

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

- Title: Spatially resolved covalent functionalization patterns on graphene
- Authors: Leoš Valenta, Petr Kovaříček, Václav Valeš, Zdeněk Bastl, Karolina A Drogowska, Timotheus A Verhagen, Radek Cibulka, and Martin Kalbáč

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201810119 Angew. Chem. 10.1002/ange.201810119

Link to VoR: http://dx.doi.org/10.1002/anie.201810119 http://dx.doi.org/10.1002/ange.201810119

WILEY-VCH

WILEY-VCH

COMMUNICATION

Spatially resolved covalent functionalization patterns on graphene

Leoš Valenta,^[a,b] Petr Kovaříček,*^[a] Václav Valeš,^[a] Zdeněk Bastl,^[a] Karolina A. Drogowska,^[a] Timotheus A. Verhagen,^[c] Radek Cibulka,^[b] Martin Kalbáč*^[a]

Abstract: Spatially resolved functionalization of 2–D materials is highly demanded but very challenging to achieve. The chemical patterning is typically tackled by preventing contact between the reagent and material, with various accompanying challenges. Photochemical transformation on the other hand inherently provides remote high spatiotemporal resolution using the cleanest reagent – a photon. Here, we combine two competing reactions on a graphene substrate to create functionalization patterns on a micrometre scale via the Mitsunobu reaction. The mild reaction conditions allow introduction of covalently dynamic linkages, which can serve as reversible labels for surface- or graphene-enhanced Raman spectroscopy characterization of the patterns prepared. The proposed methodology thus provides a pathway for local introduction of arbitrary functional groups on graphene.

Graphene holds a prominent position among two-dimensional (2-D) materials due to its unique properties,^[1-3] which can be further tuned for particular application^[4-6] by several methods. Among them, chemical functionalization offers the broadest variety of possibilities.^[7–9] Although several protocols for covalent grafting have been reported in the literature, [10-15] only recently has the advancement towards specific applications revealed the need for spatially resolved methods that would provide patterned surface functionalization on the 2-D material,[16-18] aiming at sophisticated sensor arrays or device mass production.^[19] This non-trivial task has been approached from several directions, using for instance photolithography,^[20] dip-pen lithography^[21-23] or various writing techniques.^[24-26] Using covalent modification for spatially resolved functionalization typically relies on preventing contact of the reagents with graphene, thus implying the use of a resist mask^[27] or controlled deposition^[28,29] at the nanoscale, which either adds more steps (with concomitant contamination^[30]) or severely limits the processing speed, respectively. Photochemical reactions represent a unique alternative to the abovementioned

- University of Chemistry and Technology Prague, Technická 5, 166 28 Praha, Czech Republic [c] Dr. T. A. Verhagen
 - Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 121 16 Prague 2, Czech Republic
 - Supporting information for this article is given via a link at the end of the document.

two approaches^[31] because photochemistry responds to illumination patterns without the need for a resist or spatially confined reagent deposition.

The critical challenge for the surface functionalization of the 2–D materials is unambiguous characterization of the reaction products facing the detection and resolution limits of many methods due to the strict monolayer nature of the materials.^[32] Typical methods such as Raman spectroscopy^[33–35] and X-ray photoelectron spectroscopy^[36] (XPS) provide only limited insight into the actual chemistry taking place at the surface, an issue which has been tackled recently by the use of surface- and graphene-enhanced Raman spectroscopy (SERS and GERS, respectively)^[14,37] and also by other methods.^[38,39] Application of SERS/GERS allows direct assignment of characteristic vibrational modes to particular species and thus provides solid evidence for species being grafted to the material.

Here, we report on the use of a photo-modulated Mitsunobu reaction on oxygen plasma-treated monolayer graphene to create patterned functionalization. In this setup, the oxygenated graphene serves both as the substrate for introduction of carboxylate species as well as the reagent in the reductive deoxygenation by triphenylphosphine (PPh₃). By the use of a and UV photomask light inducing azodicarboxylate spatially decomposition in irradiated areas, resolved functionalization patterns are created, which can then be detected by Raman and SERS spectroscopy. The proposed method provides a way to form spatially resolved arbitrary functional group 2-D structures on graphene in an easy, clean and rapid manner.

