a simple yet powerful method for subtractive micropatterning of C–C covalent grafts via mechanochemical degrafting upon contact with PDMS stamps. Such mechanochemical imprint lithography (MCIL) does not necessitate reactive functional groups on the PDMS or grafts, nor does it require complex preparation steps or expensive equipment. Multiple imprinting sessions can be combined with surface functionalization steps to fabricate multi-component covalently grafted substrates characterized...
by well-defined microscale structure, nanoscale thickness and spatially localized chemical functionality. Whether used alone or in combination with other micro-/nanopatterning methods, MCIL offers convenient direct patterning of covalently functionalized spatially localized chemical functionality. Whether used alone or in combination with other micro-/nanopatterning methods, MCIL offers convenient direct patterning of covalently functionalized spatially localized chemical functionality. Whether used alone or in combination with other micro-/nanopatterning methods, MCIL offers convenient direct patterning of covalently functionalized spatially localized chemical functionality. Whether used alone or in combination with other micro-/nanopatterning methods, MCIL offers convenient direct patterning of covalently functionalized spatially localized chemical functionality. Whether used alone or in combination with other micro-/nanopatterning methods, MCIL offers convenient direct patterning of covalently functionalized spatially localized chemical functionality. Whether used alone or in combination with other micro-/nanopatterning methods, MCIL offers convenient direct patterning of covalently functionalized spatially localized chemical functionality.

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Data availability

Data for this article, including original CV, AFM, STM, SEM and Raman measurements are available at Zenodo repository at https://doi.org/10.5281/zenodo.12525524.

Conflicts of interest

There are no conflicts to declare.

Notes and references