

Logic Control of Interface-Induced Charge-Trapping Effect for Ultrasensitive Gas Detection with All-Mirror-Image Symmetry

Chuancheng Jia, Qing Wang, Na Xin, Jian Zhou, Yao Gong, Lidong Li, Qiang Sun, and Xuefeng Guo*

Controlling the type and concentration of charge carriers is at the heart of modern electronics because of its importance to realize functional devices for potential applications in broad areas ranging from integrated circuits and energy conversion to catalysis and chemical/biological detection. Toward this objective, here a straightforward design of a high-performance stimuli-responsive hybrid optoelectronic device with high-level mirrorimage symmetry is presented. The device consists of suspended pristine graphene that is in direct contact with photoactive TiO₂ quantum dots. Through a combination of photoexcitation and gate regulation, two types of photoinduced free electrons trapped at the TiO₂/graphene interface with different behaviors are identified, allowing logical control of both the carrier type and charge trapping/detrapping process. Such control leads to the TiO₂-decorated graphene displaying high chemical environment sensitivity. Upon exposure of the photoexcited hybrid device to different gases, such as O₂ as an electron acceptor and NH₃ or H₂ as an electron donor, all-mirror-image sensing with controllable fast response rate and ultralow detection limit in a single optoelectronic device is established. This approach offers novel interface engineering insights to develop highperformance multifunctional environmental/chemical sensors and other optoelectronic devices.

1. Introduction

Solid-state optoelectronic sensors can be widely used for both light sensing over the broad spectral range from the UV-visible to the infrared region and the detection of trace chemical and biological agents in natural environments or warfare attacks.^[1,2] Because of these potential civilian and military applications, they are becoming a central part of modern science. Many nanocircuit-based sensors incorporating different nanostructures as sensing elements, such as nanobelts/ nanowires,^[3-6] carbon nanotubes,^[7-9] nanoparticles,^[10,11] nanopores,^[12] and nanoclusters,^[13] have been successfully developed. Advantages of such sensors include high sensitivity, low production cost, miniature size, and integrability. Recently, there has been an explosion of interest in the use of graphene-like nanomaterials in new nanoscale biosensors.^[14-28] However, because of the inert and nonselective surface of graphene, intrinsic impurities or defects on graphene and specific strong

C. Jia, Q. Wang, N. Xin, Y. Gong, Prof. X. Guo Beijing National Laboratory for Molecular Sciences State Key Laboratory for Structural Chemistry of Unstable and Stable Species College of Chemistry and Molecular Engineering Peking University Beijing 100871, P.R. China E-mail: guoxf@pku.edu.cn J. Zhou, Prof. Q. Sun, Prof. X. Guo

Department of Materials Science and Engineering

School of Materials Science and Engineering

University of Science and Technology Beijing



to realize the sufficient sensing performance, especially for a pure graphene layer.^[14,21,23,25] For example, Schedin et al.^[14] demonstrated the detection of individual events of a gas molecule attaching onto and detaching from a graphene surface. This single-molecule sensitivity might result from unintentional functionalization with the residual polymer auxiliary adsorption layer, as demonstrated by a later study, which proved that a thermal cleaning process led to a decline in sensitivity of two orders of magnitude.^[15] In addition, recent experiments confirmed that graphene grain boundaries can substantially enhance device sensitivity to adsorbed gas molecules (≈300 times).^[23] Cumulatively, all previous experimental reports and theoretical works^[29,30] indicate that graphene-based sensors require specific functionalization to achieve desired functionality or to detect target analytes with high sensitivity and selectivity.

interactions with target analytes are needed for these devices

Two general approaches to achieve desired functionalities are covalent and noncovalent modification of graphene surfaces. The low reactivity of graphene means that only a few chemical

DOI: 10.1002/admt.201600067

College of Engineering

Beijing 100083, P.R. China

Peking University Beijing 100871, P.R. China

Prof. L. Li



reactions, such as hydrogenation, diazonium chemistry, cycloaddition, photochemistry, and fluorination, are suitable to modify its electronic properties.[31-33] Covalent modification results in the transition of the graphene carbon atoms from sp² to sp³ hybridization, leading to partial impairment of the planar π -conjugation and consequently mechanical or transport properties of graphene.^[34,35] In contrast, noncovalent functionalization is a less invasive process, preserving the primary sp² hybrid structure of graphene and thus its remarkable conductance and mechanical properties. Pristine single-layer graphene (SLG) is highly desirable as a basic building block to produce future nanoelectronics because of its unique characteristics.[36-38] First, SLG is a 2D defect-free crystalline monolayer made of sp²-hybridized carbon atoms arranged in a honeycomb lattice, and exhibits ballistic ambipolar transport with low resistivity, high chemical stability, and low noise level. Through the combination of gate modulation and chemical doping, it is possible to control the type and concentration of charge carriers in graphene to tailor SLG transistor performance.^[21,39] Second, SLG has the simplest chemical composition and a 2D atomic bonding configuration that maximizes the surface-to-volume ratio of graphene. Each carbon atom on the surface of SLG is exposed to the environment and any tiny changes of the environment could cause drastic changes in its electrical properties, thus forming the basis for new types of sensors and optoelectronic devices.^[14,24,25,38] Third, SLG is

(a)

(b)

entirely composed of carbon atoms, and can be easily micro/ nanofabricated on a large range of substrates. All these features strongly promote the use of pristine SLG as an active material in high-quality optoelectronic devices for switching and sensing applications.