The Mitsunobu reaction involves PPh3 activated by dialkyl azodicarboxylate (i-propyl in our case, DIAD) to convert a hydroxyl into an easily leaving group, which is then replaced by a nucleophile, such as carboxylate. On the oxygenated graphene, both hydroxy and epoxy functions can undergo this transformation. Several reports in the literature also employ chemical reduction of graphene oxide by various agents,^[40] among others hydrazine^[41] or phosphine^[42] derivatives. Finally, azodicarboxylates are sensitive to irradiation in the blue/UV region, leading to their photochemical decomposition.^[43] We have thus outlined a system in which oxygenated graphene is subjected to the Mitsunobu reaction under photomasked UV irradiation, anticipating that a) the non-irradiated areas will undergo the Mitsunobu substitution reaction and b) at the irradiated part DIAD will decompose, leaving unreacted PPh₃ available for oxygenated graphene reduction (Scheme 1).

 [[]a] L. Valenta, Dr. P. Kovaříček, Dr. V. Valeš, Dr. Z. Bastl, Dr. M. Kalbáč, Dr. K. A. Drogowska
 J. Heyrovský Institute of Physical Chemistry of the Czech Academy

of Sciences, Dolejškova 2155/3, 182 23 Praha, Czech Republic E-mail: <u>petr.kovaricek@jh-inst.cas.cz</u>, <u>martin.kalbac@jh-inst.cas.cz</u> [b] L. Valenta, Prof. R. Cibulka

COMMUNICATION



Scheme 1. a) Scheme of chemical transformation of monolayer CVD-grown graphene. Oxygen–plasma treatment causes introduction of, among others, hydroxy- and epoxy-groups which can either be removed by the reverse reaction with PPh₃, or subjected to nucleophilic Mitsunobu substitution in the presence of DIAD and PPh₃. b) By photochemical decomposition of DIAD, spatially resolved functionalization-reduction patterns can be prepared using a photomask.

Graphene was synthesized on copper foil using the chemical vapor deposition method (CVD) and transferred onto Si/SiO_2 wafers (300 nm SiO₂ layer) by a polymer-assisted copper etching method, as described previously.[30,44] Material quality was confirmed by spectroscopic Raman mapping^{[33-35]} showing the typical G and 2D modes at approximately 1600 and 2700 cm⁻¹, respectively, without any detectable D mode. Oxygen plasma treatment was then performed using the previously published protocol,^[45] which resulted in appearance of clear D mode at 1346 cm-1 (Figure 1). This process produces various oxygencontaining functional groups on graphene, namely hydroxyls, epoxy bridges, carbonyl and carboxyl functions, [46,47] it is therefore necessary first to investigate the feasibility of the oxygenated graphene reduction by PPh_3 . The sample with median I_D/I_G ratio of 0.51 was immersed into the PPh₃ solution (20 mM) in dichloroethane (DCE) for 12 hours at room temperature, after which the sample showed a strong decrease of the D band to median $I_D/I_G = 0.17$. Using the published model,^[48] the change in the D mode intensity corresponds to the average 'defect' distance changing from 16 nm to 29 nm. Hence, PPh₃ is a feasible reducing agent for oxygenated graphene, yet some oxidative defects, presumably carbonyl and carboxyl functions, may remain at the surface (Figure 1). It is also important to note that the reduction efficiency decreases rapidly with increasing oxidation degree (i.e. with an I_D/I_G ratio above 0.7) as a result of graphene overoxidation to carbonyl and carboxyl stages.



Figure 1. Raman spectra of as-transferred graphene on Si/SiO₂ wafer (black), after oxidation in oxygen plasma (red) and reduced back to pristine form by PPh₃ (blue). Oxidation leads to a considerable D mode visible in the spectra, but the reduction leads to almost complete removal of oxidative defects.

