2D Chemistry: Chemical Control of Graphene Derivatization

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Supporting Information

ABSTRACT: Controllable synthesis of graphene derivatives with defined composition and properties represents the holy grail of graphene chemistry, especially in view of the low reactivity of graphene. Recent progress in fluorographene (FG) chemistry has opened up new routes for synthesizing a plethora of graphene derivatives with widely applicable properties, but they are often difficult to control. We explored nucleophilic substitution on FG combining density functional theory calculations with experiments to achieve accurate control over the functionalization process. In-depth analysis revealed the complexity of the reaction and identified basic rules for controlling the 2D chemistry. Their application, that is, choice of solvent and reaction time, enabled facile control over the reaction of FG with Nu species, focusing on the solvent effects and possible activation of the C–F bond by electron transfer from a Nu. We also considered possible nucleophilic attack on the solvent and reaction time.

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the strength of the C–Nu bond formed by the reaction. It should be noted that OH\(^{-}\) and CN\(^{-}\) have previously been shown to successfully react with FG.\(^{31,44}\) Besides gas-phase reaction, we also considered four solvents commonly used in syntheses of graphene derivatives from FG,\(^{31,32,34,40}\) that is, tetrahydrofuran (THF), acetone, methanol and N,N-dimethylformamide (DMF). Among them, THF is the least polar and inert with respect to FG. Acetone can promote the reduction of FG\(^{47}\) and has been used as a solvent in the reaction of FG with NaOH.\(^{40}\) Polar protic solvents like methanol can form hydrogen bonds with FG and do not promote the rupture of C–F bonds.\(^{38,49}\) Finally, DMF causes defluorination, which can be initiated via hydrogen transfer to radical sites on FG.\(^{44}\)

Energy profiles of the S\(_{N2}\) reaction of FG with Nu\(^{-}\) in the gas phase were found to significantly differ from those in solvents (Figure 1). Stabilization of the reactants, that is, small anions, in polar environments caused an increase in the energy barrier to about 50 kcal mol\(^{-1}\), whereas in the gas phase, it was significantly lower (about 20 kcal mol\(^{-1}\) for OH\(^{-}\) and NH\(_2\)^{−} and 37 kcal mol\(^{-1}\) for CN\(^{-}\)). After the first transition state (TS1), the reaction proceeded through an intermediate state (IMS), where the departing F\(^{-}\) remains trapped between carbon atoms and neighboring fluorine atoms carrying partial negative charge. To release these F\(^{-}\), the system must overcome another energy barrier (TS2) ranging from 10 to 20 kcal mol\(^{-1}\) in solvent to reach the final state (P). The product of CN\(^{-}\) attack was less stable than those of OH\(^{-}\) and NH\(_2\)^{−} due to their different nucleophilicity (the natural bond orbital (NBO) partial charge on the carbon atom of CN\(^{-}\) is approximately 0.2 e, whereas the charges on oxygen/nitrogen atoms of OH\(^{-}\)/NH\(_2\)^{−} are approximately 1.4 e and 1.6 e, respectively) and the ability of OH\(^{-}\) and NH\(_2\)^{−} to form hydrogen bonds with neighboring fluorine atoms. In the reaction of FG with OH\(^{-}\) in methanol, the protic solvent caused an overall increase in the energy profile. This can be rationalized by the formation of strong hydrogen bonds between the hydroxide anion and methanol, leading to a higher solvation energy of OH\(^{-}\) (92.8 kcal mol\(^{-1}\)) compared with NH\(_2\)^{−} (78.0 kcal mol\(^{-1}\)) and CN\(^{-}\) (63.1 kcal mol\(^{-1}\)).

