Emerging and Future Possible Strategies for Enhancing 1D Inorganic Nanomaterials-Based Electrical Sensors towards Explosives Vapors Detection

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Due to the necessity for maintaining homeland security and antiterrorism, a greatly growing demand exists for sensors that can detect explosives vapors. One-dimensional inorganic nanomaterials represent one kind of the most promising materials for sensor fabrication due to the large surface-to-volume ratios, quantum confinement, high reaction activities, excellent electrical, optical, and chemical properties, unique anisotropic morphologies, and abundant structure tuning capabilities. All of these properties make the 1D inorganic nanomaterials ideal nanoscale building blocks in explosives vapors sensing applications. However, due to the big challenges, such as manufacturing technique with high cost and energy consumption, the difficulty of the assembling and patterning of 1D inorganic nanomaterials into functional devices, the weak repeatability for surface modification which hinder the development of sensors with high sensitivity, selectivity, low power consumption, simple structure, fast response and recovery procedures, high reliability and biocompatibility, more advanced strategies are needed for enhancing 1D-inorganic-nanomaterials-based electrical sensors towards explosives vapors detection. In this article, a comprehensive review of the recent progresses on emerging and future possible strategies for enhancing 1D-inorganic-nanomaterials-based electrical sensors towards explosives vapors detection is provided.

1. Introduction

The detection of the explosives which contain a great amount of potential energy is attracting extensive attention because of plenty of adverse events, increasing threat of terrorism attacks, and the need for homeland security, environmental and humanitarian implications.[1–5] Based on the differences of chemical compositions, explosives can be classified into acetylides explosives, fulminates explosives, nitroexplosives, nitrates explosives, amines explosives, peroxides explosives and so on. Among them, nitroexplosives such as trinitrotoluene (TNT), nitrates explosives such as ammonium nitrate (AN), and peroxides explosives such as triacetone triperoxide (TATP) are three kinds of the most commonly used explosives. Sensing methods towards explosives vapors can meet the requirements of noncontact sampling, real-time analyzing and wireless detection. However, the sensitive, selective and rapid detection of explosives vapors is still a challenge due to their low vapor pressure,[6] especially in open environment. The nitroexplosives and nitrates explosives can be decomposed into NO_x under light illumination. Sometimes the detection of explosives is realized via the conductance changes induced by NO or NO_2.[3]

Recently, the rapidly and dramatically developed sensors which convert chemical and physical stimuli into certain form of response that can be easily detected, such as electronic signals, fluorescent changes, or resonant frequency shifts have become a research focus.[7–15] A series of researches have proved that sensors can be used as powerful tools for explosives detection.[16–19] Many detection strategies have been explored in the past decades, such as the ion mobility spectrometry method,[20–22] mass spectrometry method,[23,24] fluorescent method,[25–28] the colorimetric method,[29,30] the surface-enhanced Raman scattering method,[31–34] the electrochemical method[35–37] and the electrical method. Among these detection methods, the electrical method is regarded as one of the most widely used ones due to its high stability, mature fabricating technology, simple sensing structure, low costs and low power requirement. Besides, by introducing the sensory array, the recognizing or fingerprinting of different explosives can be realized.[16,38] In general, for an electrical sensor whose output signals are resistance, voltage or current, the adsorption of the charged molecules will form a depletion layer and lead to the conductance change.

Nanosensors are one kind of potential sensors for the detection of trace species due to the large surface-to-volume ratio, quantum confinement effect and high reaction activity.[39,40]

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Among them, 1D inorganic nanomaterials (such as nanowires, nanotubes, nanorods, nanofibers, nanoribbons, etc) have been regarded as substantially promising candidates due to their excellent electrical, optical and chemical properties, unique anisotropic morphologies, and abundant structure tuning capabilities.[41–43] Although numerous works have used 1D inorganic nanostructures as the sensing materials to fabricate electrical sensors, most of these works are based on chemiresistors or field effect transistors (FETs).

A chemiresistor is a simple device in which both ends of the materials form Ohm contact with electrodes. The chemiresistors are usually operated in air. Oxygen molecules adsorb onto the semiconductor surface and trap electrons from the material, leading to the formation of negative oxygen ions species. Adsorption of charged molecules onto the surface of materials will lead to the change of concentration of charge carriers. The advantages of the chemiresistors involve simple fabrication process, low cost and low power requirement. However, chemiresistors rely on the change in conductance of the whole device which depends highly on the analyte's concentration,[44,45] leading to lower sensitivity. Besides, when exposed to high gas concentrations, the chemiresistors lack reversibility and need long time and additional assistant methods such as UV illumination or air purge to recover.

FETs are emerging as promising candidates for signal transduction and recognition of chemical species.[46–50] In a typical FET device, the 1D nanomaterial acts as a conductive channel. Both of the two ends form Ohm contact with electrodes which are called source and drain contacts. A front or back gate electrode located at the insulation layer will change the density of the charge carriers by a variable applied voltage.[51–54] FETs provide several advantages over other sensing strategies, owing to the methodical controllability over the sensing signals by changes of gate voltages, the ability to provide multiple device features to evaluate the sensing signals, the low power requirement, and the miniaturization features of the device size[55–58]. When a gate voltage is applied, charge carriers electrostatically accumulate or deplete in the semiconductor at the semiconductor/gate dielectric interface. Owing to the field-effect, the charge carrier density in the semiconductor can be modulated and the current through the active layer can be varied over orders of magnitude. The key advantage of transistors over chemiresistors is the amplified sensor response due to the current modulation by the gate voltage.[59] Similar with chemiresistors, FETs have faced the challenge of diffusion dependent response and recovery for gas species.

Up to now, a series of investigations related to the 1D inorganic nanomaterials for sensing applications have been summarized in several excellent reviews.[40,60–63] Although these reviews have complete coverage, they either focus on certain topic such as one kind of specific materials or more wide coverage from synthesis to a series of applications. So far, no comprehensive and professional review has covered the overall sensing strategies and possible platforms for electrical sensing using 1D inorganic nanomaterials towards explosives vapors detection. In this article, we would like to update the latest researches about recent progresses on emerging and future possible strategies towards explosives vapors detection, as shown in **Figure 1**.

We first introduce emerging strategies for enhancing 1D inorganic nanomaterials-based explosives sensors in Section 2. These strategies include aligned array, surface modifications, optoelectronic sensing, flexible design, Schottky junction and sensory array. Section 3 introduces possible strategies for enhancing 1D inorganic nanomaterials-based electrical explosives sensors in the near future. Section 4 summarizes this article and provides a brief perspective for the future research in this field. The aim of this article is to present comprehensive coverage of last five year's progresses targeting at the emerging and future possible strategies for enhancing 1D inorganic nanomaterials-based sensors towards explosives vapors detection, and to stimulate future research in this field.

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2. Emerging Strategies for Enhancing 1D Inorganic Nanomaterials-Based Explosives Sensors

Although there exists plenty of inorganic semiconductors, however, limited by the intrinsic characteristics, only few ones, namely silicon nanowires, ZnO, TiO_2 and carbon nanotubes (CNTs), have been proven to exist sensitive response towards explosives vapors, especially nitroexplosives. The gas sensing performances of them are highly influenced by the size, morphology, surface state, exposed facet and other

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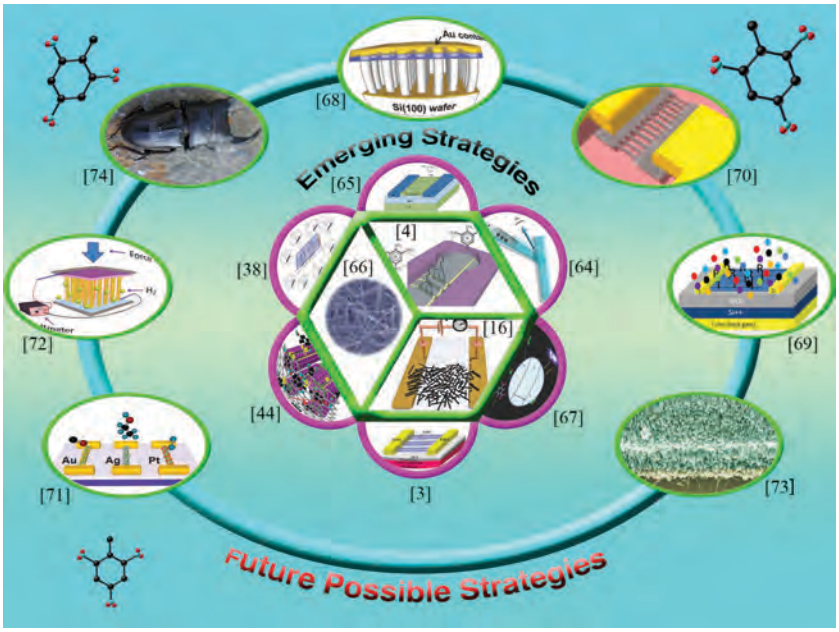

Figure 1. Illustration of the main topics of this article, showing emerging strategies, future possible strategies, and platforms towards explosives vapors detection. Reproduced with permission.[3,4] Copyright 2010, Wiley-VCH. Reproduced with permission.[68] Copyright 2012, Wiley-VCH. Reproduced with permission.[16] Copyright 2014, Wiley-VCH. Reproduced with permission.[73,44] Copyright 2015, Wiley-VCH. Reproduced with permission.[71] Copyright 2013, American Chemical Society. Reproduced with permission.[69–74] Copyright 2014, American Chemical Society. Reproduced with permission.[64] Copyright 2015, American Chemical Society. [66] Copyright 2011, Royal Society of Chemistry. Reproduced with permission.[65] Copyright 2012, Royal Society of Chemistry. Reproduced with permission.[38] Copyright 2014, Macmillan Publishers Limited. Reproduced with permission.[72] Copyright 2014, Elsevier Ltd. Reproduced with permission.[67] Copyright 2013, Royal Society of Chemistry.

intrinsic characteristics. Although these four materials own different unique properties, the sensing applications of inorganic nanomaterials towards explosives vapors have been limited by a series of reasons such as complicated fabrication processes due to a lack of solubility of the nanomaterials, sensitivity to different kinds of species and low interference immunity towards ambient gases like water vapor which could cause false positives.[64] In order to achieve the goal of supersensitive, selective and real-time vapor detection, some strategies for enhancing 1D inorganic nanomaterials-based sensors towards explosives vapors detection emerged, including aligned array, surface modifications, optoelectronic sensing, flexible design, Schottky junction, and sensory array. In this section, we will review the recent researches, mainly published during the five years from 2010 to 2015 (**Table 1**), and focus on the research progresses on improving the 1D inorganic nanomaterials-based electrical sensors towards explosives vapors detection.

2.1. Aligned Nanowires for Integration Priority

Aligned nanowire (NW) (nanoribbon, nanorod, nanotube) arrays, which contain planar ones and vertical ones, offer distinct advantages over single nanowire in terms of more adsorption sites, the integration density of individual active nanocomponent and high signal to noise ratio.[65,68] Besides, compared with random 1D nanomaterials, planar aligned array provides advantages in optimizing sensor designs, reducing sensor's resistance and facilitating the electrodes fabrication.[42] For the detection of explosives vapors with rather low concentration, aligned nanowires could do better.