In the Mitsunobu reaction, hydroxy and epoxy groups on the oxygen plasma-treated graphene were subjected to formal nucleophilic exchange by *p*-bromobenzoic acid.^[49] The bromine atom is a suitable probe for quantification of the on-surface reaction yield. Performing the reaction on oxygenated graphene with PPh₃ and DIAD (20 mM each reagent) in DCE for three hours under ambient conditions did not result in a significant change of the I_D/I_G ratio, indicating that PPh₃ activation by DIAD is a faster process than graphene reduction and thus the concentration of sp3 'defects' in the monolayer remains rather constant during the reaction. Based on the XPS data, the C:Br atomic concentration ratio was determined to be 60:1 as a result of substitution of only part of the oxygen-containing groups created by the plasma treatment. The product of the Mitsunobu reaction was further confirmed by SERS after evaporation of 12.5 nm silver film on top of the sample. The SERS spectra provided homogeneously distributed characteristic vibrational bands, which have been attributed to the p-bromobenzoate ester species bound to the surface. The signal assignment was performed using a bulksynthesized benzyl p-bromobenzoate as a reference (see Supplementary information, SI) as follows (in cm⁻¹): 1586 C=C str., 1280 and 1140 for asym and sym C-O-C str., 1073 for Ar-Br, 930 for C-C-O str. and 896 for C-O-C def; other bands overlap with graphene signals and were not considered in the assignment.

Photochemical decomposition of DIAD provides the opportunity to switch the reaction pathway on oxygenated graphene remotely with high spatiotemporal resolution. To verify the concept, we have drop-casted the reaction mixture onto oxygen-plasma treated graphene, placed a half-masked cover slide to create only a thin liquid film and placed the sample under a laboratory UV lamp for three hours. After removal of the mask and sample washing, Raman spectra were recorded on both irradiated and photomasked regions. The non-irradiated area showed merely an unchanged I_D/I_G ratio of 0.57, but at the irradiated parts, the I_D/I_G ratio decreased to 0.27. These results clearly demonstrate that decomposition of the DIAD reagent in the

WILEY-VCH

COMMUNICATION

irradiated parts leaves PPh_3 in the solution, which is then responsible for the reductive de-oxygenation of graphene, but in the masked regions the Mitsunobu reaction proceeds undisturbed.

Spatial control of the reaction pathway is in principle limited only by the diffraction limit of UV light, therefore it should be possible to adopt photolithography to the fine patterning of the graphene functionalization. As described above, different transformations were anticipated to occur in irradiated vs. nonirradiated areas. The reaction was performed in a DCE liquid film in between the Si/SiO₂ substrate with oxygenated graphene and a metal on a glass photomask. After three hours of reaction under UV light at 30 mM concentration of all components, the sample was thoroughly washed and 12.5 nm thick Ag film was evaporated on top of it. Results of the SERS mapping are shown in Figure 2. Indeed, the mapped intensity of graphene's 2D mode and the ester C-O-C and C-C-O vibrations are fully complementary, showing the 5- μ m wide stripe pattern imprinted by the photomask. This pattern is in fact even visible in optical microscope because the Ag film exhibited slightly different morphology as observed with scanning electron microscopy.



Figure 2. a) Raman spectra of graphene recorded after oxidation (black) and after photomasked Mitsunobu reaction at non-irradiated (red) and irradiated (blue) regions. b) Image taken after Ag film evaporation, a line is visible due to different film morphology. c) SERS spectra taken at irradiated (red) and non-irradiated (blue) areas, C-O-C def vibration is only present in non-irradiated part (d) and *vice versa* 2D mode appears only at irradiated one (e), band at 850 cm⁻¹ due to the omnipresent C-O def vibration (black scale bar = 5 µm).

