Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

On-chip assembly of 3D graphene-based aerogels for chemiresistive gas sensing

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Experimental

Synthesis of graphene oxide

Graphene oxide was synthesized by an improved Hummers method[1]. Briefly, a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (360:40 mL) was prepared. Then 3 g graphite flakes were added to the flask and mixed by magnetic stirring. 18.0 g $KMnO_4$ was slowly added into the reaction to keep the temperature low. The reaction was then heated to 50 ^oC and stirred for 12 h. The reaction was cooled to room temperature and poured onto ice (600 mL) with 30% H_2O_2 (8 mL). Then, the mixture was centrifuged (6000 rpm for 1 h), and the supernatant was decanted away. The remaining solid material was then washed in succession with 200 mL of water, 200 mL of 15% HCl, and 200 mL of ethanol. For each wash, the mixture was centrifuged (6000 rpm for 1 h) and obtains the remaining material. The final resulting material was freeze-dried for 24 hours to obtain graphene oxide.

Synthesis of $W_{18}O_{49}$ nanowires

Uniform $W_{18}O_{49}$ nanowires were prepared by a modified solvothermal method. Typically, 0.1 mg of poly (vinylpyrrolidone) (PVP, MW≈ 40000) and 0.1 g of WCl_6 were added into 60 mL of absolute ethanol. The mixture was stirred by magnetic stirring to form homogeneous solution. The solution was then added into a 120 mL Teflon-lined stainless steel autoclave and maintained at 180 ^oC for 24 h. After that, the autoclave was cooled to room temperature naturally and $W_{18}O_{49}$ nanowire suspension were obtained for further use.

Preparation of functionalized substrates

The substrates were first treated in Piranha solution (98% H_2SO_4–30%H_2O_2, 7: 3 v/v) kept at 90^{o}C for 30 min followed by thoroughly rinsing with ultrapure water and drying with flowing N_2 to obtain a fresh and clean surface.

In situ assembly of polypyrrole coupled graphene/$W_{18}O_{49}$ nanowires aerogels (PGWA) on chip

Graphene oxide (GO) was dispersed in deionized water by ultrasonication for 2 h in cold water to acquire GO suspension (3 mg/ml). The as-prepared $W_{18}O_{49}$ nanowire suspension was first centrifuged with absolute ethanol and deionized water twice respectively. Then, the resulted solid was dispersed into GO suspension (3mg/ml) in the weight ratio $W_{18}O_{49}$ to GO equal to 5:1. After vigorous vibration for 2 min and ultrasonically dispersing for 30 min in cold water, pyrrole monomer (mass ratio of GO and Py =1:5) was added in the above mixed suspension and ultrasonicated for 30 min in cold water. To in situ growth of the graphene aerogels on the substrates, 3 drops of the mixed solutions transferred to the substrate at 50 °C for 2h and then at RT for 24h statically. After dialyzing the black hydrogel with ethanol (20 Vol %) for 24 h to remove residual pyrrole monomer and ploypyrrole oligomer, polypyrrole/reduced graphene oxide/$W_{18}O_{49}$ nanowires aerogel (PPy-rGOWA) was obtained by freeze-drying for 24 h. Then, GOA was thermally reduced at 250 °C for 1h in a tube furnace under argon atmosphere to form polypyrrole/graphene/$W_{18}O_{49}$ nanowires (PGWA). For comparison, polypyrrole/graphene aerogel (PGA) was synthesized applied same procedure without adding $W_{18}O_{49}$ nanowires.

