Artificial Olfactory System for Trace Identification of Explosive Vapors Realized by Optoelectronic Schottky Sensing

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Explosives detection-related terrorist attack has become a major threat to the homeland security and social stability, and thus the exploration of reliable detection methods toward trace explosives is of great urgency.[1] Up to now, much efforts have been made in the field of trace explosives detection, such as ion mobility spectrometry method,[2] fluorescent method,[3] and gas sensing method.[4–7] Among them, the detection of vapor-phase explosives has the merits of noncontacting and simple sampling. Nanosensors have emerged as powerful strategies for the detection of trace explosive vapors due to the large surface-to-volume ratios and high reaction activities.[5,6,8] As a representative example, our group demonstrated the fabrication of a silicon nanowires (SiNWs) array/TiO2/reduced graphene oxide (rGO) Schottky sensor working in dark, which utilizes Schottky barrier height (SBH) modulation to realize the ultrasensitive detection toward nitroexplosive vapors but suffers a relatively long time for responding and recovering (≈120 s).[7] Furthermore, an inherent limitation of an individual nanosensor is the weak recognition ability and high misinforming chance due to the limited specific binding property and myriad species of targeted analytes.[8,9] Hence, the real-time, supersensitive, and recognizable detection of explosive vapors remains a severe challenge.

The best way to realize trace vapor recognition is mimicking the natural nose, such as a superbioelectronic nose that mimics the human sense of smell, can not only realize odorant discrimination but also reach a superhigh sensitivity of 0.1 femtomole (fM) toward the target odors.[11] Thus, if an artificial olfactory system could be facilely constructed, the ultrasensitive and selective odor sensing system for the detection of explosive molecules will be promisingly realized. Array of cross-reactive sensors is usually utilized to construct an artificial olfactory system.[6,10,12–14] Although selective detection has been partially achieved with array of sensors, complex surface modification or tedious chemical synthesis steps are always necessary in the fabrication,[10,15] which result in high cost and complicated sensing structure. What is more, the stability of the sensory array is always a stubborn problem since each sensor may encounter device fault. It would be extremely attractive if the fabrication of a sensory array can be realized by only employing one sensor.

Optoelectronic sensing shows great advantages when compared with the other gas sensing method, due to that light can be used to regulate the density of charge carriers and the molecular desorption process, nominally, the light enhanced response value[16] and light accelerated recovery process.[14,17] Thus, a sensory array based on a single optoelectronic sensor could be built by regulating the light intensity. In order to build a single optoelectronic sensor realized sensory array, three items are needed: (1) the component sensor should be very sensitive to explosive vapors; (2) the sensor should have quick and varied photoresponse under different light illumination; and (3) the sensor illuminated with a specific light intensity should be semiselective to realize molecule identification. However, up to now, no one has any trial on it and it remains a significant challenge to realize the instant detection and discrimination toward explosive vapors by an individual sensor.

We demonstrate here the development of a rapid, ultrasensitive artificial olfactory system based on an individual optoelectronic Schottky junction for the discriminative detection of explosive vapors, including 2,4,6-trinitrotoluene (TNT), dinitrotoluene (DNT), paranitrotoluene (PNT), picric acid (PA), hexogen (RDX), urea, black powder (BP), and ammonium nitrate (AN). The rationale behind this approach is that an optoelectronic SiNWs/ZnO/rGO Schottky sensor, which possesses ultrasensitivity toward explosive vapors, rapid photoelectric response, and light intensity modulated sensing response, has been adopted to realize the function of a sensory array, rather than using a common Schottky sensor operating in dark. The practical application chance was verified by the excellent anti-interfering performance and the preliminary semiquantitative identification ability. Therefore, a rapid, supersensitive, and recognizable method by a single sensor to detect explosive vapors is explored, which will make the real-time detection of explosive vapors in practical occasions come true.

