

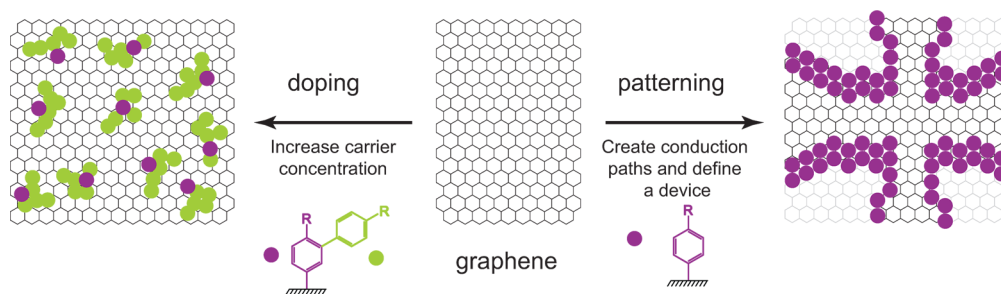
## Organic Synthesis on Graphene

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### CONSPECTUS



Graphene is a two-dimensional crystalline carbon allotrope that has fascinated researchers worldwide and has extended the interest in carbon structures such as fullerenes and nanotubes. In this Account, we use electrical characterization tools to study chemistry on supported graphene. These experiments elucidate the way covalently bound phenyl units can change graphene's physical properties. Can we use chemistry to control electronic properties of graphene? What can we learn from well-known carbon allotropes like fullerenes?

The surfaces of fullerenes and graphene show distinct differences in reactivity because of the high strain of  $sp^2$  carbon in fullerenes compared with the complete lack of strain in graphene. Diazonium chemistry provides a versatile tool for attaching phenyl units covalently to carbon to produce advanced materials and electronic components, but diazonium-based carbon chemistry is strongly influenced by strain. Although fullerenes are highly reactive, graphite (stacks of graphene) remains relatively inert. We chemically introduce n- and p-like doping patterns in two-dimensional graphene using photolithography and extend the ability to chemically control doping to the chemical design of conducting and insulating areas. Thereby we can shape graphene surfaces into functional electronic devices.

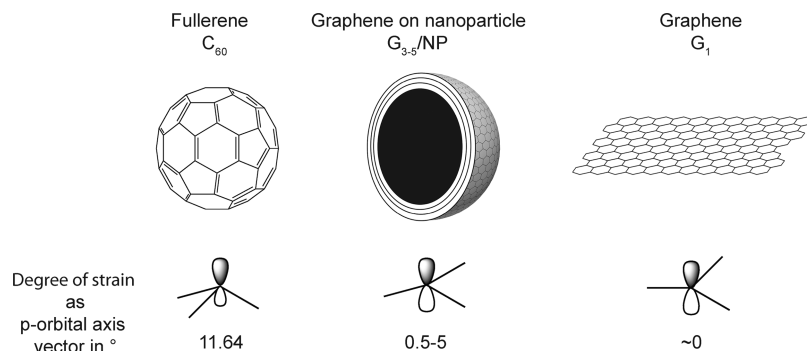
This Account also describes multistep synthesis on graphene-coated nanoparticles and the introduction of various functional groups on graphene surfaces. Only few functional groups can be produced directly via diazonium chemistry. To overcome this issue, we used these functional groups as starting points for more demanding organic reactions. We covalently attached chelating agents, catalysts, or polymers on the carbon surface. These more complex reactions facilitate the design of electronic modifications, intergraphene connections, and anchors for polymer incorporation. Diazonium chemistry forms strong covalent bridges between graphene and other areas of chemistry.

### Introduction

Organic chemistry has excelled at the formation of stable carbon–carbon bonds.<sup>1,2</sup> A colorful variety of reactions create bonds in high yield, selectivity, and often stereospecific. What happens if we transfer such knowledge to carbon allotropes? Can we make organic synthesis on very large, two-dimensional planes? Or has this been around for a while, largely unnoticed? Industrially important products like black ink already consist of chemically modified carbon particles.<sup>3,4</sup> And carbon black was just the beginning of a most remarkable story when in the last decades a plethora

of carbon forms have become functionalized with small organic molecules by carbon–carbon bond forming reactions. Making carbonaceous material soluble or putting it into a polymer matrix has been the driving force behind efforts to chemical modification. Most famous representatives of carbon allotropes are 0D fullerenes,<sup>5</sup> 1D carbon nanotubes,<sup>6</sup> highly ordered graphites, and nowadays also the 2D form of carbon: graphene.<sup>7</sup>

What makes  $sp^2$  carbon allotrope chemistry so diverse? From fullerenes to graphene, the strain at  $sp^2$  carbon atoms is reduced, step-by-step as shown in Scheme 1, due to a

**SCHEME 1.** Fullerene, Bend Graphene on a 20 nm Nanoparticle, and Flat Graphene Are Characterized in Terms of Strain by p Orbital Axis Vector (POAV) Analysis<sup>a</sup>

<sup>a</sup>The POAV is the angle between the p and the three sp<sup>2</sup> orbitals of an sp<sup>2</sup> hybridized carbon atom. For simplicity, the POAV is normalized by -90° to set a planar sp<sup>2</sup> carbon to 0°. Fullerene has a higher intrinsic strain (larger POAV) than the two other systems.

