Molecular embroidering of graphene

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Structured covalent 2D-patterning of graphene with different chemical functionalities constitutes a major challenge in nanotechnology. At the same time, it opens enormous opportunities towards tailoring of physical and chemical properties with limitless combinations of spatially defined surface functionalities. However, such highly integrated carbon based 2D-architectures (“graphene embroidery”) are so far elusive. We report here for the first time a practical realization of molecular graphene embroidery by generating regular multiply functionalized patterns consisting of concentric regions of covalent addend binding. These spatially resolved 2D-hetero-architectures were generated by repetitive electron-beam lithography (EBL)/reduction/covalent-binding sequences starting with (polymethyl methacrylate) PMMA covered graphene deposited on a SiO\textsubscript{2}/Si substrate. The corresponding functionalization zones carry bromobenzene-, deutero- and chloro-addends. We employed statistical Raman spectroscopy together with scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) for an unambiguous characterization. The exquisitely ordered 2D-nanoarchitectures of these covalently multi-patterned graphene sheets were clearly visualized.

Multiply functionalized and hierarchically patterned graphene sheets with a spatially defined 2D-architecture are still elusive. The realization of this challenge constitutes the next higher level of graphene chemistry. Such tailored nano-surfaces are highly attractive for high-performance applications, for example, in the fields of optoelectronics and sensors\textsuperscript{1-4}. Key to this endeavor is
providing facile and flexible synthetic approaches for 2D-patterning of graphene. So far, shape control over graphene nanostructures has been targeted either by top-down etching\textsuperscript{5-10} or by bottom-up synthesis of nanoribbons using low-molecular precursors on surfaces\textsuperscript{11-15}. Covalent graphene chemistry, in principle, provides another opportunity by addend binding to defined lattice regions. This approach also has the advantage that next to spatial structuring of graphene chemical surface functionalities can be introduced which are located in the proximity of the conductive regions of intact graphene. To date a few first examples of covalently 2D-patterened graphene have been prepared by a combination of wet-chemical and classical patterning techniques\textsuperscript{16-25}. However, all covalent patterning protocols established so far are limited to one-step chemical patterning of graphene only. For the realization of more complex 2D-architectures involving the regular arrangement of addend regions with different surface functionalities, a detailed understanding of covalent reaction mechanisms and concepts such as surface activations are required. In the macroscopic world, such a 2D-engineering approach finds an analogy in embroidery. This is a long-existing decoration technique, in which a needle is used as a tool for applying patterns onto fabric and other materials. Following a similar manner, once the chemical needle (as referred to graphene chemistry) was manipulated, the analogous chemical embroidery will provide access to structured graphene nano-architectures with a multifunctional array of addend zones next to patterns of intact graphene. Owing to its versatility and chemical tailor ability, lithography-assisted chemical functionalization\textsuperscript{17,20} is assumed to be one important component for the realization of “graphene embroidery”. Very recently, we demonstrated one-step patterned graphene functionalization with diazonium salts involving lithography as a pattern defining tool.\textsuperscript{24} We were able to fabricate well-defined nanostructures down to the sub-micrometer-scale. Another pillar for this success was the realization of comparatively high functionalization degrees in the addend zones by using reductively activated graphene and allowing for substrate-mediated antaratopic additions.

We now demonstrate for the first realization of the desired “graphene embroidery” by generating regular multiply functionalized patterns consisting of concentric regions with covalent addend binding. These spatially resolved 2D-hetero-architectures were generated by repetitive electron-beam lithography (EBL)/reduction/covalent-binding sequences starting with polymethyl methacrylate (PMMA) covered graphene deposited on a SiO\textsubscript{2}/Si substrate. We employed the statistical Raman spectroscopy together with scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) for an
unambiguous characterization, which clearly shows that covalently multi-patterned graphene exhibits an exquisitely ordered nanostructure.