The SiNWs/ZnO/rGO Schottky junction-based optoelectronic sensor was fabricated by the steps shown in Figure S1 (Supporting Information). SiNWs were employed for optoelectronic Schottky sensing due to the ultrafast and sensitive light responding characteristics,[18] good response toward explosive vapors, and the sufficient gaps for target molecules diffusing. The highly ordered and vertically aligned SiNW array with a length of ≈10 µm was first obtained by wet etching (Figure 1a).
To further enhance the light-induced electron–hole separation efficiency, the specific surface area, and molecular adsorption capability, ZnO nanoparticles (NPs), which have been proven to show sensitive response to different species including nitro-explosives and improvised explosives,[5,10,13] were modified on the SiNWs/rGO Schottky device. ZnO NPs with an average size of 3–5 nm were grown both on top and around the body of the SiNWs (Figure 1b; Figure S2a, Supporting Information). The corresponding powder X-ray diffraction (XRD) of SiNWs decorated with ZnO NPs is depicted in Figure S2b (Supporting Information). Although the peak intensities of ZnO are weak due to the small amount, it can still prove the formation of wurtzite ZnO.[19] From the high-resolution transmission electron microscopy comparison (Figures S3 and S4, Supporting Information), a distinct interface between the single-crystalline SiNW and the wurtzite ZnO NPs can be observed. RGO sheets were then transferred onto the top of the SiNW array to form the top electrode (Figure 1c; Figures S5a and S6, Supporting Information), one can see that the semitransparent rGO sheets lie tightly on the top of the ZnO NPs decorated SiNW array, the uniform and compact contact is beneficial for carriers transporting. The intensity ratio (I_D/I_G = 1.11) of D band (=1351 cm⁻¹) over G band (=1592 cm⁻¹) in the Raman spectrum of rGO film shows an increase compared to that of graphene oxide (GO) (I_D/I_G = 0.91), indicating the reduction of GO after the hydrothermal and annealing processes (Figure S5b, Supporting Information).[20] Finally, a Schottky sensor was fabricated and could either work in dark (Figure S1d, Supporting Information) or under light illumination (Figure S1e, Supporting Information).

As shown in Figure S7 (Supporting Information), the typical I–V curve of the sensor in air exhibits a nonlinear behavior, with forward/reverse current ratio of ~466 at ±10 V, implying the successful formation of Schottky barrier between the decorated SiNW array and rGO sheets. It should be noted that the high forward/reverse current ratio can be largely own to the rGO sheet transfer method, which ensures the uniform and compact contact between rGO and the array. Thus, a more efficient Schottky junction was built compared to our previous SiNWs array/TiO₂/rGO Schottky sensor which uses the spin coating method.[7] Here, reverse bias is defined as negative voltage applied to the rGO sheets. The I–V characteristic of a Schottky device can be expressed by the thermionic emission model[21]

\[
I = I_s \left[ \exp\left(\frac{qV}{\eta kT}\right) - 1 \right]
\]

\[
= A A^* T^2 \exp\left( - \frac{\Phi_B}{kT} \right) \left[ \exp\left(\frac{qV}{\eta kT}\right) - 1 \right]
\]

