Akademie věd
České republiky

Teze disertace
k získání vědeckého titulu "doktor věd"
ve skupině chemických věd

# Towards controlled functionalization of single-layer graphene

Komise pro obhajoby doktorských disertací v
oboru fyzikální chemie

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Praha, 12. února 2021

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## 1. Introduction

Graphene is a one-atom-thick layer of $sp^2$ connected carbon atoms. The experimental preparation of this material and demonstration of the quantum hall effect in 2007 sparked enormous research interest.

Although the research on pristine graphene remains unexhausted, there is growing interest in analogous materials. For example, several research groups have successfully prepared 2D materials from other elements or compounds, such as P, BN, $MoS_2$, $MoSe_2$, $WS_2$, and $WS_2$, showing the possibility of preparing 2D material featuring a plethora of properties, including, electrically, the capacity to act as anything from isolators to semiconductors to metals. Additionally, such materials have potential as light-emitting diodes, transistors, sensors, and emitters.

However, true 2D materials are defined by not only their thickness but also allowing charge carriers to travel without significant scattering. That is, the 2D materials are presumably perfect, an important requirement for many phenomena that is simultaneously very hard to achieve. Almost perfect graphene samples can be obtained by mechanically exfoliating the flakes from graphene, with a similar approach applied to obtain flakes from other 2D materials. Nonetheless, this requires perfect crystal and, because the procedure typically leads to a locally strained material, it still contains both impurities from the tape and some defects or cracks. The mechanical-exfoliation–based approach is useful for fundamental science because many experiments can be done using sample size of few micrometers.

For practical applications, it is more important to obtain a large amount of the material, which can involve chemical exfoliation from bulk materials, a procedure that is typically quite harsh and therefore produces material that is poorly defined and features significant defects, as well as leading to the presence of multilayers and potentially broad flake-size distribution. Therefore, such a material is not suitable for high-end applications. The chemical vapor deposition compromises between high-quality but tiny exfoliated samples and large scale but poor quality chemically exfoliated samples. In the case of graphene, the chemical vapor deposition (CVD) process can produce samples of relatively high quality because the process has been developed over more than a decade, a striking advantage in comparison to other 2D materials, for which there are few reports of CVD synthesis leading to samples of reasonable quality. It should also be noted that it is much less challenging to determine graphene quality compared to other 2D materials. Consequently, high-end applications of 2D materials other than graphene must wait for the development of adequate preparation and characterization methods. However, given CVD for graphene is already at an advanced stage, graphene can be considered as a starting material for more complex materials, with its modification altering its properties. This suggests another approach: graphene’s chemical functionalization, which could potentially produce various modifications capable of broadening the number of potential applications depending on the specific functional groups attached to the graphene.

Although the functionalization of graphene has also been studied widely, it is necessary to distinguish between the functionalization of chemically exfoliated graphene and CVD graphene or mechanically exfoliated graphene. Chemically exfoliated graphene allows a large amount of material to be prepared and, moreover, the exfoliation and functionalization to proceed in one step; this saves costs and simplifies the whole process. However, the material obtained material is often low quality; samples contain broadly distributed layers and sizes and are not uniformly functionalized, which further increases uncertainty. Given the system is quite complex, it is challenging to characterize the reaction product and, thus, to control or optimize the functionalization process.

Accordingly, it is more convenient to study the reactions of mechanically exfoliated graphene or CVD graphene, which enables higher quality samples with potential use in high-end applications. Additionally, if the protocol is optimized and the product well-characterized, the conditions can be transferred to chemically exfoliated graphene.

The current work demonstrates our approach to graphene functionalization, addressing three issues: i) select the right model reaction, ii) test different approaches to controlling the reaction, and iii) find a set of suitable techniques that can enable characterization and control of the functionalization process.

We chose fluorination using $XeF_2$ as our model reaction. This reaction is performed in a gas phase, and the only byproduct is xenon. Therefore, the reaction is very clean and can be performed even under low vacuum conditions. Additionally, the product—fluorinated graphene—is predictable and detectable, and the reaction's success can easily be controlled by Raman spectroscopy, which is fast and nondestructive. Finally, the fluorine can be exchanged for other functional groups. Consequently, successfully controlling the reaction would enable easily altering the fluorine by functional group of interest.

The presence of substrate constitutes a large difference between the reactivity of chemically exfoliated graphene and CVD graphene. While chemically exfoliated graphene is typically functionalized in solution, substrate is typically necessary for CVD graphene. (Note that CVD graphene can be prepared suspended, but its handling is more complicated.) Therefore, this paper studies the role of the substrate and explores the possibilities of controlling the functionalization reaction by adjusting the substrate properties.

Characterization techniques are crucial for the study of graphene functionalization because we need feedback for tested reaction conditions, with the method ideally simple, fast, and nondestructive. Unfortunately, proper characterization of functionalization is not simple: given graphene is a one-atom-thick material, the technique must be surface-sensitive and able to detect a sub-monolayer of functional groups. Furthermore, reliable characterization apparently requires combining several techniques. Therefore, this work both summarizes commonly used characterization techniques and introduces new or rarely applied approaches.