Characterization

The morphology of $W_{18}O_{49}$ nanowire and graphene-based aerogels integrated on-chip were studied via scanning electron microscopy (SEM) in a Zeiss Gemini Leo 1530 (Zeiss, Germany). Transmission electron microscopy (TEM) images of $W_{18}O_{49}$ nanowire and graphene based aerogels removed from the substrate were obtained on a FEI Tecnai G2 20 S-TWIN electron microscope equipped with an energy dispersive X-ray detector operated at 200 kV(FEI, USA). XPS spectra were performed on a Thermo Fisher Scien-tific ESCALAB 250Xi. Fourier transform infrared spectroscopy (FTIR) in Attenuated Total Reflection (ATR) mode carried out in an Equinox 55 (Bruker, Germany) in the range of 400 – 4000 cm^{-1}. X-ray diffraction was performed with Bruker D8 (Bruker, Billerica, MA, USA) with Co Kα radiation (λ=0.1789 nm) with 2θ value ranging from 10° to 90°. The specific surface area (SSA) was measured using a Brunauer−Emmett−Teller (BET) analyzer (Micromeritics; TRISTAR II 3020).

Gas sensor test

Gas tests have been conducted using a home-build setup (Figure. S1). In order to measure the dynamic change of the resistance of our sensors, we used a sensing substrate which is comprised of 0.6 mm thick polycrystalline Al_2O_3 (length 2.5 cm, width 4 mm) with 15 µm thick Pt electrodes on both sides of the substrate which were deposited by electron beam evaporation method. The electrodes on one side of the substrate are used for sensing purposes, the electrodes on another side are intended for Ohmic heating of the substrate and the sensor. The spacing between the sensing electrodes was 2 mm. After testing materials were grown onto the prepared sensor substrates, the prepared sensors were mounted onto a homemade gas-sensing setup. The temperature of the sensor was controlled by supplying power to the heating electrodes.

Formula for temperature calculations: $T = \frac{(\frac{\frac{U}{I}}{R_0}-1)}{\alpha} + 25$

Where:

T is the heater's temperature

U is the applied voltage to the heater

I is the current is the circuit

R0 is the measured heater's resistance at RT

α is the temperature coefficient of resistance for Pt

Target gases were diluted in N_2, and the flow rates were precisely controlled by a set of mass flow controllers (Bronkhorst EL-Flow Prestige Series) to obtain desired gas concentrations. The total flow rate was kept constant at 150 ml/min. The resistance signals of the studied sensors were measured by a set of multimeters (Tektronix DMM 4050 and Keithley DMM 7510) with auto range and filters off, the sampling rate was set to 1/s. Power sources (Manson SSP-8160 and Keysight U8001A) were connected to heater electrodes of the sensors. Most of the equipment was connected to a PC and programmed with Labview for cooperative functionalization. The sensor signal is defined here as R_0/R_{NO2} and the relative response is $(R_0\text{-}R_{gas})/R_0$. Resistance fluctuations are calculated according to Ref.[2]