In this work, we present an optimized design to prepare high-performance stimuli-responsive optoelectronic devices from suspended pristine SLG decorated with photoactive TiO₂ quantum dot (QD) thin films (Figure 1a). TiO2 has been extensively investigated because of its widespread use in photocatalysis and many other applications.^[40-42] The unique feature of TiO₂ thin films that we utilize here is that UV irradiation generates free electrons (e^{-}) and holes (h^{+}) as active centers on the TiO₂ QD surface. Relevant to our design are the studies that use TiO₂ and graphene mixtures to improve the photocatalysis and energy conversion performance.[43-45] In particular, we and others have recently investigated photoinduced carrier manipulation with inorganic QDs to improve and/or fine-tune the electrical properties of carbon nanomaterial-based transistors.^[17,19,46,47] In the current investigation, we examine the interesting electrical behaviors of TiO2-decorated SLG as an efficient optical switch with an all-mirror-image sensing effect. The developed switch is able to detect typical oxidizing O₂ gas

www.MaterialsViews.com



Figure 1. a) Left: Schematic demonstration of a multifunctional TiO₂/graphene hybrid transistor, where a suspended graphene flake is coated with TiO₂ QDs; Right: The exposure of TiO₂ QDs to light and ambient gases can affect the conductance of subjacent graphene. b) SEM image of a typical suspended graphene device with TiO₂/graphene in pink color and gold electrodes in yellow color. c) High-resolution TEM image of a 5 nm thick TiO₂ QD film with the corresponding TiO₂ lattice parameters marked out, *d*_{rutile} (101) = 2.48 Å and *d*_{anatase} (004) = 2.38 Å. d) AFM image of a 5 nm thick TiO₂ film on graphene.

molecules with minimum detection limit (MDL) of ~10 ppm at a response time of ~14 s and typical reducing NH₃ gas molecules with MDL of ~5 ppm at a response time of ~15 s, which are better or comparable with previous reported graphene based sensors.^[26–28] More importantly, we reveal the intrinsic trapping/detrapping processes of different carriers at the TiO₂/ graphene interface in combination with photoexcitation, gas exposure, and gate modulation, thus setting an invaluable foundation for designing future high-performance sensors.

2. Results and Discussion

Conventional nonsuspended pristine graphene transistors were fabricated by the combination of a peel-off technique and electron-beam (e-beam) lithography on a heavily doped silicon wafer substrate with a 300 nm thick layer of thermally grown silicon oxide (Figure S1, Supporting Information).^[21] Raman spectroscopy was used to confirm that the pristine SLG used has the well-preserved structure of single-layer sp^2 hybrid carbons (Figure S1c, Supporting Information).^[48] To eliminate substrate-induced perturbations on the sensing and electronic properties of graphene,^[49–51] we fabricated suspended SLG



(Figure 1b) by wet chemical etching through a window precursor patterned by another e-beam lithographic step (see the Experimental Section for details). Before resist lift-off, we deposited a 5 nm thick TiO₂ thin film on the graphene surface by e-beam thermal evaporation. High-resolution X-ray photoelectron spectroscopy (XPS) revealed characteristic Ti 2p and O 1s peaks (Figure S2, Supporting Information), indicating the successful assembly of TiO₂ on SLG. High-resolution transmission electron microscopy (TEM) and atomic force microscopy (AFM) investigations indicated that these thin films were composed of numerous anatase or rutile TiO₂ nanoparticles with a diameter of less than 5 nm^[52,53] (Figure 1c,d). Of these two crystalline forms of TiO2, rutile is the most stable phase, but both pure anatase and anatase mixed with rutile possess superior optoelectronic and photochemical properties;[41,54] therefore, the observation of these phases is a harbinger of the useful optoelectronic properties described below. To rule out potential artifacts from Schottky barrier modification between TiO2 and metal electrodes, we defined TiO₂ thin films to separate them from metal electrodes (Figure S1, Supporting Information). In a typical SLG device after removing resist (Figure 1b), the graphene layer was suspended from the source-drain leads, which ran across the sample and at the same time provided structural support for graphene.

To conduct reliable measurements, we designed and produced a sealed black box with a quartz window for light stimulation, three channels for gas flow, and multiple connectors for electrical characterization (**Figure 2**). The black box has a small chamber to allow rapid gas exchange, which is crucial to perform precise sensitivity measurements. Using this custommade testing platform, we were able to simultaneously expose the devices being tested to two or more external stimuli, such as light and gas. The devices were incorporated into the black box through a simple wire-bonding method (Figure 2b). Before sensing measurements, we purged the black box with a stream of N₂ gas to remove any trace of air or O₂ from the chamber.

The responses of the devices to different conditions of UV light and gases were first studied by measuring their gatedependent characteristics (**Figure 3**a). For the device operated in the dark under an inert N₂ atmosphere, typical ambipolar characteristics of pristine graphene with the Dirac point at \approx 40 V were observed, which implies slight p-doping of graphene. This



Figure 2. a) Schematic design drawing for light and gas sensing measurements with the hybrid transistor. b) Optical image of the home-made measurement system with the device connected by a wire-bonding method (inset).

www.advmattechnol.de

mainly originates from the p-type chemical doping effect of TiO₂ QDs assembled on graphene,^[21] which was further confirmed by a theoretical calculation (Figure S3, Supporting Information). Interestingly, when the device was exposed to UV light ($\lambda = 254$ nm, $\approx 50 \mu$ W cm⁻²), the Dirac point of the gate-dependent curves showed a marked left shift to ≈0 V (Figure 3a). This shift is attributed to the electron doping effect of photoexcited TiO₂ QDs to graphene at the TiO₂/graphene interface (Figure 3b). The left inset of Figure 3c shows that when photoinduced free electrons are injected into p-type graphene, the Fermi level of graphene rises. Through a firstorder exponential fitting, the change of the Dirac point shift as a function of UV light exposure time was calculated, giving a response time (τ) of \approx 44.0 s (Figure S4a, Supporting Information, and Figure 3c), which is defined as the time needed to reach 63.2% of the final state.

When the UV light was switched off, the device reverted back to its initial state with a recovery time (τ) of \approx 334.9 s (Figure S4b, Supporting Information, and Figure 3c). This means that trapped electrons in graphene transferred back to the TiO₂ QDs, thus lowering the Fermi level of graphene (right inset of Figure 3c). Control experiments using suspended graphene devices lacking TiO₂ QDs showed no obvious change in either Dirac point or drain current under UV light (Figure S5, Supporting Information). This confirms that the photoactivity of the TiO₂ QDs is responsible for the photoswitching effect observed above. Therefore, it is concluded that by switching UV light on and off, we are able to reversibly control the charge trapping/detrapping processes at the TiO₂/graphene interface.