where \(I_s\) is the reverse saturation current, \(q\) is the electronic charge, \(A\) is the contact area, \(A^*\) is the effective Richardson constant, \(\eta\) is the diode ideality factor, \(T\) is the absolute temperature, \(\Phi_B\) is the SBH, and \(k\) is the Boltzmann constant. From the I–V curve plotted in logarithmic scale (Figure 1d), and using the measured contact area of 7.2 × 10^{-5} m² and \(A^*\) values of 32 A cm⁻² K⁻²[22] for ZnO, \(\eta\) and \(\Phi_B\) were calculated to be 1.82 and 0.719 eV, respectively,[23] which are in close agreement with the reported result.[24] At the SiNWs/ZnO/rGO interface, the electrons have to overcome the energy barrier at a reverse bias and the reverse current highly depends on SBH (exponential relationship).[21,25] In other words, the current is dominated by SBH and the Schottky barrier plays an important role. Even a small change in SBH, such as the adsorption of TNT molecules, would lead to a huge response in current.[26]
The sensing properties of the SiNWs/ZnO/rGO Schottky sensor toward explosive vapors were first evaluated in dark condition. Figure S8 (Supporting Information) displays the current curve of the sensor upon exposure to room-temperature saturated vapors of TNT, DNT, PNT, PA, RDX, Urea, BP, and AN in dark condition with a −1 V bias. Five successive gas sensing cycles were repeated and the response of each cycle keeps nearly at the same value, indicating the excellent repeatability and stability of the sensor. The current of the sensor changed quickly once it was put into the explosive vapor due to the SBH modulating after the adsorption of the explosive molecules. In detail, the current of the sensor decreases immediately once it is exposed to RDX and BP vapors, and can recover to the initial value quickly once it is put back into air, while the current increases once it is exposed to any of the other six explosive vapors. For comparison, the saturated vapor pressure of the above-mentioned explosives at room temperature is shown in Table S1 (Supporting Information), and the structural formulas and ingredients are shown in Figure S9 (Supporting Information).

The response values toward five nitroexplosives TNT, DNT, PNT, PA, and RDX are 4.4%, 12.1%, 19%, 7.5%, and −10.6%, respectively. While for Urea, BP, and AN, the response values are 21.7%, −20.4%, and 25.6%, respectively (Figure 1e). Since the saturated vapor pressure of PNT (647 ppb) is much higher than that of TNT (9 ppb), DNT (411 ppb), and PA (0.97 ppb), the response value toward PNT at the same concentration is much smaller. Via the simulated relative electron withdrawing and electron-donating abilities (Figure S10, Supporting Information), it is obvious that TNT, DNT, and PA show much stronger electron withdrawing ability than PNT. Thus, it is considered that with the increase of the number of nitro groups, the electrostatic interaction between the target molecules and rGO is greatly enhanced, leading to a stronger change of SBH, the electrostatic interaction between the target molecules and rGO, thus, light illumination lifts the Fermi level of rGO and lowers the barrier height. As a result, a new ΦB = ΦB + ΔV would be established, and it varies with the change of the light intensity. Thus, the varied SBH under different light intensities can be used to modulate the sensing response afterward.

To evaluate the influence of the adsorption of different explosive vapors on the transport characteristics of the sensor, the I–V curves of the sensor in eight vapors were recorded and the corresponding η and ΦB were calculated (Figure S11, Supporting Information). The estimated SBH in eight saturated vapors are listed in Table S2 (Supporting Information). The SBH changes for TNT, DNT, PNT, PA, RDX, Urea, BP, and AN are −0.02, −0.03, −0.01, −0.02, 0.02, −0.04, 0.01, and −0.04 eV, respectively. That is to say, the adsorption of TNT, DNT, PNT, PA, Urea, and AN lowers the SBH, while the other two raises it.

Another two important factors for the evaluation of the gas sensing performance are the response time and recovery time. The average response time and recovery time of the sensor toward eight saturated vapors are all less than 5 s (Figure 1f), manifesting a rapid sensing behavior. This rapid sensing characteristic could be attributed to the successful formation of the efficient Schottky junction improved by the rGO sheet transfer method, which facilitates the fast charge carrier transporting. As a result, the rather high sensitivity, rapid response and recovery characteristics and the good reproducibility together make the SiNWs/ZnO/rGO Schottky sensor very suitable for explosive vapors detection and promising for real sensing applications.