SiNWs fabricated with a lithography process provides advantages in integration with microelectronic circuits that interfaced with the chemiresistive sensor. An aligned SiNWs array was prepared with a top-down nanofabrication process on a silicon-on-insulator wafer,[65] which is shown in **Figure 2**a. The responses towards vapors of nitroexplosives like dinitrotoluene (DNT), TNT, cyclotrimethylene trinitramine (RDX), pentaerythritol tetranitrate (PETN), picric acid (PA) and 2-nitrobenzene were sensitive and fast, with high signal to noise ratios. Hydrogen plasma and oxygen plasma treatment greatly improved the sensitivity and response time of the sensors. The higher sensitivities were observed in the nanowires of smaller width. Besides, the sensor showed long-term stability in ambient atmosphere. The sensor responses towards DNT with oxygen plasma treatment were continuously tested over 2000 cycles and no significant drift was observed (Figure 2b).

Compared with chemiresistors, the aligned NWs FETs have the merits of methodical controllability by changes of gate voltages to obtain the highest sensitivity. Fernando Patolsky's group has concentrated on the detection of nitroexplosives using chemically modified SiNWs FETs arrays. In 2010, the supersensitive, rapid and label-free detection of TNT in real-time with the use of large-scale SiNWs array-based FET devices containing multiple sensing elements was demonstrated.[4] As shown in **Figure 3**a, aligned SiNWs were chemically modified firstly with a monolayer of 3-aminopropyltriethoxysilane (APTES), and then used to sense TNT in liquid and gaseous phase. This sensor could detect TNT with concentrations down to the femtomolar level. Furthermore, the most sensitive device could sense TNT down to the 50–100 attomolar range in less than a minute. Approximately 100 repeated TNT injection/wash cycles were conducted with the same nanowire device for over more than a week, and remarkable sensing stability and reproducibility were obtained, which showed the superiority of the aligned FETs. The sensor array could allow for the detection of TNT vapors directly from samples in air using either a nitrogen gas or dry air stream as the TNT vapor carrier. A repeated (>50 cycles) sensing performance at low concentrations, with unprecedented sensitivities down to at least 0.01 ppt in air was obtained (Figure 3b). The sensitivity and stability of the sensors make them capable of being used for practical applications. In addition, TNT could be distinguished from other related compounds with the modification of APTES, which inspired us to look into the development of selective and supersensitive sensors boosted by surface modification.

Table 1. 1D inorganic nanomaterials-based sensors towards explosives vapors detection (The room temperature saturated pressures of explosives is based on the datum of the literature.[6])

Materails	Nanostructures	Devices	Targeted species	Concentration	Sensitivities	Ref
Silicon	NWs array	Resistor	DNT	411 ppb	50%	[65]
			TNT	9 ppb	28.5%	
			RDX	4.9 ppt	24%	
			PA	0.97 ppb	15.3%	
			PETN	10.7 ppt	30%	
Silicon	NWs array	FET	TNT	1 ppt	—	[4]
Silicon	NWs	FET	TNT	Down to ppq level	—	[38]
			RDX		—	
			PETN		—	
			HMX		—	
			AN		—	
			TATP		—	
rGO/TiO_2/SiNWs	NWs array	Schottky junction	TNT	9 ppb	6.3%	
			DNT	411 ppb	40%	
			PA	0.97 ppb	4%	
			RDX	4.9 ppt	9%	
			HMX	0.25 ppq	3%	
ZnO	NW	FET	TNT	60 to 1360 ppb	20% to 80%	[3]
TiO_2-(B)	NWs	Resistor	TNT	5 ppb	57%	[66]
			RDX	5 ppt	50%	
TiO_2-(B)	NWs	Resistor	TNT	9 ppb	47%	[75]
			DNT	411 ppb	38%	
TiO_2-(B)	NWs	Resistor	TNT	1 ppb	33%	[67]
TiO_2 decorated GaN	NWs	Resistor	TNT	100 ppb	10%	[76]
			DNT	100 ppb	2%	
CNTs	NTs	FET	TNT	8 to 1100 ppb	5% to 50%	[3]
DNA decorated SWNTs	NTs	Resistor	DNT	46 ppm	23%	[77]
Covalently Functionalized SWNT	NTs	Resistor	Nitromethane	57 ppm	0.1%	[16]
			Cyclohexanone	57 ppm	0.5%	
Oligomer-coated CNTs	NTs	Resistor	nitrobenzene	7 ppm	1.7%	[64]

abbreviations: NW: nanowire; NT: nanotube; DNT: dinitrotoluene; HMX: cyclotetramethylene tetranitramine; PA: picric acid; PETN: pentaerythritol tetranitrate; RDX: cyclotrimethylene trinitramine; TATP: triacetone triperoxide; TNT: trinitrotoluene; ppb: part per billion; ppm: part per million; ppq: part per quadrillion; ppt: part per trillion

2.2. Surface Modification for Enhanced Sensitivity and Selectivity

Surface modification, which enhances the molecules adsorption, facilitates the charge transfer and allows the sensors to recognize specific target molecules, is a commonly used choice for enhancing 1D nanomaterials-based gas sensors for trace and selective detection.[60] In general, self-assembled organic monolayer (SAM), noble metal nanoparticles (NPs), polymer and macromolecules are the commonly used species to be functionalized on the surface of 1D nanomaterials. Surface modifications can be divided into covalent functionalization and non-covalent functionalization.

The silicon oxide layer on SiNW makes it convenient to be functionalized with different types of linker chemistry, mostly using silane coupling agents.[78] Hossam Haick's group have conducted a series of representative works on the functionalization of SiNW-based FETs for volatile organic compounds detection.[50,79–82,69,83] These results have the potential to boost the combination of the SiNW FET and surface modification into sensors for gas phase species detection in real-world. For CNT-based sensors, functionalization can be done by non-covalent functionalization through π–π stacking, wrapping with functionalized polymers or by covalent functionalization through carboxy groups.[84–87] Besides, the species on the CNTs can efficiently restrain the aggregation, making CNTs-based devices more easily be fabricated. The sensors based on metal oxides also need surface modification to obtain the selectivity.

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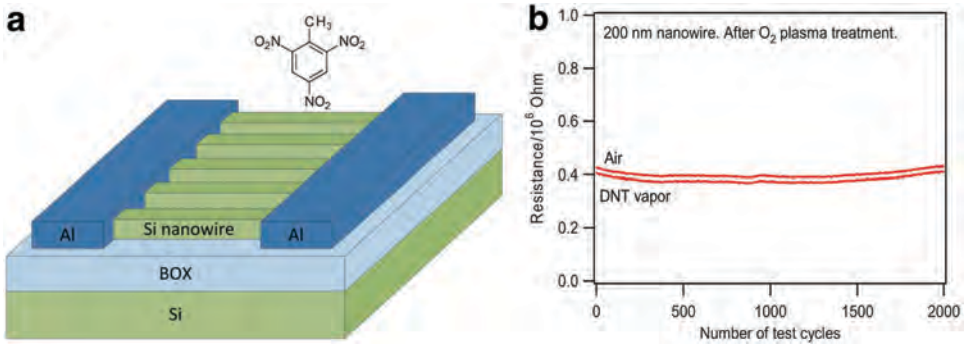

Figure 2. a) Schematic drawing of the silicon nanowire sensor. b) Test results of the silicon nanowires (200 nm width) treated with oxygen plasma through 2000 testing cycles of alternating between DNT vapor and air. Reproduced with permission.[65] Copyright 2012, Royal Society of Chemistry.

2.2.1. Covalent Functionalization for Semispecific Purpose

Covalent functionalization of 1D nanomaterials has significantly expanded the utility of the sensors for different sensing fields. The sensitivity and selectivity of gas sensors for certain explosives analytes can be enhanced by surface functionalization with specific functional groups. Furthermore, by modifying with different selectors, a variety of semispecific sensors can be fabricated and a sensory array can be built up to discriminate different species.

Swager et al. fabricated a chemiresistive sensory array for sensing cyclohexanone, a non-explosive vapor marker of RDX, and nitromethane, a solvent utilized in the formation of explosives mixtures, using single-walled carbon nanotubes (SWCNTs) that are covalently functionalized with urea, thiourea and squaramide containing selector units.[16] Using the two-step synthetic route, substituted thiourea and squaramide groups were attached to the surface of SWCNTs (**Figure 4**a). In order to obtain a higher binding affinity of the selector to its analyte, the selectors were optimized based on ^{1}H NMR binding studies and then covalently attached to SWCNTs (Figure 4b). The sensors showed a very high level of reproducibility between measurements with the same sensor and across different sensors of the same type. Furthermore, the sensors exhibit promising long-term stability.

However, the concentrations of these two species are quite high (≈1 × 10^{2} ppm level) compared with the explosives with low saturated vapor pressure (qqb–ppq level), which is far from

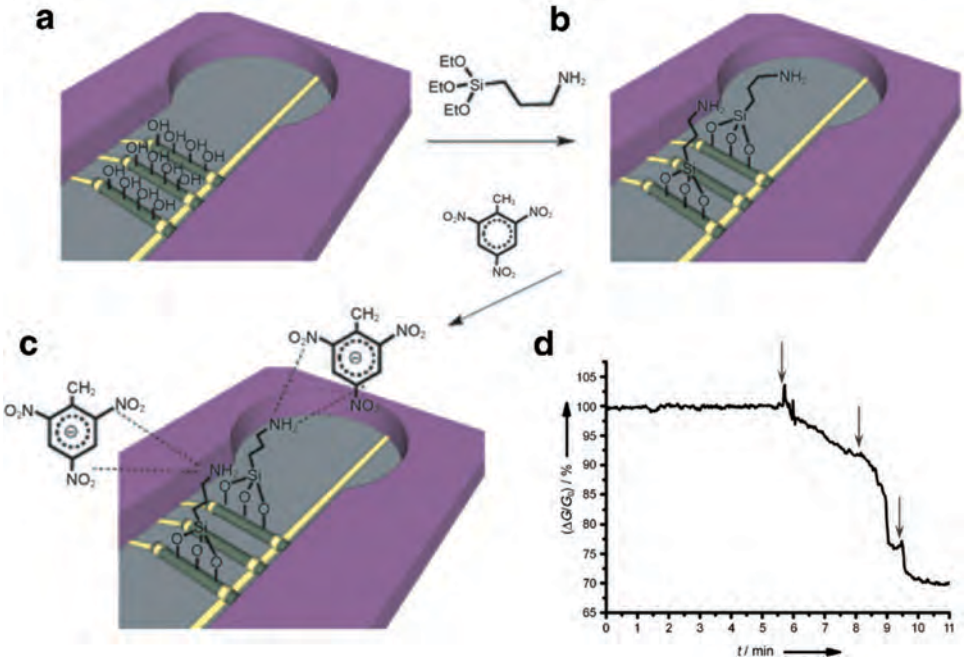

Figure 3. a– c) A representation of a silicon nanowire device from surface modification to TNT sensing. d) Relative percent conductance change versus time for an APTES functionalized p-type SiNW FET sensor after 5 s short pulses of ca. 1 ppt TNT vapors in carrier air samples (arrows denote the time when the TNT vapor pulses were applied). Reproduced with permission.[4] Copyright 2010, Wiley-VCH.