To understand the underlying switching mechanism of the $TiO_2/graphene$ devices, their responses to UV light switching under an inert N_2 atmosphere at different gate voltages (V_G) were studied. For an n-type channel ($V_G \ge 20$ V) with electron carriers, a considerable increase of electron current was observed upon UV light exposure, and reversible photoswitching occurred upon switching UV light on and off (top of Figure 3d and Figure S6, Supporting Information). These responses indicate that a reversible electron trapping and detrapping process occurs at the $TiO_2/graphene$ interface. In contrast, for a p-type channel ($V_G \le 10$ V) with hole carriers, a large reversible decrease of hole current occurred during UV light irradiation (bottom of Figure 3d and Figure S7, Supporting

Information). In addition, the changes of both electron and hole currents are gate-independent (Table S5 and Figure S9, Supporting Information). This observation is different from the case by directly photoexciting the graphene layer, where the changed energy level of graphene can affect the intrinsic photoinduced electron–hole generation processes in graphene.^[55] These results reveal a mirror-image symmetrical photoswitching effect in a single ambipolar device, which is rare.

To investigate the states of trapped electrons at the photoexcited $TiO_2/graphene$ interface, the recovery of the photoexcited devices to their initial state was analyzed. The back-conversion processes fitted a





Figure 3. a) Gate-dependent characteristics of a typical TiO₂/graphene device under different conditions. Black: in the dark with an inert N₂ atmosphere; Red: under UV light illumination with an inert N₂ atmosphere; Blue: under UV light illumination and upon exposure to O₂; Green: under UV light illumination and upon exposure to NH₃. $V_D = 100 \,\mu$ V. b) Schematic diagram of the working principle under UV light illumination, showing that the photogenerated electrons can be transferred from TiO₂ QDs to the graphene channel. c) Dynamic processes of the Dirac point shifts for the device exposed to UV light (red) and further stored in the dark (blue) under an inert N₂ atmosphere. d) I_D -time plots for a representative device under an inert N₂ atmosphere with alternate treatments of UV light (red) and in the dark (azure) at gate biases of 45 V (top) and 0 V (bottom), which lead to the n-type and p-type graphene conducting channels, respectively. $V_D = 100 \,\mu$ V.

second-order exponential relationship for both n- and p-type systems, showing that the release of photoinduced trapped electrons from the TiO₂/graphene interface involves distinct rapid and slow processes. For an n-type channel with $V_{\rm G}$ > 20 V, the fast process had a response time (τ) of about ≈ 30 s and displayed little variation as a function of $V_{\rm G}$; τ of the slow process shortened with increasing $V_{\rm G}$, ranging from \approx 34 to \approx 229 s (Figure 4a and Table S1, Supporting Information). Based on these results, it is considered that some of the trapped electrons on graphene are strongly coupled with the remaining holes in the TiO₂ QDs, thus leading to their rapid recombination with holes in a bias-independent process, as shown in the inset of Figure 4a. The remaining trapped electrons are dispersed in graphene with weak coupling with holes in the TiO₂ QDs. Because they are confined in the graphene layer by a gate electric field, these electrons are released to the TiO₂ QDs more slowly under a stronger gate electric field. Similarly, for the p-type channel with $V_{\rm G}$ < 10 V, a gate-independent fast recombination process with a response time of about ≈ 30 s, which results from release of trapped electrons that are strongly coupled with holes in the TiO₂ QDs, and a gate-dependent slow process with τ from \approx 318 to \approx 1187 s, were observed (Figure 4b and Table S2, Supporting Information). In comparison with the case in the n-type system, the latter value is much bigger. This is because with increasingly negative V_G, more positive charges will accumulate in the graphene layer and retard the release of trapped electrons from graphene to the TiO₂ QDs. Such gatedependent effects on trapped electrons also exist in the electron injection processes (Table S3, Table S4, and Figure S8, Supporting Information).^[56] As a consequence, these two types of trapped electrons behave differently at the TiO₂/graphene interface, thus rendering the TiO₂-decorated graphene with high chemical environment sensitivity in the following studies. In addition, both p-type and n-type systems displayed the high photodetecting performance, such as responsivity (*R*) of 1.1×10^5 A W⁻¹ (p-type) and 7.9×10^4 A W⁻¹ (n-type), quantum efficiency (η) of 5.7×10^7 % (p-type) and 4.0×10^7 % (n-type), and photogain (*G*) of 2.3×10^9 (p-type) and 4.4×10^8 (n-type).

In combination with photoexcitation that helped to populate carrier traps at the TiO₂/graphene interface, these functional devices were also very sensitive to chemical environment. When a photoexcited TiO₂/graphene device was exposed to oxidative gas molecules, such as O₂, the gate-dependent curves displayed a reversible right shift of the Dirac point, which reached ≈ 20 V (Figure 3a blue). The change in Fermi energy of SLG can be calculated from the magnitude of the Dirac point shift by using Equation: $\Delta E_F^{\text{SLG}} = \text{Sign}(\Delta V_G)\hbar v_F(\alpha \pi |\Delta V_G|)^{1/2}$, where α is gate capacitance (7.1 × 10¹⁰ cm⁻² V⁻¹) and v_F is the Fermi velocity of the carriers (1 × 10⁶ m s⁻¹). Therefore, O₂ adsorption on photoexcited TiO₂ QDs shifts the Fermi level of graphene to higher energy by ≈ 0.136 eV. This should be attributed to the electron-withdrawing effect of O₂, which leads to hole doping in

www.advmattechnol.de



www.MaterialsViews.com



Figure 4. Dynamic simulations for a photoexcited device in the electron detrapping process, which fit a second-order exponential relationship [a) at $V_G \ge 20$ V for the n-type channel; b) at $V_G \le 10$ V for the p-type channel]. Insets show two types of distinct trapped electrons, which have different interactions with the remaining holes in TiO₂ QDs.

the system and reduces trapped electrons at the TiO₂/graphene interface. In contrast, for a photoexcited device upon exposure to reductive gas molecules, such as NH₃, the gate-dependent curves exhibited a further reversible left shift of the Dirac point to \approx -30 V (Figure 3a green), which led to the shift of the graphene Fermi level to lower energy by \approx 0.168 eV. This is caused by the electron-donating effect of NH₃, which increases the concentration of trapped electrons at the TiO₂/graphene interface.

