Ultrasensitive Chemical Sensing through Facile Tuning Defects and Functional Groups in Reduced Graphene Oxide

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Supporting Information

ABSTRACT: Herein, we report on a facile, low-cost, and efficient method to tune the structure and properties of chemically reduced graphene oxide (rGO) by applying a transient voltage across the rGO for ultrasensitive gas sensors. A large number of defects, including pits, are formed in the rGO upon the voltage activation. More interestingly, the number of epoxide and ether functional groups in the rGO increased after the voltage activation. The voltage-activated rGO was highly sensitive to NO2 with a sensitivity 500% higher than that of the original rGO. The lower detection limit can reach an unprecedented ultralow concentration of 50 ppb for NO2 sensing. Density functional theory (DFT) calculations revealed that the high sensitivity to NO2 is attributed to the efficient charge transfer from ether groups to NO2, which is the dominant sensing mechanism. This study points to a promising method to tune the properties of graphene-based materials through the creation of additional defects and functional groups for high-performance gas sensors.

Graphene is a promising material for electronic devices due to its unique properties; various exciting applications of graphene have been demonstrated, including gas sensors, biosensors, and energy devices. Generally, graphene-based gas sensors have the advantages of high sensitivity, low-noise level, and low power consumption. However, it remains a challenge to achieve an exceptional sensitivity allowing for the detection of toxic gases at concentrations of a low parts per billion (ppb) level, which are important for industrial, environmental, and military applications.

Previous work has reported that defect sites with oxygen groups in single-walled carbon nanotubes dominated the sensing response and can be used to enhance the sensitivity. Indeed, steam-etched porous graphene oxide (GO) with abundant defect sites, including large vacancies (i.e., holes), has been shown to have more enhanced interactions with NO2, which is a toxic pollutant and has been extensively studied as a model analyte for graphene-based sensing materials. Therefore, tuning the defects and oxygen functional groups in graphene-based materials is a promising method to significantly enhance the sensing response of graphene-based gas sensors.

In this work, we report a facile, low-cost, and efficient method to tune the structure and properties of reduced graphene oxide (rGO) by applying a voltage across the rGO for a short duration in a room air environment (Figure 1a). We found that the rGO was greatly activated by creating more active defects and oxygen functional groups for gas adsorption, and as a result, the sensing performance of rGO was significantly improved. On the basis of our data, the lower detection limit of our voltage-activated rGO to NO2 can reach a very low concentration of 50 ppb, which is much lower than any other rGO-based sensor reported so far. The method also can be used to dope various elements in the graphene basal plane to further expand rGO applications. Density functional theory (DFT) calculations were carried out to understand the

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Figure 1. (a) Schematic illustration of the voltage activation process for rGO in the air. After the voltage-activation process, more defects and oxygen functional groups (epoxide and ether groups) form in the rGO. (b, c) SEM images of rGO before and after the voltage activation, respectively. The scale bars in (b) and (c) are 0.5 μm.
sensing mechanisms of the defects and oxygen functional groups.

**EXPERIMENTAL SECTION**

**Synthesis of rGO.** The rGO was obtained by chemically reducing a diluted commercial single layer GO water dispersion (ACS Material) using our previously reported method. Briefly, H₂NO·HCl (0.5 g) was added into 25 mL of GO dispersion (1 mg/25 mL) and the mixture was continuously stirred at 80 °C for 30 h. The black product was filtered and rinsed by DI water and acetone to obtain rGO powders. Then, the rGO powder was dispersed in N,N-dimethylformamide (DMF) with sonication for 2 h.

**Fabrication of Sensor Devices.** The sensor device was fabricated by drop casting the rGO dispersion onto interdigitated gold electrodes. The gold electrodes were fabricated using e-beam lithography on a silicon substrate interdigitated gold electrodes. The gold electrodes were fabricated by drop casting the rGO dispersion onto the gold electrodes, followed by drying in air, leading to rGO nanosheets bridging the gold fingers. Further annealing was carried out at 200 °C for 1 h in an Ar atmosphere to remove the residual DMF and improve contacts between rGO and gold fingers.