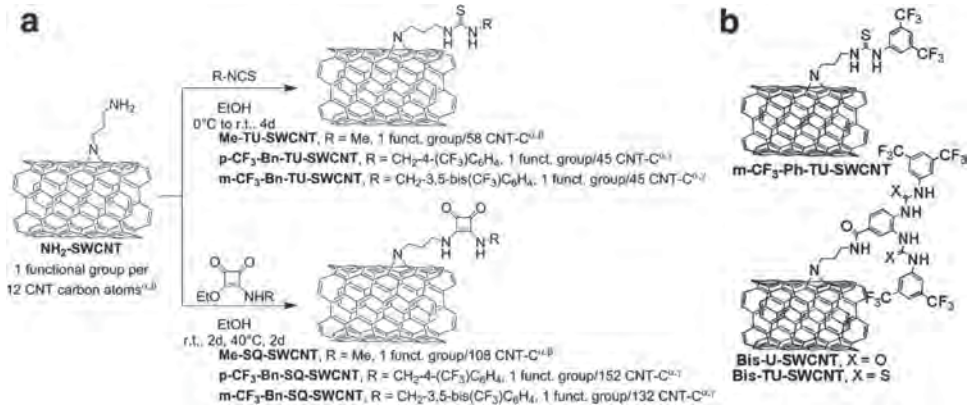

Figure 4. SWNTs based sensors for explosives detection. a) Functionalization of SWCNTs with selectors. α: Functional group density is determined by X-ray photoelectron spectroscopy. β: Based on O 1s and C 1s signals in the product compared to NH_2–SWCNT. γ: Based on F 1s and C 1s signals. b) Functionalized SWCNTs with selectors based on ^{1}H NMR binding study. Reproduced with permission.[16] Copyright 2013, Wiley-VCH.

trace detection. Thus, the problem of sensitive, selective and rapid detection towards trace explosives must be conquered and it could be of great benefit for practical explosives detecting applications. Patolsky demonstrated SiNW-FETs chemically modified in a multiplexed mode, by the surface immobilization of multiple non-specific small chemical receptors, which enabled the supersensitive discriminative detection, fingerprinting of multiple explosive molecules down to the ppq concentration range.[38] This presented an approach allowed for the clear-cut discriminative identification of multiple explosives species, which will be discussed later.

2.2.2. Noncovalent Modification with Polymers and Macromolecules

Compared with covalent modification, noncovalent modification shows the merits in terms of a wide range of functionalized materials including polymers and macromolecules which could be chosen as the modification agents without changing the band structure and electrical properties.[88] Furthermore, the affinity and response of nanomaterials to specific analytes could be increased dramatically.

Dokmeci et al. presented a wireless sensing unit based on DNA decorated SWCNTs integrated with complementary metal oxide semiconductor circuitry to detect trace explosives and chemical agents.[77] **Figure 5**a and 5b show SEM images of SWNTs assembled between single finger and multifinger microelectrodes on a complementary metal-oxide-semiconductor (CMOS) chip. The response of the SWCNTs-based sensor to DNT vapor was improved dramatically after the decoration with single stranded-DNA due to the enhanced surface affinity (Figure 5c). Besides, the response was reversible and repeatable. This versatile sensing system provided a promising platform to detect explosives and chemical agents at a trace level in a wireless manner and stand-off distance. The wireless transmission was conducted using the ZigBee protocol which is a low-cost, low-power and wireless mesh network standard (Figure 5d), which allowed longer life, high reliability and extended range. However, only a limited response of around 28% was obtained to DNT vapor of 46 ppm which is much higher than the saturated vapor pressure of DNT. Therefore, the modified species still need rational selection.

Zang et al. fabricated a high-performance chemiresistive sensor based on carbazolylethynylene oligomer (Tg-Car)-coated SWNTs for trace vapor detection of nitroexplosives.[64] The sensors could detect low concentrations of nitrobenzene (NT), TNT and DNT vapors at ppb to ppt levels. The noncovalent modification of Tg-Car not only maintains the electron transport properties of CNTs, but also improves the selectivity of the sensor to nitroaromatic explosive compounds. Besides, the Tg-Car oligomer greatly enhances the dispersion of CNTs in organic solvents and creates charge carrier tunnel barriers at the junctions of the CNT network. The mechanism of the Tg-Car/CNT sensors is due to the swelling of the Tg-Car/CNT thin film which decreases the conductivity of the CNT network by increasing the tunneling distance (**Figure 6**).

2.2.3. Surface States Tuning

Besides the surface modifications with external species, the surface states like exposed facets, density of oxygen vacancies, density of surface hydroxyl groups and nonstoichiometry created by doping play an important role, especially for metal oxides. For example, Rogach et al. demonstrated that different exposed facets of nanosheets in a hierarchical SnO_2 nanoflower could show different sensitivity.[89] Feng et al. showed that by increasing the oxygen vacancies in tungsten oxide, a higher sensitivity could be achieved.[90] Exploitation of these intrinsic properties could promote the understanding of the sensing mechanisms and facilitate the development of explosives sensors.

Antao Chen's group explored the surface properties of TiO_2-(B) nanowires towards nitroexplosives. In 2011, TiO_2-(B) nanowires were synthesized and exhibited high sensitivity, fast and reversible response at room temperature towards trace vapors of nitroaromatic and nitroamine explosives.[66] It is considered that the hydroxyl groups enriched in the surface could connect to nitro groups of the explosive molecules and acted as the bridge for charge chansfer. Further, Chen et al. investigated the role of surface hydroxyl groups on TiO_2-(B) nanowires.[75] **Figure 7**a shows the responses of nanowires to TNT, after

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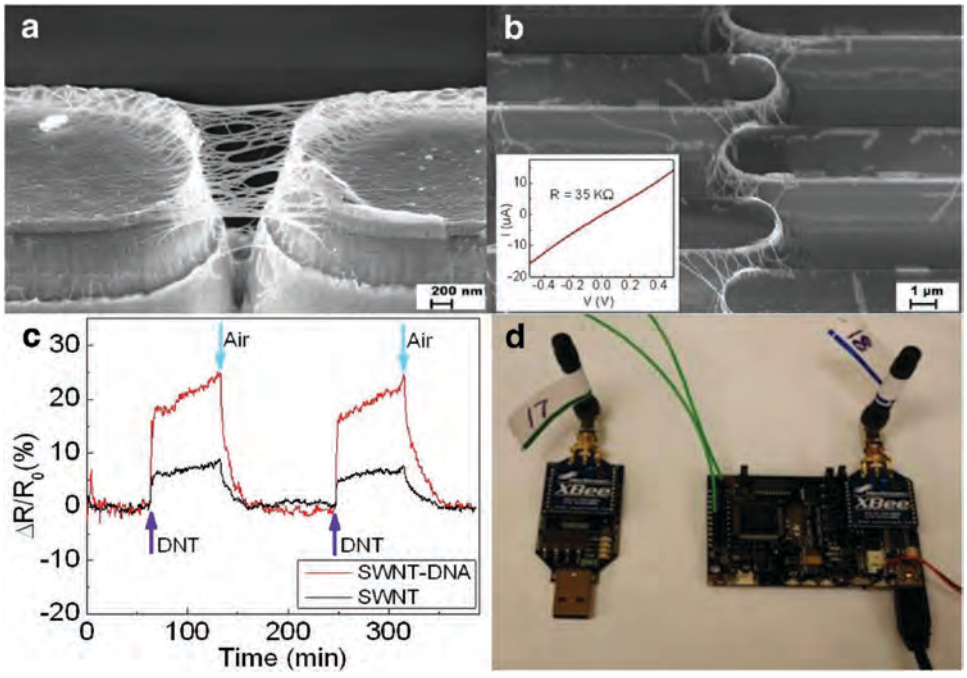

Figure 5. SEM images of SWNTs assembled between a) single finger and b) multifinger microelectrodes on a CMOS chip. Inset: *I–V* measurement of assembled SWNTs on microelectrodes. c) Responses of a DNA decorated SWNT sensor and a bare SWNT sensor to 46-ppm DNT vapor. d) Photograph of the ZigBee wireless transmitter and receiver. Reproduced with permission.[77] Copyright 2012, Institute of Electrical and Electronics Engineers.

oxygen and hydrogen plasma treatments, respectively. A higher response after an oxygen plasma treatment was observed compared with the untreated TiO_2-(B) nanowires and the nanowires with surface hydrogen plasma treatment. As shown in Figure 7b, the sensitivity of the sensor towards DNT vapor after the water treatment was almost two times higher than the untreated one. These results proved that a higher density of surface hydroxyl groups would constantly enhance the response of nanowires to nitroexplosives vapors.

Combination of surface modification and surface tuning could optimize the sensors' surface conditions which will benefit the charge transfer and enhance the affinities between the sensors' surface and molecules.

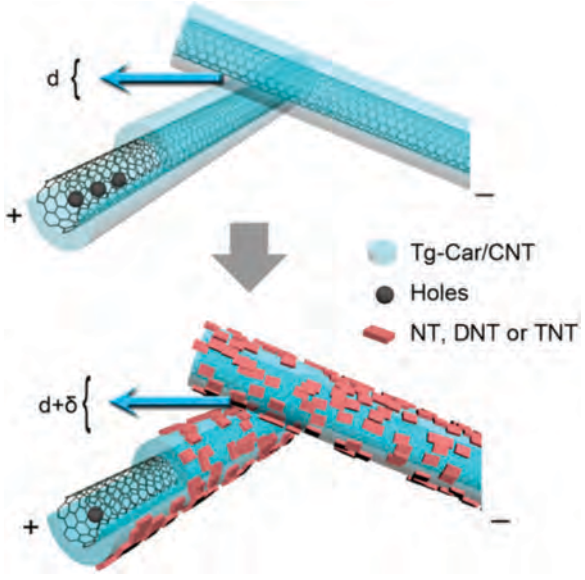

Figure 6. Schematic of the charge carriers (holes) moving in the CNT and tunneling through the Tg-Car Oligomer before and after the exposure to nitroaromatic explosive compounds. Reproduced with permission.[64] Copyright 2015, American Chemical Society.

2.3. Optoelectronic Sensing for Signal Amplification

Usually, light illumination is introduced to the sensing procedure to enhance the adsorption and desorption, resulting in the shorter response time and recovery time. However, the enhanced sensing effects induced by light illumination have been neglected. Optoelectronic trace sensing shows great advantages compared with normal gas sensing in the dark, but the mechanisms need to be fully explored.