For O_2 sensing in the presence of UV light, the reversible hole doping effect of O_2 molecules can be detected in plots of current as a function of time for the device upon alternating exposure to O_2 and inert N_2 gases. A large reversible decrease of electron current upon O_2 exposure for the n-type channel and an opposite increase of hole current for the p-type channel were observed for the TiO₂/graphene system (**Figure 5**a), thus representing another mirror-image symmetrical response. Control experiments in the dark using the same device indicated that it had negligible response to O_2 gas (Figure S10, Supporting Information), demonstrating that UV light is a prerequisite for gas detection. Therefore, it can be inferred that the electrical response of the photoexcited TiO₂/graphene hybrid devices results from O2 molecules adsorbed at the photoinduced electron sites on the TiO2 QDs.^[57] Because of the strong oxidability of O_2 molecules, the adsorbed O_2 can capture electrons from the TiO₂/graphene system and then reduce the photoinduced trapped electrons at the TiO2/graphene interface (inset of Figure 5b), thus leading to a decrease of electron current and increase of hole current in the same device. This observation is also corroborated by the calculated electronic density of states (E-DoS) spectra of both TiO₂/graphene and O₂/TiO₂/graphene systems (Figure 5b), which confirm that O_2 adsorption causes electron loss in the graphene channel and shifts the Dirac point of graphene to higher energy by ≈ 0.68 eV. More specifically, in the model $O_2/TiO_2/graphene$ system, each adsorbed O_2 molecule can withdraw 0.56 electrons from the TiO₂/graphene system, 0.44 electrons from graphene, and 0.12 electrons from each (TiO₂)₃ QD, thus resulting in O₂ having a hole doping

effect on the system. The dynamic processes during O₂ sensing and subsequent N2 purging of a photoexcited device were analyzed by applying a first-order exponential fitting to the corresponding $I_{\rm D}$ -time plots in Figure 5a according to $I_{\rm D} = A + Be^{-(t-t0)/\tau}$. For both n- and p-type operations (Table 1), the short τ for O₂ exposure (\approx 14.0 s for n-type operation and \approx 29.8 s for p-type operation) and long recovery time for subsequent N2 purging (≈493.9 s for n-type and ≈182.2 s for p-type operation) indicate that the O_2 adsorption rate is much faster than that of O_2 desorption. Furthermore, the O₂ adsorption rate under n-type operation is faster than that under p-type operation, and the O₂ desorption rate under n-type operation is slower than that under p-type. These results indicate that the O2 adsorption in an n-type system is stronger than that in a p-type one, which can be logically attributed to the enhanced affinity of the n-type channel with more gate-induced negative charges for O2 adsorption, and the weakened affinity for O2 adsorption of the p-type channel with more gate-induced positive charges.

With such controllable O2 adsorption strength on the photoexcited TiO₂ QDs, the O₂ sensitivity of both n- and p-type systems was investigated. After the TiO₂/graphene device was stabilized under UV light irradiation in N2 under either n- or p-type operation, the concentration of O2 gas exposed to the photoexcited device was gradually increased (Figure 5c,d). Following each O₂ exposure, the device was thoroughly purged with N₂ to recover its initial state. For both n- and p-type systems, linear electrical responses to O2 gas were found over nearly the full concentration range (40 ppm-100% for the n-type system and 0.5%-100% for the p-type), as illustrated in the insets of Figure 5c,d. Based on the change of current upon O_2 exposure, the ratios of the current changes (ΔI_D %) as a function of O_2 concentration (V_{O2} %) were fitted with the equation $\ln(\Delta I_D\%) = a + b \ln(V_{O2}\%)$, where *a* and *b* are intercept and slope of the fitted line. A slope of ≈0.235 was obtained for the n-type system with strong O₂ adsorption. This value is lower than that for the p-type system (≈ 0.902) with weak O₂ absorption. This suggests that for the same change in O₂ concentration, a larger variation of device current will occur for the p-type system, which in turn helps to enhance the sensitivity of the devices to O2 at a high concentration range. Using three times the







Figure 5. a) I_D -time plots for a photoexcited TiO₂/graphene device upon alternate exposure to O₂ (purple) and inert N₂ gases (cyan) at gate biases of 45 V (top, n-type) and -40 V (bottom, p-type). $V_D = 100 \ \mu$ V. b) E-DoS spectra for the TiO₂/graphene system with and without absorbed O₂ molecules on TiO₂ QDs. Inset shows the p-doping effect of O₂ absorption in the O₂/TiO₂/graphene system. O₂ concentration-dependent spectra for the hybrid device with c) the n-type channel ($V_G = 45$ V) and d) the p-type channel ($V_G = -40$ V) under UV irradiation. Insets show the linear fitting of the device response to oxygen concentration: Left: $\ln(\Delta I_D\%) = -0.833 + 0.235 \ln(V_{O2}\%)$ ($R^2 = 0.9944$); Right: $\ln(\Delta I_D\%) = -1.492 + 0.902 \ln(V_{O2}\%)$ ($R^2 = 0.9946$), respectively. $V_D = 100 \ \mu$ V.

standard deviation of the initial conductance as the minimum detection limit (MDL), MDLs of ~0.1% O₂ for the p-type system and 10 ppm O₂ for the n-type system were conservatively estimated, which lead to the conductance changes that are larger than the noise level (~0.4 nA). Therefore, a lower O₂ detection limit was realized for the n-type system than the p-type one, which should be attributed to the strong O₂ adsorption of the n-type system. These values are higher than or comparable with those obtained for high-temperature metal–oxide semiconductor sensor platforms.^[58] Because of the controllable O₂ absorption strength of the developed TiO₂/graphene devices, both high sensitivity and low detection limit for O₂ gas sensing can be realized.

For NH₃ sensing in the photoexcited $TiO_2/graphene$ system, because of the electron-donating effect of NH₃, a reversible increase of electron current for the n-type system and decrease of hole current for the p-type channel were realized upon NH₃ exposure (**Figure 6**a). These changes are opposite to the case of O₂ sensing. Therefore, an inverse mirror-image symmetrical response to NH₃ molecules was obtained for the TiO_2/gra phene device compared with that for O₂ sensing. In addition, in the E-DoS spectrum of a $TiO_2/graphene$ system with NH₃ molecules adsorbed on TiO_2 , the Dirac point of graphene shifted to lower energy by ~0.07 eV (Figure 6b). This indicates that the NH₃ adsorbed on TiO₂ has an electron doping effect. In the model NH₃/TiO₂/graphene system, an adsorbed NH₃ molecule could donate 0.13 electrons to the TiO₂/graphene system; that is, graphene accepts 0.25 electrons with 0.12 electrons donated from each (TiO₂)₃ QD. Therefore, it is reasonable to conclude that the response of the photoexcited TiO₂/graphene device should be attributed to NH₃ adsorption on the photoinduced hole sites of the TiO₂ QDs (inset of Figure 6b).

