Research article

Hui Zhang, Kangyi Zhao, Songya Cui, Jun Yang*, Dahua Zhou, Linlong Tang, Jun Shen, Shuanglong Feng, Weiguo Zhang and Yongqi Fu*

Anomalous temperature coefficient of resistance in graphene nanowalls/polymer films and applications in infrared photodetectors

<https://doi.org/10.1515/nanoph-2017-0135>

Received December 28, 2017; revised February 20, 2018; accepted March 16, 2018

Abstract: Graphene nanowalls (GNWs) exhibit outstanding optoelectronic properties due to their peculiar structure, which makes them a great potential in infrared (IR) detection. Herein, a novel IR detector that is composed of polydimethylsiloxane (PDMS) and designed based on GNWs is demonstrated. Such detector possesses an anomalous temperature coefficient of resistance of 180% K⁻¹ and a relatively high change rate of current (up to 16%) under IR radiation from the human body. It primarily attributes to the ultra-high IR absorption of the GNWs and large coefficient of thermal expansion of PDMS. In addition, the GNW/PDMS device possesses excellent detection performance in the IR region with a responsivity of ~1.15 mA W⁻¹. The calculated detectivity can reach 1.07 × 10⁸ cm Hz^{1/2} W⁻¹, which is one or two orders of magnitude larger than that of the traditional carbon-based IR detectors. The significant performance indicates that the GNW/PDMS-based devices reveal a novel design concept

and promising applications for the future new-generation IR photodetectors.

Keywords: graphene nanowalls; IR; polymer; TCR; thermal detectors.

1 Introduction

The application of infrared (IR) photodetectors keeps rapidly growing in the fields of security, night vision, astronomy, and health care. In these specific fields, thermal photodetectors without cooling that can operate at room temperature are highly desirable. Typically, vanadium oxide (VO_x) and amorphous silicon (Si) are the most widely employed thermal-sensitive materials due to their superior temperature coefficient of resistance (TCR in units of % K⁻¹ hereinafter) of up to -4.5 [1] and 7.9 [2], respectively. Those thin films, however, are unable to absorb light by themselves and require an extra light-absorbing layer that collects IR radiation and conducts IR heat into thermal-sensitive materials. Recently, there is an increasing effort in searching for novel IR sensing materials that can exhibit excellent performance with broadband absorption and competitive TCR value, such as graphene [3, 4], carbon nanotube (CNT) [5], and WSe₂ [6]. Among these materials, the investigation of graphene is most popular due to its outstanding performance [7, 8]. However, as the intrinsic absorptivity is only 2.3% for each layer [9], graphene-based IR photodetectors routinely suffer from poor light absorption. Considering this, researchers focused on exploring effective methods to improve the absorption, for example, plasmon enhancement [10, 11], waveguide [12, 13], and quantum dots [14, 15]. However, the desired absorptivity is limited by the narrowband absorption due to the optical characteristics of those structures [16]. Except for low light absorption, the intrinsic TCR of graphene also shows poor superiority, which is

*Corresponding authors: **Jun Yang**, Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, P.R. China; and University of Chinese Academy of Sciences, Beijing 100049, P.R. China, e-mail: jyang@cigit.ac.cn; and **Yongqi Fu**, School of Physics, University of Electronic Science and Technology of China, Chengdu, Sichuan 610054, P.R. China, e-mail: yqfu@uestc.edu.cn. <http://orcid.org/0000-0002-5737-4332>
Hui Zhang: School of Physics, University of Electronic Science and Technology of China, Chengdu, Sichuan 610054, P.R. China; and Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, P.R. China
Kangyi Zhao and Songya Cui: School of Physics, University of Electronic Science and Technology of China, Chengdu, Sichuan 610054, P.R. China
Dahua Zhou, Linlong Tang, Jun Shen, Shuanglong Feng and Weiguo Zhang: Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, P.R. China

$-0.05\% \text{ K}^{-1}$ only. Researchers [15–18] have done a lot of works for the purpose of enhancing the TCR of graphene in which the maximum value is $-4\% \text{ K}^{-1}$ accompanied with a complicated fabrication process. Apparently, it is challenging to simultaneously possess both broadband strong absorption and high TCR value for the bolometric sensing materials.