## 2 Graphene synthesis and basic characterization of graphene

### 2. 1 Graphene synthesis

Graphene synthesis is crucial because it determines both the initial properties of graphene and its first environment. Unless otherwise stated, this work considers “graphene” material synthesized by

CVD method, a procedure proposed by Ruoff in 2009.[1] The graphene is grown on copper foil that is heated to about 1000 °C; methane is a typical source gas, with the typical growth procedure involving mixing methane with hydrogen before introducing the mixture to the hot wall reactor in which the copper foil is placed. At a high temperature, the methane cracks and forms graphene. The reaction requires free copper surface to be available so that the reaction stops when the graphene covers all of the copper foil. That is, the growth is self-limiting, guaranteeing that, theoretically, only a monolayer grows. In praxis, the situation is more complex because the graphene grows from seeding points—for example, a defect in the copper—in the form of a multilayer. The number of multilayers can be controlled during the synthesis by, for example, increasing the amount of hydrogen, which leads to the etching of the adlayers.[2]

Copper-catalyzed CVD synthesis also enables changing feedstock to isotopically labeled methane, promoting the formation of isotopically labeled graphene sample. [3,4] Although this process has thus far been established for $^{13}CH_4$ methane, in principle, $^{14}CH_4$ can also be used. Furthermore, the feedstock $^{12}CH_4$ can be changed to $^{13}CH_4$ during the growth procedure.

Later, we discuss the significant impact of the number of layers on properties of the material, especially how the interaction of the layers changes the electronic properties and thus also the reactivity. To study the effects of layer interaction, it is useful to form multilayers from different isotopes. Previously, we have demonstrated that it is possible to realize such a structure with $^{12}C$ and $^{13}C$ graphene layers.[4] The layers are synthesized separately and then subsequently transferred onto the desired substrate. However, this approach precludes controlling the between-layers angle. Furthermore, the interaction between layers is limited by the transfer residuals between the layers.

Another possibility is the direct synthesis of isotopically labeled bilayers, which we reported previously.[5] This involves the growth condition being modified to change the formation of bilayer islands, which can be achieved by, for example, growth inside a thick copper capsule. When growth in the seed begins, the bilayer islands are already formed; by prolonging the reaction time, they grow in size. However, layer speeds are different, with one layer growing much faster than the other. After the faster-growing layer grows to about 10 um and the slower-growing layer reaches about 1 um, we switched the $^{12}CH_4$ to $^{13}CH_4$ and both layers continued growing with the $^{13}C$ carbon. This procedure produces a bilayer, where, between 1um and 10 um, each layer contains a different carbon isotope. This growth condition promotes the formation of bilayers with both random and AB stacked orientations.

## 2.2 Basic graphene characterization

There are several methods typically used to evaluate graphene properties, with the simplest being optical microscopy imaging, a method typically used for graphene samples on $Si/SiO_2$ substrate. This method can distinguish one-layer and two-layer graphene.

Raman spectroscopy is another elemental and frequently used method for characterizing graphene samples, including functionalized samples. For pristine samples, there are two main bands: the G mode and the 2D mode. The G mode originates from in-plane $E_{2g}$

vibrations; its frequency in neutral unstrained graphene is about 1582 cm$^{-1}$. Strain and doping lead the mode to shift to higher frequencies, with the 2D mode originating from second-order triple resonant processes because it includes two phonons with opposite momentum. The 2D mode is dispersive, with its shift depending on the strain and doping. The typical functionalized graphene spectrum reveals a large difference from pristine graphene, which is the D mode at about 1350 cm$^{-1}$, a mode used to quantify defects in graphene samples. Although the D mode's origin is analogous with that of the 2D mode, the momentum is conserved by scattering the phonon with defects. This also explains the frequency of the D mode being about half the 2D mode's frequency. The sp$^3$ carbon in the sp$^2$ graphene lattice can also be considered a defect.

Consequently, any covalent functionalization of graphene manifests as the D mode in the Raman spectrum. The intensity of the D mode scales with the number of scattering centers, which allows the extent of functionalization to be quantified. Note that at high levels of functionalization, the D mode intensity saturates and eventually decreases again as the sizes of defect-free crystallites in graphene start being smaller than the phonon scattering length.[6] Another mode associated with defects is D', in which defects are scattered by intravalley phonons. As in the D mode, there is also a higher-order counterpart called the 2D' mode, which is approximately twice the frequency of the D' mode.