The dynamic processes of NH₃ sensing and subsequent N₂ purging in the photoexcited TiO₂/graphene system were also found to obey a first-order exponential relationship. The fitted dynamic parameters (**Table 2**) indicated that the average NH₃ adsorption rate of the n-type system (\approx 140.0 s) was slower than that of the p-type system (\approx 15.4 s), while the desorption rate under n-type operation (\approx 248.9 s) was faster than that under p-type (\approx 350.1 s). These observations are reasonable because NH₃ adsorption in the TiO₂/graphene system can be effectively controlled with p-type positive charges enhancing NH₃ adsorption, which is opposite to the case of O₂ detection. Control experiments using a TiO₂/graphene device in the dark and a graphene device without TiO₂ QDs under photoexcitation demonstrated

Table 1. Response lifetimes (τ) for the photoexcited TiO₂/graphene system upon alternate exposure to O₂ and N₂ gases.

τ[s]	τ_{1-O2}	τ_{1-N2}	τ_{2-O2}	τ_{2-N2}	$\tau_{3.O2}$	τ_{3-N2}	$ au_{avg-O2}$	$ au_{avg-N2}$
n-type	13.99	415.5	15.99	583.3	12.04	482.9	14.01 ± 1.61	493.9 ± 68.9
p-type	31.05	250.9	29.15	162.5	29.05	133.2	29.75 ± 0.92	182.2 ± 50.0





Figure 6. a) I_D -time plots for a photoexcited TiO₂/graphene device upon alternate exposure to NH₃ (blue) and inert N₂ (cyan) gases at gate biases of 45 V (top, n-type) and -40 V (bottom, p-type). $V_D = 100 \ \mu$ V. b) E-DoS for a TiO₂/graphene system with and without absorbed NH₃ molecules on TiO₂ QDs. Inset shows the n-doping effect of NH₃ absorption in the TiO₂/graphene system. c) NH₃ concentration-dependent spectrum for a photoexcited device with the n-type channel ($V_G = 45 \ V$). Inset shows the linear fitting of the device response to NH₃ concentration: $\ln (\Delta I_D \%) = -0.697 + 0.346 \ln(V_{NH3}\%)$ ($R^2 = 0.9946$). $V_D = 100 \ \mu$ V. d) Schematic representation of a full mirror-image symmetrical sensing pattern of the TiO₂/graphene system under different operations. The central section shows twofold mirror-image symmetrical operations: dark (dark tone)—UV light (brilliant hue) and n-type gating (orange)—p-type gating (blue). The outer section shows fourfold mirror-image symmetrical operations in combination with photoexcitation: n-type gating (black solid line)—p-type gating (black dashed line), O₂ treatment (+O₂, purple solid line), and NH₃ treatment (+NH₃, blue solid line)—no NH₃ treatment (-NH₃, blue dashed line). Among these operations, in general the device with the current increase is marked with "1" and the device with the current decrease is marked with "0." Specifically, in the case of the operations without both O₂ and NH₃ treatments, the device current keeps constant. In comparison with their surrounding cases, we mark the n-type device (n-type-O₂-NH₃) with "0" and the p-type device (p-type-O₂-NH₃) with "1," respectively.

that both devices could reversibly respond to NH_3 gas and recover in N_2 atmosphere with a similar mirror-image symmetrical relationship (Figures S11 and S12, Supporting Information). These phenomena result from the intrinsic adsorption of NH_3 molecules on graphene and/or TiO_2 QDs.^[14,59] However, comparing the dynamic parameters of the control and TiO_2/gra phene systems (Table 2 and Table S6, Supporting Information) reveals that UV light excitation of TiO_2 QDs can speed up both the adsorption and desorption processes of NH_3 in the $TiO_2/$ graphene system, and thus is required to lower the detection limit and enhance the response rate of NH_3 sensing. To balance the speeds of reversible adsorption/desorption responses, we then performed concentration-dependent NH_3 detection experiments using an n-type photoexcited TiO₂/graphene device by alternately introducing NH₃ gas with sequentially increasing concentration from 10 ppm to 100% and thoroughly purging with N₂ gas (Figure 6c). A linear electrical response to NH₃ concentration was found over nearly the full concentration range, with an equation of ln (ΔI_D %) = $-0.697 + 0.346 \ln(V_{\rm NH3}$ %) (inset of Figure 6c). Correspondingly, an ultralow MDL of \approx 5 ppm NH₃ was estimated for the device under n-type operation, which is comparable with that of state-of-the-art organic semiconductor detection systems.^[60]

Another superior feature of our $TiO_2/graphene$ system is its long-term operational stability because no obvious device degradation occurred during both O_2 and NH_3 detection for

Table 2. Response lifetimes (τ) for the photoexcited TiO₂/graphene system upon alternate exposure to NH₃ and N₂ gases.

τ[s]	$ au_{1- m NH3}$	$\tau_{1.N2}$	τ _{2- NH3}	τ _{2-N2}	$ au_{3- m NH3}$	$ au_{3-N2}$	$ au_{avg-NH3}$	$ au_{avg-N2}$
n-type	186.2	241.7	134.3	238.6	99.3	266.4	140.0 ± 35.7	248.9 ± 12.5
p-type	15.69	317.8	10.99	394.4	19.56	338.2	15.41 ± 3.50	350.1 ± 32.4

www.advmattechnol.de



 ${\approx}1000$ continuous cycles with only a slight increase of the N_2 purging time. This is because both TiO_2 and graphene are stable, and very low operating voltages (100 μV) were required compared with those of organic semiconductor detection platforms.