Graphene nanowalls (GNWs), which are 3D carbon nanomaterials, can be regarded as nanostructures with few-layer graphene sheets [17] and usually have tapered structure with one to three graphene layers at the top and several layers at the bottom [18]. Therefore, GNWs are expected to reveal a great number of novel properties. According to literature review, GNWs have been mainly applied in the fields of energy storage [19, 20], bioapplications [21], and nanocomposites [22]. Actually, GNWs have been proven to possess excellent light absorption from NIR to MIR region [23–25] due to the abundance of edges and index of refraction close to unity at the interface. Additionally, our previous work [26] reported that GNWs have a considerably high TCR. Furthermore, in terms of IR detectors, GNWs also show a great market potential. Wang et al. [27] pointed out that the electrical parameters of GNWs are comparable to that of the graphene-based devices. Recently, Shen et al. [28] reported a photodetector that was designed based on GNWs, and the photodetection parameters of the devices are greatly improved. All the above-mentioned reports demonstrated that GNWs have good enough qualifications for use as high-performance sensing materials of IR detectors. Nevertheless, the influence of the height of GNWs and underlying substrate on the performance of IR detectors is still unclear. It is a drawback for the development of GNW-based IR photodetectors.

In this paper, we demonstrate a novel IR photodetector that is structured based on the GNWs acting as sensing bolometric materials. A low-temperature and sample craft plasma-enhanced chemical vapor deposition (PECVD) is applied to synthesize the GNW film and a poly(methyl methacrylate) (PMMA)-free transfer method is adopted to maintain the vertical morphology of GNWs on the target substrate, including polyethylene terephthalate (PET), Si, and polydimethylsiloxane (PDMS). The Raman spectra and absorption of MIR band from the Fourier transform IR (FTIR) spectrometer depending on the height of GNWs are given. After transferring on three substrates with significantly different coefficients of thermal expansion (CTE), the performance of the IR detector devices is characterized. The thermal expansion of substrates plays an important role in TCR. GNW/PDMS composites are confirmed as

ideal IR sensing materials with both strong broadband absorption and high TCR value. An anomalous TCR value of up to $180\% \text{ K}^{-1}$ is obtained, which is an ultra-high value compared to the previous IR detectors. Additionally, the GNW/PDMS structured device possesses high-performance IR photodetectors and has a great potential application in the field of bolometry.

2 Experiments

2.1 Synthesis of GNWs

The GNW film was grown on copper foil (25 μm thick) at a pressure of 50 Pa using RF-PECVD as reported in our previous work [26, 29]. The gas proportion ($\text{CH}_4:\text{H}_2$) was maintained at a constant ratio of 6:4 at 750°C growing temperature and 200 W RF power. Growing time varied from 30 to 90 min. Before growing, the copper substrate was annealed at 700°C for 60 min, making the quality of the GNW film greatly improved [23].

2.2 Characterization

The surface morphology and height of GNWs were analyzed using scanning electron microscopy (SEM; JEOL JSM-7800F), and the typical zooming magnification was 30,000 $\times$. The characterization of vertical nanosheets in GNWs was performed using a high-resolution transmission electron microscope (TEM; FEI Tecnai G2 F20) operating at 200 kV. The defect status of GNWs was verified using a Raman spectrometer (Renishaw inVia Reflex) with a laser excitation wavelength of 532 nm. IR absorbance was obtained using an FTIR spectrometer with the scanning of waveband ranging from 2 to 16 μm . In addition, we performed a 3D surface imaging of GNWs using atomic force microscopy (AFM). The details are discussed in Section 3.

2.3 Fabrication of PET/GNWs, Si/GNWs, and GNWs/PDMS

The GNW film is thicker and more robust than graphene. This property makes it possible to be transferred without the protection of PMMA. Therefore, the PMMA-free method is adopted here. It is important for achieving an excellent performance of the devices. Floating

GNW films were derived after 6 h etching process in ammonium persulfate solution and transferred to the target substrates, including Si, PET, and PDMS. To guarantee the integrity of the GNW films, a hydrophilic treatment for the transferred substrates was carried out via UV-ozone or O_2 plasma. Then, the Ag electrodes were pasted onto two terminals of the sample. To increase the TCR value, the GNW channel between two Ag electrodes was set as 45 mm^2 (i.e. $15 \times 3 \text{ mm}$ in length and width, respectively). The specific fabrication process is shown in Figure 1.