smaller angle between the p and sp<sup>2</sup> orbitals of the carbon atoms (p orbital axis vector analysis, POAV). The smallest species, fullerenes, are well-defined in geometry and consist only of bent sp<sup>2</sup> carbon atoms. An anomalously large reactivity is the result of the buckyball's attempts to release strain through formation of sp<sup>3</sup> carbon centers.<sup>8,9</sup> The fully relaxed other extreme, pristine graphene has theoretically no strain at carbon atoms besides at edges, wrinkles, and influences from substrates. This results in a loss of motivation to react, and, as a consequence, unstrained carbon atoms in graphene show a reduced tendency for sp<sup>3</sup> hybridization making graphene intrinsically less reactive than fullerenes. Between these two extreme forms, another form of carbon is found as graphene-coated metal nanoparticles.<sup>10</sup> Here, strain is a function of particle size and the intermediate bend graphene has most successfully been used to investigate a broad range of organic reactions on graphene-based systems.

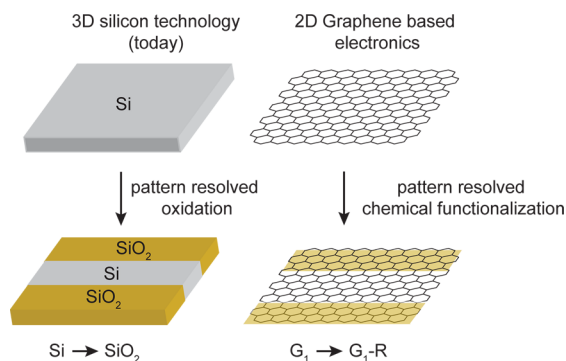
Today, chemically modified graphenes have moved into the focus of research since organic chemistry provides the necessary flexibility to adapt the fascinating 2D structures to specific performance profiles (electronic, physical, or as a material). Early work on covalent graphene chemistry often used representative model compounds or minute sample sizes derived from more cumbersome preparations, like scotch taped graphene,<sup>11</sup> and gradually shifted to large scale produced graphene on SiC,<sup>12</sup> or CVD graphene.<sup>13</sup> In addition, all kinds of solubilized graphene flakes are now exploited for chemical functionalization studies,<sup>14,15</sup> especially graphene oxide (GO)<sup>16</sup> or reduced graphene oxide (rGO).<sup>17</sup> There are several reactions possible on graphene either solubilized or supported,<sup>15,18</sup> here we focus on diazonium chemistry for functionalizing supported graphene.

As the "graphene" reactant plays a crucial role in the reactions, it is necessary to clearly characterize the starting material. It is known from several scientific reports that the parent compound graphite (G<sub>∞</sub>) itself is a rather inert material.<sup>27,28</sup> This is a result not only of the electronic configuration, but also of the planar geometry itself (rigidity of the basic graphite structure and hence difficulty to accommodate a change in geometry/size of a specific carbon atom). Single sheets of the 2D carbon crystal have a tremendously high surface to volume ratio and especially small flakes, a high edge to volume ratio making graphene flakes particularly susceptible to attack by small molecular species. From this purely geometric perspective, it is also evident that small graphene flakes (~500 nm size) or chemically processed material of lower quality (GO, rGO) are more reactive and have more defects than high quality scotch taped graphene.

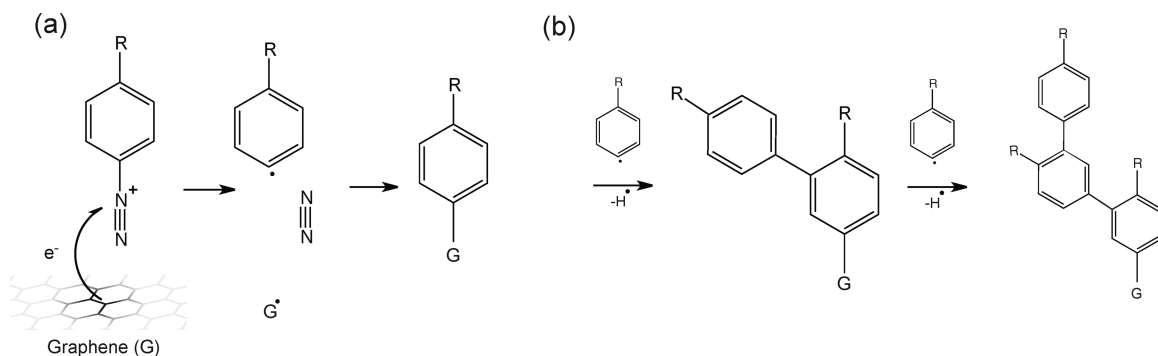
Fullerenes<sup>19,20</sup> and their larger cousins, graphene coated metal nanoparticles,<sup>21,22</sup> provide a rich source for simple but powerful functionalization studies. The probably simplest one, diazonium chemistry, has been used for generating either chemically uniform products, allowing attachment of complex organic molecules or building small polymers onto a carbon surface. This reaction forms strong, covalent carbon-carbon bonds based on the conversion of a sp<sup>2</sup> carbon in the graphene basal plane into a sp<sup>3</sup> hybridized form. In this Account, we specifically focus on the reaction between aryl diazonium ions and graphene but would like to keep in mind that other carbon-carbon bond forming reactions may provide interesting alternative derivatizations.<sup>15,18</sup> The mechanism of the diazonium reaction formally involves an electron transfer reaction and has been studied on several different carbonaceous materials. Initially, an electron is transferred to the preadsorbed aryl diazonium ion, releasing