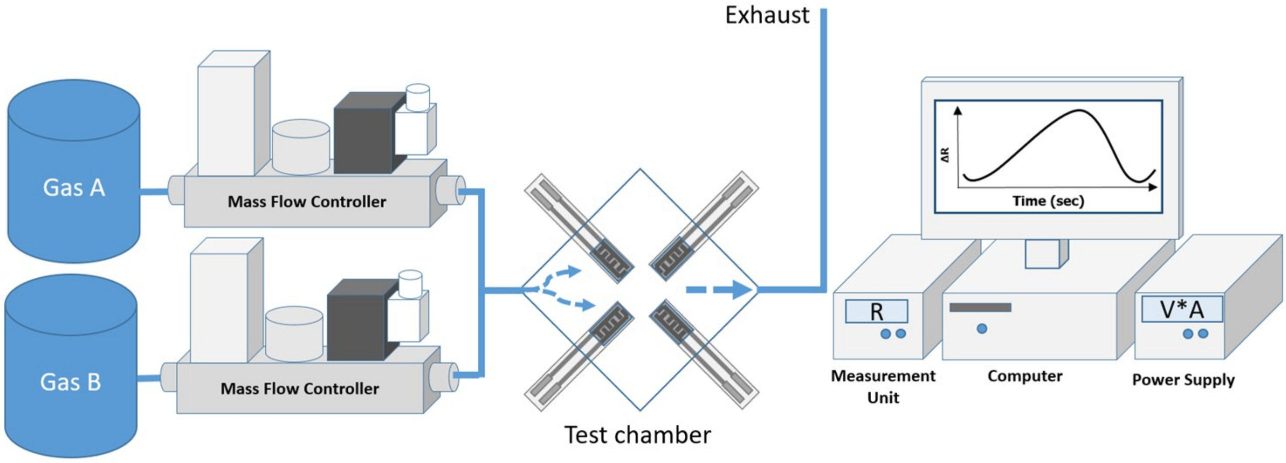
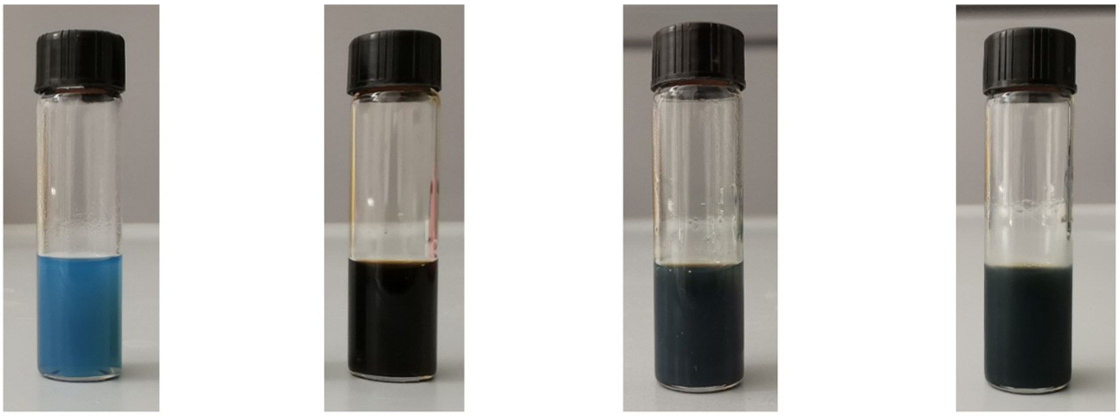


Figure S1. Scheme of the experimental set-up for gas sensing tests



$W_{18}O_{49}$ nanowires suspension (3mg/ml)

GO suspension (3mg/ml)

Mixed suspension before adding Py

Mixed suspension after adding Py

Figure S2. Optical images of as-prepared $W_{18}O_{49}$ nanowires solution, GO solution, $W_{18}O_{49}$ nanowires/GO solution and $W_{18}O_{49}$ nanowires/GO/PPy solution during the preparation process.

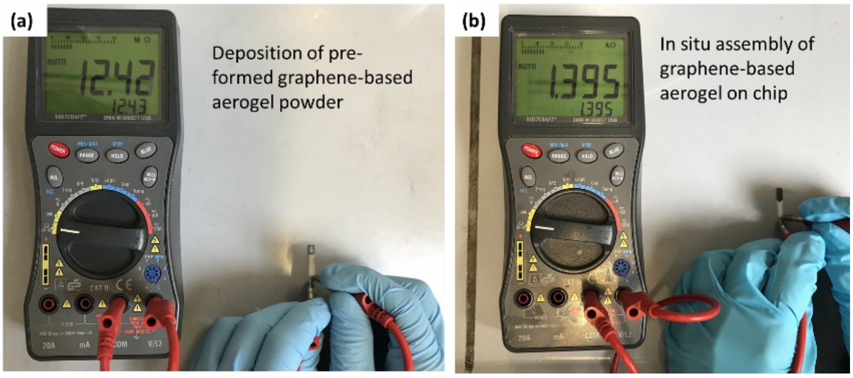


Figure S3 The resistances of traditional deposition of graphene-based aerogel powder and on-chip assembled graphene based aerogels.