2.4 Test of TCR

TCR is a key parameter for IR detectors and is given by [30]:

$$\text{TCR} = \alpha = R_0 \frac{\Delta R}{\Delta T} \quad (1)$$

where R_0 is the initial resistance. It is necessary to determine the TCR of the samples due to its importance. In our study, we used stable hot plate as a heat source to adjust the ambient temperature of the sample. Meanwhile, Keithley source-meter (2450, from Tektronix company) was employed to record the change of resistance under different temperatures (ranging from 20°C to 45°C with an interval step of 5°C) and 1 V bias voltage. To prove that it is reasonable to measure the TCR with the step of 5 K, we made an additional supplementary experiment with an interval step of 1 K (ranging from 35°C to 40°C).

3 Results and discussion

3.1 Morphology and optical performance of GNWs

The SEM images in Figure 2A and B show the morphology of the GNWs with three specific heights of 380, 740, and 940 nm, respectively. It can be seen that the entire surface of the substrate is covered with continuous wall-like vertical nanosheets and becomes densified as the growth time increases. The vertical nanosheet is further characterized using TEM as shown in Supporting Information Figure S1a and b. The results provide evidence that the vertical nanosheets consist of several graphene layers that are 0.34 nm thick for each layer. The GNWs of 940 nm in height reveal that the high density of wall-like edge structure leads to outstanding optical properties. The IR absorption of GNW films with different heights is illustrated in Figure 2C. As can be seen, the high GNWs correspond to a strong absorbance. In fact, the high GNWs possess the structure with more wall-like edges; the structure plays a crucial role in decreasing light reflection according to the gradient refractive index model [27]. The absorbance limitation of GNWs is studied as well. When the height of the GNWs reaches $1.5 \mu\text{m}$, the absorbance of the GNWs is relative unchanged (see Supporting Information Figure S2). Figure 2D shows the Raman spectra of the GNWs with different heights. Both I_{2D}/I_G ratio and D peak values diminish as height increases, which means that the graphene layers increase and defects become less. The AFM image in Figure 2E further proves that the GNWs have a taper-off structure

Figure 1: Schematic diagram of device fabrication.

(A) Growing GNWs on copper foil. (B) Etching copper foil in ammonium persulfate solution. (C) Washing residue of etchant in DI water. (D) Transferring GNWs on target substrates. (E) Annealing GNWs with 100°C for 30 min. (F) Pasting Ag electrodes on two terminals of GNWs.

Figure 2: Morphology and optical characterization of the GNWs.

(A and B) Morphology and cross-section of the GNW SEM images with height of 380, 740, and 940 nm, respectively. (C and D) IR absorbance and Raman spectrum of GNWs with different heights. (E) AFM image of the GNW film.

and ultra-high surface ratio. Moreover, this structure can respond with excellent properties of the GNWs, such as extraordinary light absorption in ultra-broad waveband and stability in a variety of surroundings [23].

3.2 TCR of GNWs with varieties substrates

Figure 3 indicates that the substrates with different CTEs have a substantial influence on TCR. The contradictory between the positive and negative values of TCR is demonstrated by the different CTEs of the substrates. For the

Si substrate with a relative low CTE ($\epsilon_{\text{Si}} = 2.5 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$), the influence of the expansion of Si can be ignored and the TCR of GNWs/Si can approximately be the pristine TCR of the GNW films. As reported in our previous work [24], the thermal expansion of the substrate leads to a positive TCR, especially for the polymer substrate. Interestingly, for the PET/GNWs, the absolute value of TCR is below 0.1% and an ultralow TCR of -0.03% is achieved. It may be the reason that the CTE of PET ($\epsilon_{\text{PET}} = 5.9 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$) is one order of magnitude larger than that of Si. The parameter causes the stretch of the GNW film with the temperature rise. The near-zero TCR means that the internal

Figure 3: Influence of different CTEs of the substrate on CTR.

