



# Advantage of graphene fluorination instead of oxygenation for restorable adsorption of gaseous ammonia and nitrogen dioxide



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## ABSTRACT

An interaction of graphene with gaseous molecules increases substantially with grafting of functional groups to its surface. However, in the efficient sensors, such interaction should not be too strong to provide an easy desorption of molecules. Here, we reveal an influence of fluorine and hydroxyl species on the graphene surface on the restorable adsorption of ammonia and nitrogen dioxide, taken as model gases having a different donor/acceptor property. Conductive films of few-layered fluorinated graphene and oxyfluorinated graphene were produced using a one-step process of the exfoliation and partial reduction of corresponding graphite derivatives. The films showed a similar sensitivity on exposure to NH<sub>3</sub> and NO<sub>2</sub>, while the fluorinated graphene-based sensor had much better recovery after a simple argon purging at room temperature. Density functional theory calculations revealed that NO<sub>2</sub> and NH<sub>3</sub> molecules are adsorbed on fluorine and oxygen from a hydroxyl group as well as bare carbon atoms located near the functionalized carbon. The strongest adsorption energy was obtained for an oxy-fluorinated graphene–NH<sub>3</sub> system due to short N···H(O) contacts. Our results show that fluorinated graphene is more perspective for gas sensing as compared to oxygenated graphene due to its higher chemical stability and weaker interactions with the adsorbed molecules.

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## 1. Introduction

Graphene is an excellent platform for gas sensing due to its unique and outstanding properties such as extremely high surface-to-volume ratio and sensitivity to charge transfer from/to adsorbed molecules through a change in electrical conductivity [1,2]. Covalent and noncovalent modifications of graphene alter the conductivity in a wide range and create the adsorption sites for gas molecules. That can drastically improve performance of specific devices [3]. The methods of graphene modification include attachment of functional species such as oxygenated groups [4,5] and fluorine atoms [6,7], introduction of structural defects [8,9] or heteroatoms [10,11] in the network, and hybridization with metal/metal oxide nanoparticles [12,13] and polymers [14]. Depending on the type of modification, the energy of interaction between molecules and graphene layer may vary substantially,

which opens the possibility to obtain sensors with fast adsorption/desorption rates and good selectivity for particular gases [15].

The most intensive attention has been paid to the testing of reduced graphene oxide (rGO), which forms stable dispersions in various solvents and can be used for wafer-scalable thin-film deposition. Oxygen functional groups remaining on the rGO surface act as binding sites for gas molecules and at the same time deteriorate the graphene conductivity. Hence, the number and type of the functional groups should be balanced in order to produce a high-response molecular sensor.

Calculations within the density functional theory (DFT) have shown that carbonyl (–C=O) and hydroxyl (–OH) groups enhance the binding energy and charge transfer for the adsorbed nitrogen oxides [16] and ammonia [17] as compared to those expected for non-modified graphene. Rotations of some hydroxyl groups during the adsorption and desorption of NO<sub>2</sub> molecules would explain a high reversibility of oxygenated graphene sensor [18]. By combining IR-spectroscopy and DFT calculation data Mattson et al. have proposed that epoxide (C–O–C) is the most reactive functional group [17,19]. This group may dissociate when interacting

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with NO<sub>2</sub> and NH<sub>3</sub> molecules with formation of nitrite ion [19] and –NH<sub>2</sub> species [17], respectively. However, other calculations found that for the NH<sub>3</sub> molecule particularly, the hydroxyl group is more attractive than the epoxide [20,21]. The differences in the results may be due to a different size and composition of the computed models. Nonetheless, a strong bonding of analyte molecules with a surface of oxygenated graphene revealed by the DFT calculations could explain a low recovery of some rGO sensors at room temperature [22–24].

Another famous member of the family of graphene derivatives is fluorinated graphene (FG). In contrast to the oxygenated graphene, the FG contains mainly a single type of the functional species, namely, the C–F bonds, which are normally directed to the basal graphene plane [25]. These bonds improve adsorption of NH<sub>3</sub> molecules that provides higher sensitivity of FG sensors compared to the pristine graphene as have been concluded from the DFT and experimental results [26]. We have previously demonstrated that the surface of a hydrazine-treated graphite fluoride is also able to sense the ammonia gas [27]. Such kind of the chemical treatment removes fluorine atoms primarily from the exposed surface [28] and the active sensor sites are the *sp*<sup>3</sup>-hybridized carbon atoms bonded with fluorine atoms located on the backside of graphene layer [27]. Park and co-authors have proposed to modify graphene oxide (GO) by fluorine in order to make ammonia gas sensor, but, all obtained sensors failed to be recovered at room temperature [29].