As illustrated above, trapped electrons can enhance electron current and lower hole current in ambipolar graphene. With UV light, which induces reversible electron trapping and detrapping at the TiO₂/graphene interface, as one operating parameter and gate bias, which produces electron carriers in an n-type channel or hole carriers in a p-type channel, as another, a mirror-image symmetrical current response was realized (Figure 3d). Such symmetry can endow the system with logic capability, such as the basic addition function of half-adder and the basic subtraction function of half-subtractor.^[21] More interestingly, for the photoexcited TiO₂/graphene system with trapped electrons at the TiO2/graphene interface, the adsorption of electrondonating molecules increases interfacial electron concentration while adsorption of electron-withdrawing molecules decreases interfacial electron concentration. Using NH₃ adsorption/desorption as one operating parameter and gate voltage as another, a different mirror-image symmetrical response was realized in the same device (Figure 6a). This kind of symmetrical response is reproducible because it was also observed for other reducing molecules like H₂ (Figure S13, Supporting Information). Similarly, by using another two operating parameters, O2 adsorption/desorption and gate voltage, an opposite mirror-image symmetrical response was achieved (Figure 5a) through alternating exposure to pure O_2 and mixed O_2 +NH₃ (Figure S14, Supporting Information). As shown in energy band diagrams of the devices at different conditions (Figure S15, Supporting Information), by comprehensively considering all these operating parameters, including gate control, photoexcitation, and O₂/NH₃ treatment, higher-level symmetrical responses can be designed. For example, Figure 6d depicts twofold mirror-image symmetry controlled by photoexcitation and gating in the center and fourfold mirror-image symmetry controlled by gas exposure (O_2 and NH_3) and gating at the outer section. Overall, our suspended TiO₂/graphene device behaves as an all-mirrorimage symmetrical sensing platform. For example, using n-type operation +O₂-NH₃ as operating parameters, the device current decreases (Figure 5a). Conversely, in the case of n-type operation and $+O_2+NH_3$ exposure, the device current increases (Figure S14, Supporting Information), forming a mirror-image symmetry based on Mirror 2. In another example, the device current decreases in the case of p-type operation and exposure to $-O_2+NH_3$ (Figure 6a), and increases in the case of n-type operation and exposure to +O2+NH3 (Figure S14, Supporting Information), forming another type of mirror-image symmetry based on Mirror 4.

3. Conclusions

We used suspended pristine graphene as a local probe to establish a mechanistic understanding of the interfacial charge trapping/detrapping processes in a TiO_2 /graphene system under multiple external stimuli. Through combination of photoexcitation and gate regulation, we identified two types of



photoinduced electrons trapped at the TiO₂/graphene interface, which have different affinities with the holes remaining on the TiO₂ QDs, thus successfully realizing rational control of both the type and concentration of charge carriers in the conductive channel. Such control was achieved because these functional hybrid materials are very sensitive to chemical environment. Upon exposure of these hybrid materials to different gases, such as O₂ as an electron acceptor and NH₃ or H₂ as an electron donor, in the presence of UV light to populate the $TiO_2/$ graphene interface with trapped electrons, all-mirror-image sensing with controllable fast response rate, high stability, and ultralow detection limit in a single graphene device was fully demonstrated. In conjunction with the sensing mechanistic understanding, these remarkable results, including the ease of device fabrication, the reproducibility, the long-term stability, and the achievement of fast response rates and high gaseous sensitivity at room temperature and ambient pressure, strongly support that graphene-based hybrid materials offer a promising platform for developing low-cost, portable, and sensitive environmental/chemical sensors and other optoelectronic devices for a wide variety of practical applications in civilian and military areas.

4. Experimental Section

Device Fabrication: Pristine SLG was obtained by a peel-off technique on silicon wafers with a 300 nm thick SiO_2 dielectric layer. After initial optical and Raman characterization of graphene, e-beam lithography and further thermal evaporation were used to pattern metal electrodes (8 nm Cr/100 nm Au) on the graphene flake. A 50 nm thick SiO₂ passivation layer was deposited on the surface of the metal electrodes by e-beam thermal evaporation. After the initial electrical characterization of the pristine graphene transistors, an exposed window defined on the SLG between metal electrodes was opened by e-beam lithography with all other parts of the device coated with a layer of polymethylmethacrylate (PMMA) (Figure S1, Supporting Information). The device was immersed in HF-NH₄F solution for 45 s to etch the SiO_2 layer below SLG, thus forming suspended SLG. Finally, through the same window, a 5 nm thick TiO₂ thin film was deposited on the surface of the SLG by e-beam thermal evaporation before PMMA lift-off. Control pristine graphene devices were fabricated by the same process without the evaporation of TiO_2 thin films.

Device Characterization: All optical microscopy images were obtained using a Nikon Eclipse LV100 POL Microscope with CCD imaging. Scanning electron microscope (SEM) images of the TiO₂/graphene devices were taken by a field-emission scanning electron microscope (Hitachi, S4800). High-resolution TEM characterization of TiO₂ QDs was carried out by a high-resolution transmission electron microscope (FEI, Tecnai F30). AFM measurements of TiO₂ films on graphene were carried out by tapping-mode AFM (Digital Instruments Nanoscope IIIa controller and multimode SPM). XPS measurements of the samples with a 5 nm thick TiO₂ film on graphene were performed using an ESCALab220i-XL electron spectrometer (VG Scientific) with 300 W AI K α radiation under 3 × 10⁻⁹ mbar base pressure. Binding energies were calibrated by the C 1s line at 284.8 eV. Raman spectra of graphene were collected using a micro-Raman spectrometer (Renishaw 1000) at an excitation wavelength of 632.8 nm.

Electrical Measurement: To carry out electrical measurements with UV light irradiation and gas injection, a novel sealed dark chamber (Figure 2) containing a quartz window to introduce UV light, three independent controllable channels for gas flow, and multiple microconnecters for electrical characterization was designed and constructed. A wire-bonding method was used to connect the device microelectrodes to a test holder (inset of Figure 2b), which was further incorporated



www.MaterialsViews.com

into the electrical testing system. A handheld UV lamp (λ = 254 nm, \approx 50 µW cm⁻²) was used to irradiate UV light through the quartz window. High-purity N₂ (99.99%), high-purity O₂ (99.99%), high-purity NH₃ gas (99.99%), and high-purity H₂ gas (99.99%) were used as sensing gases. Before gas injection, sufficient pure N2 gas was purged into the sealed chamber to completely remove the residual air or other gases in the system. The concentrations of mixed gases were precisely controlled by introducing the appropriate amounts of target gases through the corresponding flow meters. Device characterization was performed under UV light irradiation and gas treatment at room temperature with a Karl Suss PM5 manual probe station and Agilent 4155C semiconductor characterization system. The responsivity (R), quantum efficiency (η) , and photogain (G) factors of the photodetectors are defined by $R = I_{\rm ph}/P_{\rm in}$, $\eta = (I_{\rm ph} \times hv)/(P_{\rm in} \times q)$, and $G = \tau \times \mu \times V/l^2$, respectively, where I_{ph} is the photoinduced current, P_{in} is the input power falling on the TiO₂ active area of the photodetector, h is the Planck's constant, v is the frequency of the incident photon, q is the electronic charge, τ is the lifetime of the photogenerated carriers, μ is the mobility of graphene layer, and I is the spanning length of the TiO₂ active area.^[61]