(A–C) TCR as a function of temperature with different substrates. The height of the GNWs is 380, 740, and 940 nm, respectively. (D–F) Current variation tendency of the GNWs (740 nm) at different temperatures on PDMS, Si, and PET substrate, respectively.

negative TCR effect of intrinsic GNWs and the external positive TCR effect of the expanded substrate cancel each other.

To our surprise, an enormous positive TCR value of up to 180% K⁻¹ is obtained with the large CTE ($\epsilon_{\text{PDMS}} = 3.0 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$) of the PDMS substrate. Evidently, the positive TCR effect from PDMS is far superior to the negative TCR effect from the GNW film. At a temperature ranging from 35°C to 40°C, the resistance of GNWs/PDMS owns a drastic change of ~900%, which is three to four orders of magnitude higher than that of Si/GNWs and PET/GNWs, as shown in Figure 3D–F. To investigate that our device can work in a broad temperature environment, we set a large temperature interval step of 5 K. To prove that it is reasonable to measure the TCR with the step of 5 K, we made an additional supplementary experiment with an interval step of 1 K, as shown in Figure S3a. It can be seen that the calculated TCR with respect to 35°C and 40°C is 180.4% K⁻¹, which is coincident with the previous outcome shown in Figure 3. Additionally, the heating-cooling process is demonstrated in Figure S3b also, which means that our devices possess a good recoverability.

3.3 Thermoresponsive behavior of GNWs/PDMS

An *in situ* method combined with AFM and optical microscopy is adopted to investigate the enormous TCR of the GNWs/PDMS. Figure 4A shows the schematic diagram of the thermal response of the GNWs/PDMS. As discussed above, for the change of resistance, the influence that is originated from intrinsic GNWs and substrate can be considered simultaneously. For the substrate of PDMS with large TCR, it tends to form isotropic thermal expansion in all directions with the increase of temperature, as shown in red outward arrows in Figure 4A (middle). For the GNW film coated above the PDMS, the outward expansion will cause the tensile deformation of the GNW film. The deformation makes a great enhancement of the resistance. Images from both optical microscopy and AFM verify the above hypothesis. The tiny disordered cracks on the GNW film are observed and become dense and deep with increasing temperature, as shown in Figure 4B. From the AFM image (see Figure 4C and D), the cracks can separate the continuous GNWs into GNW islets. Therefore, it

Figure 4: Schematic diagram of thermal response of the GNWs/PDMS.

(A) Schematic diagram of the thermal response of GNWs/PDMS, (B and C) optical microscopy and AFM images of GNW/PDMS surface at 45°C, and (D) AFM cross-section profile of the crack region in C.

becomes clear why the GNW/PDMS device has such an enormous positive TCR value. With the increment of temperature, the compact and continuous GNW film stretches into a defective and discontinuous conductive network with vast cracks due to the large expansion of the PDMS substrate. As a result, the conductive channels between the two Ag electrodes are lengthened and the resistance of device increases sharply. On the contrary, as reported in our previous work, the conductive channels can return to its original state after cooling down to room temperature, as shown in Figure 4A (right). The GNW/PDMS composites form a revertible conductive channel under the heating-cooling process and result in a reliable stability for applications. Generally speaking, the GNW/PDMS composites possessing the anomalous TCR can be expected to be the novel materials for the fabrication of flexible IR detectors with high performance.

3.4 IR radiation response and stability of device

To demonstrate the IR radiation response and stability of the GNW/PDMS devices, we apply a constant drain-source voltage between the two Ag electrodes. A different

IR radiation is adopted, as shown in Figure 5. First, an IR lamp with a temperature control is conducted above the device that is 20 cm high. A thermocouple is placed near the device for the purpose of measuring the actual accepted temperature of GNWs/PDMS. The starting and ending temperatures are 30°C and 32°C, respectively. Figure 5A shows that the current is still changed remarkably under repeated increasing and decreasing temperature. The process of heating-cooling corresponds to the up and down of the device resistance. Thus, the GNW/PDMS composites show excellent detection performance of IR radiation.