The presented calculations indicate that the S\(_{N2}\) reaction mechanism cannot fully explain the reaction of FG with nucleophiles. Even for strong nucleophiles, such as OH\(^{-}\) or NH\(_2\)^{−}, the calculated barriers of Walden inversion are too high, in contradiction with the experimentally determined activation barrier of the FG reaction with NaOH in acetone (14 ± 5 kcal mol\(^{-1}\)).\(^{40}\) Lai et al.\(^{39}\) suggested that the defluorination of FG may start by single electron transfer (SET) from a nucleophile to FG, followed by rupture of the C–F bond and creation of a radical site on the carbon atom. Although it has been suggested that C–F \(\sigma^*\) orbitals in perfluorinated polycyclic hydrocarbons can act as electron acceptors,\(^{39,41–43}\) the electron affinity of FG is too low (about 4 kcal mol\(^{-1}\)) to explain the sensitivity of FG to reduction in the presence of mild reducing agents.\(^{14}\)

Considering that the ionization potential of OH\(^{-}\) is 38.7 kcal mol\(^{-1}\), the suggested SET mechanism does not seem to be plausible (see Table S7 in the SI).

Recent studies showed that radical defects exist in FG with enough concentration (of 1 defect per 1000 carbon atoms) to trigger the FG reactivity.\(^{44}\) The graph of reaction energies in Figure 2a shows that nucleophilic attack on radical sites existing on pristine FG\(^{28}\) was energetically favorable in all environments. A polar solvent environment generally caused a decrease in the released energy due to stabilization of the negatively charged Nu species. The amide anion had the largest affinity to FG (\(\Delta E = -60\) kcal mol\(^{-1}\)) in solvent owing to its high nucleophilicity and also the formation of a hydrogen bond between the −NH\(_2\) group and released F\(^{-}\) (structure I.a in Figure S4). On the contrary, \(\Delta E\) for CN\(^{-}\) was only about \(-10\) kcal mol\(^{-1}\). As for S\(_{N2}\) reaction on pristine FG, the stabilization of OH\(^{-}\) in methanol led to a smaller \(\Delta E\) compared with other solvents. In comparison to the S\(_{N2}\) mechanism, the reaction barriers of Nu attack on an FG radical center were much smaller (in DMF, 21 kcal mol\(^{-1}\) for NH\(_2\)^{−}, almost 8 kcal mol\(^{-1}\) for CN\(^{-}\), and ca. 15 kcal mol\(^{-1}\) for OH\(^{-}\); see Figure 3). In the case of OH\(^{-}\), the estimated barrier was in good agreement with the experimental value (14 ± 5 kcal mol\(^{-1}\)).\(^{40}\)

Because the Nu species contributes a negative charge to FG, the neighboring C–F bonds become susceptible to heterolytic cleavage, releasing fluoride anions to the environment (Figure 2b). In all cases, cleavage of a C–F bond on carbon in the ortho position was preferred. Although release of F\(^{-}\) in the gas phase is inconvenient, stabilization of F\(^{-}\) in a polar environment makes the process favorable (with low activation energies; Figure 3 and Figure S5), especially in the case of OH\(^{-}\) and CN\(^{-}\). Even for NH\(_2\)^{−}, the required energy was low in the polar solvent, suggesting that the release of F\(^{-}\) can occur at room temperature. The newly created radical center after F\(^{-}\) detachment can be attacked by another nucleophile. Figure 2c shows that this reaction is also energetically favorable in all environments and follows similar trends as the first attack.

Our results show that the radical centers on FG may play multiple roles in the reactivity of the material, as (i) electron acceptors (in the presence of a sufficiently strong reducing agent),\(^{44,50}\) (ii) triggering points for radical defluorination (if sufficiently stable radicals can be formed),\(^{44}\) or (iii) electro-