2.3.1. Light Generated Charge Carriers for Efficient Vapor Sensing

Light illumination can be utilized to enhance the sensing performance due to the increase in the number of the photogenerated electron-hole pairs participating in the reactions with target molecules.[91] For example, Zang et al. fabricated well-defined ultrathin nanoribbons from an amphiphilic electron donor-acceptor supramolecule which demonstrated high photoconductivity upon illumination and efficient vapor sensing of nitro-based explosives.[18] Although this work is based on organic material, it provided a totally new insight into the optoelectronic method for gas sensing application. Thereafter, Rao et al. demonstrated a highly sensitive and

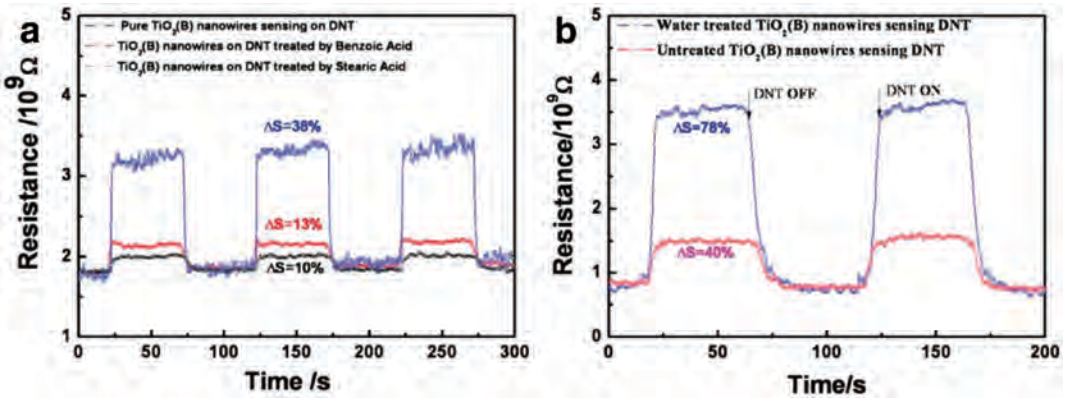

Figure 7. Sensitivities of TiO_2-(B) nanowires to a) DNT with surface modification, b) DNT before and after water treatment of the surfaces. Reproduced with permission.[66] Copyright 2011, Royal Society of Chemistry.

selective detection towards traces of nitro-aromatic explosive compounds by GaN/TiO_2 nanowire-nanocluster hybrids under UV illumination.[76] The 10 to 50 nm TiO_2 NPs interconnected into extended 2D networks. The response of the sensors towards 100 ppb of the aromatics and nitroaromatics in air and responses towards different concentrations of TNT from 8 ppm down to 500 ppt are shown in **Figure 8**a and 8b, respectively. The UV light photo-modulated hybrids were able to detect TNT at concentrations as low as 500 ppt in air with good selectivity and dinitrobenzene at concentrations as low as 10 ppb in air in approximately 30 s. The heterojunction design led to the efficient separation of photogenerated charge carriers, resulting in a longer lifetime of the photogenerated electrons. Thus, these photogenerated electrons could be attracted by nitroexplosives molecules through charge transfer, leading to the enhanced sensitivity.

2.3.2. Photocatalytic Effect Enhanced Sensing

The combination of the optoelectronic sensing method with the photocatalysis method could realize a higher detection limit towards vapor phase nitroexplosives since most of the explosive molecules could be photocatalized in air under illumination.[91] It is found that the presence of NO and NO_2, which are the decomposition products of TNT under room light irradiation, led to the sensing response of ZnO.[3] This result revealed that light illumination could play a more important role in trace detection of explosives. Chen et al. found that the cross-sensitivity could be effectively modulated when the thin film of TiO_2-(B) nanowires was exposed to a 365 nm UV light under operating conditions during the detection of explosives.[67] Usually, humidity has a negative effect on the sensing behaviors. As shown in **Figure 9**a, a significant response of TiO_2-(B) to air of relative humidity of 100% is exhibited. Figure 9b and 9c show that the cross-sensitivity of the sensor to humidity could be suppressed up to 51% when the UV light intensity was 40 mW cm^{-2}, while the overall sensitivity to TNT presents about 17% fluctuation over the entire range of UV illumination. Such a modulation of sensing responses by UV light was attributed to a photocatalytic effect. As shown in Figure 9d, water adsorbed on the TiO_2-(B) nanowire surface was splitted into the hydroxyl ($OH^{\cdot}$) and $HO_2^{\cdot}$ radicals and the number of surface hydroxyl groups was increased. Although this photocatalysis enhanced optoelectronic sensing method provides a new way to develop explosives sensors, the mechanisms should be better understood. Further, how to eliminate the interference of NO_x in ambient air is a stubborn problem.

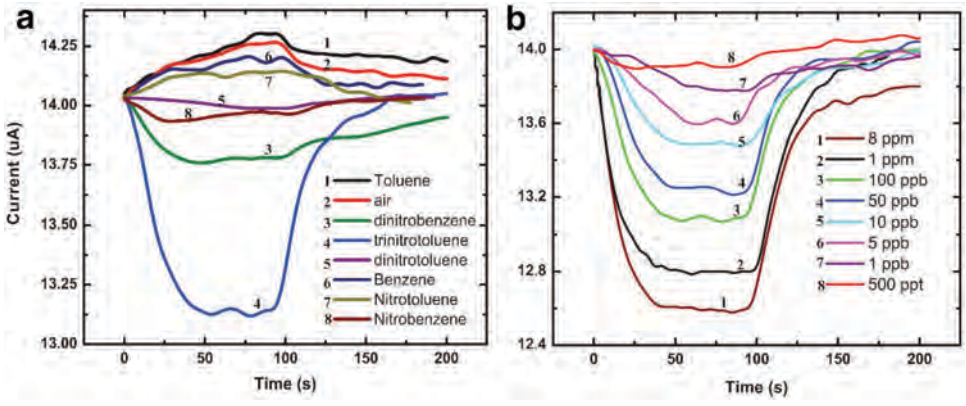

Figure 8. a) Response of a single nanowire–nanocluster hybrid sensor to 100 ppb of benzene, toluene, nitrobenzene, nitrotoluene, dinitrobenzene, DNT, and TNT in the presence of UV excitation. b) Response of the device to different concentrations of TNT under UV excitation. Reproduced with permission.[76] Copyright 2013, Institute of Electrical and Electronics Engineers.

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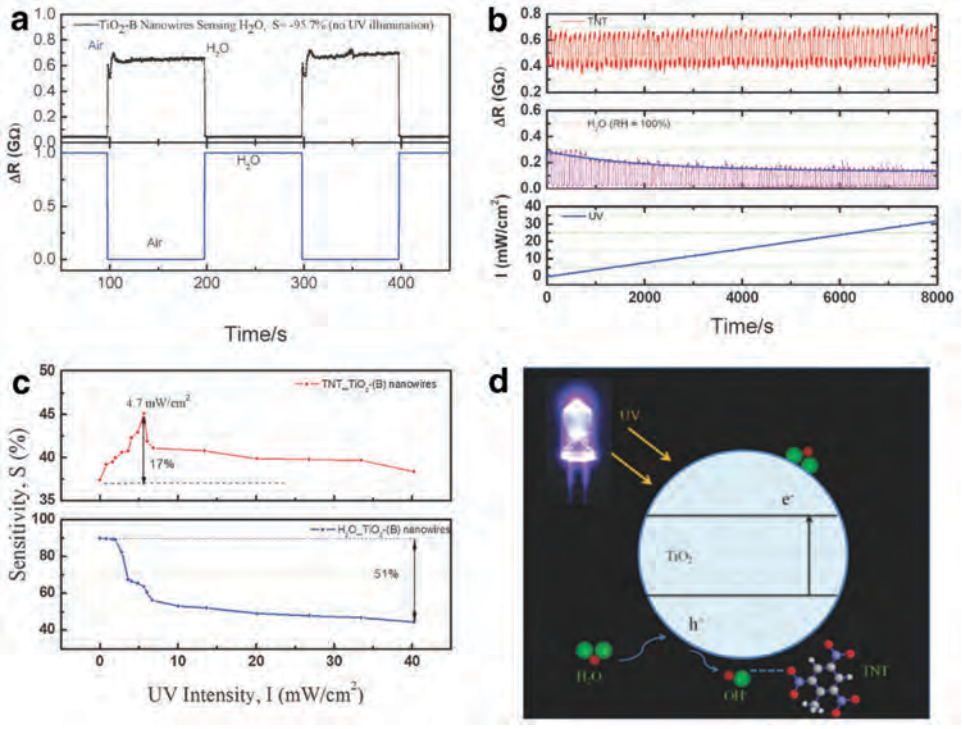

Figure 9. a) Typical resistance change of a TiO_2-(B) nanowire thin film in response to saturated water vapor at room temperature. b) Sensing response to 1 ppb concentration of TNT and saturated water vapor at room temperature based on TiO_2-(B) nanowires under controlled UV intensity from zero to 40 mW cm^{-2}. c) The variation of sensitivity to TNT and H_2O at different UV currents. d) Schematic drawing showing water splitting on the surface of TiO_2-(B) nanowires under UV irradiation. Reproduced with permission.[67] Copyright 2013, Royal Society of Chemistry.

2.4. Flexible Sensors

Most traditional nanosensors require using rigid substrates, which cannot be used in flexible electronic devices or flexible integrated systems. Advanced gas sensor requirements should include being flexible. This is also suitable for explosives sensors, which demand a higher level of practical applications. Zhou et al. reported the successful fabrication of flexible SWCNT sensor for explosives detection.[3] A schematic diagram of a flexible SWCNT sensor is shown in **Figure 10**a. The flexible aligned SWCNT FETs could be fabricated on a textile fabric with high flexibility (Figure 10b). The SEM image (right) shows that the nanotubes bridged the two electrodes. Figure 10c plots the change in SWCNT conductance normalized by the initial conductance at a gate bias of 0 V exposed to TNT vapors ranging from 8 ppb to 1.1 ppm. The detection limit was close to 1.5 ppb TNT. The flexible TNT sensor is considered to find immediate applications in systems that demand mechanical flexibility, light weight and high sensitivity.

Future flexible explosives sensors should be capable of being wearable or interfaced with flora and fauna in nature for monitoring explosives vapors. Besides, the wireless sensing ability is another key factor of flexible and transferable sensors for practical applications.

2.5. Schottky Junction for High Sensitivity and Selectivity

The above explosives sensors are all based on the traditional ohmically contacted devices. Schottky junction has several merits when compared with them in terms of the higher sensitivity, methodical controllability by changing the Schottky barrier height(SBH), and smaller adsorption area around the junction contact due to that Schottky barrier serves as a "gate" controlling the current passing through the barrier.[92–94] A small change in SBH will lead to a huge change in current, which is the basis of the Schottky barrier enhanced sensing. Besides, the diode features can make the Schottky junction realize self-powered sensing. Wang Zhonglin's group conducted a series of work to investigate the superiority of Schottky-contacted sensors for UV, liquid phase species or gas phase species.[93] Besides, by utilizing the piezoelectric effect of ZnO, they conducted a systematic research on piezoelectric effect enhanced Schottky-contacted optical, gas, chemical and biological nanosensors.[95–103]

Recent investigations on graphene/semiconductor Schottky junction which called Barristor[104] have opened up the possibility for developing interesting electronic devices. Compared with traditional Schottky junction, such Barristor are very promising for sensing applications due to the atomically thin nature of graphene, which allows modulation of the graphene Fermi level.[105] For example, Koley's group[105] developed a new chemical sensor based on reverse-biased graphene/Si heterojunction diode that exhibited extremely high bias-dependent molecular detection sensitivity and low operating power.