Using isotopically labeled graphene layers, we have previously demonstrated that the phonons in adjacent AB stacked layers can interact with each other, which also has consequences for the appearance of higher-order modes where more than one phonon is involved. The interaction of phonons from adjacent layers produces a new band corresponding to a process combining phonons from different layers.[7] For example, the spectrum of an isotopically labeled AB stacked graphene bilayer comprises three bands in the frequency corresponding to the 2D mode. One band results from combining two phonons originating in the $^{12}$C layer, one band combining two phonons originating in the $^{13}$C layer, and one band combining a phonon originating in the $^{12}$C layer and a phonon originating in the $^{13}$C layer. The intensity of the latter band is twice the intensity of the bands featuring phonons originating from the same layer. Where the layers are not AB stacked, that latter band is either missing or significantly weaker. A similar effect has been observed for the 2D’ mode. Although the 2D’ mode’s intensity is rather low, the mode is important for the evaluation of the strain in the graphene samples. Compared to the 2D mode, the 2D’ mode’s line shape interpretation is less complex and less affected by sample doping.[7]

Additionally, as previously addressed, Raman spectroscopy is an efficient and powerful tool for studying the properties and “status” of graphene. However, for complete characterization of graphene samples—especially functionalized samples—a broad range of other methods should be employed. These are discussed in a later section.

## 3 Changing the properties of graphene using external stimuli

Graphene properties can be modulated by different approaches, with the most straightforward being the use of external stimuli such as doping and strain. Sometimes, the external stimuli are unintentional, introduced through treatment or manipulation with the sample. In any case, it is necessary to understand how these external stimuli act on graphene and how they can be monitored and controlled.

### 3.1 The dependence on doping and strain

Both the G and 2D mode depend on strain and doping. The doping dependence of the shift and intensity of these modes can be efficiently probed using in-situ Raman spectroelectrochemistry It has been demonstrated that the Raman shift of the G mode is  increasing as the graphene doping increases. This effect is caused by electron-phonon coupling reducing as the graphene doping level increases. A similar effect is observed for the 2D mode, which also features a bond-strength change following doping. Injecting electrons into graphene layers promotes the bond's weakening as the extra electrons move to anti-bonding orbitals. The withdrawal of electrons leads to the removal of electrons from bonding orbitals, which also weakens the bond strength. The effects of electron–phonon coupling and bond-strength change act together; depending on the strength of that collective action, the G mode shift changes.

The frequency of the G and 2D modes also depends on the strain. In general, the strain weakens the bond, causing an upshift in Raman modes. The dependence of the shift of the G and 2D mode can be derived experimentally by putting the graphene on a plastic beam and bending it, together with simultaneous measurement of the Raman spectra.[9]

The dependences of the G and 2D modes on doping and strain are different. While the G mode is more sensitive to doping, the 2D mode is more sensitive to strain. Given the effect of isolated strain and isolated doping are known, it is possible to deconvolute the effects of strain and doping on the Raman spectrum of the graphene sample.[10] However, strain and doping typically vary from one point to another in general graphene samples. Therefore, for a complete picture, it is necessary to measure the Raman map and extract the contribution of strain and doping for each measured point, with the strain and doping distributions typically represented in G/2D space.

### 3.2 Interaction with substrate

Substrate is an important factor that influences the properties of pristine graphene (unless the graphene sample is suspended). The most popular method for preparing large single-layer graphene is CVD using copper foil. However, the copper foil comprises grains of different surface orientation; thus, graphene properties can be locally modified.[11] We combined in-situ Raman spectroscopy and heating to study graphene-copper interactions for defined surface orientations, finding that interactions on Cu(111) are not affected by heating while interactions on Cu (110) and Cu(100) can be significantly modified by heating.

A special substrate case is another layer of graphene, a situation that can be represented simply by a graphene bilayer. Furthermore, in this case, it is even important how the layers are oriented with respect to each other. For example, we have studied Raman spectroscopy on artificially assembled graphene bilayers with layer orientation varying at different locations of the samples,[12] ascertaining that the Raman maps of these bilayers follow the dependence of the Raman signal on the location of the Raman spot. These locations where the Raman signal is enhanced correspond to areas where the laser excitation energy resonates with van Hove singularities in the electronic structure of the graphene bilayer, which follows the previous suggestion that the interaction of graphene layers leads to the formation of van Hove singularities in graphene electronic structure.[13] The energy separation of singularities is a function of the angle between adjacent graphene layers. If the sample contains regions with different layer orientation, there is also variation in the energy distance; consequently, at specific places, the excitation laser eventually matches the energy difference between those singularities, and the Raman signal is strongly enhanced. This demonstrates that even very weak interaction between graphene layers can dramatically influence graphene's properties.

Another important substrate for graphene research is $SiO_2$/Si, which is widely used in the study of graphene. In this case, oxygen-containing functional groups are present on $SiO_2$ and play a significant role. Therefore, the interaction with the $SiO_2$/Si substrate can be modulated by heating, which, in turn, provides a convenient tool for studying such interactions.