nitrogen and building a most reactive intermediate species, a phenyl radical. This radical usually directly reacts with the carbon surface,<sup>23</sup> but tends to yield a product distribution (i.e., the reaction is rather unspecific). It is therefore not surprising to find reports in the literature on direct attachment of phenyl species next to formation of phenyl oligomers and polymeric species.<sup>24</sup> Well-defined C–C bond chemistry on graphene therefore requires finding specific, preferred reaction conditions that yield the desired type of reaction, using well accessible diazonium ions and suitably pretreated graphene.

Exploiting this covalent chemistry as a tool to chemically introduce dopants or isolating properties into graphene could connect to historically grown manufacturing methods of silicon.<sup>25</sup> In semiconductor manufacturing, the 2D wiring and circuitry information of dozens of layers is usually multiplied through photolithography. The conducting component, doped silicon, can locally be etched or oxidized to insulating silica (see Figure 1), thus providing a route to design electron paths within a device. For a graphene based



**FIGURE 1.** Functional analogy between silicon (3D) and possible graphene electronics (2D) based on the formation of conduction pathways in the material. The oxidation of (doped) semiconductor silicon creates insulating areas. In graphene, the analogy is the generation of high  $sp^3$  carbon density by chemical functionalization to create and increase a band gap.



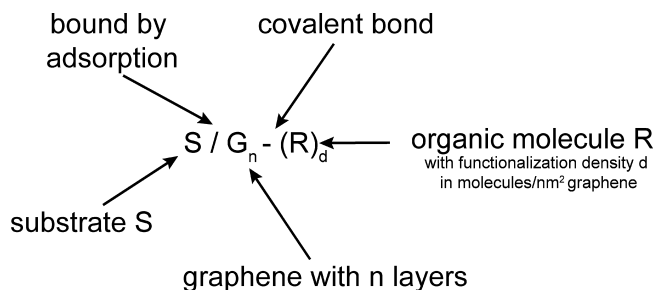
**FIGURE 2.** Mechanism for a diazonium reaction with a carbon surface, involving an electron transfer for creation of a phenyl radical. The radical species can either react further with the carbon surface (a) or with a previously attached aryl moiety forming branched oligomers (b).

device, covalent functionalization could provide a functional analogue to silicon oxidation since  $sp^2$  carbon is the building element of electrically conductive graphene and its transformation into an  $sp^3$  carbon atom results in an insulator (see Figure 1).<sup>26</sup>

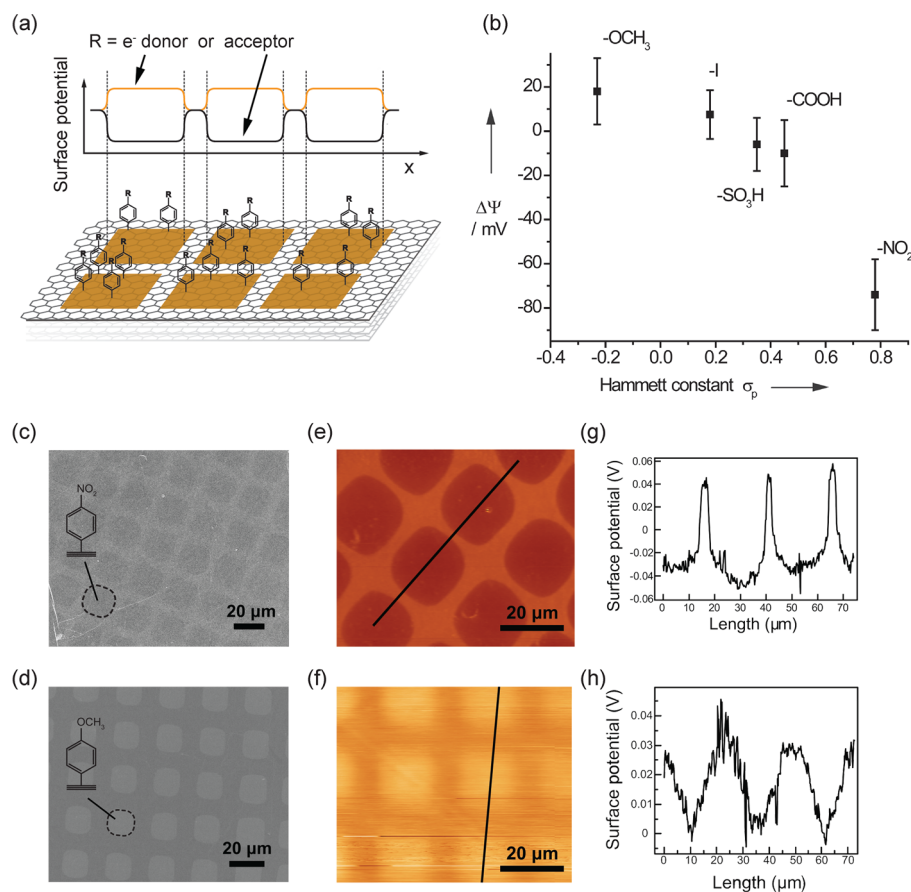
## Nomenclature for Graphene in Chemical Formulas