**Voltage Activation Process and Characterization.** Various DC voltages were sequentially applied across the electrodes in air to investigate the rGO structural changes and their influence on the sensing performance. The morphology of the rGO on the sensing devices was characterized by scanning electron microscopy (SEM) (Hitachi S-4800). Transmission infrared (IR) microspectroscopy measurements were performed at the Synchrotron Radiation Center using the Infrared Environmental Imaging (IRENI) beamline to examine the variation of oxygen functional groups in the rGO.

**Sensing Tests.** The rGO sensor device was placed in an airight chamber with electrical feedthroughs. A constant voltage was applied to the device. The variation of resistance was monitored and recorded with the changes in the gas environment using a Keithley 2602 source meter. Typically, a sensing-measurement cycle has three continuous steps: (1) introducing dry air (2 L/min) as a background, (2) then injecting an analyte gas (2 L/min) to register a sensing signal, and (3) introducing dry air (2 L/min) again for sensor recovery.

**Density Functional Theory (DFT) Calculation Method.** To further understand the sensing mechanism, DFT calculations were implemented using OPENMX. The pseudoatomic orbitals (PAOs) within the framework of norm-conserving pseudopotentials were used, and the exchange-correlation functional was treated in the formalism of the local spin density approximation (LSDA) for NO₂. The basic functions were specified by two primitive orbitals of individual s and p orbitals with the cutoff atomic radius of 7.0 in Bohr for all elements considered. A single molecular adsorbate was put in the 3 × 3 supercell composed of a centered rectangular unit cell of graphene, and the layer spacing was set to be larger than 20 Å in order to minimize the interactions between the adjacent layers and between the molecules themselves. A cutoff energy of 200 Ry in real space and a k-point density of 0.02/Å in reciprocal space were used for the numerical integrations. The structural optimizations stopped when the force was less than 0.01 eV/Å between the successive iterations.

**RESULTS AND DISCUSSION**

Figure 1b,c shows SEM images of the same rGO area before and after being activated using step-increasing voltages up to 40 V in a room air environment. The voltage interval was 5 V, and each step lasted for 1 min (Figure S1, Supporting Information). Compared with the original rGO (Figure 1b), the morphology had a significant change with some breakdown regions, as shown in Figure 1c. The locations of the failure area are both near the contact region with gold electrodes and in the middle of the gap, similar to the breakdown locations on current-passing graphene. This sheds light on the breakdown mechanism of Joule heating. It has been reported that abundant defects in GO or rGO are very active upon heating while being exposed to air, resulting in uniformly distributed etch pits throughout the entire flakes. Here, a similar result was obtained in our rGO upon the heating induced by the voltages. The etching is well evidenced by the SEM images in Figure 1. Thermal annealing of rGO could lead to similar products, which was further confirmed through controlled experiments of thermally treating rGO exposed to air using a tube furnace at a temperature of 200–450 °C for a short duration (Supporting Information). According to the SEM images upon the heating experiments (Figure S2, Supporting Information), the edges (white arrows) and central areas (red circles) of rGO were severely etched at 450 °C, leading to a large number of edges and defects. This also can be well observed from SEM images with a higher magnification (Figure S3, Supporting Information).

The electrical properties of rGO were studied before and after the voltage (Vₜ) activation in air (Figure 2). Figure 2a shows the I–V characteristics of rGO after the activation by different Vₜ. The voltages were applied on the rGO sequentially from low to high, and each Vₜ lasted for 1 min. The resistance had a significant change with some breakdown regions, as shown in Figure 1c. The locations of the failure area are both near the contact region with gold electrodes and in the middle of the gap, similar to the breakdown locations on current-passing graphene. This sheds light on the breakdown mechanism of Joule heating. It has been reported that abundant defects in GO or rGO are very active upon heating while being exposed to air, resulting in uniformly distributed etch pits throughout the entire flakes. Here, a similar result was obtained in our rGO upon the heating induced by the voltages. The etching is well evidenced by the SEM images in Figure 1. Thermal annealing of rGO could lead to similar products, which was further confirmed through controlled experiments of thermally treating rGO exposed to air using a tube furnace at a temperature of 200–450 °C for a short duration (Supporting Information). According to the SEM images upon the heating experiments (Figure S2, Supporting Information), the edges (white arrows) and central areas (red circles) of rGO were severely etched at 450 °C, leading to a large number of edges and defects. This also can be well observed from SEM images with a higher magnification (Figure S3, Supporting Information).

