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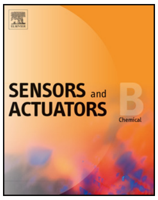

Ultra-high sensitivity, multi-parameter monitoring of dynamical gas parameters using a reduced graphene oxide microcavity

Fei Xing[a], Yong Yang[b,*], Junfeng Shen[c], Wenshuai Jiang[d], Zhibo Liu[d], Siwei Zhu[e], Xiaocong Yuan[a,*]

[a] *Nanophotonics Research Centre, Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, PR China*
[b] *Institute of Modern Optics, Key Laboratory of Optoelectronic Information Science & Technology, Ministry of Education of China, Nankai University, Tianjin 300071, PR China*
[c] *Emei campus, South West Jiaotong University, Emei, Sichuan 614200, PR China*
[d] *The Key Laboratory of Weak Light Nonlinear Photonics, Ministry of Education, Teda Applied Physics School and School of Physics, Nankai University, Tianjin 300457, PR China*
[e] *Institute of Oncology, Tianjin Union Medicine Centre, Tianjin 300121, PR China*

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ABSTRACT

An ultra-high sensitivity, multi-parameter monitoring system was established based on a 1.8 mm^3, high-temperature-reduced graphene oxide microcavity. The gas refractive index, pressure, velocity and flux can be detected in real time based on polarization-sensitive absorption of graphene, and the detection limits are 1.1×10^{-8} RIU (refractive index units), 3.5 Pa, 3.5 mm/s, and 0.1 ml/min respectively, with an experimental response time less than 0.5 s. These results are a great improvement over those measured previously with single-parameter sensors. Furthermore, the system can also recognize gas flow direction accurately, and enable applications for extreme conditions and for precision instruments with microcavity integrated.

1. Introduction

Pressure [1,2], velocity [3], flux, and flow directions[4] are essential parameters in the characterization of gases. Accurate multi-parameter detection and mapping with integrated chips show promise for precision applications such as manned spacecraft, intensive care units, and gas reaction chambers. [5,6] The gas refractive index (RI) is a comprehensive parameter[7–9] that can be correlated with other essential parameters noted above, under certain conditions. Therefore, monitoring the RI is an effective way to achieve multi-parameter detection. However, since the RI resolution of current gas sensors is only 10^{-4}–10^{-5}, [10,11] the corresponding resolution limits of correlated parameters are also low (*e.g.*, pressure at a KPa level, velocity at a m/s level, and flux at a level of tens of ml/min). These limits are far from meeting the requirements of many applications. Currently, high-sensitivity monitoring of gas parameters can be practically achieved only with single-parameter sensors, with detection limits for pressure difference, velocity, and flux of 13.3 Pa, 5 mm/s and 0.8 ml/min, respectively. [12–14]

Graphene, a truly two-dimensional (2D) crystal, has been recognized as a revolutionary material because of its remarkable electronic, optical, mechanical, and chemical properties [15–17]. Because all of its atoms are exposed in a 2D structure, its electrical and optical properties are very sensitive to changes in surface charge induced by adsorption or reaction with analytes. Hence, graphene is particularly well suited for ultra-high sensitivity gas detection. [18–22] A highly sensitive graphene-based gas RI sensor would thus be extremely useful for multi-parameter gas detection.

Here, an optimized RI sensing method, based on the polarization-sensitive light absorption of graphene, is used for real time monitoring of gases. Because of its strong broadband absorption, graphene exhibits different reflectances for transverse electric (TE) and transverse magnetic (TM) modes under total internal reflection, which is sensitive to the RI of the media in contact with

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* Corresponding authors.
E-mail addresses: yangyong@nankai.edu.cn (Y. Yang), xcyuan@szu.edu.cn (X. Yuan).