Along the chemical description of reactions in this Account, we propose a simplified nomenclature to increase the readability of chemical reactions involving graphene as a reactant. In the reactions as shown in Figure 2, the graphene representation was abbreviated as a capital G, which is used in the same manner as the short forms of ethyl (–Et) or acetate (–Ac) in chemical formulas. In Scheme 2, a short description of the used syntax is given, allowing one to discriminate for the number of layers, covalent bonds, or just adsorbed species. With this syntax, the following system  $SiO_2/HO-G_2-(Ph-NO_2)_2$  will be read as bilayer graphene ( $G_2$ ) covalently functionalized with hydroxyl groups (HO–) on one side and nitrobenzene molecules (–Ph–NO<sub>2</sub>) on the other side with a density of

**SCHEME 2.** Nomenclature for Chemically Modified Graphene Used in This Account<sup>a</sup>



<sup>a</sup>The forward slash “/” is used to characterize an interaction based on adsorption, whereas the hyphen “-” is a sign for covalent bonding like in standard chemical nomenclature.



**FIGURE 3.** Doping of the top graphene layer of graphite. Patterned functionalization results in functionalized and unfunctionalized areas (a). (b) Change of surface potential with different substituents in para position of the benzene ring. Scanning electron microscopy (c,d) and Kelvin probe analysis (e–h) reveal the different doping effect of electron withdrawing (p-type doping) nitrobenzene (c,e,g) and electron donating (n-type doping) methoxybenzene (d,f,h) functionalized 2D carbon surface. Figure adapted from ref 25.

2 molecules/nm<sup>2</sup> graphene surface, which is adsorbed on a silica surface with the hydroxyl functionalized side.

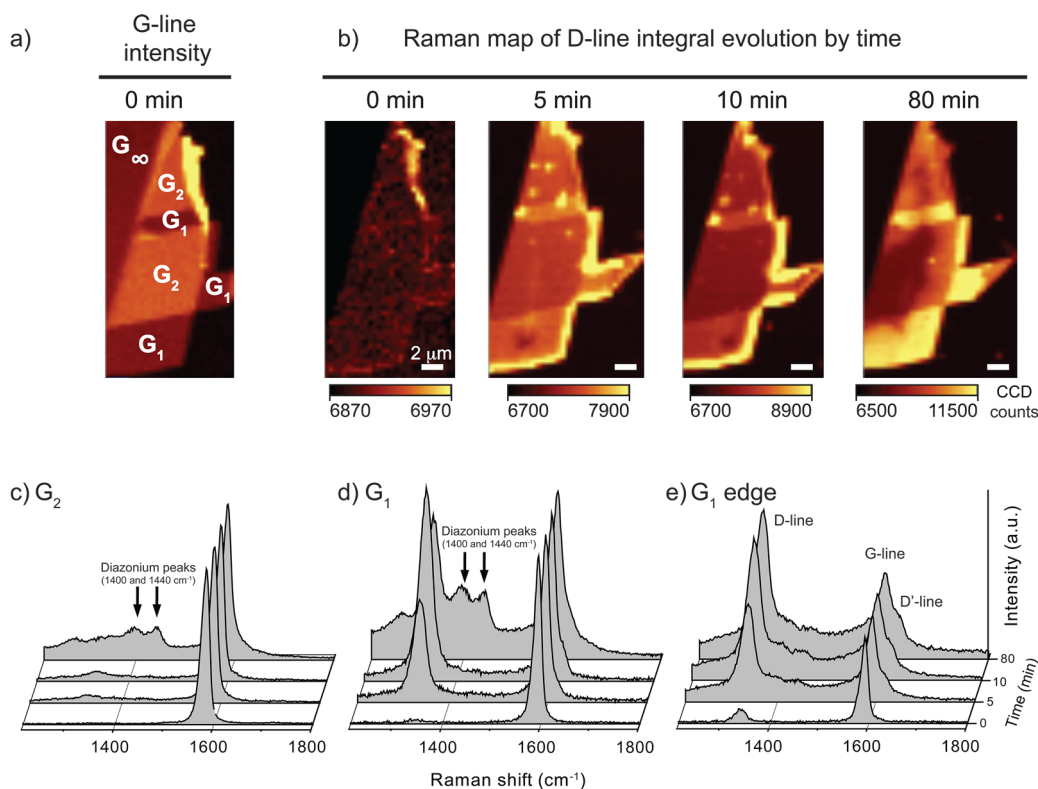
## Functionalization Methods

The low intrinsic reactivity of graphene requires all small reactants to be rather reactive in a chemical sense. Most functional group introductions on carbon have been established, documented and characterized for fullerenes where chemical analysis is accessible through nuclear magnetic resonance (NMR), gas or liquid chromatography or micro analysis.<sup>29,30</sup> The analysis of well-defined 2-D products from diazonium chemistry with high quality scotch taped graphene requires more demanding, often complex analytical methods, as derived from studies on activated-<sup>31</sup> or glassy carbon,<sup>32</sup> fullerenes,<sup>9,19,20,33</sup> carbon nanotubes<sup>34,35</sup> or graphene coated metal nanoparticles.<sup>22,36,37</sup> Raman spectroscopy<sup>38–42</sup> was found most useful to determine chemical structure and quality of graphene. The D/G intensity ratio is a measure for the quality of graphene, where the G-line ( $\sim 1580\text{ cm}^{-1}$ )