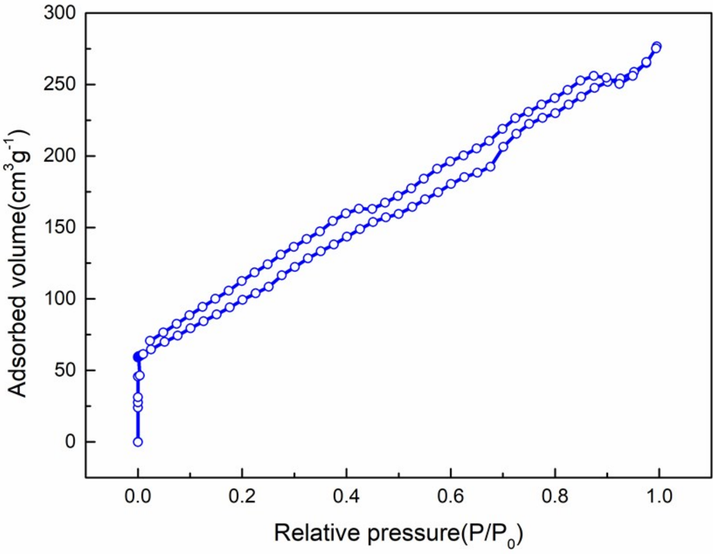


Figure S4. Nitrogen adsorption-desorption isotherms of PGWA

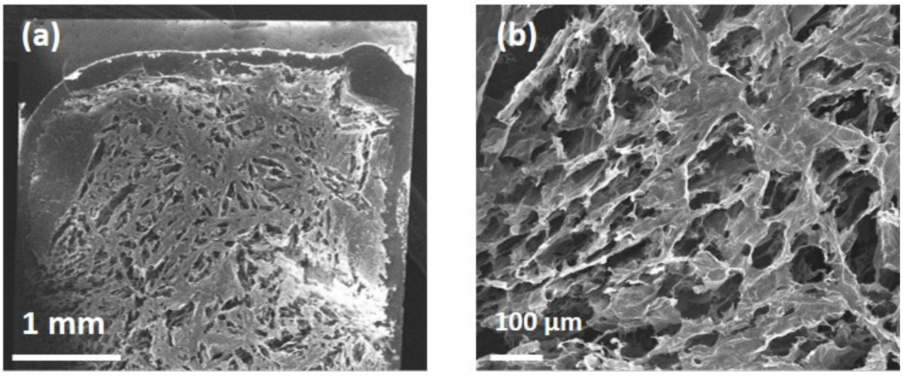


Figure S5. SEM images of PrGOA on chip after annealing at 900 ^{o}C for 1h in Ar. (a) Low magnification and (b) High magnification.

