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Radiation Enhancement by Graphene Oxide on MEMS Emitters for Highly Selective Gas Sensing

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ABSTRACT: Infrared gas sensors have been proven promising for broad applications in Internet of Things and Industrial Internet of Things. However, the lack of miniaturized light sources with good compatibility and tunable spectral features hinders their widespread utilization. Herein, a strategy is proposed to increase the radiated power from microelectromechanical-based thermal emitters by coating with graphene oxide (GO). The radiation can be substantially enhanced, which partially stems from the high emissivity of GO coating demonstrated by spectroscopic methods. Moreover, the sp² structure within GO may induce plasmons and thus couple with photons to produce blackbody radiation and/or new thermal emission sources. As a proof-of-concept demonstration, the GO-coated emitter is integrated into a multifunctional monitoring platform and evaluated for gas detection. The platform exhibits sensitive and highly selective detection toward CO₂ at room temperature with a detection limit of 50 ppm and short response/recovery time, outperforming the state-of-the-art gas sensors. This study demonstrates the emission tailorability of thermal emitters and the feasibility of improving the associated gas sensing property, offering perspectives for designing and fabricating high-end optical sensors with cost-effectiveness and superior performance.

To tackle energy and environment related challenges, smart sensors need to be widely spread in sensor networks to collect data and information under ambient conditions for wise decision-making¹. These sensors are also the essential parts for the prospective artificial intelligence, Internet of Things (IoT), and Industrial Internet of Things (IIoT)². With rising concerns on the industrial gas leakage detection, indoor and outdoor air quality monitoring, and foodstuff/cosmetic quality determination, mid-infrared (mid-IR) optical gas sensors have gained substantial interests from both scientific and industrial aspects³. The working principle of those sensors relies on the fact that different molecules register their unique absorption fingerprints in the infrared regime. Consequently, infrared gas sensors feature attractive characteristics including excellent sensitivity, selectivity, low power consumption, and long lifetime compared with the currently-used metal oxide semiconductor (MOS) chemiresistive sensors, which usually suffer from inherent issues such as high power consumption and poor selectivity^{4,5}. Although recent progresses enable highly sensitive detection of various toxic gases by MOS and other novel materials at room temperature, problems such as long-

term stability, fast response/recovery speed, and/or high selectivity need to be further addressed⁶⁻⁸. Moreover, conventional IR sensors employing solid state monolithic devices⁹⁻¹¹ or fiber based devices^{12,13} as light sources undoubtedly bring in configuration complexity and high cost, hindering their miniaturization and large-scale deployment³. Therefore, more efforts are required to design and fabricate relevant IR emitters with miniaturized size and reliable radiation as the light sources, targeted for trace gas detection.

In light of all substances emitting electromagnetic radiation above absolute temperature because of the thermally induced motion of particles/quasiparticles, microelectromechanical system (MEMS) based membrane heaters have been utilized as IR emitters and proven to be effective due to several advantages such as low power consumption¹⁴, short response time^{15,16}, compact size¹⁷, and wide emission bandwidth¹⁸. Furthermore, they are compatible with the current complementary metal-oxide-semiconductor (CMOS) fabrication technology^{15,17}, which enables the mass-production of devices with low cost and high reliability. However, the emission intensity of the MEMS emitters needs to be high to achieve large signal-

to-noise ratio (SNR) for sensing applications. In order to enhance the radiation from the resistive heaters generally composed of tungsten (W) or platinum (Pt), additional blackening layers such as carbon nanotubes (CNT) or carbon nanoparticles (CNP) can be coated^{17,19,20}. Graphene oxide (GO) possesses unique properties such as uniform, planar two-dimensional structure and bright optical emission in comparison with CNT and CNP^{21–23}. To the best of our knowledge, the radiation enhancement of thermal emitters by utilizing graphene-based materials has been rarely explored yet.

Figure 1. Scheme of MEMS emitter coated with GO sheets for enhanced infrared radiation in gas sensing.

In this work, we design and fabricate a new type of MEMS based thermal emitters and demonstrate for the first time that deposition of GO sheets on emitters enables a substantial radiation enhancement. As a proof-of-concept application demonstration, the GO-coated thermal emitter is integrated with temperature and humidity sensors into a multifunctional sensing platform for simultaneous detection of multiple environmental parameters including carbon dioxide (CO_2) concentration, temperature, and humidity. The concept of GO-coated MEMS emitter for the enhancement of infrared radiation is shown in **Figure 1**. The radiated power of the GO-coated emitter is almost three times as much as that of the bare emitter under a bias voltage of 1 V, which can be attributed to the additional emission of GO coating, the black-body radiation and/or new thermal emission sources created

through the coupling of induced plasmons with photons. Remarkably, the as-fabricated optical sensor equipped with the GO-coated emitter exhibits sensitive and highly selective response toward CO_2 over various gases/vapors including methane (CH_4), carbon monoxide (CO), and acetone. The limit of CO_2 detection is 50 ppm and the response/recovery time is within few seconds, both surpassing the state-of-the-art sensors. This study opens up a novel perspective for designing and fabricating optical gas sensors with high sensitivity, good selectivity, and short response/recovery time by exquisitely coating the thermal emitters with GO for radiation enhancement and thus for trace gas detection.