We further measured the IR optothermal response using IR laser (980 nm, 13 mW), as shown in Figure 5B. The light incident angle is normal incidence. For the purpose of intuitively observing the current change under IR radiation, the photocurrent ($I_{\text{photo}} = I_{\text{light}} - I_{\text{dark}}$) is used to evaluate the photoresponse of the photodetectors. The magnitude of photocurrent is approximately 15 μA . The responsivity is calculated to be $\sim 1.15 \text{ mA W}^{-1}$, which is one order of magnitude larger than that of the original CNT IR detector ($\sim 0.1 \text{ mA W}^{-1}$) [30]. Furthermore, the detectivity (D^*) of the device calculated from the reported method [31] reaches $1.07 \times 10^8 \text{ cm Hz}^{1/2} \text{ W}^{-1}$. Table 1 indicates that the performance of our device is better than the traditional carbon-based IR detector even with a large effective

Figure 5: IR photothermal response of the GNW/PDMS device. (A) Response of the GNW/PDMS device under illumination of IR lamp with a temperature control. In this testing, the IR lamp turns on at 30°C and turns off at 32°C. (B) Response of the GNW/PDMS device under illumination of 980 nm light source. (C) Current changed with different thermal radiation (human body) of GNW/PDMS devices. (D) Performance of device with 1000 times bending test.

Table 1: Device performance of IR photodetector based on different nanomaterials.

Type	Area (mm ²)	TCR (K ⁻¹)	Detectivity (cm Hz ^{1/2} W ⁻¹) at RT	Reference
GNWs/PDMS	~45	180%	1.07×10^8	This work
SWCNT	0.06	-0.17%	4.5×10^5	[32]
MWCNT (unsuspended)	0.073	-0.07%	8.3×10^5	[33]
MWCNT (suspended)	0.073	-0.07%	3.3×10^6	[33]
Graphene/CNT	0.12	-0.08%	1.5×10^7	[34]
Graphene oxide	N/A	-2.4 to -4%	1.18×10^8	[35]
VO _x	0.001	2-3%	1.9×10^8	[36]

working area (~45 mm²) and can be expected to easily develop a commercialized bolometer with the optimized fabrication process.

Figure 5C shows the IR thermal response with the radiation of the human body (hand). It is clearly shown that the IR radiation emitted by the human body can generate an obvious thermal response in our designed GNW/PDMS detector. From left to right of the figure, quantities

of radiation increase, so does as the change rate of current. The change rate of current in the third case is found to be about 16%. It may attribute to the ultra-high TCR of our novel IR detector. Thus, it is suggested again that the GNW/PDMS-based IR detectors have tremendous implications in human motion monitoring, IR imaging, etc.

Moreover, the flexibility and repeatability of the GNW/PDMS-based bolometer are also evaluated. A periodic

bending testing with 10 mm bending radius is applied, as shown in Figure 5D. Figure 5D demonstrates that, even after 1000 cycles of repetition, the performance of the device shows near-zero degradation. As mentioned previously, the interlaced network of the GNW film provides a reliable flexibility of the device under repeating bending. It is important for the flexible IR detectors.

4 Theory of radiation response

According to the principle of IR thermal detector [37], we have thermal equilibrium equation:

$$C \frac{d(\Delta T)}{dt} + G\Delta T = \varepsilon P_0 e^{j\omega t} \quad (2)$$

where C is the thermal capacity, G is the thermal conductance, ΔT is the temperature difference aroused by IR radiation power, ε is the absorption of GNWs, $P_0 e^{j\omega t}$ is the optical or thermal radiation power, and ω is the angular frequency of signal modulation. Then, the temperature difference generated by IR radiation power can be written as

$$\Delta T = \frac{\varepsilon P_0}{G(1 + \omega^2 \tau_r^2)^{1/2}} \quad (3)$$

where $\tau_r = C/G$ is the IR thermal response time. Combined with Eq. (1), we obtain the relationship between IR radiation power and resistance change as

$$\Delta R = \alpha R_0 \frac{\varepsilon P_0}{G(1 + \omega^2 \tau_r^2)^{1/2}} \quad (4)$$