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of the rGO gradually increased with the increase of $V_t$. The inset in Figure 2a shows the resistance evolution curve with the rate of resistance increase accelerating at 40 V, which is attributed to the large Joule heating at higher voltages that led to more defects such as holes. For some samples, there was a limited decrease in resistance during the first few voltage applications, followed by subsequent increases in resistance with further voltage application (Figure S4, Supporting Information). The thermally treated rGO (in the air) also showed similar $I$–$V$ characteristics and consistent resistance changes (Figure S5a, Supporting Information). By comparing the curve of resistance versus voltage (inset of Figure 2a) with that of resistance versus temperature (inset of Figure S5a, Supporting Information), we can estimate the critical temperatures of the sample for Figure 2. A combined chart is plotted in Figure S5b, Supporting Information, and according to the related resistance change, it is clear that there is no obvious resistance change until 40 V is applied. Thus, the temperature of the rGO can be estimated to be about 400 °C at 30 V. After 40 V is applied, the rGO can reach about 450 °C, leading to a dramatic resistance increase.

On the basis of previous studies, thermal reduction of GO in an inert atmosphere (argon or vacuum) causes a decrease in resistance.10,14 It is expected that thermal treatment can partially remove the oxygen functional groups from the GO surface, leading to more graphitic areas and a higher electrical conductivity. However, in this work, the conductance changed in an opposite direction (decreased). For example, the original rGO had a resistance of $6.1 \times 10^4 \Omega$, but after activation at 90 V, the resistance increased to $1.4 \times 10^1 \Omega$, which is 3 orders of magnitude higher than the original resistance. Therefore, the structural change of our rGO (including oxygen functional groups and basal plane) is significantly different from conventional rGO after thermal or chemical reduction of oxygen functional groups.

To observe the change in oxygen functional groups, rGO was characterized using IR microspectroscopy before and after the voltage activations. Figure 2c shows the IR absorption spectrum of the original rGO. The band at 1562 cm$^{-1}$ is assigned to the C=C stretch of the graphene lattice, while the band at 1200 cm$^{-1}$ is attributed to the asymmetric and symmetric stretching modes of epoxide groups.24 There are no other significant absorption bands observed in the spectrum. The evolution of the differential IR spectra of the rGO from exactly the same position on the sample following sequential voltage activations is shown in Figure 2d. The bands in the 800–1300 cm$^{-1}$ region can be assigned to residual epoxide and cyclic ether oxygen functional groups. In addition to the assignment of epoxide groups to the 1050–1300 cm$^{-1}$ region,25 previous studies found that edge terminations of cyclic ether groups produced collective modes in the lower frequency (800–1000 cm$^{-1}$ regions).26 While the frequency of these collective C–O–C stretching modes is ultimately determined by the lateral size of the exposed edge (higher vibrational frequency with decreasing edge length), the substantial degree of burning resulting from the voltage activation could easily expose large edge-domain sizes that rapidly become oxidized in the air. As the applied voltage increased from 10 to 100 V, a substantial increase in the intensity of epoxide (1200 cm$^{-1}$) and ether (883 cm$^{-1}$) groups was observed. These data demonstrate that the voltage activation facilitated the formation of oxygen functional groups (epoxy and ether groups) in rGO likely due to the reaction between the oxygen in the air and the carbon atoms of the rGO at a high temperature.17,18 The significant rise of cyclic ether groups also reveals the increase of defects after the voltage activation. On the basis of the above data, the voltage-activation process is proved to be an oxidation process instead of a reduction process commonly observed for the conventional chemical/thermal reduction of rGO.10,19