RESULTS AND DISCUSSION

Characterizations of exfoliated graphene oxide. The exfoliated GO was fully characterized by multiple techniques. The sheet-like morphology of GO with wrinkles and folds can be clearly observed by transmission electron microscopy (TEM, **Figure 2a-b**). Selected area electron diffraction (SAED) pattern of GO sheet unveils two concentric hexagon rings with different spot sizes (**Figure 2c**), suggesting its hexagonal atomic structure and crystalline nature. Atomic force microscopy (AFM) image also confirms the sheet-like structure with a thickness of around 3 nm (**Figure 2d**). Raman spectrum (**Figure 2e**) exhibits two distinct bands residing at 1568.4 and 1334.5 cm^{-1} , corresponding to the ordered sp^2 (G band) and disordered sp^3 (D band) structures, respectively²⁴. The D band reflects the formation of disorders and defects including grain boundaries and heteroatoms introduced into the graphitic structure. A large integral-area ratio of D band to G band, i.e., I_D/I_G , somehow testifies a high degree of oxidation of GO²⁵. X-ray photoelectron spectroscopy (XPS) survey spectrum reveals the characteristic peaks for C1s and O1s (see **Figure S1**, Supporting Information). The high-resolution C1s XPS spectrum can be deconvoluted into three Gaussian peaks centered at binding energies of 287.9, 286.6, and 284.5 eV, which can be assigned to C=O, C-O, and C-C bonds within the GO structure, respectively²⁶. The oxidation degree of GO can be also reflected by the integral-area percentage of the XPS peaks contributed by oxygen-containing species within GO. The derived value is 52.9%, which may be higher than the actual value because the adsorbed O species has not been excluded during the calculation. Moreover, attenuated total reflection Fourier transform infrared (ATR-FTIR) and ultraviolet-visible spectroscopic results also confirm the existence of GO (**Figure S3**, Supporting Information).

Figure 2. (a, b) TEM images of GO sheets. (c) SAED image of the area in (b) highlighted by red rectangle. (d) Representative AFM image of the GO sheet deposited onto Si wafer. The inset shows its height profile. (e) Raman spectrum of GO. The inset displays deconvolution of the broad peak related to D and G bands. (f) High-resolution C_{1s} XPS spectrum of GO.

Design and characterizations of MEMS emitter. The schematic cross-sectional view of the designed micro-hotplate emitter is shown in **Figure 3a**. Firstly, one thermal silicon oxide (SiO₂) layer and one tensile silicon nitride (Si₃N₄) layer were subsequently formed onto the silicon substrate by thermal oxidation and low pressure chemical vapour deposition (LPCVD), respectively. The first Pt layer (underneath) was afterward deposited and patterned via photolithography and acts as the resistive micro-hotplate so that electromagnetic radiation can be thermally induced under applied bias voltage. Another Si₃N₄ layer was then deposited onto the Pt layer as the passivation/insulating layer via plasma enhanced chemical vapour deposition (PECVD). The upmost Pt interdigitated electrodes were fabricated eventually to guarantee a uniform thermal distribution and potentially act as a capacitive gas sensor. The silicon substrate underneath the Pt layer was back-etched until reaching the SiO₂ layer. More details of the fabrication process are available in Figure S4-5, Supporting Information Note 2. **Figure 3b** depicts the cross-sectional focused ion beam (FIB)-scanning electron microscopy (SEM) image of the bare chip.