Results and discussion

Reaction sequence for the sequential pattern functionalization. As a prototype for sequential multiple functionalization of graphene we developed the generation of three concentric zones carrying bromobenzene-, deuto- and chloro-addends (Fig. 1). The activation of the graphene substrate towards addend binding was initiated by reduction with Na/K alloy, an elegant strategy that we recently developed for efficient covalent mono-patterning of graphene. First a graphene monolayer was deposited on a reactive SiO₂/Si substrate, which allows for strain-free antaratopic bond formations by quenching the initially formed dangling bonds. This allows for establishing comparatively high degrees of functionalization. The patterning process is controlled by the placement of an e-beam resist mask on top of the graphene monolayer. For this purpose, a polymer-film of PMMA was used. Then a periodic array of dots with a diameter of 5 µm was fabricated via electron-beam lithography. In this way uncovered graphene regions (zone Iₐ) are generated that are available for the first addend binding process. The uncovered graphene zone Iₐ was activated by treatment with Na/K alloy. Briefly, a drop of liquid Na/K alloy was dropped onto the graphene monolayer. As a result, graphene was negatively charged which increases the reactivity towards the electrophiles. As soon as the Na/K alloy was removed by a gentle stream of Ar, the efficient addend binding was accomplished by reaction with bromobenzene diazonium-tetrafluoroborate. As a consequence, an array of the first dot-shaped addend zones (zone Iₐ) was generated. The second concentric addend zones were generated following the same concept. For this purpose, a second lithographic procedure was applied expanding the diameter of the concentric dots to 15 µm (zone IIₐ). After activation and exposure to deuteroxide, pronounced deuteration of the second patterning zone (zone IIₐ) was accomplished. This is the first example of pronounced deuteration of a graphene monolayer. So far only bulk deuteration of graphite/graphene has been reported. A third diameter expansion of the periodic dots to 20 µm (zone IIIₐ) allows for the final concentric graphene patterning. Activation with Na/K and subsequent quenching with iodine monochloride (ICl) gave rise to a mild chlorination (no necessity of hazardous Cl₂ gas) generating the third addend zone (zone IIIₐ). Strikingly, for the first time ICl was developed...
as a new and mild chlorination source for graphene chlorination. The last step of the entire patterning procedure was the removal of the PMMA layer by treatment with acetone. The final outcome was the first demonstration of a sequential multiple patterning of graphene with different addends bound to spatially defined addend zones. The concept can be considered as a molecular embroidery analogy to the traditional embroidery manufacturing, that is, employing spatially resolved graphene chemistry (needle) to embroider regularly patterned addend zones to graphene (fabric). It can be expected that with this pioneering concept any type of complex 2D-pattern on graphene can be realized.

This multifunctional graphene patterning has enormous potential to realize unprecedented spatially resolved combinations of properties such as hydrophilic-, hydrophobic-, opto-electronic-, molecular recognition-, magnetic-, catalytic- and sensing behaviour. Significantly, these 2D-structured functions are always combined with the electric conductivity of the surrounding intact graphene regions (zone IV), the geometry of which can be easily tailored and adjusted.

Figure 1. Reaction sequence. A): Schematic illustration of the reaction sequence for the multiple patterning functionalization of graphene monolayer. EBL = electron-beam lithography; zone Ia, IIa and IIIa: the step-wise EBL exposed graphene areas (with diameters of 5 µm, 15 µm and 20 µm) before functionalization; zone IV: the graphene areas covered by PMMA; zone Ib, IIb
and IIIb: the step-wise EBL exposed graphene areas after functionalization. The PMMA layer finally is removed by washing with acetone leaving the 2D-patterned graphene embroidery. The first addend zone (zone Iₐ) is indicated in red; the second addend zone (zone IIₐ) is indicated in blue; the third addend zone (zone IIIₐ) is indicated in orange; zone IV is indicated in black. During the entire reaction procedures, strain-free antaratopic additions provided by surface atoms (O, H) of the underlying SiO₂/Si substrate were enabled. Inert substrates would allow only for successive supratopic additions, which however are forbidden due to the enormous amount of strain energy that would be built up. B): A typical traditional fabric embroidery is comparable with that of the graphene embroidery.