Although the increase of oxygen functional groups may also cause a resistance increase of rGO due to the effect of sp$^3$ carbon bonds,20 we believe that the additional defects dominate the resistance increase in this work because a dramatic resistance change can only occur with the creation of a large number of defects. This speculation was confirmed through controlled experiments by adding a gradual step-increasing voltage to the rGO until it was completely broken down. Figure S6, Supporting Information, shows the current versus time curve of the sequential voltage application. The rGO resistance did not show an obvious change until the applied voltage reached 15 V, which caused a sudden increase in the electrical resistance. The resistance kept increasing for a voltage up to 20–22 V, and the breakdown occurred at the end of 22 V. The corresponding structure change was captured (Figure S7, Supporting Information). After being maintained at 15 V for 1 min, some defects appeared on the suspending rGO near the contacts with the gold electrodes (Figure S7b and inset, Supporting Information). Considering the sudden increase of resistance, the defects are likely responsible for the dramatic resistance increase. With a higher voltage (20 V), more defects near the electrode contacts were induced (Figure S7c, Supporting Information), leading to another dramatic resistance increase. This defect-induced resistance increase is also consistent with that of thermally treating rGO (Figures S2, S3, and S5a, Supporting Information).

The structural change of rGO also significantly affects its field-effect transistor (FET) properties. Figure 2b shows the evolution of the rGO FET characteristics before and after four $V_t$ activations. We measured the current-gate voltage ($I$–$V$) curve immediately after each $V_t$ activation. To normalize the curves, the $Y$ axis represents the ratio of current ($I$) to the minimum current ($I_{min}$) at Dirac points. The $I/I_{min}$–$V_g$ curves show that the Dirac point gradually shifted from a $V_g$ of ~20 V for the original rGO to a $V_g$ of 0 V for the rGO after being treated with a $V_t$ of 90 V, indicating the removal of the p-doping sources.21,22 Although the oxygen functional groups increased on the basis of the IR data, a large number of other p-doping sources from the air (e.g., physisorbed oxygen molecules) were removed. These p-doping sources strongly induce p-type behavior of rGO even for n-doped rGO.23 Previous studies showed that chemical doping on graphene only rigidly shifts the Dirac point without any significant change in the $V$ shape of the conductivity-gate voltage curve.24 However, the shape of FET curves in Figure 2b becomes sharper and the electron transport is enhanced with the increasing $V_g$, further confirming the removal of extrinsic p-doping sources. Meanwhile, the on/off current ratio ($I_{on}/I_{off}$) increased with the increasing $V_t$, and it can be well fitted by a linear line as shown in the inset of Figure 2b. For narrow graphene or graphene nanoribbons (GNRs), the bandgap ($E_g$) can be estimated by $I_{on}/I_{off} \propto \exp(E_g/k_BT)$ (where $k_B$ is the Boltzmann constant and $T$ is the temperature) and the $I_{on}/I_{off} \propto 1/w$ (w is the width of GNRs).24 In this study, all the FET measurements were conducted at room temperature. Therefore, our results suggest the bandgap of our rGO increases with increasing $V_t$ and can be tuned by the voltage activation. However, further investigation is needed to confirm...
the bandgap tuning. Although the n-type transport in the rGO was enhanced after the voltage activations, the p-type transport was still stronger than the n-type transport, likely due to the intrinsic p-type doping sources (epoxide and ether groups) on the rGO.

Nitrogen dioxide (NO₂) was selected to evaluate the sensing performance of our voltage-activated rGO. The voltage application curves are shown in Figures 3a and S8, Supporting Information. Each $V_t$ was applied for 1 min with a base voltage of 0.5 V. The rGO showed a significant conductance drop after a voltage of 25 V was applied, suggesting the formation of a large number of defects. The sensing performance was evaluated against 100 ppm of NO₂ for the original rGO and the rGO after being activated with $V_t \geq 25$ V. The sensor sensitivity was defined as $S = \Delta G/G_0$, where $\Delta G$ is the change in conductance before and after gas exposure and $G_0$ is the average conductance before the gas exposure. Figure 3b shows the responses of rGO before and after voltage activations. Because of the p-type semiconducting behavior of rGO and the oxidizing NO₂ that can withdraw electrons from rGO, all the sensor devices showed an increased conductivity upon exposure to NO₂. The sensitivity of the original rGO was 36%. For the voltage-activated rGO, however, the sensitivity gradually increased to 180%, which is five times that of the original rGO.