Top-view SEM image of the bare thermal emitter is displayed in **Figure 3c**, onto which the wire bonding has already been done. **Figure 3d** presents the input power as a function

of bias voltage applied on the micro-hotplate of the bare emitter. High magnification SEM image of the GO-coated emitter confirms the appearance of thin GO sheets with wrinkles as highlighted by the red dotted line (**Figure 3e**). The emission properties of the emitters with and without GO coating were evaluated using the setup shown in **Figure 3e**. **Figure 3f** compares the real-time radiation intensities of the bare emitter and the GO-coated emitter under the same bias voltage of 1 V. The comparisons under 0.8 and 1.4 V are available in Figure S6. An enhancement factor of 2.2 for emission intensity at steady state was observed under the measured wavelength range. The rise time (from 10% to 90%) for the emitters with and without GO coating was measured to be 15.43 and 6.49 ms, respectively. The corresponding fall time (from 90% to 10%) for the two emitters is 5.82 and 2.49 ms, respectively. Such difference in rise time and fall time between emitters with and without GO coating can be attributed to GO's ability in converting thermal energy into photons, as well as the different thermal transfer resistance between the emitters. It is worth mentioning that the resistances of emitters with and without GO coating are quite similar (See Figure S7, Supporting Information), ruling out the possibility of emission enhancement caused by resistance.

Figure 3. (a) Schematic illustration of the as-fabricated micro-hotplate thermal emitter. (b) Cross-sectional FIB-SEM image of the bare emitter. (c) Front-view SEM image of the bare thermal emitter. (d) Input power of the bare emitter under variable voltages. (e) Schematic of the emitter measurement apparatus (upper); the lower left depicts SEM images of GO-coated emitter; the lower right displays the optical image of the set-up. (f) Real-time radiation intensity within the range of 1.5 - 4.8 μm of the bare emitter and the one with GO coating under a bias voltage of 1 V. Note that the photodetector here can only detect wavelength in the range of 1.5 - 4.8 μm , within which the characteristic absorption fingerprint of CO_2 coincidentally resides.

To further justify the observed radiation enhancement, we measured the surface reflectance of the two emitters by a Fourier-transform infrared (FTIR) spectrophotometer at room temperature. **Figure 4a** shows the obtained spectral profiles in the wavelength range of 2 to 14 μm . The reflectance of the bare emitter varies from 70% to 94%, whereas that for the GO-coated emitter varies between 15% and 32%. Since both emitters are non-transparent, the radiation illuminated on them will either be reflected or absorbed. Moreover, the emissivity

equals to the absorbance under thermal equilibrium according to Kirchhoff's law^{27,28}. Hence, the emissivity of the surface can be calculated by subtracting the reflectance from 1 as shown in Figure 4a (dotted lines). Clearly, the emissivity of GO-coated emitter is nearly quadruple of that of the bare emitter, testifying our foregoing observation.

By replacing the light source of the FTIR spectrophotometer with our own emitter, the emission spectra of the two emitters under heating were obtained (Figure 4b). More details

regarding spectra acquisition are provided in the Experimental Section). It can be clearly observed that the GO-coated emitter exhibits a larger emission intensity than that of the bare emitter under the same bias voltage of 1 V, in agreement with our aforementioned results. The impact of applied voltage was also investigated, and the obtained spectra are presented in Figure 4b in which the red, green, and magenta curves represent the ones under 0.8, 1, and 1.4 V, respectively. A higher applied voltage contributes to a higher temperature and hence a higher radiated emission. All the emission spectra localize within the mid-infrared regime, with the peak centered at around 10 μm . Peaks from the absorption of water and carbon dioxide in the ambient environment were also observed in the spectra. The integral-area percentages of the emission intensity within the short wavelength range (3 - 9 μm) for 0.8, 1.0, and 1.4 V were calculated to be 54.0%, 57.7%, and 64.7%, respectively. This suggests that the electromagnetic irradiation with short wavelengths arises as the emitter temperature increases, consistent with Planck's law³. The apparent enhancement in emission of the GO-coated emitter can be ex-

plained as follows. On one hand, GO can enhance the top surface emissivity, justified by the spectroscopic results presented in Figure 4a. Thus, it conduces to the emission enhancement under heating from the underneath micro-hot-plate. On the other hand, the existence of sp^2 C-C sheets within GO may induce plasmons that can be efficiently coupled to photons in the surrounding to produce antenna-coupled blackbody radiation and even create new optical pathways^{27,29}. The appearance of plasmons also allows extremely efficient thermal energy transfer in the infrared range, and the merging optical pathways can also act as thermal emission sources³⁰. All of these factors contribute to the emission enhancement under heating.

The optical power in the range of 0.19 - 20 μm from the relevant MEMS emitters was also measured by a thermal detector connected with a powermeter (Figure 4c). The GO-coated emitter generally outperforms the bare one under the same applied voltage and a modulation of 10 Hz with one half cycle. Specifically, the total radiated power from the GO-coated emitter reaches 0.6 mW and triples that of the one without GO coating under 1.4 V.