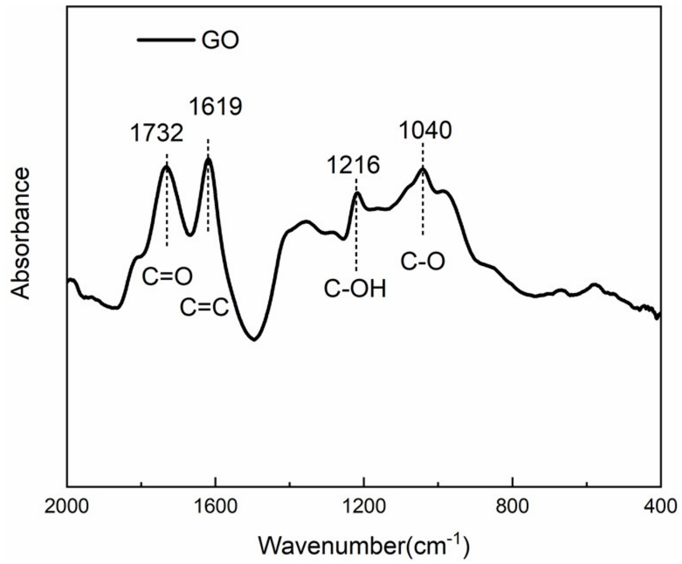


Figure S6. The ATR-FTIR spectrum of GO

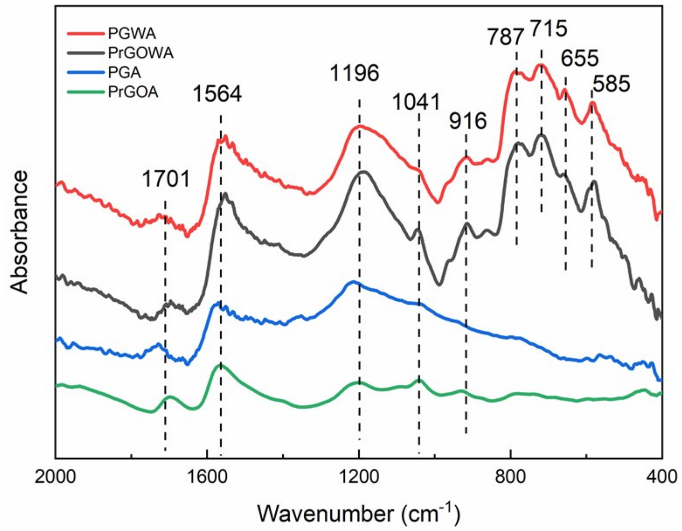


Figure S7. The ATR-FTIR spectra of graphene based aerogels

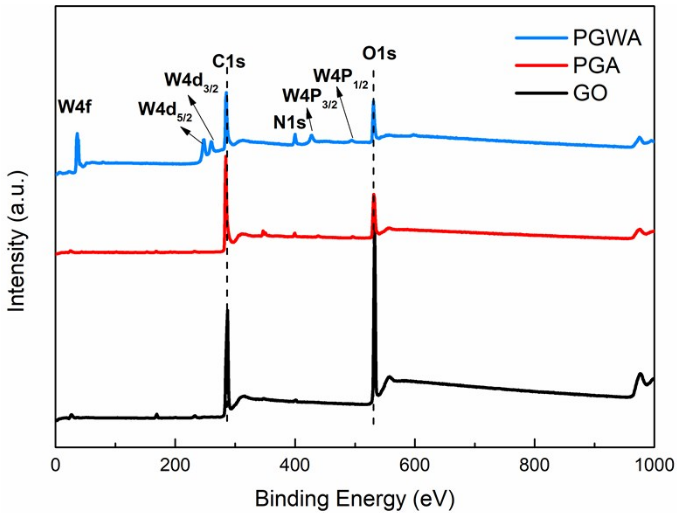


Figure S8 XPS survey spectra for all elements (C, N, O and W) of GO, PGA and PGWA.

Table S1 Atomic concentration of each constituent from the survey scans of GO, PGA and PGWA.

Sample	C	O	N	W
GO	65.62	34.38	-	-
PGA	78.75	19.12	2.13	-
PGWA	68.65	19.02	4.26	8.07