**Statistical Raman analysis.** For the characterization of the concentrically patterned graphene sheets we applied statistical Raman spectroscopy (SRS). The mean Raman spectra of the patterned zones are shown in Fig 2. The zone Iₐ (before functionalization) show a pronounced G-band at 1582 cm⁻¹ indicating a sp² carbon lattice along with a negligible defect-induced D-band at 1350 cm⁻¹. This is indicative of intact monolayer graphene. The absence of a D-band demonstrates that during the EBL process no defects in the graphene lattice were generated. After arylation a very intense D-band emerged, demonstrating the efficient conversion of sp² into sp³ carbon within the corresponding carbon lattice of zone Iₐ. The I_D/I_G ratio raised from < 0.1 to 2.6 after arylation (Fig. 2A and 2D). This high I_D/I_G ratio indicates a high degree of functionalization, which is superior to previously reported covalent graphene patterning, emphasizing the advantage of our reductive protocol. The observed G-band at 1593 cm⁻¹ is upshifted relative to that measured before functionalization. This reflects the expected influence of the covalent binding of electron-withdrawing molecules to the remaining conjugated π-system in zone Iₐ. ³⁴,³⁵

Significantly, the unpatterned regions (zone IV), which were covered by PMMA during the chemical treatment remains completely intact as no D-band was observed. Consequently, our graphene functionalization protocol selectively takes place only in the patterned region. To visualize this spatially resolved 2D chemistry, large-scale Raman mapping was conducted and the corresponding pattern images can be clearly recognized through I_D/I_G mapping (Fig. 3D). In addition, the rather uniform distribution of I_D/I_G ratio within patterned region suggests the homogeneous arylation.

For the zone IIₐ a similar result is observed, that is, a high and very broad D band with a I_D/I_G ratio of 1. Again, the surrounding
zone IV remains unaffected and stays as defect free monolayer graphene (Fig. 2B and 2D). It is noteworthy that this very broad D-band is indicative for a rather high degree of functionalization with the corresponding \( I_D/I_G \) ratio begins located at the right side of the Cançado curve (high-functionalization-regime).\(^{36} \) In contrast, relative to the arylated graphene (zone I\(_b\)) deuteration causes n-doping of the remaining conjugated \( \pi \)-system within zone II\(_b\) as manifested by a downshift of the Raman G-band to 1567 cm\(^{-1}\) (the G-band locates at 1582 cm\(^{-1}\) before functionalization)\(^{34,35} \). The large-scale Raman \( I_D/I_G \) mapping clearly reveals a turquoise pattern of the deuterated zone II\(_b\) concentrically arranged around zone I\(_b\) (Fig. 3E). The chlorinated zone III\(_b\) was confirmed by Raman investigation as well by the dramatically increased D-band with a \( I_D/I_G \) ratio of 2.4 (Fig. 2C and 2D). Considering the electron-withdrawing effect of the Cl-atoms the remaining conjugated \( \pi \)-system within zone III\(_b\) is expected to show p-type semiconductor behavior. This was indeed corroborated by an upshift of the Raman G-band to 1592 cm\(^{-1}\). The chlorination of zone III\(_b\) is further reflected by large-scale Raman \( I_D/I_G \) mapping (Fig. 3F).
Figure 2. Statistical Raman analysis of a multiple patterned graphene monolayer. A): Raman spectra of zone I_a (before arylation), zone IV (after arylation and PMMA removal) and zone I_b (after arylation). B): Raman spectra of zone II_a (before deuteration), zone IV (after deuteration and PMMA removal) and zone II_b (after deuteration). C): Raman spectra of zone III_a (before chlorination), zone IV (after chlorination and PMMA removal) and zone III_b (after chlorination). D): Statistical Raman histograms extracted from Raman spectra of A (zone I_b), B (zone II_b), C (zone III_b), D (zone IV). Averaged spectra (~200 single point spectra) of the respective zones, $\lambda_{exc} = 532$ nm.

Figure 3. Large-scale Raman $I_D/I_G$ mapping. Optical image of PMMA patterned graphene (precursor masks) for each step (A, B, C). The purple areas are the exposed graphene regions and the light green areas are covered by PMMA. The corresponding Raman $I_D/I_G$ mapping images after addend binding and removal of the PMMA layer (D, E, F).