In our study, we heated and cooled graphene samples on $SiO_2$/Si substrate in two subsequent cycles, while simultaneously measuring the Raman spectra of graphene.[14] It has been shown that with increasing sample temperatures the G-mode frequency is shifting to higher frequencies. When the temperature decreases, the G mode shifts back to lower frequencies. However, at room temperature, it remains upshifted compared to its pre-heating position. During the second heating cycle, the G mode follows the first cycle's cooling dependence. After cooling, the G-mode frequency returns to the second cycle starting frequency. This behavior can be understood by considering the thin layer of water present between the graphene and the $SiO_2$/Si substrate, which is strongly bound to surface hydroxyl groups. When the sample is heated to a high temperature, the water is removed, putting the graphene in direct contact with the $SiO_2$/Si substrate. Given the interaction changes the position, the G-mode the frequency does not return to its original position. Water is absent for the second cycle; thus, the G-mode frequency returns to its original position for the start of the cycle.

We have performed analogous studies on the graphene bilayer, allowing comparison of the results on $SiO_2$/Si substrate with the situation in which where graphene itself serves as a substrate.[15] In that case, the main difference between the top and bottom layers was the effect of the strain. While the bottom layer appeared pinned to the substrate, the top layer slid, making it more relaxed following the heating cycle.

The same experiment can be performed on a sample containing the isotopically labeled AB stacked bilayer Ref.[16] Doing so demonstrates that the behavior of the AB stacked and turbostratic graphene bilayers during heating is similar if both samples are grown directly because such cases involve the turbostratic graphene bilayer being prepared by subsequent transfer layer transfer, producing different behavior. Consequently, it seems that the layers’ orientation to each other has less impact than the preparation procedure. This can be explained by the presence of impurities or random wrinkles in the top and bottom layers if the sample is prepared by the subsequent transfer of layers.

# 4 Graphene functionalization

## 4.1 Fluorination

Studying the reactions of graphene can be very complex; therefore, it is advisable to begin with a simple and clean model reaction. For this, we used the fluorination of graphene by $XeF_2$ to model graphene reactivity dependence for different substrates. The reaction is very clean because the only byproduct is inert gas xenon. Additionally, because the reaction is realized in a gas phase, there is no contamination from solvents. Finally, it is very easy to monitor the reaction progress. Attaching fluorine to graphene changes $sp^2$ carbon to $sp^3$; as previously discussed, this can be semi-quantitatively identified by monitoring the intensity of the D mode in the Raman spectrum. The degree of functionalization also increases the intensity of the D mode.

Meanwhile, as previously demonstrated, the substrate significantly affects the properties of graphene. Hence, the reactivity of graphene can also be expected to be driven by interactions with the substrate.

The easiest test is to compare the reactivity of graphene on $Si/SiO_2$ and graphene on graphene substrate. The $Si/SiO_2$ substrate is most commonly used because graphene can be easily optically imaged on this substrate. Meanwhile, study of the reactivity of graphene on graphene substrate can be realized practically by studying the reactivity of the graphene bilayer. In this case, it is possible to take advantage of isotopically labeled graphene to distinguish between probed graphene and the underlying graphene substrate.

The study was performed on a sample containing both the graphene monolayer and the bilayer on Si/$SiO_2$ substrate.[17] The bilayers were either AB stacked or turbostratic, such a setup is preferred because both bilayers and monolayer can be simultaneously fluorinated, which eliminates problems with slightly different reaction conditions, in the case of subsequent experiments.

It has been demonstrated that fluorination induced the largest increase for the D mode in graphene on Si/$SiO_2$ substrate. This means that the extent of fluorination was the largest of cases probed. The increase of D-mode intensity was smaller for the turbostratic graphene bilayer. This indicates that graphene's reactivity on graphene substrate was lower than the reactivity of graphene on Si/$SiO_2$. Finally, the lowest D-band intensity increase was found for the AB stacked bilayer. This indicates that graphene reactivity is also influenced by stacking order even if the graphene is placed on the same material. Here, AB stacking represents a stronger interaction between substrate and sample than turbostratic stacked graphene layers.

Copper is another important substrate regularly used to grow graphene. This typically involves a polycrystalline copper foil, and, therefore, it contains grains with different surface orientations. This can be monitored by Electron backscatter diffraction (EBSD) in Scanning electron microscope (SEM). For this experiment, we first grew graphene on copper foil and then identified the grains on a specific area of copper foil.[18] Then, the graphene on the copper was fluorinated. For the analysis, the area identified by EBSD was examined by Raman spectroscopy, demonstrating that the reactivity of graphene strongly depends on surface orientation. We have constructed a map of orientations, with column size corresponding to a particular D/G ratio of fluorinated graphene sample at a specific grain orientation. For example, for copper grain surface orientation close to (111), reactivity was highest; for copper grain orientation close to (110), reactivity was smallest. These results confirm the importance of graphene-substrate interactions, indicating the significance of not only the material but also the specific surface orientation.