![Figure 1. Reaction profiles of the SN2 reaction of fluorographene (a) NH\(_2\)^{−}, (b) CN\(^{-}\), and (c) OH\(^{-}\) in different solvents obtained at the oB97X-D/6-31+G(d,p)/SMD level of theory. (d) Reaction scheme. Carbon atoms, gray; fluorine, green; nitrogen, blue; oxygen, red; hydrogen, white.](image-url)
philic centers for nucleophilic attack (Scheme 1). Scheme 1 shows that whereas paths A and B lead to partial or complete defluorination, path C results in substitution. All three pathways can occur concurrently. However, the different kinetic and thermodynamic parameters of individual steps and their dependence on solvent characteristics enable control over the processes of defluorination and substitution. For instance, reaction of FG with a nucleophilic agent (e.g., NaCN) in an inert solvent (e.g., methanol) under mild conditions should preferentially proceed via path C, resulting in a high content of sp³ carbon atoms in the lattice, whereas the degree of substitution (CN/F ratio) could be controlled by the reaction time. Use of the same nucleophile in a defluorinating solvent (e.g., DMF) leads to Gr-CN with very low content of fluorine, as reported in ref 31. Another option could be to control the topology of functionalization. Namely, instead of using a nucleophile in reducing solvent, as in the previous case, one could start with the reducing phase (without Nu), during which sp² carbon domains would be preferentially formed in the lattice, and then a Nu would be added afterward.

To demonstrate the potential for controlling FG reactivity, we used an amine-group-bearing compound (N-octylamine) as a nucleophile and carried out the reaction in two types of solvents (o-dichlorobenzene (o-DCB) and DMF) using...
variable reaction time. o-DCB was chosen as an inert, that is, nondefluorinating solvent (see the SI), unlike DMF. The progress of reaction of FG with OA significantly differed in the two solvents. In the case of DMF, the reaction proceeded quickly. Within 20 min, the purified FG derivative displayed intense C−H stretching vibrations originating from the attachment of OA aliphatic chains (Figure 4a). After 6 h, the

**Figure 4.** FT-IR spectra of graphene−octylamine derivatives after reaction in (a) DMF and (b) o-DCB, along with spectra of pristine octylamine, graphene, and products from control reactions. C 1s HR-XPS spectra and atomic analysis results (insets) of the graphene-octylamine derivatives after reaction in (c) DMF and (d) o-DCB. (e) Raman spectra of the N-octylamine-functionalyzed FG derivatives after 6 h of reaction in the two solvents.

sp² band in XPS visibly increased, and almost complete defluorination (3.5 at % of F, Figure 4c) occurred. In the case of o-DCB, after 6 h of reaction, a C−H stretching vibration band appeared, but the C−F band was still prominent (Figure 4b) and the F content remained high at 31.5 at % (Figure 4d). The nitrogen content also differed considerably (7.5 and 3.8 at % for DMF and o-DCB, respectively), corroborating the previous results. Slower kinetics of the reaction in o-DCB is in line with the higher activation barrier predicted by the DFT calculations (Figure S6). According to the N content (after subtraction of the N content measured in control reactions, Table S9), the functionalization degree was calculated as 11.4 and 6.5% for the derivatives prepared in DMF and o-DCB, respectively. Apart from the very low F content in the 6 h derivative in DMF, after 20 and 30 min, the F/N atomic content could be further controlled at 21.5:3.7% and 14:5.4%, respectively. The Raman spectra of the 6 h products displayed high I_D/I_G ratios (ca. 1.3 and 1.4 for DMF and o-DCB samples, respectively), which, along with the band broadening, indicated high functionalization degree51 (Figure 4e). Finally, chemical mapping with energy-dispersive X-ray spectroscopy in STEM showed the homogeneous incorporation of N (thus OA) in the flakes, suggesting the production of similarly homogeneous OA-functionalized graphene derivatives (Figure S7). These results clearly demonstrate that the composition of functionalyzed graphenes prepared by FG chemistry can be controlled by varying the solvent and reaction time, opening new doors for fine-tuning the properties of graphene derivatives.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.8b01596.

Further computational details, assessments of model size, basis set, and method, and theoretical and experimental data on the reaction of butylamine with FG (PDF)

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**Notes**

The authors declare no competing financial interest.

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