By introducing interface modulation strategy, sensitive and selective response towards nitroexplosives vapors can be realized on a nanowires array based Schottky-gated system. Recently, our group fabricated a high performance SiNWs array/TiO_2/reduced graphene oxide (rGO) Schottky sensor for the detection of trace

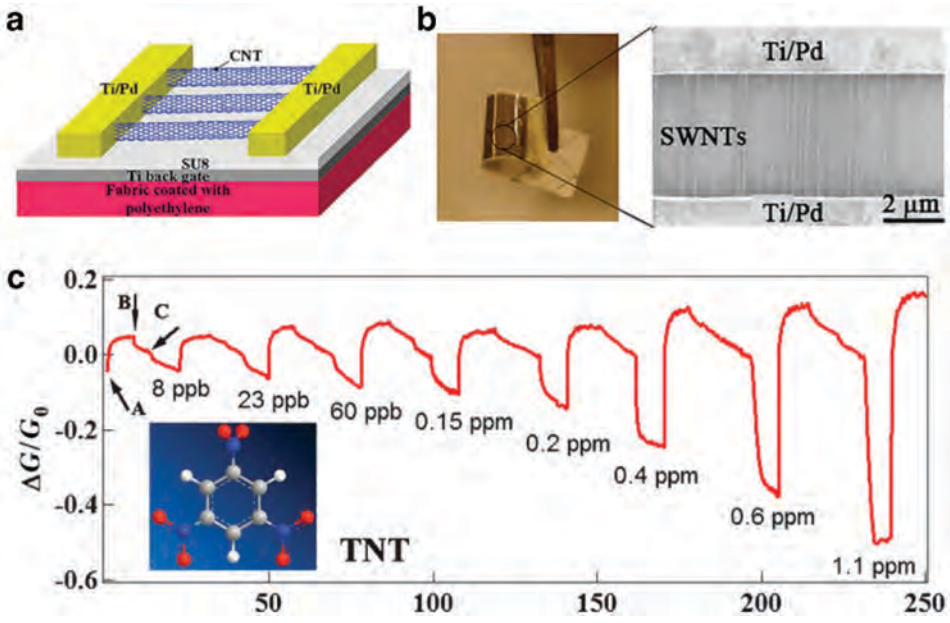

Figure 10. a) Schematic diagram showing a transistor structure that uses polyethylene-coated fabric as the substrate, 50-nm Ti film for the back-gate electrode, 2-mm SU-8 as the dielectric layer, and the transferred aligned nanotube array as the active channel. b) The optical microscopy image showing an array of such transistors built on a flexible fabric. c) Sensing response of a flexible SWNT sensor to TNT. The normalized conductance change is plotted as a function of time with the sensor exposed to TNT of different concentrations. Recovery was made by UV light (254 nm). Reproduced with permission.[3] Copyright 2010, Wiley-VCH.

nitroexplosives vapors.[44] **Figure 11**a shows the energy band diagrams of our sensor. Under reverse bias, the electrons have to overcome the energy barrier to transport through the rGO top electrode. The adsorption of TNT molecules would decrease the SBH, leading to the dramatic increase of current. The NWs array structure could benefit molecules' diffusion into the gaps between SiNWs and adsorption on both sides of the rGO sheets to change the SBH (Figure 11b). The selection of the components of the Schottky junction is of vital importance to improve the sensor performance, which highly depends on the energy band structure and adsorption characteristics. Herein, with the introduction of TiO_2, the responses for nitroexplosives increased remarkably, especially 2.4 times for TNT, 7.5 times for RDX and 5 times for HMX (Figure 11c). Superior selectivity was shown even compared with interfering gases of 10 ppm. The calculated adsorption energy towards TNT and DNT increased with the decoration of TiO_2 nanoparticles on a SiNW (Figure 11d), explaining the improved and selective detecting results. This is the first Schottky heterojunction-based sensor for nitroexplosives vapors detection and the concept illustrated here presents a new sensing method that can be applied to the ultra-sensitive detection of trace molecules such as nitroexplosives vapors.

The sensing performance of Schottky-gated explosives sensors can be further improved by rational design of the sensor components to get an optimized SBH, by surface functionalization to realize ultraselectivity and light illumination to enhance the sensitivity and realize self-powered operation.

2.6. Sensory Array for Exact Discrimination

It is very hard to determine the existence of certain explosives just rely on one sensor since there exists various explosives and many other interfering gases. Besides, it is almost impossible to develop a sensor only responds to a specific species. Exact discrimination is essential to prevent misdeclaration, thus, based on the other strategies, a sensory array is needed. A common method to build a sensory array is to employ a group of semi-specific sensors which are fabricated by modifying with different selectors. Recognition can be achieved by the composite response of the analytes to the entire array of semi-selective receptors in the sensory array.[106]

Among the different statistical analysis tools, principal component analysis (PCA) is a commonly used method to process the sensing datum and to realize molecule identification. A chemiresistive sensory array for cyclohexanone and nitromethane using covalently functionalized SWCNTs was fabricated.[16] Six sensors were exposed to a variety of analytes and the sensing responses of an array of SWCNT devices to different analytes were obtained. By further analyzing with PCA, the clear discrimination of different explosives vapors was shown (**Figure 12**a). The sensor-to-sensor reproducibility as well as the long-term stability were also studied. The response of three sensors based on m–CF_3 –Benzene–Thiourea–SWCNT to 57 and 283 ppm cyclohexanone was firstly evaluated (Figure 12b). The variances between different devices were small. Then device 2 was retested after 16 days as well as after 236 days of storage under ambient conditions without special precautions, and a clear response towards 57 ppm of cyclohexanone could still be observed. These repeatability and long-term stability make them suitable for practical applications.

Although PCA can partly be used to recognize different species, however, with the increase of the analytes' types, the PCA gradually fails to discriminate the explosives species. What's more, the concentration of explosives vapors in ambient air is

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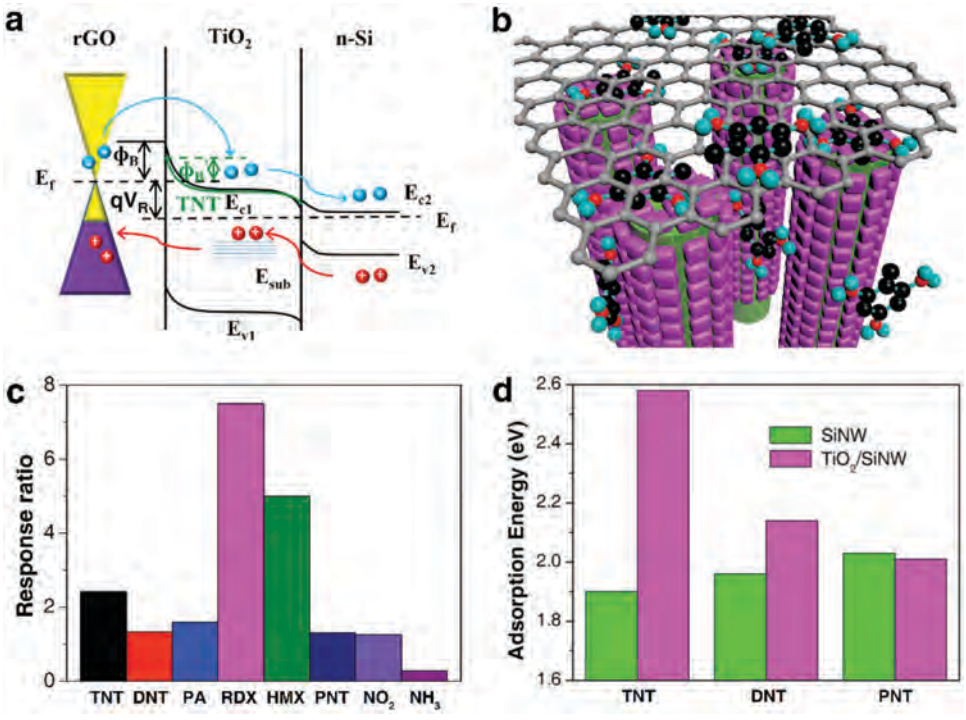

Figure 11. a) Energy band diagrams of the heterojunction showing the carriers transfer process under reverse bias. V_R is the reverse bias, E_f is the quasi Fermi level of rGO, and Φ_B is the SBH. The red surface on the Dirac cone of graphene denotes the holes injected from TiO_2. b) Schematic sensing mechanisms of SiNWs array/TiO_2/rGO Schottky heterojunction-based sensors. c) Response ratios of the SiNWs array/TiO_2 /rGO-based sensor over the SiNWs array/rGO-based sensor. d) Calculation of the adsorption energy of SiNWs and TiO_2 NPs decorated SiNWs toward nitroexplosives molecules. Reproduced with permission.[44] Copyright 2015, Wiley-VCH.

always changing, which puts forward a severe challenge to pattern recognizing methods.

Patolsky et al. presented the development of an ultrasensitive and highly selective platform for the detection and discriminative identification of different explosive chemical species, down to the low ppq concentration range in gas and aqueous samples, using a different recognizing method.[38] **Figure 13**a shows scheme of a chip bearing eight chemically differentiated nanoFETs. (1) APTES, (2) *N*-octadecyltriethoxysilane (OTS), (3) n-(2-aminoethyl)-3-3aminopropyltrimethoxysilane, (en-APTAS), (4) (heptadecafluoro-1,1,2,2-tetrahydrodecyl) dimethylchlorosilane (fluorosilane), (5) p-aminophenyltrimethoxysilane (p-APhS), (6) aminopropyldimethylmethoxysilane (APDMES), (7) 4-amino-3,3-dimethylbutyl triethoxysilane (tBu), and (8) silicon oxide, nonmodified SiNW, or NPs-decorated devices. All the devices modified with silanes showed considerable electrical shifts and cross-reactivity towards different explosive species. Different from the previous PCA analysis commonly based on the difference in sensor responses, the discriminative identification of explosives was done based on the real-time mathematical analysis, both kinetically and thermodynamically (Figure 13b-f), which practically exemplified the complete set of results obtained when exposing the multireceptor nanosensor array to a certain explosive sample. This sensing platform could also directly and sensitively detect and identify peroxide-based explosives such as TATP and hexamethylene triperoxidediamine (HMDT), which are notorious improvised explosives. In addition, the capability of this platform to directly detect practical gas systems and remotely detect various explosive species was preliminarily demonstrated, which proved its practical applications.

Although this work provided a supersensitive, rapid and real-time analytical platform for the ultra-trace detection and identification of a broad range of explosives species, this fingerprinting methods still need more works to verify its universal applicability. More works on the relations between intrinsic properties of explosives and output signals and the development of new recognizing method should be paid extensive attention. Besides, the number of sensors in a sensory array should be reduced to simplify the device structure.

3. Possible Advanced Strategies for Enhancing 1D Inorganic Nanomaterials-Based Electrical Explosives Sensors in the Future

Numerous investigations on gas sensing using 1D inorganic nanomaterials have been carried out. Among the various gaseous species, explosives vapors are just a drop in the ocean. The sensors in the previous section represent the development direction of electrical explosives sensors, however, many other advanced sensing strategies and platforms towards other airborne species based on 1D inorganic nanomaterials can be utilized to inspire and boost the development of sensing device towards explosives vapors. In this section, we will introduce some typical and advanced gas sensing strategies and platforms which may be introduced to explosives sensing in the future.