Figure 4. (a) FTIR reflectance spectra and the estimated emissivity of the emitter surfaces without and with GO coating. (b) Radiation spectral profiles of the GO-coated emitter under different bias voltages and the bare emitter under a bias voltage of 1.0 V. (c) Total radiation power (from 0.19 to 20 μm) of the bare emitter and the one with GO coating under 10 Hz square wave modulation with one half duty cycle. (d) Stability performance of the GO-coated emitter under different applied voltages.

The thermal stability of the GO-coated MEMS emitter under different applied voltages was also investigated (Figure 4d). The emission intensity under 0.8 V remains almost unchanged after 10 h testing. Whereas, the emission intensity witnesses a drop by around 10% under 1 V after 3 h testing, and

then reaches the steady state. A higher voltage (1.4 V) contributes a higher emitter surface temperature of approximately 300 $^{\circ}\text{C}$ estimated by an infrared camera. As such, the emission intensity experiences an obvious decrease attributed to the

decomposition of oxygen-containing functional groups anchored at the carbon skeleton, consistent with the literature results that the oxygenated groups of GO start to be removed at above 200 °C^{31,32}.

MEMS GO-coated emitter for photonic gas sensing. As a proof-of-concept functionality demonstration, the MEMS

GO-coated emitter was integrated into one home-made platform that contains multiple sensor arrays as shown in **Figure 5a**. The multifunctional platform was evaluated for environmental parameter monitoring, including CO₂ concentration, humidity, and temperature. The schematic in Figure 5(a) also includes the rest components implemented in the gas sensing setup.

Figure 5. (a) Scheme of the experimental set-up for gas sensing tests. (b) Dynamic response of the multi-integrated optical sensor with the GO-coated thermal emitter as the light source toward variable CO₂ concentrations in the range of 200 and 2500 ppm. Note that the increasing concentration step is 200 ppm. (c) Sensor response versus CO₂ concentration. The discrete points stand for the experimental data whereas the solid red line denotes the exponential fitting results. On the right y axis, C₁ to C₅ represent the concentrations of the diluent gases. For CH₄ and CO, the C₁-C₅ concentrations are 200, 360, 520, 680 and 840 ppm, respectively. For acetone, the C₁-C₅ concentrations are 240, 432, 624, 816 and 1008 ppm, respectively. (d) Zoomed-in plot as highlighted in (b). (e) Cyclic sensing property toward 2500 ppm CO₂ of the optical sensor integrated with the GO-coated emitter.

Figure 5b presents the dynamic response-recovery transient of the as-fabricated sensor integrated with the GO-coated emitter toward CO₂ in the range of 200-2500 ppm at room

temperature. Obviously, the as-fabricated optical sensor with the GO-coated emitter exhibits sensitive response (defined as

$(V_0 - V_{\text{analyte}}) \cdot V_0^{-1}$, where the V_0 and V_{analyte} represent the photo-voltages in N_2 and in the analyte, respectively) toward variable concentrations of CO_2 , with response values of 4% and 20% upon 200 ppm and 2500 ppm, respectively. Nevertheless, the optical sensor integrated with the emitter without GO coating shows indistinguishable response toward 200–2500 ppm CO_2 (See Figure S8, Supporting Information), in correspondence with our foregoing observation that the bare emitter has a much lower power. The zoomed-in response-recovery curve (Figure 5d) toward 1400 and 1600 ppm CO_2 clearly demonstrates that the response and recovery time periods of the optical sensor are all astonishingly short (within few seconds). In the meanwhile, the variations of the humidity and temperature inside the chamber were also recorded (see Figure S9, Supporting Information). The gas response as a function of CO_2 concentration is presented in Figure 5c. The fitting result with an R square value of 0.996 demonstrates that the response versus CO_2 concentration follows an exponential relationship, which agrees with the Beer Lambert law well³. In addition, the detection limit was estimated to be 50 ppm by multiplying the standard deviation of the background by a factor of $3^{\text{ref}33}$, and mapping the ppm value based on the fitting curve. More calculation details are provided in Supporting Information Note 4.

Since the selectivity is of paramount importance to commercial sensors regarding their practical applications, we therefore inspected the influence of the interference from other gases to our sensor. The co-existence of variable amounts of CH_4 , CO, or acetone vapor exerts no influence on the response of the relevant sensor toward a certain ranges of CO_2 (Figure 5c and Figure S10). This explicitly indicates the superior selectivity of the optical sensor system toward CO_2 , promising for practical application and commercialization. Furthermore, the sensitivity of the sensor toward 2500 ppm CO_2 remains almost unchanged after more than 4 weeks (Figure 5e), suggesting its excellent stability and repeatability. Comparing with the state-of-the-art CO_2 sensing performance (See Table S1, Supporting Information), the as-fabricated optical sensor integrated with the GO-coated emitter exhibits superior gas sensing performance in terms of sensitivity, selectivity, and response/recovery time.