Thermal stability and reversibility. Temperature-dependent Raman spectroscopy was employed to investigate the thermal stability of this concentric graphene patterning. As shown in Fig 4, the thermal stabilities of the zones I_a, II_b and III_b differ from each other significantly, which implies their individual chemical nature reflected in different strengths of the addend-graphene
lattice bonds. For zone I\textsubscript{b}, as temperature rises, the intensity of the D-band continuously decreases and eventually leads to a spectroscopic feature at 350 °C, which is the same as that for monolayer graphene (Fig. 4A). The thermally induced decline of the D-band is due to the restoration of sp\textsuperscript{2} carbon lattice initiated by the cleavage of the C-C bonds between covalently linked aryl addends and graphene. The predominant defunctionalization process starts around 250 °C.

The thermal behavior of the deuterated zone II\textsubscript{b} is significantly different. In this case the intensity of the D-band keeps constant up to 500 °C, indicating very high thermal stability (Fig. 4B). Further increasing the temperature to 600 °C causes the complete loss of all Raman features including the G- and 2D-bands and the establishment of a flat line. This demonstrates the complete destruction of the graphene framework rather than just cleavage of C-D bonds. Similar to zone I\textsubscript{b}, the temperature-correlated D-band alteration was also found in zone III\textsubscript{b} and the D-band decrease continuously with increasing temperature (Fig. 4C). The decline of the D-band is a result of the C-Cl bond cleavage accompanied by sp\textsuperscript{3} to sp\textsuperscript{2} rehybridization. A closer look at the addend cleavage as a function of temperature nicely reflects the different thermal stabilities of the zone I\textsubscript{b} and III\textsubscript{b}. For the chlorinated zone III\textsubscript{b}, the Raman features approaches that of pristine graphene at 300 °C instead of 350 °C, observed for the arylated zone I\textsubscript{b}. Besides, the main addend cleavage sets in at 200 °C for zone III\textsubscript{b} and at 250 °C for zone I\textsubscript{b}. The experimentally observed different thermal stabilities for zone I\textsubscript{b} (C-C bond cleavage), zone II\textsubscript{b} (C-D bond cleavage) and zone III\textsubscript{b} (C-Cl bond cleavage) correlate very well with the corresponding bond strengths (BE (C-Cl) = 328 kJ/mol, BE (C-C) = 332 kJ/mol and BE (C-D) = 414 kJ/mol).

As mentioned above, the reversible defunctionalization process mainly occurs in the temperature range between 200-350 °C for zone I\textsubscript{b} and III\textsubscript{b}. Therefore, for instance, upon heating to 250 °C, we can tune the I\textsubscript{D}/I\textsubscript{G} ratio of zone I\textsubscript{b} and zone III\textsubscript{b} to around 1.8 and 1, respectively. The large-scale Raman mapping clearly displayed the pattern image with the corresponding decreased I\textsubscript{D}/I\textsubscript{G} ratios, respectively, encoded in yellow for zone I\textsubscript{b} and green for zone III\textsubscript{b} (Fig. 4E). The 400 °C heating treatment resulted in the complete defunctionalization of both zone I\textsubscript{b} and III\textsubscript{b} and leave only zone II\textsubscript{b} intact, which is confirmed by large-scale Raman mapping that the corresponding pattern image changes from the previous concentric circle to the hollow circle (Fig. 4F). Taking into account that the electronic character of the remaining conjugated π-system within a functionalized zone depends on the extent of functionalization such as chlorination, this reversible defunctionalization process enables the adjustment of
electronic properties (band gap engineering).

Figure 4. Temperature-dependent Raman analyses. Temperature-dependent statistical Raman spectra of zone Ib (A), zone IIb (B) and zone IIIb (C). D: Mean Raman ID/IG ratio extracted from temperature-dependent Raman spectra of A, B and C. Raman ID/IG mapping after 250 °C (E) and 400 °C (F) annealing.