of the Raman spectra is due to the doubly degenerate zone center  $E_{2g}$  mode<sup>38</sup> and the D-line is due to a diamondlike atomic arrangement ( $sp^3$  carbon atoms) corresponding to edges or defects within functionalized graphene.<sup>43</sup> Atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS)<sup>25,44–46</sup> provide both chemical and structural information. In addition, electronic property measurements help to identify the influence of the chemical reaction on the fascinating physical properties of graphene. However, the graphene flakes used for electronic measurements need processing for production of electrical contacts and sometimes must be shaped in special geometries, which by themselves can severely influence electron transport properties.<sup>47</sup>

## Doping

Physicists add or remove electron density by doping; chemists use the right substituents. The linear free enthalpy relationship and Hammett concept are probably globally taught to chemistry students when discussing in a quantitative



**FIGURE 4.** Raman analysis of a graphene flake with single- and bilayer regions during the functionalization. (a) overview of the analyzed graphene flake with G<sub>1</sub> and G<sub>2</sub> regions. The three different areas on bilayer (low functionalization density), single layer (medium functionalization density), and single layer edge (high functionalization density) are seen in the maps (b) and more clearly in the point spectra analysis corresponding to the regions G<sub>2</sub> (c), G<sub>1</sub> (d), and G<sub>1</sub> edge (e). Figure adapted from ref 55.

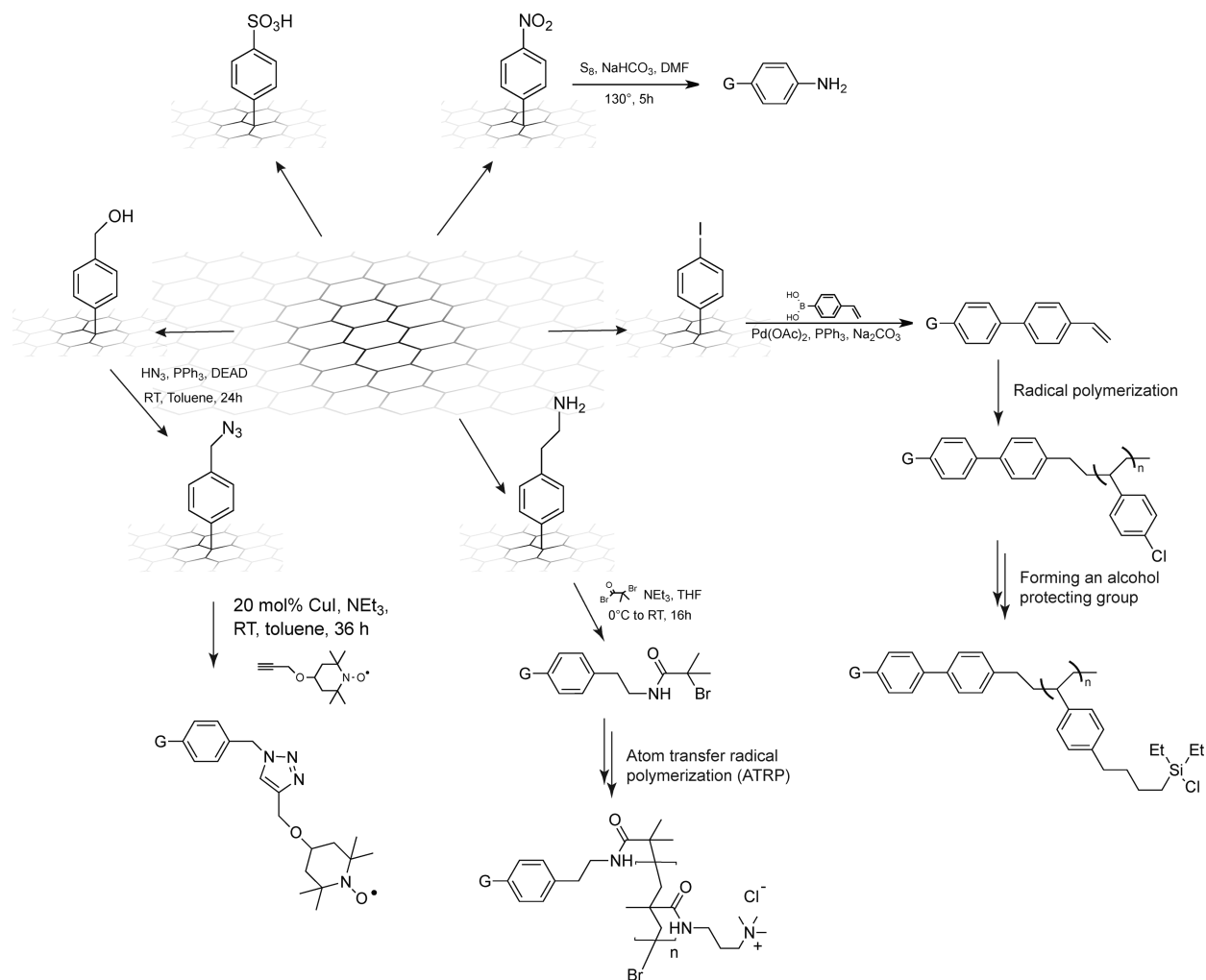
way how substituents influence chemical reactivity.<sup>48</sup> Pushing or pulling electrons is a chemist's talk for doping. We most recently extended the Hammett concept from connected benzene rings to 2D graphene systems and showed how substituents in graphene-functionalization allow control on electron density, surface potential, and therefore the Fermi level.<sup>25</sup>