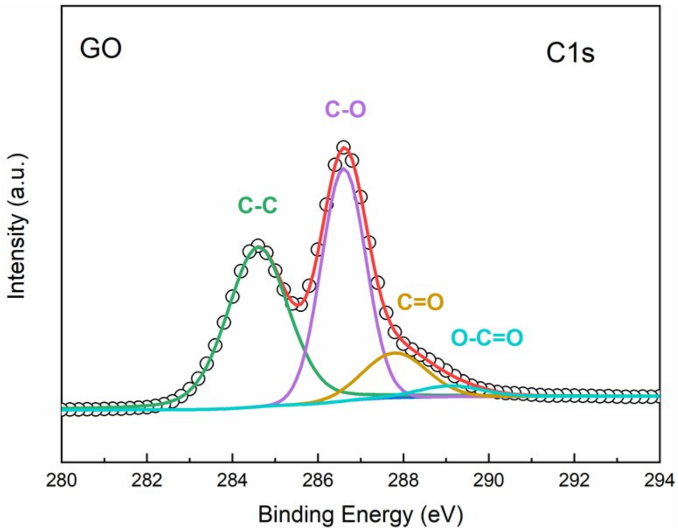


Figure S9. C1s XPS spectrum of GO

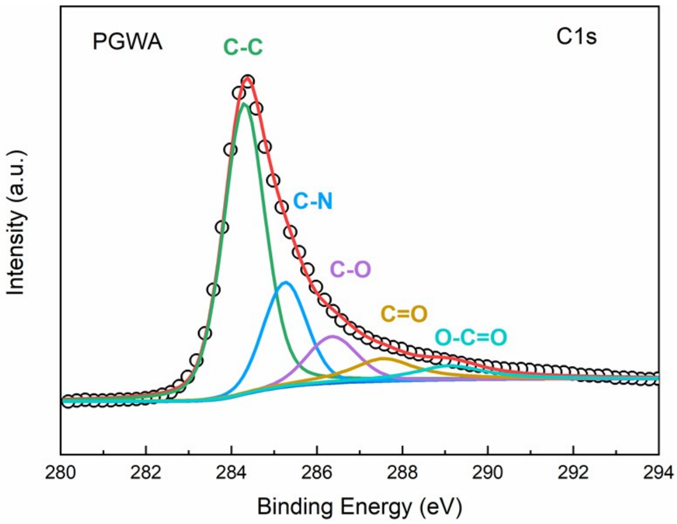


Figure S10. C1s XPS spectrum of PGWA