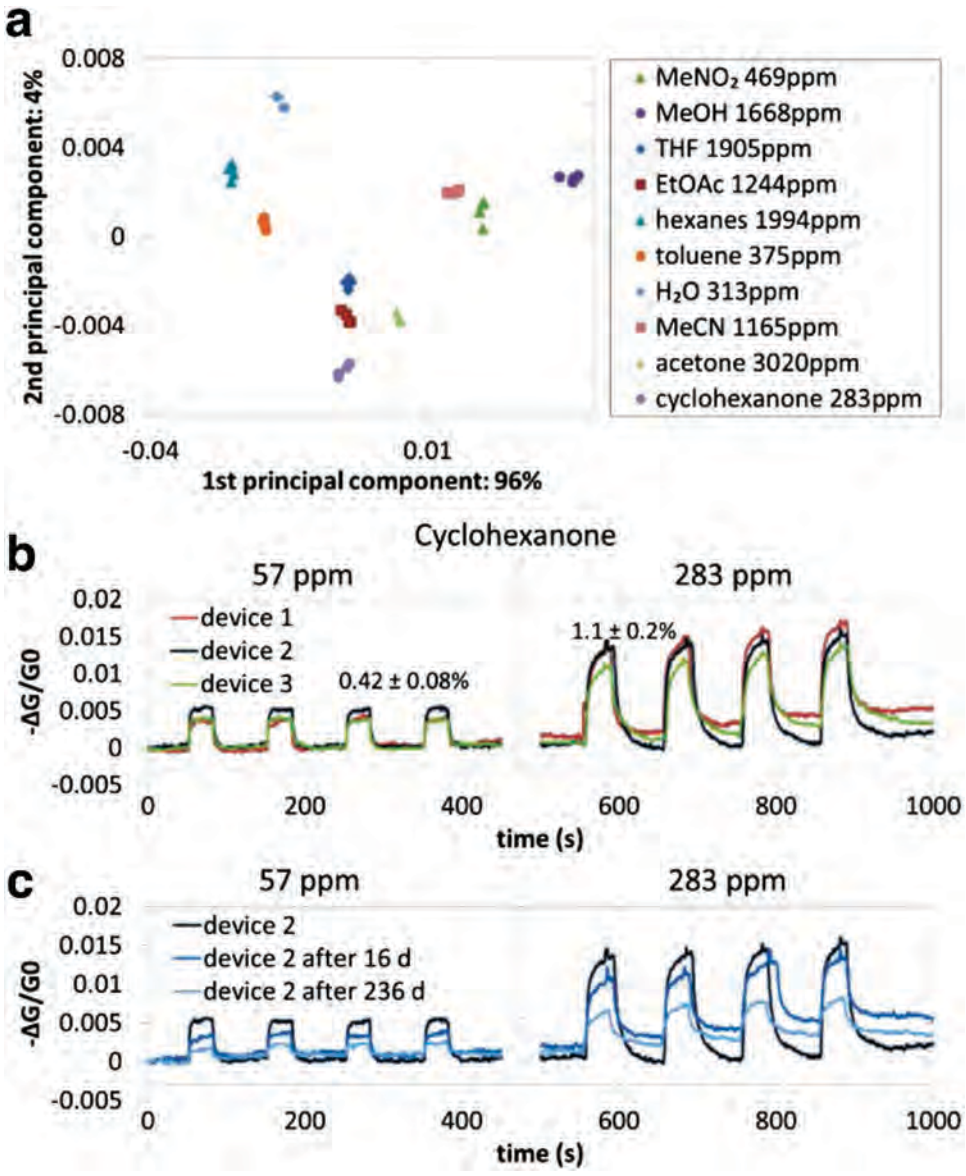

Figure 12. a) Principal component analysis of sensing response to different analytes using two sensors each based on the urea-based selector with two binding sites (Bis–U–SWCNT), its thiourea counterpart (Bis–TU–SWCNT), the phenyl analogue (m–CF_3 –Ph–TU–SWCNT), m–CF_3–Bn–TU–SWCNT, and m–CF_3 –Bn–SQ–SWCNT (Bis: two binding sites; U: urea; TU: thiourea; Bn: benzene; SQ: squaramide). b) Sensing response of three different devices prepared with m–CF_3–Bn–TU–SWCNT to 57 ppm and 283 ppm cyclohexanone. Averages and errors are based on four measurements per analyte concentration and all three devices. c) Sensing response of one device prepared with m–CF_3–Bn–TU–SWCNT to 57 ppm and 283 ppm cyclohexanone, directly after device fabrication, after 16 days and after 236 days of storage under ambient conditions without additional precautions. Reproduced with permission.[16] Copyright 2013, Wiley-VCH.

3.1. Vertical Nanowires Array

Compared with lateral ones, vertically aligned nanowires have merits such as more easily synthesis procedure, higher surface area and more diffusion channels for molecules. Besides, due to the big cross-sectional area of the dense NWs array, increased current capability and higher signal to noise ratio will be obtained. However, integrating vertically aligned NWs array with electrode contacts into a sensing device is a challenge. Lee et al. developed a generic approach for constructing an air-bridged top electrical contact on an extended array of vertically aligned nanowires.[68] **Figure 14**a–c show a schematic outline of the experimental procedure for construction of air-bridged Ohmic contact on vertically aligned SiNWs (left column) and SEM images of the corresponding sample structures (right column). A suspended polystyrene layer was firstly formed on the array of vertical SiNWs by performing partial impregnation of polystyrene at its glass transition temperature and then utilized as a deposition barrier for selective sputter deposition of metal on the tips of nanowires. The ultra-high integration density of the sensing elements for NWs array effectively maximized the signal to noise ratio and reduced the response

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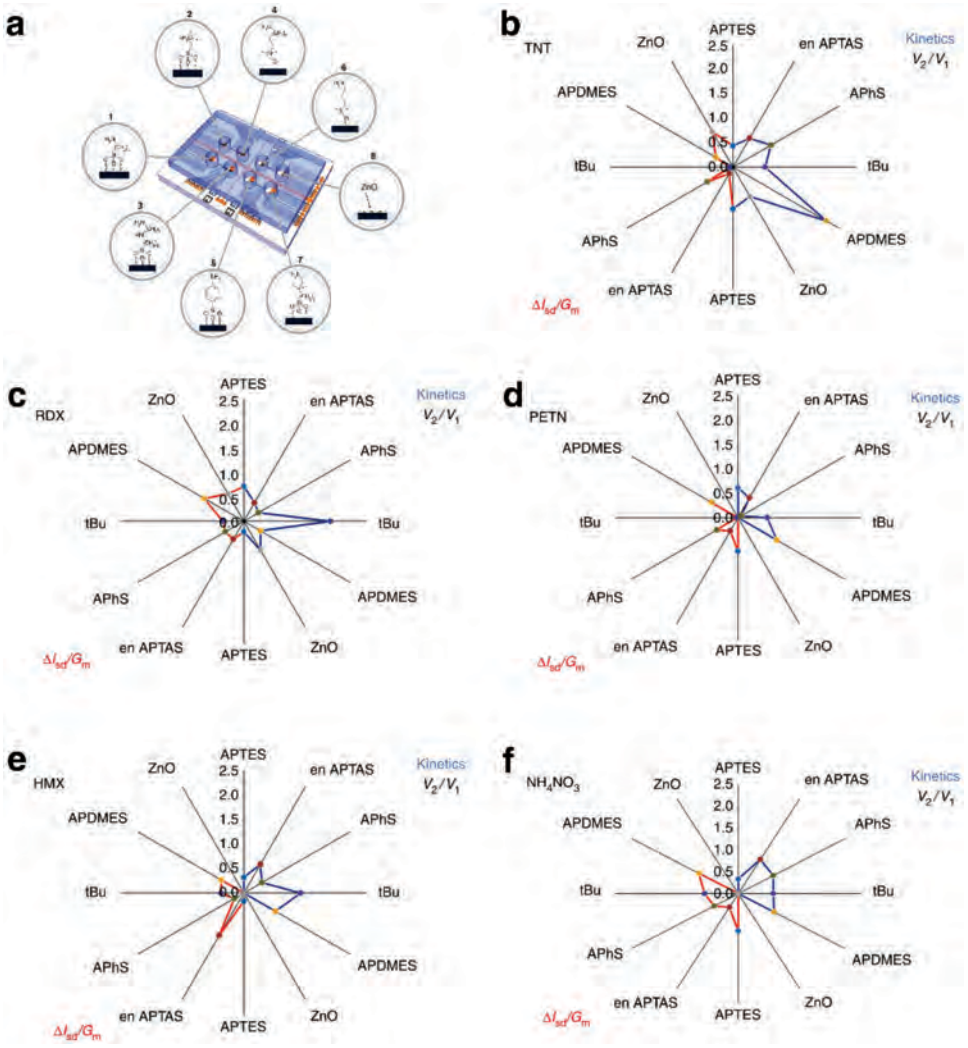

Figure 13. a) Scheme of a nanoFET devices sharing a common liquid gate, arrayed into eight separate chemically differentiated subregions. 1) aminopropyltriethoxysilane (APTES), 2) *N*-octadecyltriethoxysilane (OTS), 3) n-(2-aminoethyl)-3-3aminopropyltrimethoxysilane, (en-APTAS), 4) (heptadecafluoro-1,1,2,2-tetrahydrodecyl)dimethylchlorosilane (Fluorosilane), 5) p-aminophenyltrimethoxysilane (p-APhS), 6) Aminopropyldimethylmethoxysilane (APDMES), 7) 4-amino-3,3-dimethylbutyl triethoxysilane (tBu), 8) silicon oxide, nonmodified SiNW, or NPs-decorated devices. Fingerprinting explosives by combining kinetics and thermodynamics: the algorithm-derived analysis results of the interaction of the multireceptor sensor platform (consisting of 1, 3, 5, 6, 7 and 8) after its exposure against b) TNT, c) RDX, d) PETN, e) HMX, and f) NH_4NO_3 explosive species. Left side $\Delta I_{sd}/G_m$ represents the thermodynamic-derived results for each explosive (red color), and the right side represents the kinetics-derived results for each explosive species (blue color). Reproduced with permission.[38] Copyright 2014, Macmillan Publishers Limited.

time and recovery time compared to the single NW-based device. Thus, an explosive sensing device incorporting vertical nanowire array structure should be a good choice to effectively improve the sensing performance. However, for the detection of ultra-trace species even down to single molecule, this kind of vertical chemresistor could be replaced with vertical FET and vertical Schottky-gated sensors.

Like planar NWs array, the vertical one can be fabricated into a FET device which could benefit the diffusion and modulate the sensitivity at the same time. Han et al. demonstrated a high performance FET implemented on massively parallel dense vertical SiNWs array with silicided source/drain contacts and scaled metallic gate length fabricated using a simple process.[107] The proposed structure offered several advantages including better immunity to short channel effects, reduction of device-to-device variability, and nanometer gate length patterning without the need for high-resolution lithography, which will benefit its use in explosives sensing device.

Other interesting works include the fabrication of graphene/semiconductor devices, which could transform into a Schottky device. Choi et al. fabricated a wafer-scale graphene/Si-nanowire array heterostructures for molecular sensing by vertically contacting single-layer graphene with high-density SiNWs.[108] A high sensitivity with a high signal to noise ratio, very fast response time and recovery time was obtained. These studies suggest that the construction of the top electrode onto a vertical NWs-based device should be paid extensive attention to further boost the priority of a vertical array-based sensor, and different types of explosives sensing devices could be fabricated into vertical ones.