The doping behavior of various substituents attached perpendicular to the graphene base plane (see Figure 3) was studied in detail using patterned, highly ordered pyrolytic graphite chips (HOPG, graphene sheets stacked together, G<sub>∞</sub>). Photolithographic patterning allowed surface selective functionalization of carbon chips, which are functionalized by immersion into reaction solutions. We used either commercially available aryl diazonium salts or a 1% HCl solution containing sodium nitrite and the corresponding aromatic amine, thus creating the diazonium ion *in situ*. Photoresist covered areas were protected from derivatization. For analysis, the remaining photoresist was removed and revealed the pattern structure on the chips. Characterization by scanning electron microscopy (SEM, see Figure 3c,d) and atomic force microscopy (AFM) confirmed

nanometer-high, thin organic films on the exposed areas. Kelvin probe measurements showed a clear change in surface potential from unfunctionalized to functionalized areas (Figure 3e–h). Kelvin probe spectroscopy measures the electrostatic interaction between a sample and the AFM tip, that is used to calculate the surface potential of a sample.<sup>49</sup> Different aryl diazonium ion substituents allowed changing the surface potential, by the use of the Hammett constant as design parameter (Figure 3b). Strong electron donor (–OCH<sub>3</sub>) groups resulted in a more positive surface potential on the functionalized areas compared to the unfunctionalized areas. Strong electron acceptors (–NO<sub>2</sub>) yielded a negative surface potential on the functionalized areas.

## Covalent Functionalization

The above ability to control electronic potentials using organic chemistry concepts provides in principle a basis to print (molecular) electric circuits on graphene. High sp<sup>3</sup> density provides barriers for charge carriers (i.e., serves as an insulator) and allows one to define wiring and circuitry.<sup>50</sup> Such insulating areas may be accessible through hydrogenated graphene with a small band gap around the charge

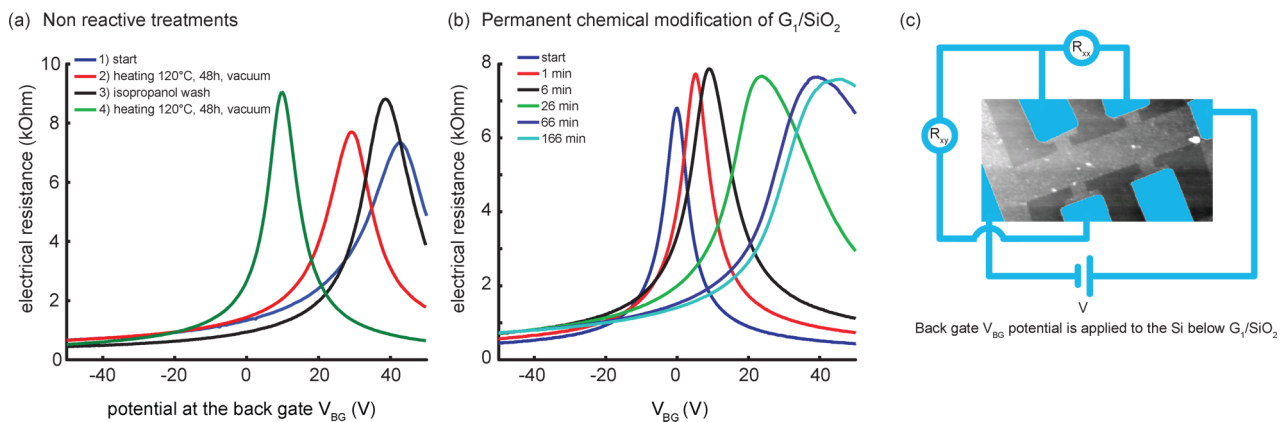


**FIGURE 5.** Chemical reactions on few layer graphene ( $G_{3-5}$ ) supported on metal nanoparticles show defined multistep organic reactions. Increasing the distance from the surface allows carrying out standard organic reaction protocols.

neutrality point<sup>26</sup> or the here introduced ambient condition C–C bond chemistry. Using chemically easily accessible graphene-like carbon model compounds such as carbon coated metal nanoparticles or carbon nanotubes the group of Tour and us showed that diazonium chemistry indeed results in covalent attachment directly to the carbon surface.<sup>22,51</sup>