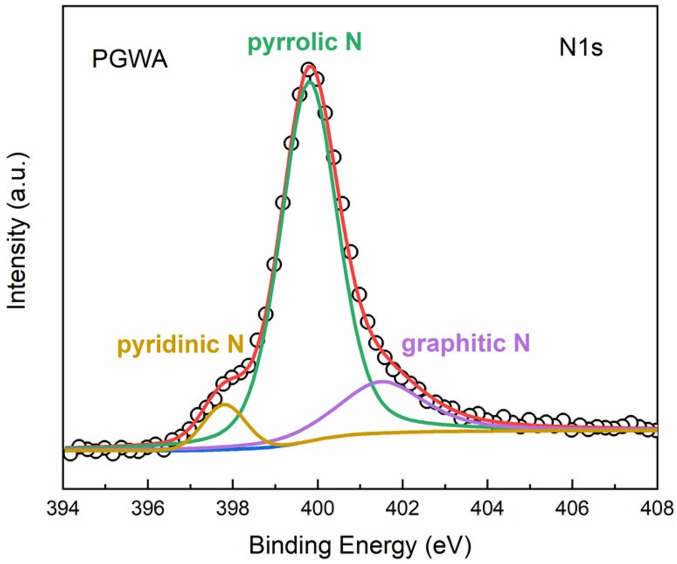


Figure S11. N1s XPS spectrum of PGWA

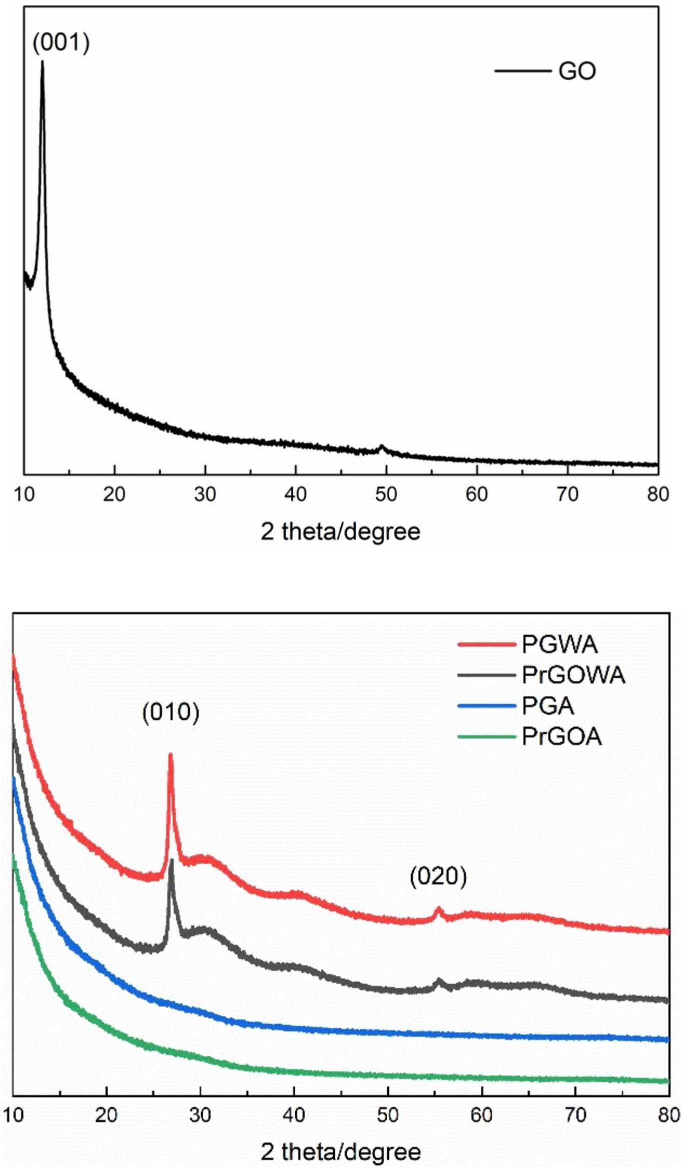
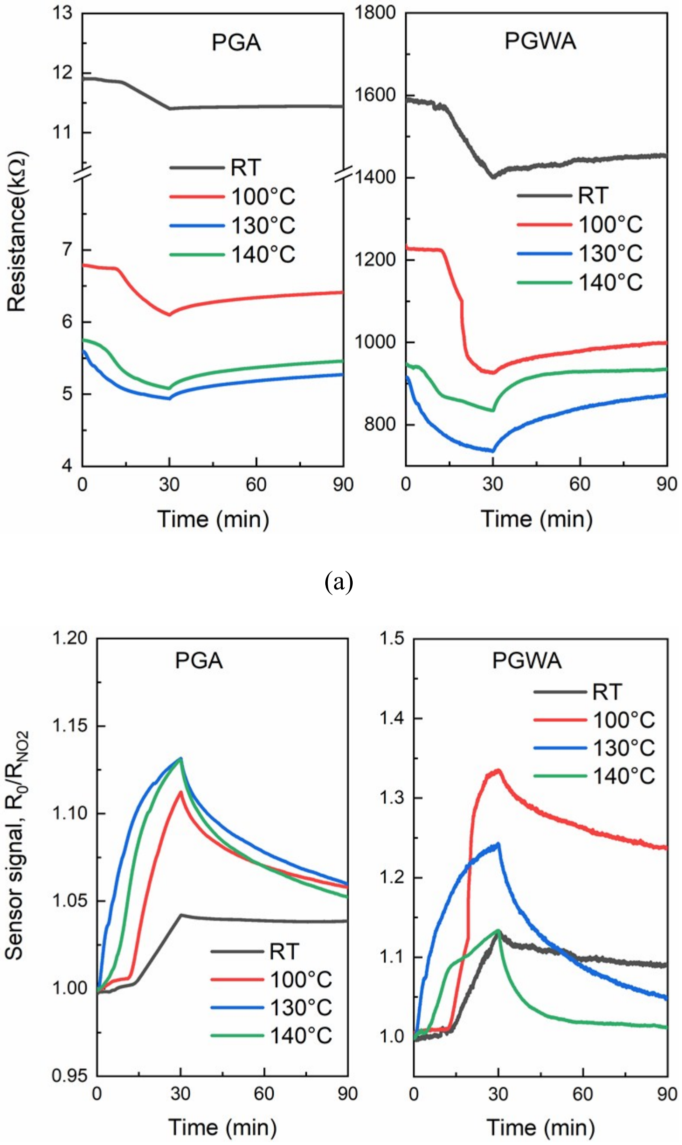