The highest sensitivity corresponded with the highest $V_t$, which was likely due to the highest concentration of defects and oxygen functional groups (Figure 2d). For the original rGO, it took overnight to recover to its initial state; however, the voltage-activated rGO fully recovered within 1 h, which is likely related to the high defect density in the rGO.11 Similarly, the sensitivity of the thermally treated rGO also gradually increased with increasing temperature and longer duration (Figure S9, Supporting Information). The largest increase in the sensitivity occurred in the heating duration from 1 to 2 min at 450 °C, where the resistance had the largest increase with a large number of defects created (Figures S3 and S5, Supporting Information). Furthermore, the defects are very reactive to adsorbed O₂ to form oxygen functional groups (i.e., ether groups).26 Therefore, it is reasonable to conclude that defects with ether groups dominate the sensing response. Moreover, this activated rGO can be used as an enhanced sensing layer in thick rGO film sensors. We thermally treated a thick rGO film (~50 nm) at 450 °C for 2 min in air. It is clear that the top layer was seriously etched with the treatment (Figure S10a,b, Supporting Information). However, the inner layers kept their original status due to the protection of the top layers. The sensing performance of the thick rGO film to 100 ppm of NO₂ shows that the sensitivity was greatly enhanced after the treatment due to the enhancement of the top sensing layer (Figure S10c, Supporting Information). However, the sensitivity is still much lower than that of the single- or few-layer rGO sensors treated under the same condition. The possible reason is that the treated rGO with defects has better semiconducting properties than the original rGO, leading to a better response than that of the original rGO as the conductance channel.

To further investigate the removal of extrinsic p-doping sources through voltage activation, the same device (after voltage activation of 35 V) was exposed to a room air environment for 2 weeks to adsorb p-type doping sources from the air. It was found that any short exposure of rGO to the room environment lead to dramatic p-type doping.27 In addition, electrical properties of the device were characterized (Figure S11a,b, Supporting Information), and the sensing response of the device to 100 ppm of NO₂ was measured. It was found that the sensitivity further increased to about 200% (Figure S11c, Supporting Information). The adsorbed p-type doping sources are very likely responsible for this increase in response. Furthermore, the recovery time of the device was prolonged to overnight. To remove the dopants, a voltage of 35 V was applied to the rGO again for 1 min to activate the removal of p-dopants without significant modification of the rGO structure. Because the voltage had already been applied to the rGO once, part of the rGO was burned, accompanied by the increase of resistance. Here, with the same voltage and a much lower current passing through the rGO, the relatively small Joule heating can only lead to the desorption of some physisorbed p-doping sources without further burning the rGO. Indeed, the electrical conductivity of the device increased due to the recovery of graphitic areas (Figure S11a, Supporting Information). The desorption of p-type dopants also caused the Dirac point to shift negatively (Figure S11b, Supporting Information), which is consistent with the results in Figure 2b.

The voltage activation can also significantly enhance the lower detection limit of rGO sensors. Figure 3c shows the responses of an rGO sensor before and after voltage activations (up to 28.6 V) upon exposure to different concentrations of NO₂.
respectively. The lower detection limit reported here is 50 ppb, which is superior to other high-performance rGO-based NO$_2$ gas sensors. For example, the calculated lower detection limits of rGO conjugated with Cu$_2$O nanowires and chemically modified rGO are 64 and 70 ppb, respectively. The lower detection limit reported here is even comparable with the calculated lower detection limit of single-walled carbon nanotubes (SWNTs) to NO$_2$ (44 ppb). The same sensor was exposed to 1 ppm of NO$_2$ for multiple successive cycles as shown in Figure S12, Supporting Information. Consistent sensing responses were observed, indicating the excellent repeatability of our sensor. However, the sensor needs a relatively long time to recover to its initial state, leading to a baseline drift. This is likely due to the relatively strong binding between the sensing material and the gas molecules, and an inert gas or UV light can facilitate the recovery. The baseline drift of the sensing curve can also be suppressed with a longer recovery time (Figure S12, Supporting Information).