It is worth noting that the periodic photoresponses of the sensor under 468 nm monochromatic light-emitting diode (LED) with different light intensities at −1 V show a highly stable characteristic (Figure 2a). The photocurrent of each cycle keeps consistent with each other. The SiNWs/ZnO/rGO Schottky junction yields a significant photocurrent change with the increase of the light intensity. Both the rise time and decay time are confirmed to be less than 0.4 ms (Figure 2b), indicating the ultrafast photorespose, which could make the instant sensing come true. I–V curves of the sensor under illumination exhibit rectifying behavior (Figure 2c), implying that the Schottky barrier maintains well with light illumination.[29] The inset shows the amplified I–V curves of the reverse bias, indicating that the reverse photocurrent is very sensitive to the light intensity. Based on the I–V characteristics, the Schottky junction structure can suppress the recombination of light-induced electron–hole pairs. On the other hand, the sub-band states behave as the intermediate band for holes injection from SiNWs to ZnO,[32] and the injected holes are completely collected by the sufficient accessible states opened up by the Dirac cone of rGO,[33] thus, light illumination lifts the Fermi level of rGO and lowers the barrier height. As a result, a new SBH (ΦB = ΦB + ΔV) would be established, and it varies with the change of the light intensity. Thus, the varied SBH under different light intensities can be used to modulate the sensing response afterward.

The optoelectronic sensing properties of the sensor toward saturated vapors of TNT, DNT, PNT, PA, RDX, Urea, BP, and AN were evaluated under periodic illumination with different light intensities at room temperature (Figure 3a; Figure S12, Supporting Information). Compared with the photocurrent of the sensor in air (Figure 2a), the photocurrent in explosive vapors under the same light intensity changes obviously. For example, the photocurrent in air at 8 W m−2 is ≅−550 nA, while those in the vapors of TNT, DNT, PNT, PA, RDX, Urea, BP, and AN are ≅−559, ≅−580, ≅−770, ≅−615, ≅−450, ≅−633, ≅−530, and ≅−650 nA, respectively. Besides, the photoresponses in explosive vapors are rapid and stable. Figure 3b displays the sensor responses toward eight explosive vapors with the increase of the light intensity. It can be obviously observed that the responses for TNT, DNT, PNT, PA, Urea, and AN are positive, while those for RDX and BP are negative, which is consistent with the response behaviors in dark condition. Meanwhile, the response highly depends on the light intensity and the
response change trends with light are different from one vapor to the other. For BP and DNT, with the increase of the light intensity, the response decreases, while for RDX, the trend is opposite. For the rest five vapors, the responses increase first and then decrease. As shown by Figure 3c, it should be noted that the final response is not absolutely determined by the varied SBH ($\Phi_B$) induced by light illumination with different light intensities. The energy band diagram of the Schottky junction under light illumination. $E_{c1}$, $E_{v1}$, and $E_g1$ are the conduction band, the valence band and energy bandgap of ZnO, respectively; $E_{c2}$, $E_{v2}$, and $E_g2$ are the conduction band, the valence band and energy bandgap of Si, respectively; $E_{f}(\text{Gr})$ is the Fermi level of rGO, $\Phi_B$ is the Schottky barrier height, $V_R$ is the reverse bias, $\Delta'$ is the decrease of SBH induced by light illumination with a fixed intensity. The red surface on the Dirac cone of graphene denotes the holes injected from ZnO; Application of a reverse bias raises $E_f(\text{Gr})$ and opens up a large number of accessible states that can be occupied by photoexcited holes injected from ZnO under illumination.[30] $E_{sb}$ is subband state in ZnO.

As shown in Figure S13 (Supporting Information), one should note that the response values calculated from the eight groups of optoelectronic responses under dark are almost the same with the values directly measured in Figure 1e. Therefore, the present optoelectronic sensing method based on the photoresponse is highly reliable. Furthermore, since the response value of the sensor is different between each light intensity, the sensor working under the illumination of a specific light intensity is equivalent to an independent sensing element in the olfactory system. Therefore, the sensory array can be built by simply changing the light intensity illuminated on an individual sensor. The principal component analysis (PCA) of the above sensing responses shows well-separated clusters of each explosive vapor (Figure 3d), and thus each one