Visualization of the functionalization patterns by SERS is a powerful technique. However, in some cases it can be impractical because evaporation of the silver film on the sample is a destructive step; thus, we have designed a different approach using GERS and dynamic covalent bonds.[37,50] In this setup, Raman signals of a given molecule are enhanced (and luminescence quenched) by interactions with graphene when more fundamental conditions are met without the need for further sample processing. Also, the dynamic linkage between graphene and the selected molecule enables for subsequent removal of the labelling species from the surface and its reuse for the final application. Hence, we have performed the photomasked Mitsunobu reaction with 4-formylbenzoic acid in acetonitrile in a similar manner as in the previous case and afterwards reacted with 7-(diethylamino)coumarin-3-carbohydrazide. The reaction sequence functionalized the CVD graphene with aldehyde moieties, which then underwent reversible condensation with the hydrazide to provide the corresponding acylhydrazone. The coumarin species features a bandgap which is in resonance with a 532 nm excitation laser and thus the essential condition for GERS is fulfilled.^[37] Optical images did not show any visible features on the surface; however, Raman mapping clearly resolved the photoimprinted stripped patterns periodically changing between strong coumarin Raman signals and pristine graphene spectra (Figure 3).



Figure 3. Functionalization patterns visualized by GERS. a) Raman spectra recorded at irradiated (black) and non-irradiated (green) areas showing strong GERS enhancement of coumarin moiety. b) Optical picture with area subjected to Raman mapping shown in green, no macroscopic features can be observed. c) Raman map with plotted intensity of coumarin signals (red scale bar = 5 µm).

We have demonstrated a photochemical spatially resolved functionalization using a Mitsunobu reaction and/or reduction of oxygenated CVD graphene. Mild graphene oxidation by oxygen plasma generates predominantly hydroxy and epoxy groups on the sp^2 carbon monolayer, both of which were efficiently reduced by the action of PPh₃. In presence of DIAD, these groups are substituted by carboxylates via the Mitsunobu reaction, with the on-surface reaction products being confirmed by a series of techniques including XPS, SERS and GERS. The spatiotemporal control was achieved using UV light-initiated decomposition of the azodicarboxylate reagent. Employing a photomask, we were able to couple the reduction and substitution reaction within one sample, creating arbitrary patterns of functionalized and pristine graphene. These structures can be prepared with a spatial resolution of approximately 2 µm. The presented approach provides a simple, efficient and scalable method for spatially resolved graphene functionalization.

Experimental Section

The experimental details can be found in the Supporting Information.

Acknowledgements

Authors acknowledge the support provided by the Czech Science Foundation (project No. 18-09055Y) and COST project (LTC18039). We also acknowledge assistance provided by the Research Infrastructure NanoEnviCz, supported by the Ministry of Education, Youth and Sports of the Czech Republic under project no. LM2015073 and project no. CZ.02.1.01/0.0/0.0/16_013/0001821.

Keywords: graphene • patterned functionalization • Raman spectroscopy · Mitsunobu reaction · photochemistry

- A. K. Geim, K. S. Novoselov, Nat. Mater. 2007, 6, 183-191. [1]
- K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666–669. [2]
- [3] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, A. A. Firsov, Nature 2005, 438, 197-200
- K. Kostarelos, K. S. Novoselov, Nat. Nanotechnol. 2014, 9, 744-745.
- F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 652–655. M. Sharon, M. Sharon, *Graphene: An Introduction to the* [5]
- [6] Fundamentals and Industrial Applications, John Wiley & Sons, 2015.
- F. V. Ferreira, L. Cividanes, F. S. Brito, B. R. C. de Menezes, W [7] Franceschi, E. A. N. Simonetti, G. P. Thim, Functionalizing Graphene and Carbon Nanotubes: A Review, Springer, 2016.
- [8] A. Criado, M. Melchionna, S. Marchesan, M. Prato, Angew. Chem. Int. Ed. 2015. 54. 10734-10750.
- [9]
- Ed. 2015, 34, 10734–10730.
 G. Zhao, X. Li, M. Huang, Z. Zhen, Y. Zhong, Q. Chen, X. Zhao, Y.
 He, R. Hu, T. Yang, et al., *Chem. Soc. Rev.* 2017, 46, 4417–4449.
 J. R. Lomeda, C. D. Doyle, D. V. Kosynkin, W.-F. Hwang, J. M. Tour, J. Am. Chem. Soc. 2008, 130, 16201–16206. [10]
- D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, [11]
- M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim, et al., *Science* **2009**, 323, 610–613. M. Dubecký, E. Otyepková, P. Lazar, F. Karlický, M. Petr, K. Čépe, P. [12]
- Banáš, R. Zbořil, M. Otyepka, J. Phys. Chem. Lett. 2015, 6, 1430-1434.
- R. Stine, J. W. Ciszek, D. E. Barlow, W.-K. Lee, J. T. Robinson, P. E. [13] Sheehan, Langmuir 2012, 28, 7957-7961
- [14] P. Kovaříček, Z. Bastl, V. Valeš, M. Kalbáč, Chem. - Eur. J. 2016, 22, 5404-5408.
- [15] K. Drogowska, P. Kovaříček, M. Kalbáč, Chem. - Eur. J. 2017, 23, 4073-4078
- M. Gobbi, S. Bonacchi, J. X. Lian, Y. Liu, X.-Y. Wang, M.-A. Stoeckel, [16] M. A. Squillaci, G. D'Avino, A. Narita, K. Müllen, et al., Nat. Commun. 2017, 8, 14767.