In the present work, we reveal an influence of oxygen and fluorine functional species on gas sensing performance of chemically modified graphene at comparative study of FG and oxyfluorinated graphene (OFG) thin films. The FG and OFG were produced by a mechanochemical exfoliation resulted in a partial recovering of the parent graphite derivatives and characterized by atomic force microscopy (AFM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The XPS showed that the obtained samples are good systems for the comparative study, because the former graphene sample contained mostly fluorine as a foreign element, while near equal amounts of oxygen and fluorine were found in the latter sample. The sensor response was studied to NH<sub>3</sub> and NO<sub>2</sub> gases, which are problematic air pollutants from industry. These molecules are also complementary model analytes because the change in graphene conductivity upon their adsorption has opposite sign that allows identifying NH<sub>3</sub> or NO<sub>2</sub> in the environment. The tests revealed a superior sensing performance of the FG film with the more balanced sensitivity and recovery behavior. The experimental results were supported by DFT calculations of model structures.

## 2. Experimental section

### 2.1. Material

A starting material for chemical modifications was purified natural graphite from Zaval'evsk deposit (Ukraine). The fluorination of graphite was performed at room temperature using a procedure described elsewhere [30]. Graphite crystallites were placed into a Teflon flask containing liquid bromine to prepare a bromine-intercalated graphite, which then was transferred into another flask with a solution of BrF<sub>3</sub> in Br<sub>2</sub> and kept there for several days. A simultaneous attachment of oxygenated groups and fluorine atoms to graphite layers was achieved using a solution of CrO<sub>3</sub> in liquid anhydrous HF [31]. After one-month reaction at room temperature, the solution was decanted and solid product was repeatedly washed with concentrated HCl to remove chromium salts. Finally, the samples of chemically modified graphite were dried in a nitrogen flow.

For film preparation, fluorinated graphite or oxyfluorinated

graphite powder in an amount of ~0.5 mg was grinded in an agate mortar for 30 min and then dispersed in 10 mL of toluene under sonication (100 W, 35 kHz) for 10 min. Microscopic aggregates were removed by a mild centrifugation. 5 mL of dispersion was sprayed onto a 3 × 5 mm<sup>2</sup> SiO<sub>2</sub>/Si substrate using an air gun system. Small drops were delivered onto substrate preheated to ~110 °C by argon gas with a purity of 99.95% and inlet pressure of 4 bar. The spraying rate was 0.1 mL/min.

### 2.2. Characterization

Samples were structurally characterized by scanning electron microscopy (SEM) on a Carl Zeiss AG – SUPRA 40 microscope and AFM on a Solver Pro microscope (NT-MDT). The AFM measurements were performed in tapping mode using cantilevers NSG10 (NT-MDT) with a tip curvature radius of 6 nm and an average value of the force constant of 11.8 N/m. Raman spectra were obtained on a Spex 1877 triple spectrometer using the 488-nm line from an argon laser. XPS spectra were collected with a Phoibos 150 SPECS spectrometer using a monochromatic Al K $\alpha$  radiation with the energy of 1486.7 eV. The binding energy scale was internally calibrated to the energy 284.4 eV of the 1s line of *sp*<sup>2</sup>-hybridized carbon. The C 1s spectra were fitted using a symmetric Gaussian/Lorentzian product function after subtraction of the background signal by Shirley's method.

### 2.3. Sensor fabrication and testing

A film deposited on SiO<sub>2</sub>/Si substrate was used for device fabrication. Two silver electrodes of a width 5 mm were formed by a silver glue on the top of the film at a distance of ~1 mm from each other. The device was mounted in a test chamber and investigation of gas sensor properties was carried out under nearly practical conditions (atmospheric pressure and room temperature) against ammonia and nitrogen dioxide diluted by argon. More details about the experimental setup are given elsewhere [27]. A change in electrical resistance of the device was monitored when the sensor was periodically exposed to an analyte gas and pure Ar. Resistance was measured using a Keithly 6485 picoammeter at a DC voltage drop of 1 V. The fractional method [32] was employed to compare the changes in the resistance of different devices. The relative response was calculated as the following:

$$\text{Relative response} = \frac{R_g - R_0}{R_0}, \quad (1)$$

the sensor recovery was defined as:

$$\text{Recovery} = \frac{R_g - R_a}{R_g - R_0}, \quad (2)$$

where  $R_0$  is the sensor initial resistance (baseline),  $R_g$  is the sensor resistance after explosion to the analyte gas, and  $R_a$  is the resistance after regenerating the sensor to its original state using pure Ar.

### 2.4. DFT calculations

Calculations were carried out using the three-parameter hybrid functional Becke [33] and Lee–Yang–Parr correlation functional [34] with a dispersion correction developed by Grimme et al. [35,36] (B3LYP-D3 method) in the framework of the Jaguar program package [37]. Atomic orbitals were described by 6–31G<sup>++</sup> basis set with polarization and diffuse functions for all atoms except hydrogen. Initial graphene fragment had a composition of C<sub>80</sub>H<sub>22</sub>, where hydrogen atoms saturated the dangling bonds of the

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