Theoretical Calculation: The electronic structures of pristine graphene, $TiO_2/graphene$, $O_2/TiO_2/graphene$, and $NH_3/TiO_2/graphene$ systems were calculated by the first-principles spin polarized density functional theory. The structure of the simulated TiO₂/graphene system is shown in Figure S3a,b (Supporting Information). The periodically repeating graphene unit contained 50 [a (5 \times 5) supercell] carbon atoms, and on the middle of each graphene unit was a TiO_2 cluster with three Ti atoms and six O atoms. For $O_2/TiO_2/graphene$ or $NH_3/TiO_2/graphene$ systems, the two O atoms of O₂ or N atom of NH₃, respectively, were bonded to one Ti atom site in each unit cell. The geometries of the systems were optimized with the Vienna ab initio simulation package using the projector augmented wave method to model the atomic cores, and the Perdew-Burke-Ernzerhof exchangecorrelation functional with a plane wave basis set. The energy cut-off and convergence criterion of the total energy were set as 400 and 1×10^{-4} eV, respectively. The reciprocal space was represented by a (5 \times 5) Γ -centered k-grid. Grimme's method was used to incorporate van der Waal's interactions. The geometries of the systems were fully relaxed without any symmetry constraints and the convergence of each force component on atoms was set as 0.02 eV ${\rm \AA^{-1}}$. The Bader charge analysis scheme was used to reveal the charge state on atoms. Because the TiO₂ QD was a closed shell system, it bound to the graphene through a weak physical interaction, and the distance between the TiO₂ and graphene was \approx 3 Å. As a result, the Dirac point character of the graphene sheet was preserved upon TiO₂ QD adsorption. For the electronic density of states calculation, a Gaussian broadening width of 0.2 eV was applied. The position of the Fermi level in all E-DoS spectra was shifted to 0 eV.

Supporting Information

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

Acknowledgements

C.J. and Q.W. contributed equally to this work. The authors acknowledge primary financial support from NSFC (21225311, 91333102, and 21373014), and 973 Project (2012CB921404).

Received: April 23, 2016 Published online:



- [4] Y. He, C. Fan, S. T. Lee, Nano Today 2010, 5, 282.
- [5] S. Liu, Q. Shen, Y. Cao, L. Gan, Z. X. Wang, M. L. Steigerwald, X. F. Guo, *Coord. Chem. Rev.* 2010, 254, 1101.
- [6] Y. Z. Long, M. Yu, B. Sun, C. Z. Gu, Z. Fan, *Chem. Soc. Rev.* 2012, 41, 4560.
- [7] J. Kong, N. R. Franklin, C. W. Zhou, M. G. Chapline, S. Peng, K. J. Cho, H. J. Dai, *Science* 2000, 287, 622.
- [8] D. R. Kauffman, A. Star, Chem. Soc. Rev. 2008, 37, 1197.
- [9] X. Guo, Adv. Mater. 2013, 25, 3397.
- [10] I. L. Medintz, H. T. Uyeda, E. R. Goldman, H. Mattoussi, Nat. Mater. 2005, 4, 435.
- [11] R. Wilson, Chem. Soc. Rev. 2008, 37, 2028.
- [12] S. Howorka, Z. Siwy, Chem. Soc. Rev. 2009, 38, 2360.
- [13] L. Soleymani, Z. Fang, E. H. Sargent, S. O. Kelley, Nat. Nanotechnol. 2009, 4, 844.
- [14] F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, K. S. Novoselov, *Nat. Mater.* 2007, *6*, 652.
- [15] Y. P. Dan, Y. Lu, N. J. Kybert, Z. T. Luo, A. T. C. Johnson, *Nano Lett.* 2009, 9, 1472.
- [16] Q. Wang, X. F. Guo, L. C. Cai, Y. Cao, L. Gan, S. Liu, Z. X. Wang, H. T. Zhang, L. D. Li, *Chem. Sci.* 2011, *2*, 1860.
- [17] D. Y. Zhang, L. Gan, Y. Cao, Q. Wang, L. M. Qi, X. F. Guo, Adv. Mater. 2012, 24, 2715.
- [18] S. Liu, X. F. Guo, NPG Asia Mater. 2012, 4, e23.
- [19] G. Konstantatos, M. Badioli, L. Gaudreau, J. Osmond, M. Bernechea, F. P. G. de Arquer, F. Gatti, F. H. L. Koppens, *Nat. Nanotechnol.* **2012**, *7*, 363.
- [20] Q. He, S. Wu, Z. Yin, H. Zhang, Chem. Sci. 2012, 3, 1764.
- [21] C. Jia, H. Li, J. Jiang, J. Wang, H. Chen, D. Cao, J. F. Stoddart, X. Guo, Adv. Mater. 2013, 25, 6752.
- [22] X. Wang, Z. Cheng, K. Xu, H. K. Tsang, J. B. Xu, Nat. Photonics 2013, 7, 888.
- [23] P. Yasaei, B. Kumar, R. Hantehzadeh, M. Kayyalha, A. Baskin, N. Repnin, C. Wang, R. F. Klie, Y. P. Chen, P. Kral, A. Salehi-Khojin, *Nat. Commun.* 2014, *5*, 4911.
- [24] G. S. Kulkarni, K. Reddy, Z. Zhong, X. Fan, Nat. Commun. 2014, 5, 4376.
- [25] N. Dontschuk, A. Stacey, A. Tadich, K. J. Rietwyk, A. Schenk, M. T. Edmonds, O. Shimoni, C. I. Pakes, S. Prawer, J. Cervenka, *Nat. Commun.* 2015, *6*, 6563.
- [26] J. Zhang, C. Zhao, P. A. Hu, Y. Q. Fu, Z. Wang, W. Cao, B. Yang, F. Placido, RSC Adv. 2013, 3, 22185.
- [27] W. Yuan, G. Shi, J. Mater. Chem. A 2013, 1, 10078.
- [28] S. S. Varghese, S. Lonkar, K. K. Singh, S. Swaminathan, A. Abdala, Sens. Actuators, B 2015, 218, 160.
- [29] O. Leenaerts, B. Partoens, F. M. Peeters, Phys. Rev. B 2008, 77, 125416.
- [30] S. Z. Liang, G. Chen, A. R. Harutyunyan, J. O. Sofo, *Phys. Rev. B* 2014, 90, 115410.
- [31] D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim, K. S. Novoselov, *Science* **2009**, *323*, 610.
- [32] C. K. Chua, M. Pumera, Chem. Soc. Rev. 2013, 42, 3222.
- [33] L. Liao, H. Peng, Z. Liu, J. Am. Chem. Soc. 2014, 136, 12194.
- [34] L. Yan, Y. B. Zheng, F. Zhao, S. Li, X. Gao, B. Xu, P. S. Weiss, Y. Zhao, Chem. Soc. Rev. 2012, 41, 97.
- [35] E. Bekyarova, S. Sarkar, F. Wang, M. E. Itkis, I. Kalinina, X. Tian, R. C. Haddon, Acc. Chem. Res. 2013, 46, 65.
- [36] K. Kim, J. Y. Choi, T. Kim, S. H. Cho, H. J. Chung, Nature 2011, 479, 338.
- [37] K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim, *Nature* **2012**, *490*, 192.
- [38] F. H. L. Koppens, T. Mueller, P. Avouris, A. C. Ferrari, M. S. Vitiello, M. Polini, Nat. Nanotechnol. 2014, 9, 780.
- [39] L. Ju, J. VelascoJr., E. Huang, S. Kahn, C. Nosiglia, H. Z. Tsai, W. Yang, T. Taniguchi, K. Watanabe, Y. Zhang, G. Zhang, M. Crommie, A. Zettl, F. Wang, *Nat. Nanotechnol.* **2014**, *9*, 348.