- Z. Xia, F. Leonardi, M. Gobbi, Y. Liu, V. Bellani, A. Liscio, A. Kovtun, [17]
- R. Li, X. Feng, E. Orgiu, et al., ACS Nano 2016, 10, 7125-7134. Q. H. Wang, Z. Jin, K. K. Kim, A. J. Hilmer, G. L. C. Paulus, C.-J. [18] Shih, M.-H. Ham, J. D. Sanchez-Yamagishi, K. Watanabe, T.
- Taniguchi, et al., Nat. Chem. 2012, 4, 724-732. M. Hirtz, A. Oikonomou, T. Georgiou, H. Fuchs, A. Vijayaraghavan, Nat. Commun. 2013, 4, 2591. [19]
- [20]
- J. Li, M. Li, L.-L. Zhou, S.-Y. Lang, H.-Y. Lu, D. Wang, C.-F. Chen, L.-J. Wan, *J. Am. Chem. Soc.* **2016**, *138*, 7448–7451. U. Bog, A. de los Santos Pereira, S. L. Mueller, S. Havenridge, V. [21]
- Parrillo, M. Bruns, A. E. Holmes, C. Rodriguez-Emmenegger, H. Fuchs, M. Hirtz, ACS Appl. Mater. Interfaces 2017, 9, 12109–12117. [22]
- M. Hirtz, S. Varey, H. Fuchs, A. Vijayaraghavan, *ACS Appl. Mater. Interfaces* **2016**, *8*, 33371–33376. W. M. Wang, N. Stander, R. M. Stoltenberg, D. Goldhaber-Gordon, Z. Bao, *ACS Nano* **2010**, *4*, 6409–6416. [23]
- R. K. Puddy, P. H. Scard, D. Tyndall, M. R. Connolly, C. G. Smith, G. [24]
- a. C. Jones, A. Lombardo, A. C. Ferrari, M. R. Buitelaar, Appl. Phys. Lett. 2011, 98, 133120.
- D. Ye, S.-Q. Wu, Y. Yu, L. Liu, X.-P. Lu, Y. Wu, *Appl. Phys. Lett.* **2014**, *104*, 103105. [25]
- Y. Stubrov, A. Nikolenko, V. Strelchuk, S. Nedilko, V. Chornii, Nanoscale Res. Lett. 2017, 12, 297. Z. Sun, C. L. Pint, D. C. Marcano, C. Zhang, J. Yao, G. Ruan, Z. Yan, [26]
- [27] Y. Zhu, R. H. Hauge, J. M. Tour, *Nat. Commun.* **2011**, *2*, 559. R. D. Piner, J. Zhu, F. Xu, S. Hong, C. A. Mirkin, *Science* **1999**, *283*,
- [28] 661-663.
- [29] M. Jaschke, H.-J. Butt, Langmuir 1995, 11, 1061-1064.
- [30]
- Hallam, N. C. Berner, C. Yim, G. S. Duesberg, *Adv. Mater.* Interfaces 2014, 1, 1400115.
 H. Liu, S. Ryu, Z. Chen, M. L. Steigerwald, C. Nuckolls, L. E. Brus, *J. Am. Chem. Soc.* 2009, *131*, 17099–17101.
 G. Bottari, M. Á. Herranz, L. Wibmer, M. Volland, L. Rodríguez-Pérez, [31]
- [32] D. M. Guldi, A. Hirsch, N. Martín, F. D'Souza, T. Torres, Chem. Soc. Rev. 2017, 46, 4464-4500.
- A. Jorio, M. S. Dresselhaus, R. Saito, G. Dresselhaus, Raman [33] Spectroscopy in Graphene Related Systems, Wiley-VCH, Weinheim, 2011
- [34] L. M. Malard, M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, Phys. Rep. 2009, 473, 51-87.
- A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. [35] Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, et al., Phys. Rev. Lett. 2006, 97, 187401