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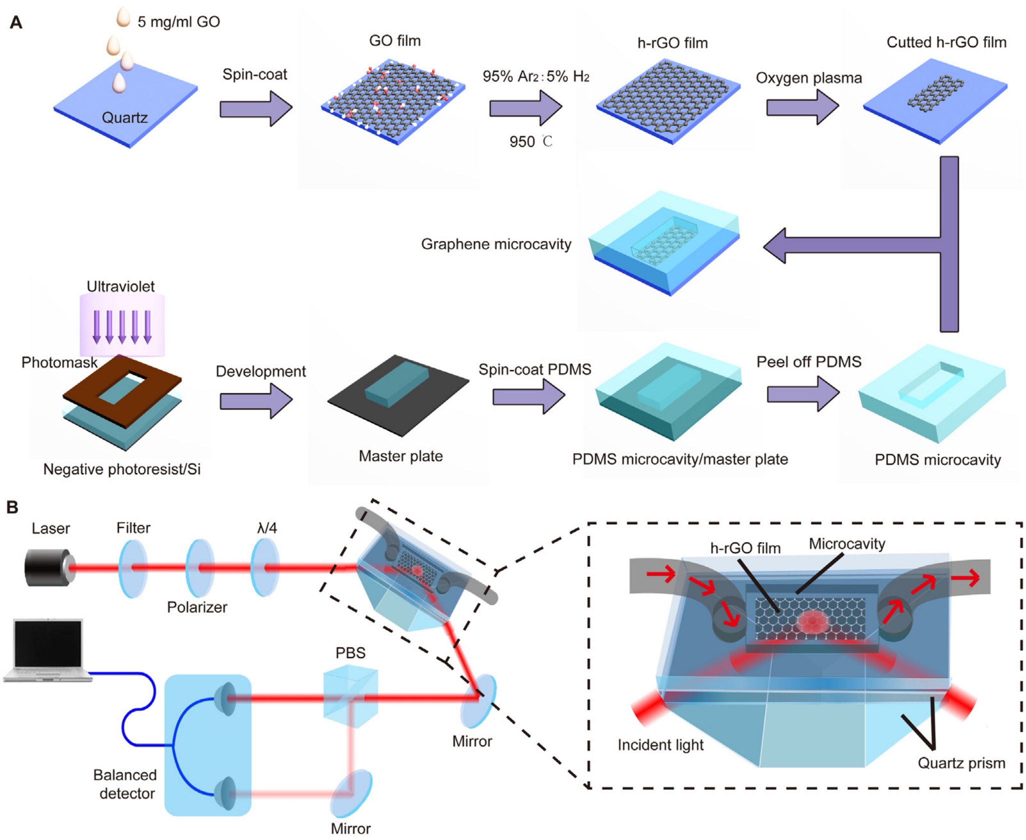

Fig. 1. Strategy for ultra-high sensitivity, multi-parameter monitoring of dynamical gas parameters using a reduced graphene oxide microcavity. (A) Fabrication of a graphene (h-rGO) microcavity. PDMS forms the microcavity material. (B) Multi-parameter OGMGS system. A 632.8 nm He-Ne laser is the light source, and details are shown at right.

the surface. [23–25] In particular, we show that a 8.1-nm thick, high-temperature-reduced graphene oxide (h-rGO) film can be used as a sensing layer because of its strong polarization-sensitive absorption. The sensitivity and resolution limits for gas RI sensing are 6.2×10^7 mV/RIU and 1.1×10^{-8}, respectively. The resolution is the highest value reported for a gas RI, and is three orders of magnitude higher than that for the same type of sensors reported. Combined with the graphene microcavity, the ultra-high sensitivity gas RI sensing method has detection limits for pressure, velocity and flux of 3.5 Pa, 3.5 mm/s, and 0.1 ml/min, respectively, with a response time of less than 0.5 s. The multi-parameter optical graphene microcavity gas sensor (OGMGS) also can recognize the direction of gas flow. It can be easily integrated, has strong corrosion resistance, and can be fabricated at low cost.

2. Materials and methods

2.1. Fabrication of h-rGO films

The fabrication of h-rGO films is depicted in Fig. 1A. Graphene oxide (GO) is prepared from graphite by the modified Hummer method. [26] Pre-cleaned quartz is treated with an oxygen plasma for 1 min prior to use. Subsequently, a 5 mg/ml GO dispersion in water is spin-coated on the glass surface at 2000 revolutions/min for 45 s. The supported GO films are then thermally annealed at 950 °C for 1 h in a mixed (by volume) atmosphere of 95% nitrogen and 5% hydrogen gases.

2.2. Preparation of graphene microcavity

Because of its chemical stability and biocompatibility, poly(dimethylsiloxane) (PDMS) was used for the fabrication of the microcavity. A photoresist mask was etched *via* electron beam lithography, and a negative photoresist was spin-coated on the silicon substrate and dried at 110 °C. The photoresist was exposed to ultraviolet light through a mask. After resist developing, a PDMS pre-polymer mixture of 70 g of Sylgard 184 silicone elastomer base and 7 g of Sylgard 184 elastomer curing agent (10:1 ratio) covered the master plate. The plate was then placed in a 70 °C oven for 3 h to form the solidified PDMS microcavity, which matched the dimensions of the h-rGO film. Other parts of h-rGO film were cleaned in an oxygen plasma. Finally, the PDMS microcavity was bonded to the surface of the trimmed h-rGO film to form the graphene microcavity.

2.3. Multi-parameter OGMGS apparatus

The experimental arrangement is shown in Fig. 1B. Light from a 632.8 nm He-Ne laser is circularly polarized with a polarizer and a quarter-wave plate. A neutral density filter is used to control the laser power. The light is incident (1 mm spot size) in the center of OGMGS chip. The TE and TM modes are separated by a polarization beam splitter and are monitored with a balanced detector. The OGMGS chip consists of the PDMS microcavity and h-rGO/quartz sandwich structure on a prism, and micro-pipes for gas flow.

2.4. Characterizations

Atomic force microscopy (AFM) was performed using a Dimension 3100 microscope (Veeco, America) in tapping mode at a scan rate of 1.003 Hz. The resonant frequency and force constant of the cantilever were 300 kHz and 40 N/m, respectively. A micro Raman spectrometer (Renishaw, RM2000) was used to acquire Raman spectra. The optical transmittance spectroscopy measure-