Meanwhile, using $XeF_2$ appears to complicate the control of fluorine quantity. The reaction time varied for different batches of the sample depending on either or both the vacuum condition and the age of $XeF_2$. This promoted our search for more reliable control of the amount of fluorine on graphene, leading to the possibility of using $SF_6$ activated by laser pulses.[19] During the experiment, the $Si/SiO_2$ target was exposed to $SF_6$ and intense 532 nm laser pulses. There was graphene sample in the vicinity of the target, which was fluorinated by reactive species within the plume. The amount of fluorine attached to the sample could seemingly be controlled by the number of laser pulses.

### 4.1.1 Stability

The stability of the chemically functionalized samples also requires consideration, especially the loss of fluorine from fluorinated graphene over time. The speed of this process increases when fluorinated graphene is heated. In[20], we followed changes in the fluorinated graphene samples using Raman spectroscopy. It appeared that most fluorine loss occurred at a relatively low temperature. However, this removal was incomplete; some residual fluorine could be traced at temperatures as high as 800K. Additionally, we tested the evolution of spectra for graphene bilayer, finding that both the monolayer and bilayer showed similar degrees of functionalization after heating cycle despite the amount of fluorine on the monolayer being significantly higher before a heating cycle.

Furthermore, we investigated the process by analyzing the product of decomposition using temperature-programmed desorption in combination with XPS and Raman spectroscopy.[21] We found that gradual annealing leads to decomposition associated with the desorption of CO and HF, as well as fractional desorption of CF species, which can explain the formation of defects associated with decomposition. Nevertheless, some fluorine atoms remain bonded to graphene even at very high temperatures (1000 K); accordingly, their bonding has to be strong. This work also importantly recognized that intercalated water catalyzed the decomposition of fluorinated graphene.

## 4.2 Defects in graphene: Formation evaluation and role in further reactivity

Graphene defects can also be viewed as specific functionalization, having the same signature in the Raman spectrum—the D mode—as functional fluorine groups. Although it is difficult to determine what defects "look like," it is possible to exclude unsaturated carbon atoms, with the expectation that carbon atoms around a vacancy are saturated with oxygen-containing functional groups (e.g., OH, COOH, and CHO).

Defects can be created in different ways, with our study taking the approach of bombardment with Ar ions. Moreover, we examined how defects are created in the top and bottom layers of isotopically labeled graphene using defects created by high energy (100 eV) argon atoms at different doses.[22] The results showed that increasing the dose increases the number of defects. However, the number of defects was significantly different for the top and the bottom layers. The energy of the Ar ions is high enough to remove carbon atoms upon impact. Without impact, the Ar ion passes through the graphene layer almost unaffected. As such, the same number of defects can be expected in both layers. In contrast, carbon atoms removed from the bottom layer have more difficulty escaping; consequently, there is a greater probability of their recombining with the defect, thus fixing it.

As discussed, Raman spectroscopy can usefully quantify the number of defects in graphene samples. However, our experiments have indicated that this can be more complex for graphene bilayers, leading to the use of oxygen plasma to create defects for this work.[23] At low concentrations of defects, it was believed that there were only single atom vacancies, a supposition confirmed by the appearance of the D´ mode in the Raman spectrum. Consequently, defects were expected to form in the top layer and not the bottom layer. However, the D mode also appears in the bottom layer. More strikingly, the D mode also appears in the bottom layer of AB stacked bilayer, with the interlayer interaction much stronger than for the turbostratic bilayer. This in contrast with the fact that, reactive oxygen could be expected to have more difficulty penetrating between the layers in the case of AB stacked bilayer. The results can be understood by considering phonon–defect interactions. The D mode is caused by a phonon scattered at a defect; it is possible that a phonon in one graphene layer can be scattered by defects in an adjacent layer, an effect expected to be significantly stronger for AB stacked bilayer because there is stronger interaction between the layers. Indeed, in our experiment, 45% of phonons were scattered by defects in adjacent layers for AB stacked layers compared to 20% for turbostratic layers. This observation importantly demonstrates that if the quantification of defects is based on D-mode intensity, the number of defects can be substantially overestimated. Although this is less concerning for turbostratic layers, it still demands attention.

The defects are assumed to increase graphene reactivity. In[24] , we attempted to address this issue by fabricating a series of samples with an increasing number of defects using oxygen plasma. Then, we exposed the sample to $XeF_2$ and, through Raman spectroscopy, monitored changes in the Raman spectra, especially D-mode intensity, showing that, for 1-LG, defect formation does not increase reactivity. This can be explained by the defects being saturated immediately after creation and thus establishing stable non-reactive structures.

## 4.3 Other reactions

Fluorine in fluorinated graphene has been demonstrated as being changeable by nucleophilic substitution. Accordingly, by controlling the fluorination reaction, the fluorinated graphene can be used as a master template for controlled functionalization by different functional groups.

In addition to fluorination, we explored hydrogenation. For this reaction, we exposed the sample to gaseous hydrogen at elevated temperatures and high pressures.[25] Again, this reaction is very clean because the only reactant is hydrogen; additionally, it is realized without any liquid being present. The hydrogen atoms can be further exchanged by electrophilic substitution, which broadens the spectrum of possible substituents and functional groups that can be attached to graphene by means of exchange reaction.