Naturally, we have current change formula expressed as

$$\Delta I = \frac{V \alpha \varepsilon P_0}{R_0 G(1 + \omega^2 \tau_r^2)^{1/2}} \quad (5)$$

Further, current responsivity can be described as

$$R_i = \frac{V \alpha \varepsilon}{R_0 G(1 + \omega^2 \tau_r^2)^{1/2}} \quad (6)$$

For the optothermal effect (see Figure 4E), the parameters in Eq. (6) are listed as angular frequency of signal modulation $\omega = 2\pi/40$ s, rise time @90% of ~ 4 s, thermal conductance of PDMS 0.15 W/(m K), $V/R_0 = 3.37 \times 10^{-4}$ A, and $\alpha \approx 180\%$ K $^{-1}$. According to Eqs. (5) and (6), the calculated change of current and responsivity are 46.4 μ A and 3.38 mA W $^{-1}$, respectively. There is a slight difference compared to the measured values. It may be the reason

that the real thermal power accepted by device is less than 13 mW because of heat loss.

For the thermal radiation (see Figure 4F), there is no action of modulation (i.e. $\omega = 0$). Therefore, Eqs. (5) and (6) can be replaced by $\Delta I = V \alpha \varepsilon P_0 / R_0 G$ and $R_i = V \alpha \varepsilon / R_0 G$. The former means that the change of current is proportional to the power of thermal radiation, which is in agreement with the results in Figure 5C. Moreover, we know that the responsivity of the thermal radiated devices has no relationship between wavelength and power. The latter shows that our model has no conflict with the existed theory.

4.1 Change of resistance

Two parts are relevant to the resistance transformation followed by $\alpha = \alpha_{\text{GNWs}} + \alpha_{\text{substrate}}$. It means that the study of resistance change needs to consider the influence of both GNWs and substance simultaneously. For GNWs/PDMS, when radiation illuminates onto the device, the resistance of GNWs begins to decrease because of the negative TCR effect. Meanwhile, for a great CTE of PDMS, under the effect of ΔT , PDMS begins to expand and results in cracks on the surface of device, which makes the resistance of GNWs greatly increased. Consequently, the TCR of this structured device is positive and enormous as well.

4.2 Rise time and detectivity

In our experiment, the working area of GNWs is 3×15 mm and the spot size is approximately 3×3 mm. The response time we obtained is 4 s. The time seems too long compared to that of the traditional IR detectors. The reason may be that the relative low thermal conductivity (G) of the PDMS substrate (0.15 W mK $^{-1}$) leads to a long response time according to the relation of $\tau_r = C/G$ [5]. It is reasonable to use the formula to estimate the dark current noise $I_n = (2I_d e \Delta f)^{1/2}$ [38], where e is the numerical value of charge and $\Delta f = 1$ Hz usually. Therefore, the detectivity $D^* = R_i \times (A \Delta f)^{1/2} / I_n = 1.07 \times 10^8$ cm Hz $^{1/2}$ W $^{-1}$ is obtained.

Theoretically, the smaller working area of the device is, the smaller of thermal exchange outside will be. It means that small working area of the device will contribute to a large ΔT as well as a significant responsivity R_i . Therefore, it is reasonable to believe that no matter how intensive the optothermal or radiation thermal is, the responsivity will be greatly improved as long as the area of GNWs is reduced. Further study can be done for the optimization of the devices in the future.

5 Conclusions

Devices with different substrates designed based on GNWs are studied. The fabrication process of the devices is competitive due to the advantages of simple synthesis process, large area structuring, and reliable performance. We investigated their properties of TCR at a temperature ranging from 20°C to 45°C. Our experimental results demonstrate that GNW/PDMS structured devices have an ultra-high TCR, and the maximum value can reach 180% K⁻¹. Furthermore, our devices show an excellent detection performance of IR optothermal and thermal radiation with competitive detectivity and change rate of current. These unique features indicate that GNWs/PDMS can be promising candidates for flexible IR photodetectors and can be used for applications in bolometry, where they act as sensing coatings.