CONCLUSION

In summary, a new type of MEMS based thermal emitters has been designed and fabricated. The radiated power from the emitter can be tuned by intentionally coating the bare emitter with GO. The substantial enhancement of radiation under heating partially stems from the enhancement of top surface emissivity contributed by GO. In the meanwhile, the possibly induced plasmons by GO can be efficiently coupled to phonons and even create new thermal emission sources. Those factors synergistically conduce to the radiation enhancement. As a proof-of-concept demonstration, the GO-coated thermal emitter was successfully integrated into a multifunctional monitoring platform containing humidity and temperature sensors for CO_2 detection. The as-fabricated optical sensor exhibits a highly selective detection toward CO_2 in the range of 200–2500 ppm at room temperature. Moreover, the response and recovery time periods are surprisingly short (within few seconds). The overall CO_2 sensing performance demonstrated in this study outperforms that of the state-of-the-art sensors in terms of sensitivity, selectivity, and response/recovery time.

This study demonstrates for the first time the emission tailorability of thermal emitters via GO coating, offering perspectives for the designing and fabrication of high-end optical gas sensors.

EXPERIMENTAL SECTION

GO film preparation: To prepare GO films on thermal emitters, a certain amount of GO bulk powder was dispersed into ultra-pure water, mechanically exfoliated and drop-casted onto the rinsed emitter device. Afterward, the device was placed in an oven at 80 °C for 2 h to vaporize the solvent. The GO deposition process has no damage to the device from CMOS foundry and hence is compatible with the standard CMOS fabrication process.

Radiation intensity measurement: The emitter was mounted within a compound parabolic concentrator (CPC) to provide collimated light. Figure 3e displays the schematic testing setup where the signal generator provided 10 Hz square wave electrical signal with one half duty cycle. A unity gain amplifier was adopted before the thermal emitter to ensure consistent delivery of the voltage. A photodetector with a detection wavelength range between 1.5 and 4.8 μm was used to measure the intensity of the emission because CO_2 molecules register their absorption fingerprints within this range (peak value localized at 4.2 μm)³.

Emission spectra and optical power measurement: The measured emitter placed within the CPC acted as the light source for the FTIR measurement. The bias voltage was set as continuous wave instead of square wave throughout the measurement to ensure the stability of the optical spectra. The emission spectra were captured using a FTIR spectrometer (Bruker Vertex 70 series) with a resolution of 4 cm^{-1} and a calibrated HgCdTe detector at room-temperature. The optical power measurement was conducted with a mid-IR power meter (Ophir, model 3A-fs P/n 7z02628) covering a spectral range of 0.19 – 20 μm .

Optical gas sensing: The GO-coated emitter and photodetector were controlled and driven by an electronic circuit board, which resided at the top of the gas sensing chamber. The gas flow rate was controlled by mass flow controllers (MFCs). The electrical output of a commercial chip-scale photodetector was processed by a microcontroller on the electric circuit board, which communicated with the computer for data acquisition.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

A PDF file containing XPS survey spectrum of GO, one more AFM image of GO sheet and its profile, ATR-FTIR pattern of GO, UV-Vis absorption spectrum of GO dispersed in water, fabrication process and characterizations of the bare thermal emitter, real-time radiation intensity of the emitters under bias voltages of 0.8 and 1.4 V, R-V curves of the bare emitter and the one with GO coating, summary of recent studies on CO_2 sensing, real-time voltages of the sensors integrated with the bare emitter and GO-coated emitter upon exposure to variable CO_2 concentrations, real-time humidity and temperature levels within the chamber during gas detection, response plots toward variable CO_2 concentrations in the presence of

interfering gases, and the method to calculate the limit of detection.

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Author Contributions

N.L., H.Y. and J.T. conceived the idea. N.L. conducted the emission, spectroscopic and gas sensing measurements. H.Y. conducted the GO characterizations, fabricated the GO film and contributed to the gas sensing test. N.L. and H.Y. analyzed the data and drafted the manuscript. L.X. constructed the gas sensing platform and helped gas sensing tests. J.T. designed the emitter. D.K.T.N. and Y.T.L. helped FTIR reflection measurement. D.D.C. fabricated the emitter. Y.Z., B.Q., and Q.W. helped the acquisition of emission spectra and measurements of optical power as well as data analysis. H.C., N.S. and D.Z. supervised the project. All authors approved the manuscript.

‡These authors contributed equally.

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