As discussed, the fluorination reaction progress can be efficiently controlled by monitoring D-mode intensity in the Raman spectra. This is also valid for hydrogenation. However, D-mode intensity cannot be used to monitor the exchange reaction. The intensity of the D mode does not change with this reaction’s progress because the $sp^3$ carbon number does not change. Therefore, it is necessary to consider other methods for identifying the functionalization.

Given functionalization only takes place on the surface, the actual number of functional groups is extremely small, a situation that might easily promote misinterpreted results. For example, the presence of even tiny amounts of contamination—in the form of bulk byproduct—will be averaged by X-ray photoelectron spectroscopy (XPS) and significantly contribute to the measured surface composition of the sample. Accordingly, it is necessary to combine several techniques to confirm successful functionalization. This is particularly important for testing new reactions.

## 4.4 Local functionalization of graphene on a large-scale

Given demonstration of the importance of strain and doping, modifying strain and doping on-demand could enable control of the reactivity of graphene at specific spots. One approach to this is using specifically modified surfaces. We have probed different methods, including creating pillars and depositing particles or fullerenes on the surface.

It is assumed that changing surface roughness promotes nanoscale corrugation in graphene. Local corrugations with different doping and strain can modify the reactivity of the graphene at specific spots. To be able to control these effects, it is necessary to relate surface changes to corrugation changes. The measurements by AFM indicated that it is possible to anticipate a higher concentration of particles promoting the formation of more graphene corrugations. To quantify the number of corrugations, we calculated the fraction of graphene delaminated from the surface, demonstrating that the higher nanoparticle concentration corresponds to a larger delaminated area.

Given performing AFM measurements and analysis is quite time consuming, it can only be conducted for a small sample area. Therefore, faster and more robust detection would be highly appreciated. Raman spectroscopy can usefully address this problem. As previously discussed, the G mode for the Raman spectrum of graphene is sensitive to strain and doping, and, thus, the delaminated area should exhibit locally differentiated doping and strain. Consequently, an area containing wrinkles should manifest as a G mode with differential shift compared to the area with the non-corrugated graphene. If the graphene sample is corrugated, the G mode appears to split into two peaks: in addition to the main peak (G1), there is a new peak at a lower frequency, marked as G2. The G2 peak intensity increases as the area of graphene corrugation and delamination increases. By measuring several samples, we determined the relation G1/G2=x*c(NP). Consequently, Raman spectroscopy can identify both delaminated areas and the corrugation.[26] Given Raman measurement is rapid and can be used to map an area of several hundred micrometers, the method can also be used to quickly check samples and evaluate potential corrugated fractions.

As discussed previously, the reactivity of graphene should be influenced by sample corrugation. To retest this hypothesis, we allowed the graphene to fluorinate over different extents of delamination and analyzed the results using Raman spectroscopy. It has been shown that indeed the I(D)/I(G) intensity ratio increases with nanoparticle concentration.[27] For more precise information about the number of fluorine atoms, we also measured XPS. showing the spectrum. The XPS analysis allowed us to derive the C/F ratio and plot the value against the delimited area. The degree of functionalization appeared to correlate with the number of nanoparticles on the substrate, indicating that surface corrugation represents the area of higher reactivity and allowing functionalization to proceed locally. Additionally, given the proportion of corrugated area corresponds to the concentration of the nanoparticles on the surface, the procedure can be used to efficiently control local functionalization on a large scale.

### 4.5 Specific characterization

This chapter introduces and discusses several different characterization methods. For ease of comparison, we use the model reaction of $XeF_2$ with graphene, which leads to graphene fluorination, following which fluorine is substituted by a phenylsulfanyl group.[28]

### 4.5.1 X-ray photoelectron spectroscopy

Often used to characterize functionalized graphene, XPS can uncover the chemical states of elements and is a quantitative approach. In contrast, the typical spot size is about 5 mm, which increases the risk of the measured spectra containing contaminations. Additionally, it is difficult to interpret the results of the chemical state, potentially making confirmation of specific bonding challenging. We have measured XPS of the sample following its change from fluorine to phenylsulfanyl group. The observed sulfur peak in the XPS spectrum could be clearly identified, which suggested a successful exchange.

### 4.5.2 Mass spectroscopy

We have also employed two mass spectroscopy methods: surface-enhanced laser desorption ionization/time-of-flight analyzer (SELDI) and thermal programmed desorption electron ionization (TPD). Using SELDI in the negative mode, functionalization by phenylsulfanyl groups clearly detected the molecular [M-H] ion mass at 109, corresponding to thiophenol ($PhS^-$); it was accompanied by signals of its oxidation products (up to $PhSO_3^-$, at 157). The remarkable sensitivity of the measurement allowed us to probe the SELDI method's imaging mode and, thus, map the distribution of the grafted species over a large area of about 1 mm x 1 mm.