Figure 2. Time-dependent photoresponse of the sensor a) measured by periodically turning on and off a 468 nm monochromatic LED light at a bias of $-1$ V (light intensity ranging from 1–8 W m$^{-2}$, respectively) and b) showing both a rise time and a decay time of 0.4 ms under 468 nm light (6 W m$^{-2}$) at a bias of $-1$ V. c) The corresponding $I$–$V$ characteristics of the sensor (inset: the enlarged curves at reverse part). d) Variation of $\Phi_B$ and $V_{oc}$ at different light intensities. e) The energy band diagram of the Schottky junction under light illumination. $E_{c1}$, $E_{v1}$, and $E_{g1}$ are the conduction band, the valence band and energy bandgap of ZnO, respectively; $E_{c2}$, $E_{v2}$, and $E_{g2}$ are the conduction band, the valence band and energy bandgap of Si, respectively; $E_{f}(\text{Gr})$ is the Fermi level of rGO, $\Phi_B$ is the Schottky barrier height, $V_R$ is the reverse bias, $\Delta'$ is the decrease of SBH induced by light illumination with a fixed intensity. The red surface on the Dirac cone of graphene denotes the holes injected from ZnO; Application of a reverse bias raises $E_f(\text{Gr})$ and opens up a large number of accessible states that can be occupied by photoexcited holes injected from ZnO under illumination.[30] $E_{sb}$ is subband state in ZnO.
can be distinguished clearly. Considering the excellent recognition ability toward different vapors via cross-selective sensing elements building and data processing, the function of an artificial olfactory system is undoubtedly realized.

In real world, there exists varied gases that may intervene the sensing performance. Herein, four common species, NO₂, NH₃, ethanol, and relative humidity (RH) were selected to test the sensor’s recognition ability. The optoelectronic sensing properties toward 50 ppm NO₂, 50 ppm NH₃, 50 ppm ethanol, and 100% RH are shown in Figure 4a and Figure S14a–c (Supporting Information), respectively. The responses toward the interfering gases have the same order as those toward nitro-explosives. For example, the sensing responses toward NH₃ range from −10% to −43%, while those toward RDX range from −7.3% to −18.5% and those toward PA range from 5% to 38%.

Since all the concentrations of NO₂, NH₃, and ethanol in the test are 50 ppm, which are much higher than those of explosives and the concentrations of NO₂, NH₃, and ethanol in daily life, the sensor is less susceptible to be intervened by NO₂, NH₃, or ethanol. However, the photoresponses in the 100% RH air are quite unstable and irregular (Figure S14c, Supporting Information). In other word, the sensor can be easily disturbed by the high RH. Thus, from the perspective of practical application, special measures should be adopted to eliminate humidity. The sensing responses toward NO₂, NH₃, ethanol (Figure S14d, Supporting Information) and sensing responses toward eight explosive vapors are analyzed together using PCA (Figure 4b), in which one can see that all the species can be obviously distinguished except AN, NH₃, and ethanol. An enlarged PCA in Figure S15 (Supporting Information) shows that these three species also separate well with each other. It is known that the variation of the amount of oxygen at the surface of a gas sensor could remarkably influence the sensing performance. However, the present test was conducted in air with standard atmospheric pressure rather than in a vacuum environment, thus, the influence of oxygen to the sensing performance can be ignored and will not affect the practical application of the sensor. These results prove that the optoelectronic sensory array based on an individual sensor is reliable and can be used to recognize the explosive vapors.