An alternative, second reaction path to doping graphene is local polymer formation on its surface.<sup>24</sup> Here, two reactions (Figure 2) compete with each other and aryl diazonium ions also react with graphene-bound aryl moieties. Both reaction pathways can be nicely distinguished by Raman spectroscopy: Physicists see defect generation (chemists call this  $sp^3$  carbon formation)<sup>52</sup> through an increase of the so-called D-line (Figure 4). The final defect density can be estimated by the intensity ratio of the D- and G-line.<sup>53,54</sup> Surface polymer formation shows no D-line but associated doping shifts the G-line.<sup>39,42</sup> Observing G-line shifts only therefore

indicates second reaction pathway. In a Raman study<sup>55</sup> on scotch taped graphene, a flake on  $SiO_2$  ( $SiO_2/G_{1-2}$ ) wafer was immersed for a certain time into the diazonium reaction media and extensively cleaned. Point spectra, line scans, and Raman maps on  $G_1$  and  $G_2$  areas revealed different reaction kinetics.<sup>55</sup> Before treatment, Raman spectra showed a D-line at the edges. With increasing functionalization, three distinct regions emerged: A low defect region directly laying on  $G_2$  is characterized by almost no D-line and formation of Raman peaks attributed to adsorbed diazonium ion species. Partial overlaps with the D-line complicate identification and determination of quantitative defect formation caused by the diazonium chemistry. Sharma et al. washed functionalized  $G_2$  for several hours to remove adsorbed species and found a small D-line.<sup>44</sup> A second region of intermediate defect density area covers part of the single layer graphene. Here, D-line and adsorbed diazonium ions are visible. The D- and G-line ratio



**FIGURE 6.** Electron transport measurements on graphene Hall bars. (a) Pretreatment of one graphene device with isopropanol and heating steps before functionalization. (Reproduced from ref 47.) (b) Functionalization of another graphene Hall bar device with 4-nitrobenzenediazonium tetrafluoroborate after an identical pretreatment. (Reproduced by permission of The Royal Society of Chemistry.<sup>65</sup>) (c) AFM topography with measurement/electrode setup.

is about 1, indicating a functionalization density of  $2 \times 10^{11} \text{ cm}^{-2}$ .<sup>54,56</sup> The difference between low and medium defect areas was explained on the basis of an altered reaction rate of the diazonium species toward a specific region of the carbon surface. From this experiment, it has become clear that higher reaction rates and therefore higher defect densities are found on  $G_1$  rather than  $G_2$ . From a chemical perspective, what is the key difference between single- and bilayer graphene?

The two-dimensional carbon arrangement in the graphene base plane is putting severe steric restrictions on rehybridization. The large rigid graphene sheet can hardly accommodate any size changes during reaction (e.g., distortion when forming an  $sp^3$  base within the space of an  $sp^2$  carbon). The most flexible form,  $G_1$ , is thought to adapt the roughness of the underlying substrate. Thus, in plane strain due to a chemical reaction can be better accommodated than in  $G_2$ .<sup>26</sup> From a physical point of view, charge impurities of the substrate cannot be effectively screened through single graphene layers,<sup>57</sup> giving rise to charge-induced roughness of single layer graphene on  $\text{SiO}_2$ . The associated lack in material perfection and symmetry reduce charge carrier mobility. Following the same arguments, bilayer graphene is more crystalline with a flat surface independent of the substrate and more effectively screens substrate charges. Naturally, this more rigid and homogeneous carbon<sup>58</sup> is chemically less reactive.

A third graphene region is the high defect area originating from  $G_1$  edges. Here, signals from adsorbed diazonium ion species are covered through a large, dominant D-line. The associated high amount of defects facilitates a high degree of functionalization. Such high defect region is only observed at the edges of the single layer graphene, which is in line with a less defined geometry at edges (zigzag or

armchair structures; functional groups like hydroxyl or carboxyl) and facilitates the accommodation of strain (highest D/G ratio or degree of functionality). With prolonged reaction time the high defect region grows into the medium defect area (see Figure 4). The expansion of the high functionality region may be explained through lowering of the activation energy when considering attachment of a phenyl functionality near a previous reaction site.

### Multistep Organic Synthesis on Graphene Coated Nanoparticles

Organic chemistry on metal nanoparticle bound graphene (NP/G) has yielded a broad range of accessible structures (see Figure 5) and thus opens graphene chemistry to the wide and fascinating field of organic synthesis and material design. The introduction of nitro-, hydroxyl-, carboxyl-, halogen-, and amine groups<sup>22,59</sup> provides an anchoring point for further synthetic work. An example of second reaction step is the modification of amine groups with chelating agents, allowing the capture of metal ions like lead or gold in solutions.<sup>36,60</sup> Experimentally, it was found that functional group reactivity on the graphene coated nanoparticle surface was often modified as a result of the proximity to the graphene plane (bulky ligand with electron pushing/pulling effects on functional groups). This behavior was shown for Suzuki cross coupling reaction using boronic acids where phenyl bromide on the graphene nanoparticle surface did not react to form covalent carbon-carbon bonds; instead phenyl iodide was used, as iodide is the better leaving group.<sup>61</sup> The Suzuki coupling reactions yielded aldehyde, epoxy, and vinyl groups on the graphene nanoparticle surface in high yield. Polymerizing vinyl groups, as the styrene