Acknowledgments: This work was supported by the National Natural Science Foundation of China (grant nos. NSFC U1532133, 61504148, and 11574308) and The Basic Science and Frontier Technology Research Program of Chongqing (grant nos. cstc2016jcyjA0315, cstc2015jcyjA50018, and cstc2015jcyjA50016).

References

- [1] Andresen BF, Jin Y, Basantani HA, et al. High-resistivity and high-TCR vanadium oxide thin films for infrared imaging prepared by bias target ion-beam deposition. *Proc SPIE* 2013;8704:87043C.
- [2] Calleja C, Torres A, Rosales-Quintero P, Moreno M. Amorphous silicon-germanium films with embedded nanocrystals for thermal detectors with very high sensitivity. *J Nanotechnol* 2016;2016:1–9.
- [3] Liu N, Tian H, Schwartz G, Tok JB, Ren TL, Bao Z. Large-area, transparent, and flexible infrared photodetector fabricated using P-N junctions formed by N-doping chemical vapor deposition grown graphene. *Nano Lett* 2014;14:3702–8.
- [4] Sahatiya P, Puttapati SK, Srikanth VVSS, Badhulika S. Graphene-based wearable temperature sensor and infrared photodetector on a flexible polyimide substrate. *Flexible Printed Electron* 2016;1:025006.
- [5] Huang ZL, Gao M, Yan ZC, Pan TS, Liao FY, Lin Y. Flexible infrared detectors based on p-n junctions of multi-walled carbon nanotubes. *Nanoscale* 2016;8:9592–9.
- [6] Zheng Z, Zhang T, Yao J, Zhang Y, Xu J, Yang G. Flexible, transparent and ultra-broadband photodetector based on large-area WSe₂ film for wearable devices. *Nanotechnology* 2016;27:225501.
- [7] Avouris P, Freitag M. Graphene photonics, plasmonics, and optoelectronics. *IEEE J Sel Top Quant* 2014;20:72–83.
- [8] Bonaccorso F, Sun Z, Hasan T, Ferrari AC. Graphene photonics and optoelectronics. *Nat Photonics* 2010;4:611–22.
- [9] Koppens FHL, Mueller T, Avouris P, Ferrari AC, Vitiello MS, Polini M. Photodetectors based on graphene, other two-dimensional materials and hybrid systems. *Nat Nanotechnol* 2014;9:780–93.
- [10] Liu Y, Cheng R, Liao L, et al. Plasmon resonance enhanced multicolour photodetection by graphene. *Nat Commun* 2011;2:579.
- [11] Echtermeyer TJ, Britnell L, Jasnos PK, et al. Strong plasmonic enhancement of photovoltage in graphene. *Nat Commun* 2011;2:458.
- [12] Gan XT, Shiue RJ, Gao YD, et al. Chip-integrated ultrafast graphene photodetector with high responsivity. *Nat Photonics* 2013;7:883–7.
- [13] Wang XM, Cheng ZZ, Xu K, Tsang HK, Xu JB. High-responsivity graphene/silicon-heterostructure waveguide photodetectors. *Nat Photonics* 2013;7:888–91.
- [14] Sun ZH, Liu ZK, Li JH, Tai GA, Lau SP, Yan F. Infrared photodetectors based on CVD-grown graphene and PbS quantum dots with ultrahigh responsivity. *Adv Mater* 2012;24:5878–83.
- [15] Nikitskiy I, Goossens S, Kufer D, et al. Integrating an electrically active colloidal quantum dot photodiode with a graphene phototransistor. *Nat Commun* 2016;7:11954.
- [16] Chen Z, Cheng Z, Wang J, et al. High responsivity, broadband, and fast graphene/silicon photodetector in photoconductor mode. *Adv Opt Mater* 2015;3:1207–14.
- [17] Hiramatsu M, Kondo H, Hori M. Eds. *Graphene Nanowalls*, London, INTECH, 2013.
- [18] Zhao J, Shaygan M, Eckert J, Meyyappan M, Rummeli MH. A growth mechanism for free-standing vertical graphene. *Nano Lett* 2014;14:3064–71.
- [19] McClure JP, Thornton JD, Jiang RZ, Chu D, Cuomo JJ, Fedkiw PS. Oxygen reduction on metal-free nitrogen-doped carbon nanowall electrodes. *J Electrochem Soc* 2012;159:F733–42.
- [20] Hassan S, Suzuki M, Mori S, Abd El-Moneim A. MnO₂/carbon nanowall electrode for future energy storage application: effect of carbon nanowall growth period and MnO₂ mass loading. *Rsc Adv* 2014;4:20479–88.
- [21] Stancu EC, Stanciuc AM, Vizireanu S, et al. Plasma functionalization of carbon nanowalls and its effect on attachment of fibroblast-like cells. *J Phys D Appl Phys* 2014;47.
- [22] Davami K, Shaygan M, Bargatin I. Fabrication of vertical graphene-based nanocomposite thin films. *J Mater Res* 2015;30:617–25.
- [23] Evlashin S, Svyakhovskiy S, Suetin N, et al. Optical and IR absorption of multilayer carbon nanowalls. *Carbon* 2014;70:111–8.
- [24] Krivchenko VA, Evlashin SA, Mironovich KV, et al. Carbon nanowalls: the next step for physical manifestation of the black body coating. *Sci Rep* 2013;3:3328.
- [25] Davami K, Cortes J, Hong N, Bargatin I. Vertical graphene sheets as a lightweight light absorber. *Mater Res Bull* 2016;74:226–33.
- [26] Yang J, Wei D, Tang L, et al. Wearable temperature sensor based on graphene nanowalls. *RSC Adv* 2015;5:25609–15.
- [27] Wang Z, Shoji M, Baba K, Ito T, Ogata H. Microwave plasma-assisted regeneration of carbon nanosheets with bi- and trilayer of graphene and their application to photovoltaic cells. *Carbon* 2014;67:326–35.
- [28] Shen J, Liu X, Song X, et al. High-performance Schottky heterojunction photodetector with directly grown graphene nanowalls as electrodes. *Nanoscale* 2017;9:6020–5.
- [29] Yang J, Ran QC, Wei DP, et al. Three-dimensional conformal graphene microstructure for flexible and highly sensitive electronic skin. *Nanotechnology* 2017;28:115501.