Although the above tests have been done on the same sensor; however, they are not simultaneously conducted. Besides, in the practical sensing case, the concentration of explosives will not be a certain value, most likely far below the saturated vapor pressure. In order to realize the real-time recognition of a specific explosive vapor regardless the concentration by an individual sensor, a typical military explosive PA (100%, 25%, and 50% of the saturated value) and typical improvised explosive BP (100%, 25%, and 75% of the saturated value) were used as examples to conduct a tentative exploration. The optoelectronic sensing under eight light intensities were simultaneously done in one test (Figure S16, Supporting Information, and Figure 4c) and the photoresponses under the same light intensity were repeated three times. The corresponding response of each atmosphere was calculated and plotted in Figure S17 (Supporting Information). Both of the
response values increase with the increase of the vapor concentration under a certain light intensity, which is consistent with the common gas sensing principle. It should be noted that the obtained results (Figure S18, Supporting Information) and the datum in Figure 3c are synchronized, which proves that the execution of real-time test is feasible.

Twelve clusters were obtained with excellent separation in the PCA plot and the clusters for PA and BP with different concentrations line up separately (Figure 4d). As a result, with the help of PCA diagram, the present optoelectronic sensory array can not only distinguish different saturated explosive vapors but also tentatively estimate the approximate concentration of a certain explosive by the location of the cluster, namely the semi-quantitative detection. As a result, the function of a sensory array can be realized on an individual optoelectronic sensor just by periodically changing the illuminated light intensity. And when it is exposed to an unknown species, via PCA analysis, the rough concentration of the vapor can be determined if the unknown vapor is in the database.

Here, the time period is limited by our experimental setups (minimum sampling period 0.2 s). However, the time period can be as short as ms level according to the rise and decay time of our sensor. As a result, the entire recognition time of the present optoelectronic sensor to semiquantitatively detect a recorded explosive vapor with unknown concentration can be within one second.

In conclusion, a supersensitive, real-time sensory array based on an optoelectronic SiNWs/ZnO/rGO Schottky sensor is demonstrated, representing the exploration of a new principal artificial olfactory system. The very sensitive character to explosive vapors, quick and varied photoresponse, as well as the semiselective characteristic at varied light illumination of the optoelectronic Schottky sensor, together facilitate the realization of a sensory array with a single sensor. The sensor is capable of sensitive, qualitative, and semiquantitative detection toward vapor phase explosives with concentrations below their room-temperature saturated vapor pressure. Although it is still a proof-of-concept study, we envisage that this method will become a new trace detection paradigm and hold new opportunity for the detection of other hazardous chemicals and biological toxicants in the near future.

**Experimental Section**

**Chemicals:** AN, 2,4-dinitrotoluene (DNT), PNT, PA, and urea were purchased from Sigma-Aldrich. TNT, RDX, and BP were obtained from the National Security Department of China. Graphite powder (SP-1 grade 325 mesh) was purchased from Bay Carbon Inc. All other chemicals were of analytical grade and used without further purification.

**Pretreatment of Si Wafers:** (100)-oriented n-Si wafers (N-doped, $\rho = 1–10 \ \Omega \ cm$) were cut into rectangular strips and sequentially cleaned with acetone, ethanol, a Piranha solution (98% $\text{H}_2\text{SO}_4$/30% $\text{H}_2\text{O}_2$, v/v = 3/1), deionized water, and diluted hydrofluoric acid (HF) solution.

**Wet Etching Process:** The synthesis of SiNW array was conducted in a Teflon-lined stainless steel autoclave. The autoclave was filled with etching HF solution (4.6 μ) containing silver nitrate (0.02 μ) up to 80%
of its total volume. The cleaned silicon strips were then immediately immersed into the etching solution and treated at 50 °C for 1 h. After the etching progress, the obtained samples were rinsed in nitric acid to remove the silver. The resulting samples were then thoroughly rinsed with deionized water and dried by N₂ blowing. Then, oxygen plasma treatment of SiNW array was carried out in a plasma cleaner to form enough hydroxyl groups.