The same rGO was treated in an Ar atmosphere to examine the effect of activation atmosphere on the oxygen functional groups, stimulated defects, and gas sensing performance. Since the Ar atmosphere is an inert environment, it is anticipated that oxygen functional groups on rGO could be effectively reduced by the electrothermal heating without significantly damaging the graphene basal plane. Indeed, the electrical conductivity of the rGO had a significant increase before partial breakdown occurred (here at 20 V for this device) due to the recovery of the graphitic basal plane (Figure 3e), which is different from the case in a room air environment. After the partial breakdown at 20 V, the resistance of the rGO greatly increased. The morphology was observed after the complete breakdown at 30 V. It was found that narrow cracks in rGO only appeared in the middle of the electrode gap (Figure S13, Supporting Information). Therefore, the defect area was smaller than that for the rGO exposed to air. The sensing performance was measured against 100 ppm of NO$_2$ after each treatment step. The sensing results (Figure 3f) show that the sensitivity started at 10 V, suggesting a substantial structure change in the rGO after being treated with V$_f$ > 10 V. However, the sensor had a slow recovery process, likely due to the irreversible NH$_3$ molecule dissociation at defects. This experiment suggests a facile method to dope graphene with selected dopants (e.g., N, S, and Cl) in a designed gas environment through voltage activation.

To show a typical example, the NH$_3$ atmosphere was selected to dope N in the rGO using our voltage activation method. The same voltage-activation process was carried out in a gas environment of pure NH$_3$ instead of air. Each voltage treatment lasted for 1 min, and the electrical properties were measured after the treatments under N$_2$ protection to examine the doping effect (Figure 4a,b). As shown in Figure 4b, the original rGO showed highly p-type semiconducting behavior and the Dirac point was at a V$_g$ much higher than 40 V. However, after activation at 20 V, the Dirac point negatively shifted to a V$_g$ of −20 V and the rGO showed a very weak p-type transport but a strong n-type transport, indicating the successful N doping in the rGO. To further confirm the N-doping, the same rGO was voltage treated using the same process in a pure N$_2$ atmosphere. However, the Dirac point remained at a positive V$_g$ until the device reached breakdown (Figure 4d).

It is well-known that gas molecules tend to adsorb to sites with a larger binding energy. For each type of adsorption site (e.g., ether groups) on the rGO, the Langmuir equation can be adopted to estimate the coverage $\theta_i$ at equilibrium:

$$\Delta R/R = \theta_i$$
Article

The optimized structures are shown in Figure 5 for different adsorption sites and allowed to relax until it reaches the simulation, a single gas molecule is placed near the adsorption site. The characteristic frequency of gas molecules with mass \( m \) can be expressed as a function of binding energy \( E_b \), i.e., the defects only appear with oxygen groups on them in the air environment.26 From eqs 1 to 3 for 1 ppm of NO2 diluted in air at room temperature, we found that the coverage is 0.92 for NO2 on the ether groups, 0.541 for NO2 on the aromatic carbon atoms and 0.371 for NO2 on the epoxide groups. Compared with the coverage of 0.016 \( \times 10^{-2} \) for NO2 adsorbed on the aromatic carbon atoms and 4.65 \( \times 10^{-3} \) on the epoxide groups, ether groups in rGO are very reactive and can greatly enhance the adsorption of NO2. Together with the experimental results, we can conclude that the ether groups dominate the sensing response to NO2. The enhanced sensitivity of NO2 is due to the potential charge transfer from the ether to NO2 with the oxygen atoms in NO2 pointing toward ether, which is unlike the case of forming the NO3 complex between NO2 and carbonyl at the edge of rGO or between NO2 and oxygen atoms at the surface of metal oxides.34,35

\[
\theta = \frac{K_{cc} C_g}{1 + K_{cc} C_g}
\]

(1)

and

\[
C_g = \frac{P_g}{P_{air}} C_{air}
\]