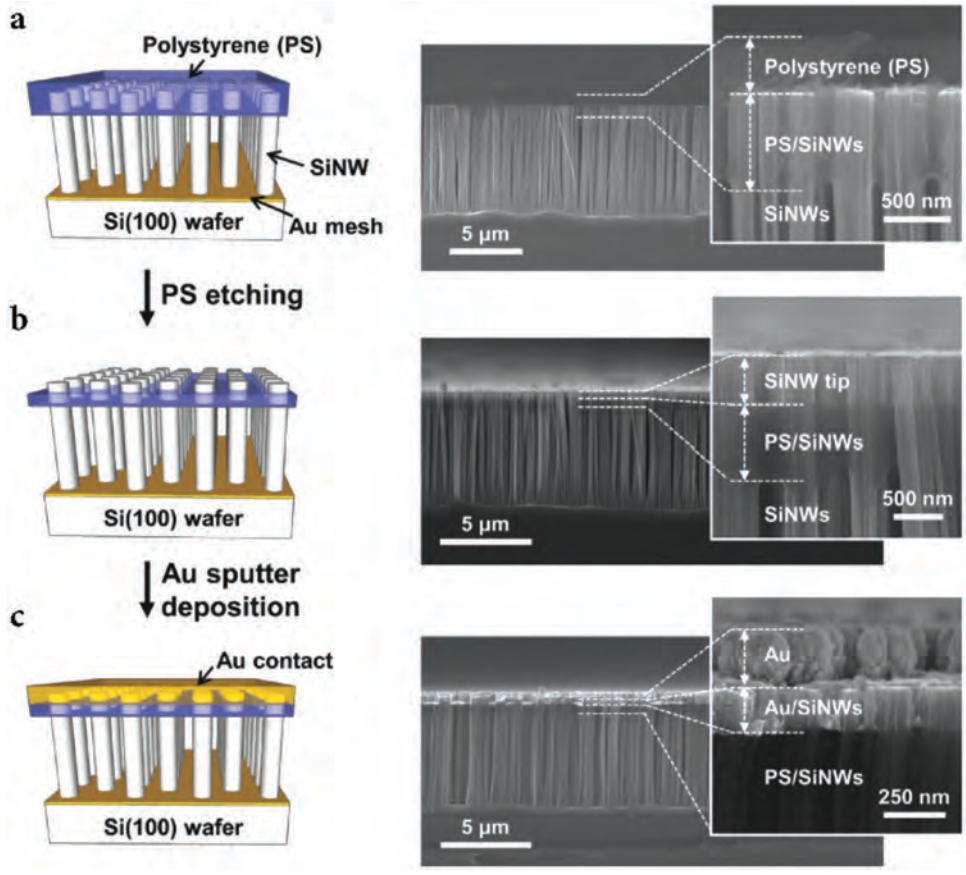

Figure 14. Fabrication process of air-bridged top metal contact on vertically aligned SiNWs; a) formation of thin suspended layer of polystyrene on the uppermost part of vertical SiNWs, (b) partial removal of PS layer by oxygen plasma etching to expose the tips of SiNWs, and (c) sputter deposition of gold for electrical contact. SEM images of the corresponding sample structure are presented on the right side. Reproduced with permission.[68] Copyright 2012, Wiley-VCH.

3.2. Direct-Patterned Aligned Nanostructures

As mentioned before, the aligned nanowires could facilitate the explosives sensing. Direct patterning the aligned nanowires can achieve better control of the transistor channel orientation and carriers transporting behaviors, which is necessary for FET devices with high quality, and would create advantages for various sensing applications including explosives detection.

The 1D graphene, namely graphene nanoribbons (GNR), narrow (<10 nm) and straight-edged stripes of graphene, is predicted to exhibit band gaps useful for room temperature transistor operations with excellent switching speed and high carrier mobility.[109–112] Compared with 2D graphene film, the 1D GNRs are more advantageous for gas sensing application and FET devices. Wi et al. implemented directed self-assembly of block-copolymers in combination with nanoimprint lithography to pattern sub-10 nm half-pitch GNRs over large areas.[113] Multichannel FETs made from such GNRs exhibited a relatively high on/off current ratio >10. The nanofabrication method and the device structure presented could be further developed to realize the massive production of high-quality GNRs based sensing devices. Zhou et al. reported patterning, characterization and superior chemical sensing of ultranarrow aligned GNR arrays down to 5 nm width using helium ion beam lithography (HIBL) for the first time.[70] The patterned GNR arrays using HIBL possess narrow and adjustable widths, high aspect ratios and relatively high quality. FETs were fabricated on such GNR arrays for gas sensing application. Edge states of GNRs could provide more active sites and HIBL would lead to the transition from a semimetal to a semiconductor and result in a better current modulation. The aligned GNRs could be a new class of 1D sensing materials towards gas phase explosives detection due to the possibility of optoelectronic sensing utilizing the existed bandgap, the superior electrical characteristics and the capability of being functionalized.

For ordinary metal oxides explosives sensor device, usually, either single nanowire or random nanowires were used. However, patterning the 1D metal oxides nanomaterials is always a problem. Zhou et al. demonstrated aligned, planar SnO_2 nanowires grown on *A*-plane, *M*-plane and *R*-plane sapphire substrates which could be patterned photolithographically for FETs and sensor devices.[114] These parallel nanowires could reach 100 μm in length with sufficient density. A straightforward photolithography process was demonstrated for patterning the aligned nanowires for working FETs with high mobilities and on/off ratios sufficient for driving an external organic light-emitting diode (OLED), surpassing network SnO_2 nanowire FETs. The proposed synthesizing method could offer

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a straightforward method to fabricate scalable nanodevices like ZnO and TiO_2 for sensitive explosives sensing applications.

3.3. "One Key to One Lock" Concept

The development of highly sensitive, selective and real-time detection method towards specific target gas like explosives vapors in a highly complex background is a great challenge. The approach of lock-and-key recognition using electrical sensors and fluorescent sensors has allowed low detection limits (down to ppb even ppt level) and high sensitivities towards explosives vapors.

Combination noble metal modification with other strategies can partly realize the "one key to one lock" concept. Llobet et al. demonstrated a quinoxaline-walled thioether-legged deep cavitand functionalized MWCNTs with unprecedented sensitivity and partial selectivity.[115] The cavitand which acted as a specific recognizing "lock" was grafted onto AuNP decorated oxygen plasma treated MWCNT by a self-assembled monolayer process to selective bind the "key" benzene vapor. Nitroaromatic compounds such as TNT have the similar structures with benzene and are one kind of the most commonly used explosives. Designing cavitands which have specific binding with nitroaromatic molecules will benefit the "one lock to one key" detection.

However, due to the multiplicity of explosives family, designing and synthesizing ultra-selective receptors towards each explosive vapor is impossible. Recognition of a group of substances with same feature, such as nitroexplosives, may cause misdeclaration, since many analogues are not explosives. The cross-reactive sensor arrays concepts have been successfully demonstrated for the detection of explosives through sophisticated pattern recognition algorithms. However, explosives species used in this concept are either with high concentration (ppm level) or in fluid phase. Besides, this approach requires complicated circuitry and hardware as well as high energy consuming to host the pattern recognition analysis of the wide variety of the output sensing signals.[50]

The combination of noble metal modification and FET operation might be a solution to this problem. Using Mg-doped In_2O_3 nanowire E-mode FET sensor array decorated with various metal NPs (Au, Ag, and Pt) as illustrative prototypes, Liao et al. designed and demonstrated a "one key to one lock" hybrid sensor configuration for the target-gas-specific, highly sensitive, and promptly responsive chemical gas sensing operated in a complex ambient background.[71] The sensing device was based on three criteria: (i) the Mg-doped In_2O_3 nanowire as sensing platform which exhibited good electron mobility and chemical and thermal stability; (ii) the FETs with appropriate threshold voltages to suppress the response to all gases; (iii) Au, Ag, and Pt NPs decoration onto the nanostructure surface to introduce the gas-specific selectivity towards different gases. This "one key to one lock" hybrid sensor could allow the real-time detection of a single compound among a mixture of ambient gases. Thus, the "one key to one lock" concept could be a good choice to selectively detect the exact species of certain explosives.

Like other sensor arrays, the number of FETs should not be less than the number of explosives species. However, the kind of noble metals is limited. An individual FET which combines the selectivity of the lock-and-key approach with the ability to tailor the cross-reactive sensors array for complex gases will be an answer.

Haick et al. demonstrated an ultrasensitive, molecularly modified SiNW FET that brings together the lock-and-key and cross-reactive sensing worlds for the diagnosis of (gastric) cancer from exhaled volatolome.[69] As shown in **Figure 15**a, on one hand, the FET was modified with different species that supplies an assortment of independent features, each of which responds differently to the various species at ppb concentration level. On the other hand, the collective output of these features can be treated via simple pattern recognition methods to enable recognition of complicated mixtures. Figure 15b–c show the representative FET features (V_{th}, μ_h, and I_{ds} @ $V_{gs} = 0$) of sensor 1 to sensor 7, on exposure to the various concentrations of VOC1 to VOC5, on a hot plot. The application of this artificial intelligence on the SiNW FET device parameters could allow identifying VOCs in multicomponent environments as well as estimating the constituent VOC concentrations. Using breath samples collected from actual patients with gastric cancer and from volunteers who do not have cancer, blind analysis validated the ability of the reported sensor to discriminate between gastric cancer and control conditions with >85% accuracy, irrespective of important confounding factors such as tobacco consumption and gender. The reported sensing approach could pave the way to use the power of silicon nanowires for simple, inexpensive, portable and noninvasive diagnosis of cancer and other disease conditions. This concept of using single FET sensor to discriminate the desired species from complex ambient background could be further used in explosives sensing systems for selective explosives vapors recognition and concentration prediction.

3.4. Self-Powered Sensors

One of the major problems for wireless sensors is the batteries needed to drive individual sensor for sustainable and maintenance-free operation.[116] Batteries would increase the required space for integration, introduce potential hazard towards environment and consume huge amount of power. It would be highly desirable if sensors could be self-powered and without external power sources. The self-powered sensors can greatly reduce the power consumption and boost the development of wireless sensors. For explosives detection which requires remote and noncontact monitoring, the development of self-powered sensors is of extraordinary significance.

Nanogenerators which are based on the piezoelectric effect were developed by Wang Zhonglin's group.[117,118] Using ZnO nanostructures, nanogenerators convert mechanical energy into electric energy. Different works have proven that ZnO-based nanoarray nanogenerator could be a powerful tool for gas sensing applications.[72,119,120] For example, without any external electric power source, the portable device could be self-powered under the driving of human motion, in which the piezoelectric output of the nanoarray could act as both the power source of the device and the room-temperature sensing signal.[72] Since ZnO shows outstanding performance for explosives detection, the combination of excellent gas sensing properties of ZnO and advances of nanogenerators might make the self-powered wireless explosives sensing come true.