**Decoration of ZnO Nanoparticles (NPs):** First, to grow ZnO seeds, the SiNW array was wetted with a droplet of 0.005 M zinc acetate in ethanol, rinsed with clean ethanol after 10 s, and then blown dry with a stream of N₂. This step is repeated five times. Then the SiNW array is heated to 350 °C in air for 30 min. Second, to grow ZnO NPs, zinc acetate dihydrate (0.01 M) was dissolved in methanol (25 mL) under vigorous stirring and heated at about 60 °C. Subsequently, a 0.03 M solution of KOH (13 mL) in methanol was added dropwise at 60 °C. Then the SiNW array was immersed into the solution and the reaction was maintained for 2 h at 60 °C. The reaction was repeated twice. Then the ZnO NPs decorated SiNW array was rinsed with ethanol and deionized water and dried by N₂ blowing.

**RGO Top Electrode Fabrication:** First, GO was synthesized using a modified Hummers’ method and diluted into a concentration of 1 mg mL⁻¹. Second, the GO solution was spin coated at 3000 rpm onto a monocrystalline Si/SiO₂ substrate (oxide layer thickness: 500 μm) to form GO films. Subsequently, GO films were further dried by placing them in a vacuum oven at 80 °C for 3 h, and then were reduced by hydrazine vapor at 40 °C for 1 h. Then, ≈300 nm thick polymethyl methacrylate (PMMA, Sigma-Aldrich) was coated on Si/SiO₂/rGO followed by annealing at 180 °C for 2 h to dry the PMMA film. Successively, SiO₂ was etched away in 2 M NaOH solution at 70 °C, and the PMMA-supported rGO film was obtained. After that, the PMMA/rGO film was transferred onto the ZnO NPs decorated SiNW array and carefully dried with N₂ gas. Then, the SiNWs/ZnO/rGO film was dried at 80 °C for 5 min and followed at 145 °C for 45 min before the top PMMA film was etched with aceton. Finally, the obtained SiNWs/ZnO/rGO Schottky junction was annealed at 400 °C in N₂ for 3 h before the sensing device fabrication.

**Characterization:** Field-emission scanning electron microscope (FESEM, ZEISS SUPRA 55VP) and transmission electron microscope (JEM-2011 TEM, 200 kV) were used to characterize the morphology of the samples. XRD measurement was conducted using powder XRD (Bruker D8 Advance, with Cu Kα radiation operating at 40 kV and 40 mA, scanning from 2θ = 20° to 80°). The powder was obtained by scraping the ZnO NPs decorated SiNWs from the Si substrate. Raman spectrometer system (RTS-B, Titan Electro-Optics Co., LTD), with an effective power of the laser source (532 nm) and integration time of about 20 mW and 5 s, respectively, was used to characterize the Raman shift of GO and rGO.

**Device Fabrication, Electrical Properties, and Gas Sensing Properties Testing:** The top contact was produced by depositing an Au film and connecting a copper wire with silver paste. The back ohmic contact was then formed by depositing an Ag film on the back side of the silicon substrate. The photoductive response, gas sensing properties, and I–V curves were recorded by a Controlled Intensity Modulated Photo Spectroscopy (CIMPS-2, ZAHNER) system under a 468 nm monochromatic LED light. The saturated explosive vapors were obtained following the procedure below. Briefly, a 50 mL quartz tube with plug was filled with 0.5 g solid explosive powder and equilibrated for 48 h to ensure saturation. For gas sensing test in the dark, the sensor was inserted into the saturated vapor of the explosive. After the sensor current reached a new constant value, the sensor was then inserted into a same quartz tube full of air to recover the sensor. The gas sensing test under light illumination is based on the photoresponse curves in air and in the explosive vapor.

Here, we define the relative sensor response in current as \( \frac{(I_{\text{vapor}} - I_{\text{air}})}{I_{\text{air}}} \times 100\% \), where \( I_{\text{vapor}} \) and \( I_{\text{air}} \) are the currents of the sensor in explosive vapor and in air, respectively (definition is same both in dark condition and under light illumination).

The response time is defined as the period in which the sensor response reaches 90% of the maximal response value upon exposure to the explosive vapor, while the recovery time is defined as the period in which the sensor response comes back to 10% of the maximal response value after the explosive vapor is removed.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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