### 4.5.3 Temperature programmed desorption

Although rarely used, TPD is another very useful method. The sample is heated in a vacuum chamber, and the mass spectra are simultaneously recorded, enabling the fragment composition to be followed as the temperature increases. The method can usefully distinguish between chemically bonded and physisorbed molecules on the graphene surface because a specific fragment composition is expected in each case. Results obtained by measuring the sample after its change from fluorine to phenylsulfanyl, indicated that there is no parent compound at low temperatures and the majority of the signal comes from decomposition products. This confirms that the phenylsulfanyl group is covalently bonded. Note that where there is sufficient doubt, it is possible to perform a blank experiment with physisorbed molecules.

### 4.5.4 Atomic force microscopy

Atomic force microscopy (AFM) can detect even extremely small changes in graphene layer thickness, which also enables us to visualize functionalization changes. We have compared fluorinated graphene with the same sample following exchange of fluorine by the phenylsulfanyl group. This procedure increased both the graphene substrate’s thickness and the sample’s roughness. Although the method cannot identify the composition of the ad-layer simply, it can provide insight into the homogeneity of functionalization and, potentially, the spatial distribution of the functional groups.

### 4.5.5 Surface-enhanced Raman spectroscopy

Surface-enhanced Raman spectroscopy (SERS) enables the measurement of even extremely small numbers of active Raman molecules. Despite the obvious potential of this method, it has not been previously applied in the identification of functional groups on graphene. Our work successfully implemented this method and demonstrated the possibility of identifying covalently attached functional groups on graphene.[29] For the model case of the exchange of fluorine atoms for phenylsulfanyl, we covered the sample with a thin layer of silver and measured the Raman spectra. Compared to the sample with no silver layer, there are clear bands, which can be attributed to the vibrations of the phenylsulfanyl.

It should be noted that the graphene signal is enhanced by metal layers. Although this enhancement is relatively weak (about 100–1000 times), it remains sufficient for the observation of the graphene signal in conditions where standard Raman spectroscopy fails, such as at laser excitation energies lower than about 1.8 eV. In our study, we considered the dependence of the enhancement on the distance from the gold using the graphene layer as a probe as well as a spacer.[30] This could be realized using isotopically labeled samples. We found that the layer closer to gold enhanced the Raman signal more than the layer further from the metal. The intensity ratio of about 0.7 corresponds to a decreased electromagnetic field intensity affecting the signal. That is, the intensity of the total spectrum proportionally corresponds to the number of layers when the theoretical electromagnetic field intensity is considered.

### 4.5.6 Surface-enhanced infrared spectroscopy

Surface-enhanced infrared spectroscopy (SEIRA) complements Raman spectroscopy. Although it is nondestructive and fast, infrared absorption is very weak for monolayer materials. Accordingly, the method is rarely used and has, thus far, not given conclusive results. There have been some reports of surface-enhanced infrared; however, such observations are generally quite rare. Our study tested gold and silver coating but obtained no signal. In the next experiments, we functionalized graphene directly on copper substrate, with the copper also able to serve as an active substrate for vibrational enhanced spectroscopy. Furthermore, during the reaction, the copper surface was partly etched, increasing the roughness; consequently, there was a greater chance of achieving an enhanced signal. Indeed, measuring the infrared spectrum was successful in this case.[31] We compared the surface-enhanced infrared spectrum of fluorinated graphene and graphene following exchange of fluorine for phenylsulfanyl in comparison to spectra of pristine graphene after exposure to thiophenol. The characteristic signals corresponding to the phenylsulfanyl moiety are only observed on the sample representing the reaction of fluorinated graphene and thiophenol.

### 4.6 Application of graphene functionalization

Mastering the functionalization process and efficient characterization of the products enables the tailored application of functionalized graphene. Her we show some examples of these applications.

#### 4.6.1 Composite with conductive polymer

Although the conductive polymer PEDOT is very popular in various industries, for its proper functioning, it is necessary to keep it in its charged form; consequently, the compensating polymer PSS is used to compensate for the PEDOT charge. This motivated our study, which used functionalized graphene. Given graphene can serve as a reservoir for a charge, we assumed that functionalizing it with phenylsulfanyl would enable it to mimic the function of the PSS.[32] Beginning with CVD-grown graphene, we subsequently functionalized phenylsulfonic acid. The process was monitored by XPS, SERS, and Raman spectroscopy to ensure sufficient characterization of the samples. Then, the EDOT was polymerized on the functionalized graphene, with polymer thickness monitored by AFM. The results obtained served as feedback for controlling PEDOT thickness. It is worth mentioning that using patterned graphene sample leads the PEDOT to grow preferentially on graphene and not on the $SiO_2$/Si substrate. After optimizing polymer thickness, we performed measurements using in-situ Raman spectroelectrochemistry, a method enabling monitoring of the electrical communication between graphene and polymer. The results indicate that both Raman bands of graphene and polymer are significantly affected by the applied voltage, which confirms efficient charge transfer from graphene to PEDOT.