SEM-EDS analyses. To track the chemical nature of this multiply-patterned graphene, we carried out scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) (Fig. 5). Our patterned graphene containing the three addend zones Ib-IIIb contains the SEM-EDX detectable elements Br (zone Ib) and Cl (zone IIIb). As expected, SEM-EDX investigation of the Br distribution in zone Ib revealed periodic solid circular dot configurations correlating very well with the extension of zone Ib. When it comes to the element Cl, a distribution related to zone IIIb, namely, a periodic ring configuration, is observed. The SEM-EDS results strongly correlate with the Raman data outlined above. In addition, the Br and Cl elements are quite homogeneously distributed with the corresponding addends zones Ib and IIIb, demonstrating homogeneous addend coverage. Moreover, no further element signals are found, which indicates the efficiency of all washing procedure and work-up procedures and underlines the covalent nature of the patterned regions.
Conclusions

In summary, we have realized the first prototype of multiply functionalized and hierarchically patterned graphene sheets with a spatially defined 2D-hetero-architecture. The chemical embroidery was accomplished by repetitive electron-beam lithography (EBL)/reduction/antaratopic-covalent-binding sequences starting with PMMA covered graphene deposited on a SiO₂/Si substrate. The corresponding functionalization zones carry bromobenzene-, deutero- and chloro-addends. The successful covalent patterning was unequivocally demonstrated by statistical Raman spectroscopy and SEM-EDS. In addition, the constructed concentric hetero-architectures were very clearly visualized by large-scale Raman I_D/I_G mapping. Moreover, the different thermal stabilities for each addend zone were revealed by temperature-dependent Raman investigations and the reversibility of covalent binding, as seen for the chloro- and bromobenzene groups, provides a feasible means for property engineering (e.g. electronic structure). The construction principle of 2D-patterning that we have disclosed here for the first time opens enormous opportunities towards tailoring the physical and chemical properties of graphene sheets with apparently limitless combinations of spatially defined surface functionalities. Such tailored nano-surfaces are highly attractive for high-performance applications, for example, in the fields of optoelectronics, sensors and catalysis.

Methods

**Covalent Patterning of graphene.** The details on multi-step covalent patterning of graphene and the involved chemicals are given in the Supplementary Information.

**Raman Spectroscopy.** The Raman spectroscopic characterization was performed on a Horiba Jobin Yvon LabRAM Aramis.
The spectrometer was calibrated by using crystalline graphite. All measurements were conducted using a laser (Olympus LMPlanFl50x, NA 0.50) with an excitation wavelength of 532 nm, with an acquisition time of 2s. Spectral data was obtained through a motorized x-y table in a continuous line scan mode (SWIFT-module). The step sizes in the Raman mappings were kept in the range of 0.1-0.5 μm depending on the experiments. The corresponding data processing were performed using software of Lab Spec 5. The temperature dependent Raman measurements were performed in a Linkam stage THMS 600, equipped with a liquid nitrogen pump MS94 for temperature stabilization under a constant flow of nitrogen. Nitrogen gas needs to be filled for 20 min before starting the measurements to remove air. The measurements were carried out on SiO₂/Si wafers with a heating rate of 10 K/min.

**Scanning electron microscopy-energy dispersive X-ray spectroscopy.** Scanning electron microscopy-energy dispersive X-ray spectroscopy was performed on GeminiSEM 500 equipped with Oxford X-max 150. The working conditions were set at an operating at accelerating voltage of 5 kV, working distance of 7.3 mm, the elevation angle of detector is 35° and the sample is vertical to the secondary-electron emission.

**Data availability**

The data supporting the findings of this study are available within the paper and its Supplementary Information, and also from the authors upon request.

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**Author contributions**

A. H and T. W. conceived the research, designed the experiments and co-wrote the paper. A. H. and F. H. supervised the project as scientific group leader and principal investigator. T. W. synthesized the samples, performed Raman spectroscopy, SEM/EDS measurement and analysed the data. M. K and H. B. W. prepared the patterns on graphene. All the authors discussed the results and contributed to writing the manuscript.
Competing interests

The authors declare no competing interests.