- [30] Zeng QS, Wang S, Yang LJ, et al. Carbon nanotube arrays based high-performance infrared photodetector [invited]. *Opt Mater Express* 2012;2:839–48.
- [31] Fang Y, Huang J. Resolving weak light of sub-picowatt per square centimeter by hybrid perovskite photodetectors enabled by noise reduction. *Adv Mater* 2015;27:2804–10.
- [32] Lu R, Li Z, Xu G, Wu JZ. Suspending single-wall carbon nanotube thin film infrared bolometers on microchannels. *Appl Phys Lett* 2009;94:163110.
- [33] Lu R, Shi JJ, Baca FJ, Wu JZ. High performance multiwall carbon nanotube bolometers. *J Appl Phys* 2010;108:084305.
- [34] Lu R, Christianson C, Weintrub B, Wu JZ. High photoresponse in hybrid graphene-carbon nanotube infrared detectors. *ACS Appl Mater Interfaces* 2013;5:11703–7.
- [35] Bae JJ, Yoon JH, Jeong S, et al. Sensitive photo-thermal response of graphene oxide for mid-infrared detection. *Nanoscale* 2015;7:15695–700.
- [36] Chen CH, Yi XJ, Zhao XR, Xiong BF. Characterizations of VO₂-based uncooled microbolometer linear array. *Sens Actuat A Phys* 2001;90:212–4.
- [37] Rogalski A. Infrared detectors. Netherlands, CRC Press, 2010.
- [38] Schmiedmayer J. Atom interferometer that puts noise in the shade – Bose-Einstein condensates could help physicists to measure the fundamental constants with greater accuracy. *Phys World* 2002;15:26–7.

Supplemental Material: The online version of this article offers supplementary material (<https://doi.org/10.1515/nanoph-2017-0135>).