### 4.6.2 Direction-controlled movement of nanoparticles

Another application of the tailored chemical functionalization of graphene is presented in Ref.[33], in which we induced directed motion of nanodiamond particles on the functionalized graphene surface. This involved functionalizing graphene with a 4-aminophenyl group and modifying the nanodiamond particle surface using salicylaldehyde. The amine and aldehyde groups can form dynamic covalent bonds, with the equilibrium given by the environmental pH. Given the nanodiamond particle size was about 30 nm, it could not be tracked by optical microscopy. However, the particles contained nitrogen-vacancy (NV) centers, which exhibit photoluminescence, enabling particles to be tracked despite their small size. The first experiment was designed to confirm the reversible formation of the covalent bond. Therefore, the particles and functionalized surface were immersed in a solution with acidic and basic pH. It has been observed that particles are attached to the surface when a solution has a basic pH and are released when the solution is acidic. The process is reversible, provided that there is not already too much salt in the solution. The next experiment was performed in the buffer solution, with pH adjusted such that the formation and release of the nanodiamond proceeded at the same speed, leading to periodic attachment and detachment of the particle, which, when visualized during the same specific time period, exhibited a Brownian motion. Finally, we performed the experiment in a solution with a linear pH gradient. In this case, the bonds tended to form in front of the particle before being released behind the particle, producing a linear motion.

### 4.6.3 Patterned functionalization of graphene

For more complex applications, it is desirable to functionalize graphene only at specific locations. This can be achieved by lithography when part of the graphene is covered by resist, an approach compatible with current industrial technology and, hence, easy to apply. However, it features certain disadvantages. First, resist should be deposited and then removed; these are potentially costly additional steps that can damage fragile graphene samples. Furthermore, the resist must be selected carefully for compatibility with the wet chemistry used to functionalize graphene. In our work[34], we introduced a resist-free approach to functionalizing graphene at specific locations, an approach based on two competing reactions: first, reducing oxygen groups to pristine graphene, which leads to, second, graphene functionalization or the reduction of oxygen groups. Thus, the graphene sample is first oxidized using oxygen plasma, immersed in a solution of triphenylphosphine and dialkyl azidodicarboxylate. Then, selected areas of the sample are irradiated by UV using a mask. Azidocarboxylates are sensitive to UV light; if irradiated, they decompose. Consequently, they stay intact only in the areas not irradiated, undergoing a Mitsunobu reaction, which promotes graphene functionalization. In the irradiated areas, triphenylphosphine reduces oxygen groups to form pristine intact graphene. Consequently, only the photomasked masked area of the sample is functionalized.

### 4.6.4 Self-assembled structures driven by graphene morphology

Nanomaterial patterns are often either or both difficult and expensive to make on a large scale. An efficient solution is self-assembly of the molecules or polymers, which can allow local and even oriented modification of graphene properties. In Ref.[35] ,we tested the assembly of specially designed oligomers, with the interplay between molecular physisorption and dynamic polymerization at the solid-liquid interface driving the formation of longer chains at the surface with higher rates than in solution.

The physicochemical properties of such assemblies were investigated for different scales on graphene, indicating that reaction and assembly are actually dependent on graphene substrate morphology. Although polymers form in random orientations on squared samples, for graphene stripes, polymer chains tend to align along the graphene stripe axis.

## 5 Conclusions and outlook

Given the technological importance of graphene as a new material, it is desirable to understand how the properties of this material are influenced by external stimuli and how they can be controlled. The electronic properties depend on several such stimuli; thus, graphene reactivity is also influenced by several effects. We have discussed strain, doping, defects, and orientation with respect to substrate, with gaining control of reactivity demonstrated to open multiple pathways for further applications.

On-going and future research should focus on precise control of functionalization. This includes the specific quantity of functional groups and their specific location. Although this research is challenged by both realization and characterization, possible pathways can be suggested based on, for example, localized control of graphene reactivity using nanoobjects.

Current applications of graphene are relatively rare, especially with respect to given previous predictions. This is also the case for chemically exfoliated graphene. Among the explanations for this are problems with the proper characterization of the material and the reproducibility of the desired properties in a large-scale production context. However, we believe that the understanding of reactivity CVD graphene can be transferred to large-scale productions of chemically exfoliated graphene, where proper characterization is a challenge. That is, using knowledge of the behavior of CVD, graphene, and optimized protocols, it is possible to solve these problems.

The knowledge accumulated for graphene functionalization can also be transferred to other 2D materials in some cases. For example, although the reactivity of other 2D materials is already understood to be significantly different, similar principles can be used for external stimulation and the adoption of characterization tools. A disadvantage in the case of other 2D materials is that there is no “D band” enabling easy monitoring of the extent of functionalization. In this respect, using SERS can beneficially allow direct measurement of functional groups. Accordingly, further developments could improve the quantification of functional groups of 2D materials in the SERS context.

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# List of publications that form the basis of the dissertation