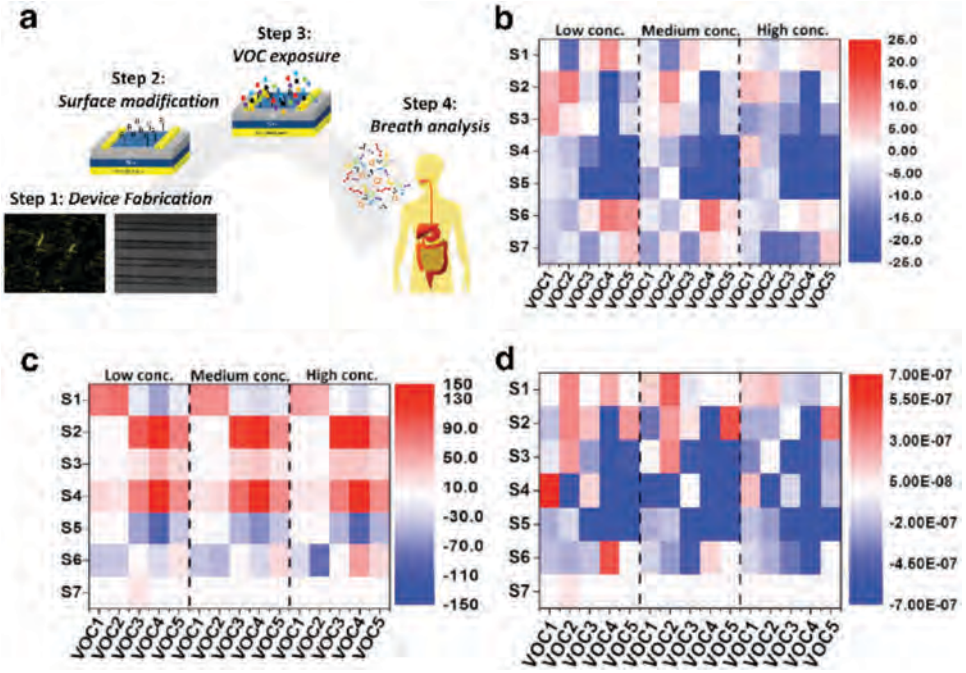

Figure 15. a) Schematics demonstrating the main steps implemented in the present study: fabrication of SiNW FETs (step 1); modification of the SiNWs with molecular layers (step 2); exposure of the molecularly modified SiNW FETs to VOCs that are linked with gastric cancer conditions, and for comparison, to VOCs that serve as confounding environmental factors (step 3); and exposure of the molecularly modified SiNW FETs to real breath samples collected from volunteers who have gastric cancer or from volunteers with control (healthy) conditions (step 4). Hot plot of the average response of b) V_{th}, c) μ_h, and d) I_{ds} @ $V_{gs} = 0$ of S1 – S7 on exposure to various concentrations of VOC1 to VOC5. Low concentration stands for 5 ppb (50 ppb for VOC1); medium concentration stands for 50 ppb (80 ppb for VOC1); and high concentrations stand for 150–500 ppb. Reproduced with permission.[69] Copyright 2014, American Chemical Society.

Different from the nanogenerators which are based on the wurtzite materials like ZnO, P-N junction is abundant in the selection of materials. Besides, at the contact area of a P-N junction structure, the conduction and valence bands usually bend and the Femi levels are equalized with the formation of the depletion layer, resulting in the improvement of the conductivity and the decrease of the response time and recovery time.[121,122] Furthermore, P-N junction can accomplish self-powered/low-powered sensor operation under light illumination since p–n junctions are commonly used structure to fabricate solar cells. [73]

Prades et al. presented a semiconductor-based gas sensor concept that combines self-powered operation and high gas selectivity in a singular sensor device.[73] n-ZnO nanowires were grown onto the p-Si and followed by surface modification of adding a SAM of functional groups, which can be shown in the SEM image of a singular p-Si/n-ZnO diode. The sensor signal was generated by microfabricated p-Si/n-ZnO diodes upon visible-light illumination. This configuration resulted in a linear increase of the measured V_{oc} signal, proportional to the number of diodes in series under light. Beyond the combination of self-powered sensing and high selectivity, a high sensitivity could also be demonstrated for the example target gas. This work shows the feasibility of transferring chemical signals from specific organic-gas interactions into active electronic signals solely driven by visible light.

The p–n junction can also be combined with surface modification, optoelectronic enhanced sensing and other strategies to realize the advanced sensing requirements.

3.5. Transferrable Flexible Sensors for Wearable and Bioimplantable Applications

Advanced flexible gas sensor requirements not only include being stretchable but also being transferrable and bioimplantable to enable smart electronics applications, such as, biointegrated/implantable applications and systems with epidermal electronics.[100,123] Besides, the remote and non-contact sensing requirements for explosives sensors demand the wearable and bioimplantable device.

Park et al. reported an unconventional approach for the single-step synthesis of monolithically integrated electronic devices based on multidimensional carbon structures.[74] Integrated array of FETs and sensors composed of CNT channels and graphitic electrodes and interconnects were formed directly from the synthesis. These fully integrated, all-carbon devices are highly flexible and could be transferred onto both planar and nonplanar substrates, including papers, clothes and fingernails, as shown in **Figure 16**a. 10 000 cycles of mechanical bending had been done without significant structural deformations or degradation of electrical performance. Furthermore, the

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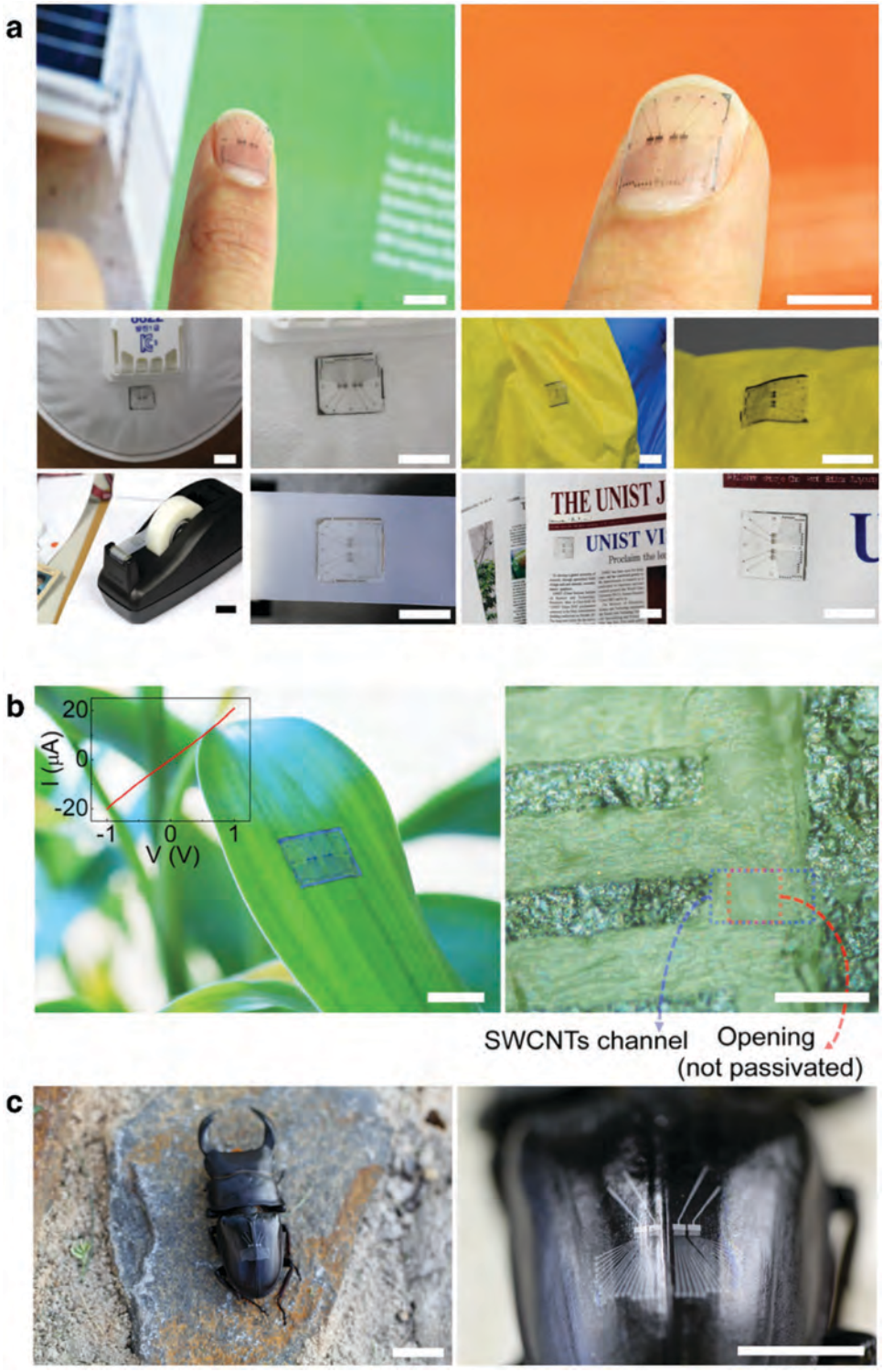

Figure 16. a) Photographs of the sensor arrays transferred onto a fingernail, a particulate mask, a protective arm sleeve, an adhesive tape, and a sheet of newspaper. Scale bars: 1 cm. b) A photograph (left, scale bar, 1 cm), an optical microscope image (right, scale bar, 50 μm) of SWCNTs–graphite arrays transferred onto surface of a live leaf. c) Photographs of SWCNTs–graphite arrays transferred onto surface of the insect. Scale bars: 1 cm. Reproduced with permission.[74] Copyright 2014, American Chemical Society.

sensor network could be interfaced with inherent life forms in nature like live plants (Figure 16b) and insects (Figure 16c) for real-time, wireless sensing of toxic gases. From this example, it is believed that the capability to synthesize flexible and transferrable devices could also be expanded to explosives vapors detection in the future since there is a strong demand in this area.

4. Conclusions and Future Perspectives

In this review, we make a detailed and comprehensive analysis of the recent emerging strategies for enhancing 1D inorganic nanomaterials-based explosives sensors. Further, an analysis of possible strategies for enhancing 1D inorganic nanomaterials-based electrical explosives sensors is given.

Strategies and materials for the detection of explosives are necessary in a variety of fields such as homeland security, battlefield detection and anti-terrorist. Owing to the outstanding physical, chemical and biological properties, over the last five years, the electrical detection methods using 1D inorganic nanomaterials-based gas sensors have been the research focus and witnessed the fast development and striking achievement, which also promoted the development of explosives sensing materials and strategies. However, due to the urgent demand of explosives sensors with high sensitivity, selectivity, low power consuming, simple structure, fast response and recovery procedures, high reliability and biocompatibility, more advanced strategies are urgently needed for enhancing 1D inorganic nanomaterials-based electrical sensors towards explosives vapors detection. Compared with fluorescent sensing methods, there exists a huge gap between lab experiments and commercial products for electrical explosives sensors. Although numerous 1D inorganic nanomaterials-based electrical sensors have been fabricated and applied, there is still much work to do to accelerate and perfect the 1D inorganic nanomaterials-based electrical sensing approach towards explosives detection. Huge challenges like manufacturing technique with high cost and energy consumption, the difficulty of the assembling and patterning of 1D inorganic nanomaterials into functional devices, the weak repeatability for surface modification, the oxidation induced aging and the gaps between lab experiments and practical application, still remain to be resolved. All of these difficulties hinder the development of electrical explosives sensors into practical application. Besides, most of the current researches focus on the detection of military explosives like nitroexplosives, while the detection towards improvised explosives made from fertilizers and industrial chemicals containing oxidizers such as chlorates, perchlorates and nitrates has got little attention. These homemade explosives which have no certain compositions are more and more frequently used by terrorists due to rigid controlling on military explosives. Therefore, the development of the sensing materials and devices towards sensitive and accurate identification of improvised explosives should be drawn enough attention.

It is anticipated that future efforts on simplifying device structure, improving the modification procedure, combining experimental results and theoretical calculation, developing new sensing concepts and identification methods will make 1D inorganic nanomaterials-based electrical sensors towards explosives vapors detection become commercial and sophisticated products, and thus, contribute to the social safety.

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