moiety<sup>61</sup> allows covalent combination of carbon materials with more traditional polymers by radical reactions. Fuhrer et al. showed how the direct incorporation of styrene functionalized graphene coated metal nanoparticles yielded a homogeneous and stable magnetic hydrogel.<sup>62</sup> Another most versatile functionality is the recently introduced azide group,<sup>37</sup> enabling very efficient click reactions, particularly for biochemical protocols. With this linker, a TEMPO catalyst was attached to the graphene coated magnetic particles, resulting in a highly active oxidation catalyst for primary and secondary alcohols, due to the magnetic properties the catalyst could be recycled several times.<sup>37</sup> The same azide linker provided a route to covalently attach a palladium phosphine catalyst onto graphene nanoparticle surfaces, for achieving Suzuki-Miyaura cross coupling reactions.<sup>63</sup> For biochemical reactions, the thiol linker is a useful group for attaching proteins to the graphene coated nanoparticle surface. The coupling reaction uses maleimide-modified biomolecules, which are covalently bound to the thiol groups.<sup>59</sup> The recent covalent linkage of a silane with carbon<sup>64</sup> chemically bridges graphene with its heavier element cousin silicon that has found prominent use in electronics.

## Chemistry as a Tool for Electronics

In order to measure the fundamental physical effects of covalent chemistry on graphene, we recently prepared graphene flakes on silica wafer ( $\text{SiO}_2/\text{G}_{1-2}$ ), connected them electronically, and applied diazonium chemistry onto this wired piece of carbon. Figure 6 gives the electronic resistance as a function of exposure time to the diazonium reagent. The plot gives the electrical resistance as a function of the so-called back-gate voltage (an electrical field applied perpendicular to the graphene device). This geometry allows physicists to derive electron and hole mobility information, type of charge carriers and degree of doping.<sup>47,65</sup>

Measuring electronic effects is challenging. Even simple treatments of a graphene sample with water or organic solvents can lead to altered doping concentrations due to impurities in the solvent, removal of charge impurity from the graphene plane, or even changing the surface charge distribution. A simple isopropanol treatment significantly improved graphene quality<sup>47</sup> resulting in a doubled electron mobility. Electronic effects are further complicated by a hypothetical thin water layer between the graphene and  $\text{SiO}_2$  wafer surface.<sup>66,67</sup> Salts or nonreactive species can change carrier concentration by physisorption and demand careful graphene sample pretreatment before any electron transport and functionalization experiment.

Chemical functionalization of a so-called graphene Hall bar (Figure 6) at short exposure times resulted in a minor shift of the charge neutrality point to more positive values and increase in minimum conductivity. This is in line with a direct functionalization, that is, formation of  $\text{sp}^3$  carbons and Raman measurements (small D-line; G-line shift due to doping). Continued derivatization does not dramatically affect the minimum conductivity but further shifts the charge neutrality point as a result of polymer formation onto previously attached phenyl units.<sup>65</sup> Hossain et al. confirmed such polymer formation and growth with scanning tunneling experiments on functionalized graphene on SiC wafers<sup>12</sup> with only a small polymer directly attached over an  $\text{sp}^3$  carbon.

With the above-mentioned method, we were able to heavily dope graphene devices in a simple and permanent way, resulting in a low resistance sheet without the requirement of a backgate potential. The mobility was partially decreased as expected from surface charges acting as scatter centers. Using above covalent C–C chemistry, modified graphene remains well conducting at any back gate potential and shows a minor increase in minimum conductance around the charge neutrality point. Doping is preferred if an integrated, wired, and mechanically fixed graphene flake with limited possibility for edge access is used.<sup>47,65</sup> Flexible and free to move, scotch taped graphene without any additional preparation steps, in contrast, is amenable to preferred edge functionalization.<sup>55</sup> Device preparation and processing of graphene devices reduces its reactivity, particularly with respect to direct attachment of functionalities to the graphene plane. It seems that the oligomer formation pathway is less influenced by device preparation. Zhang et al. showed that an additional reactant tetrabutylammonium hexafluorophosphate<sup>68</sup> helps to increase direct attachment and reduces polymerization reactions (strong doping). With a high degree of functionalization, chemical band gap engineering is indeed coming closer to realization.

## Conclusion

Chemistry is a most versatile tool for simple modification of the extraordinary physical properties of graphene, such as mobility and carrier concentration. Besides electronics, pattern-resolved formation of functional groups on the otherwise rather monotonous  $\text{sp}^2$  carbon structures opens up most creative research directions by covalently connecting graphene to polymers, proteins, and defined organic synthesis. Here, diazonium chemistry builds a strong and covalent bridge by a simple reaction yielding the basic functionality on the graphene surface.



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## BIOGRAPHICAL INFORMATION

**Fabian M. Koehler** received his M.Sc. degree in Chemical- and Bioengineering from ETH Zurich along with the Willi-Studer Award for outstanding master students. He obtained the Ph.D. degree for his thesis about electronic transport analysis of chemically modified graphene from ETH Zurich in 2011. Currently, he is a Pioneer Fellow at the Functional Materials Laboratory of ETH Zurich responsible for the development of next generation diagnostics focused on rapid and quantitative point of need analysis.

**Wendelin J. Stark** received his Master in Chemistry in 2000, followed by a Ph.D. in Mechanical Engineering in 2002, both from ETH Zurich. In 2004, he founded the Functional Materials Laboratory within the Department of Chemistry and Applied Bioscience at the ETH Zurich. His research group pursues application-oriented research at the interface of chemistry with material science and medicine.

## FOOTNOTES

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