(2)

where \( P_g \) is the partial pressure of the target gas; \( P_{air} \) is the air pressure; \( C_{air} \) is a constant (2.9 \( \times 10^4 \) m\(^{-3}\)) for air at room temperature; \( K_{cc} \) is the equilibrium constant that is defined as the ratio of the classical adsorption rate constant \( K_{cc} = (k_b T/2\pi m)^{1/2} \) to the classical desorption rate constant \( K_{dc} = \omega_g \exp(-E_g/(k_b T)) /2\pi \), where \( \omega_g = \gamma(2E_g/m_g)^{1/2} \) is the characteristic frequency of gas molecules with mass \( m_g \) and \( k_b \) is the Boltzmann constant; and \( \gamma \) is the fitting parameter in the Morse potential. The exact value of \( K_{cc} \) depends on \( \gamma \) from fitting the Morse potential; however, \( \gamma \) has been fitted to be around 1.5 Å\(^{-1}\) for gas adsorption on different sites, and \( K_{cc} \) can thus be expressed as a function of binding energy \( E_{b,i} \) alone with a high accuracy,

\[
K_{c,i} = \frac{K_{cc}}{K_{dc}} \approx \frac{k_b T}{E_{b,i}} \exp\left(\frac{E_{b,i}}{k_b T}\right) \times 1.2 \times 10^{-10} \text{m}
\]

(3)

To obtain the binding energies and to further understand the sensing enhancement by the voltage activation, DFT calculations were performed for gas adsorption on sp\(^2\) carbon, ether groups, epoxide groups, and defects without oxygen. For the simulation, a single gas molecule is placed near the adsorption site and allowed to relax until it reaches the minimum potential. The optimized structures are shown in Figure 5. The binding energy of a single gas molecule is calculated as \( E_b = E_{G,O} + E_{g} - E_{G,O,gas} \), where \( E_{G,O} \), \( E_{g} \), and \( E_{G,O,gas} \) are the energies of the rGO, the isolated gas molecule, and the rGO-gas system. The results show that the binding energy is 0.371, 0.212, and 0.545 eV for NO2 adsorbed on the sp\(^2\) carbon, the epoxide group, and the ether group, respectively. For the defects, NO2 will be dissociated into NO molecule and atomic O atoms bonded to the dangling C atom forming carbonyl (Figure S16, Supporting Information). However, the defects are very reactive to dissociate the O2 molecules into ether groups for the lowest energy structures; i.e., the defects only appear with oxygen groups on them in the air environment.20 From eqs 1 to 3 for 1 ppm of NO2 diluted in air at room temperature, we found that the coverage is 0.92 for NO2 on the ether groups. Compared with the coverage of 0.016 \( \times 10^{-2} \) for NO2 adsorbed on the aromatic carbon atoms and 4.65 \( \times 10^{-3} \) on the epoxides, ether groups in rGO are very

![Figure 5. Top (upper panel) and side (lower panel) views of gas adsorption on different sites of rGO: (a) NO2 on sp\(^2\) carbon, (b) NO2 on ether groups, and (c) NO2 on epoxide groups in rGO. The yellow, red, and light blue balls represent carbon, oxygen, and nitrogen atoms, respectively.](image)

### CONCLUSIONS

In summary, transient high voltage activation on rGO can deeply remove extrinsic p-doping sources from air, increase oxygen functional groups (epoxide and ether groups), and create a large number of defects in rGO, leading to significant changes in electrical properties of rGO such as electrical conductivity and FET behavior. Compared with the original rGO, the voltage-activated rGO shows significantly enhanced sensing responses to both NO2 and NH3. The lower detection limit of the voltage-activated rGO to NO2 can reach an ultralow concentration of 50 ppb. The ether groups are primarily responsible for the ultrahigh sensing response to NO2. The method also can be used to dope various elements (e.g., N, S, and Cl) in rGO. This study suggests a facile and effective method to fabricate high-performance graphene-based gas sensors through in situ modulation of rGO properties using transient voltages.

### ASSOCIATED CONTENT

#### Supporting Information

More experimental details, SEM images, electrical properties, and sensing responses. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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