^[1] J. Liu, Z. Cao, Y. Lu, Chem. Rev. **2009**, 109, 1948.

^[2] N. L. Rosi, C. A. Mirkin, Chem. Rev. 2005, 105, 1547.

^[3] F. Patolsky, G. F. Zheng, C. M. Lieber, Anal. Chem. 2006, 78, 4260.

www.advmattechnol.de



www.MaterialsViews.com

- [40] C. Jia, H. Yin, H. Ma, R. Wang, X. Ge, A. Zhou, X. Xu, Y. Ding, J. Phys. Chem. C 2009, 113, 16138.
- [41] J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, D. W. Bahnemann, *Chem. Rev.* 2014, 114, 9919.
- [42] L. Sang, Y. Zhao, C. Burda, Chem. Rev. 2014, 114, 9283.
- [43] M. Q. Yang, N. Zhang, M. Pagliaro, Y. J. Xu, Chem. Soc. Rev. 2014, 43, 8240.
- [44] L. Wang, T. Sasaki, Chem. Rev. 2014, 114, 9455.
- [45] C. Chen, Y. Wen, X. Hu, X. Ji, M. Yan, L. Mai, P. Hu, B. Shan, Y. Huang, Nat. Commun. 2015, 6, 6929.
- [46] S. Liu, J. M. Li, Q. Shen, Y. Cao, X. F. Guo, G. M. Zhang, C. Q. Teng, J. Zhang, Z. F. Liu, M. L. Steigerwald, D. S. Xu, C. Nuckolls, *Angew. Chem.*, *Int. Ed.* **2009**, *48*, 4759.
- [47] D. Shao, J. Gao, P. Chow, H. Sun, G. Xin, P. Sharma, J. Lian, N. A. Koratkar, S. Sawyer, *Nano Lett.* **2015**, *15*, 3787.
- [48] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, A. K. Geim, *Phys. Rev. Lett.* **2006**, *97*, 187401.
- [49] J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, T. J. Booth, S. Roth, *Nature* 2007, 446, 60.

- [50] Z. Cheng, Q. Li, Z. Li, Q. Zhou, Y. Fang, Nano Lett. 2010, 10, 1864.
- [51] A. A. Balandin, Nat. Nanotechnol. 2013, 8, 549.
- [52] J. K. Burdett, T. Hughbanks, G. J. Miller, J. W. Richardson, J. V. Smith, J. Am. Chem. Soc. 1987, 109, 3639.
- [53] A. G. Thomas, K. L. Syres, Chem. Soc. Rev. 2012, 41, 4207.
- [54] D. O. Scanlon, C. W. Dunnill, J. Buckeridge, S. A. Shevlin, A. J. Logsdail, S. M. Woodley, C. R. Catlow, M. J. Powell, R. G. Palgrave, I. P. Parkin, G. W. Watson, T. W. Keal, P. Sherwood, A. Walsh, A. A. Sokol, *Nat. Mater.* 2013, *12*, 798.
- [55] B. Y. Zhang, T. Liu, B. Meng, X. Li, G. Liang, X. Hu, Q. J. Wang, Nat. Commun. 2013, 4, 1811.
- [56] G. Haider, P. Roy, C. W. Chiang, W. C. Tan, Y. R. Liou, H. T. Chang, C. T. Liang, W. H. Shih, Y. F. Chen, *Adv. Funct. Mater.* **2016**, *26*, 620.
- [57] Y. F. Li, U. Aschauer, J. Chen, A. Selloni, Acc. Chem. Res. 2014, 47, 3361.
- [58] V. Aroutiounian, Int. J. Hydrogen Energy 2007, 32, 1145.
- [59] K. Hadjiivanov, J. Lamotte, J. C. Lavalley, Langmuir 1997, 13, 3374.
- [60] H. W. Zan, W. W. Tsai, Y.-R. Lo, Y. M. Wu, Y. S. Yang, IEEE Sens. J. 2012, 12, 594.
- [61] Y. Lin, X. Guo, Small 2015, 11, 2856.