Figure S12 XRD patterns of (a) GO and (b) graphene based aerogels



(a)

(b)

Figure S13. (a)Transient resistance and (b) sensor response of the sensors at different temperatures towards 0.975 ppm NO_2

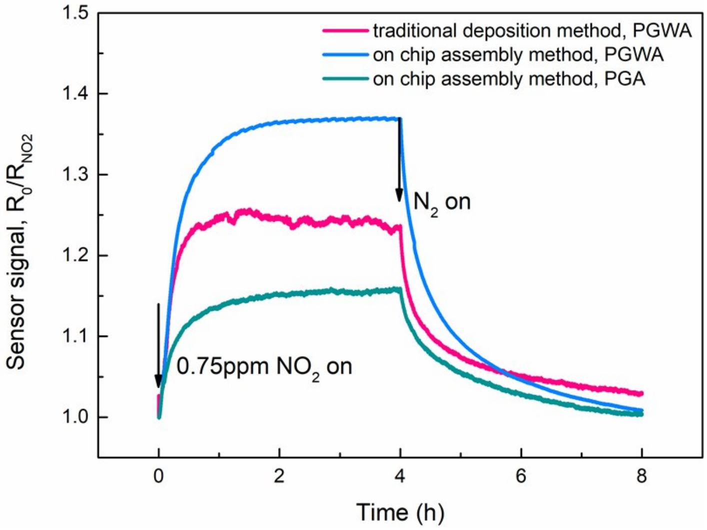


Figure S14 Transient sensor response towards 0.75ppm of NO_2 at 140℃

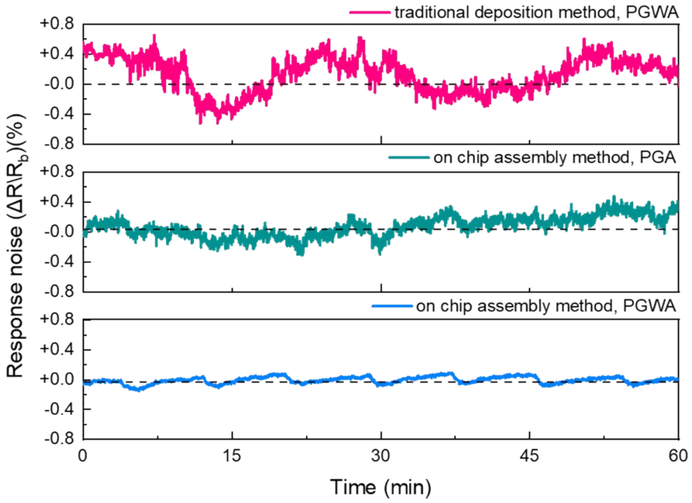


Figure S15. Resistance fluctuations during sensing for graphene aerogel sensors fabricated by different methods

[1] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, J. M. Tour, *ACS Nano* **2010**, *4*, 4806-4814.

[2] S. J. Kim, H.-J. Koh, C. E. Ren, O. Kwon, K. Maleski, S.-Y. Cho, B. Anasori, C.-K. Kim, Y.-K. Choi, J. Kim, Y. Gogotsi, H.-T. Jung, *ACS Nano* **2018**, *12*, 986-993.