- D. Ferrah, J. Penuelas, C. Bottela, G. Grenet, A. Ouerghi, Surf. Sci. [36] 2013. 615. 47-56.
- V. Valeš, P. Kovaříček, M. Fridrichová, X. Ji, X. Ling, J. Kong, M. S. [37] Dresselhaus, M. Kalbáč, 2D Mater. 2017, 4, 025087
- [38] P. Kovaříček, V. Vrkoslav, J. Plšek, Z. Bastl, M. Fridrichová, K.
- Drogowska, M. Kalbáč, Carbon 2017, 118, 200-207. [39]
 - D. Dasler, R. A. Schäfer, M. B. Minameyer, J. F. Hitzenberger, F. Hauke, T. Drewello, A. Hirsch, J. Am. Chem. Soc. 2017, 139, 11760-11765.
- C. Kiang Chua, M. Pumera, Chem. Soc. Rev. 2014, 43, 291–312.
 S. Park, R. S. Ruoff, Nat. Nanotechnol. 2010, 5, 309–309. [40]
- [41]
- [42] J. Liu, H. Jeong, J. Liu, K. Lee, J.-Y. Park, Y. H. Ahn, S. Lee, Carbon 2010, 48, 2282-2289.
- [43] S. T. Reid, in Photochem. Vol. 5 (Ed.: D. Bryce-Smith), The Royal
 - Society Of Chemistry, **1974**, pp. 638–688. M. Kalbac, O. Frank, L. Kavan, *Carbon* **2012**, *50*, 3682–3687.
- [44] [45] S. D. Costa, J. Ek Weis, O. Frank, M. Kalbac, Carbon 2016, 98, 592-598.
- A. Bagri, C. Mattevi, M. Acik, Y. J. Chabal, M. Chhowalla, V. B. Shenoy, *Nat. Chem.* **2010**, *2*, 581. [46]
- [47] Y. C. G. Kwan, G. M. Ng, C. H. A. Huan, Thin Solid Films 2015, 590, 40-48
- L. G. Cançado, A. Jorio, E. H. M. Ferreira, F. Stavale, C. A. Achete, R. [48] B. Capaz, M. V. O. Moutinho, A. Lombardo, T. S. Kulmala, A. C. Ferrari, Nano Lett. 2011, 11, 3190-3196.
- The mechanism of nucleophilic exchange in this case cannot proceed [49] via the typical S_N2 substitution of the alcohol. Instead, allylic migration or activation of the carboxylate are considered to be the most likely mechanisms to occur, perhaps even simultaneously. All of these mechanisms lead to identical products for the on-surface reaction
- [50] P. Kovaříček, A. C. Meister, K. Flídrová, R. Cabot, K. Kovaříčková, J.-M. Lehn, Chem. Sci. 2016, 7, 3215-3226.

WILEY-VCH

WILEY-VCH

COMMUNICATION

Entry for the Table of Contents

Layout 1:

COMMUNICATION

Patterns of chemical functional groups are grafted to graphene via photomodulated Mitsunobu reaction. Enhanced Raman spectroscopy employing covalently dynamic linkages provide easy and direct mapping of the structures prepared. Arbitrary patterns with micrometer resolution can be prepared.



Leoš Valenta, Petr Kovaříček,* Václav Valeš, Zdeněk Bastl, Karolina A. Drogowska, Timotheus A. Verhagen, Radek Cibulka, Martin Kalbáč

Page No. – Page No.

Spatially resolved covalent functionalization patterns on graphene