Supplementary information

Au@ZnO/rGO nanocomposite based ultra-low detection limit, highly sensitive and selective NO_2 gas sensor

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A. Calculation of threotical Detection limit & limit of quantification (LOQ):

1. Generally, the threotical detection limit (DL) is the minimum concentration in which the sensor response is different from the noise signal. Typically, it is three times to that of standard deviation of noise signal present [1-3].

$$DL\ (in\ ppb) = 3\frac{S_D}{Slope}$$

2. The limit of quantification is the lowest analyte concentration that can be quantitatively detected with a stated accuracy and precision and it is given by:

$$LOQ\ (in\ ppb) = 10\frac{S_D}{Slope}$$

where S_D is the standard deviation of blank measures.

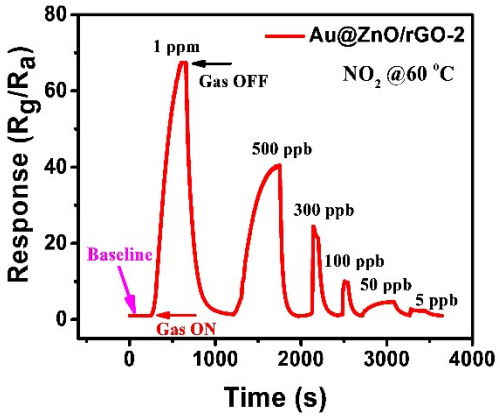


Fig. 1. Time-response curve of Au@ZnO/rGO-2 sensor.

The calculation of threotical detection limit and limit of quantification are performed for Au@ZnO/rGO-2 sample as shown below. The similar procedure is followed for other samples as well.

The following table explains the calculation of theoretical detection limit.

Parameters/samples	ZnO	Au@ZnO/rGO-1	Au@ZnO/rGO-2	Au@ZnO/rGO-3
N	100	100	100	100

S_D	0.0003128	0.0006042	0.0030708	0.0004093
Slope	0.00255 /ppb	0.0092 /ppb	0.0665 /ppb	0.0373 /ppb
LOQ	1.226 ppb	0.656 ppb	0.461 ppb	0.109 ppb
Threotical Detection limit	0.368 ppb or 368 ppt	0.197 ppb or 197 ppt	0.138 ppb or 138 ppt	0.0329 ppb or 32.9 ppt

References:

1. A. M. Committee, *Analyst*, 1987, **112**, 199–204.
2. J. Gonzalez-Chavarri, L. Parellada-Monreal, I. Castro-Hurtado, E. Castaño and G. G. Mandayo, *Sensors Actuators B Chem.*, 2018, **255**, 1244–1253.
3. J. Krupčík, P. Májek, R. Gorovenko, J. Blaško, R. Kubinec and P. Sandra, *J. Chromatogr. A*, 2015, **1396**, 117–130.

Figure S1: Schematic illustration for synthesis of ZnO nanospheres and Au decorated ZnO/rGO nanocomposite.

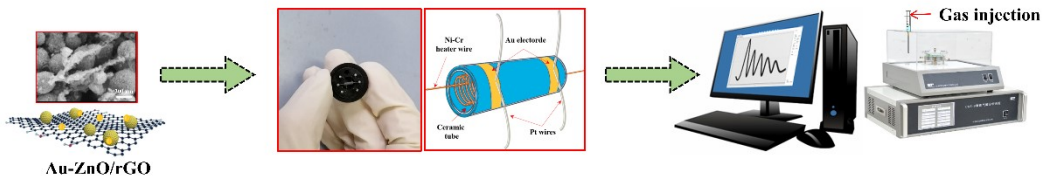


Figure S2: Illustration for fabrication of gas sensor device based on Au@ZnO/rGO for NO_2 gas detection.

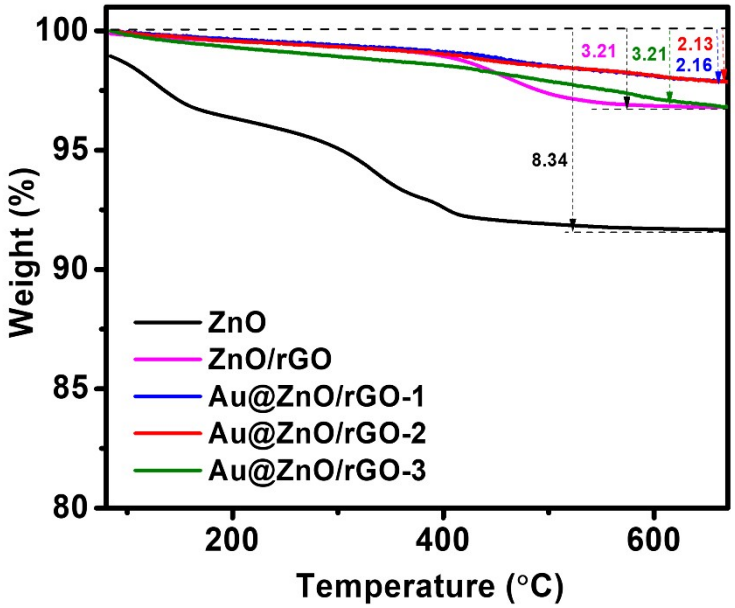
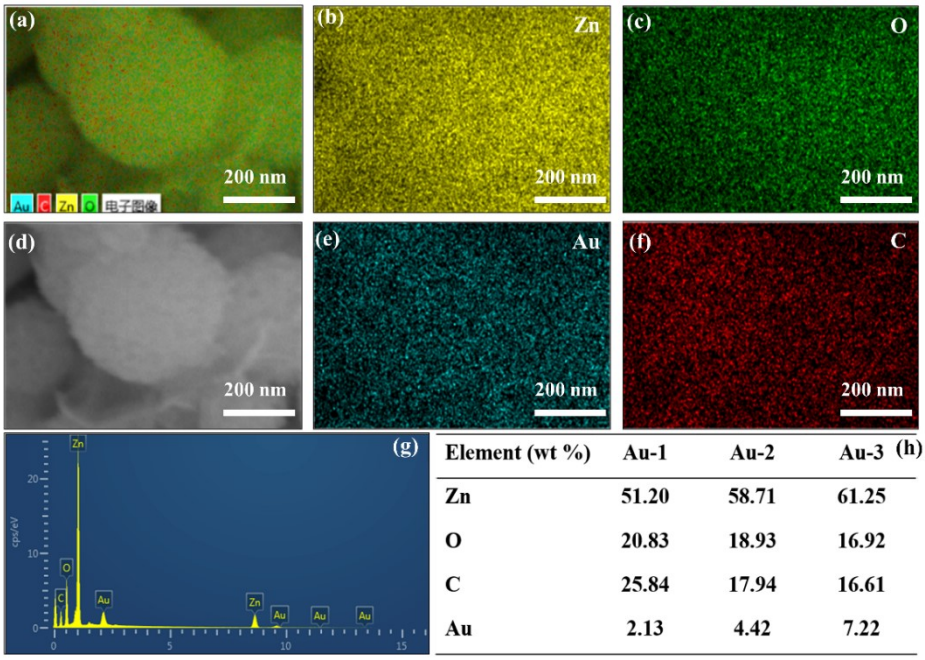


Figure S3: Thermogravimetric analysis of ZnO, ZnO/rGO, and Au@ZnO/rGO nanocomposite materials.

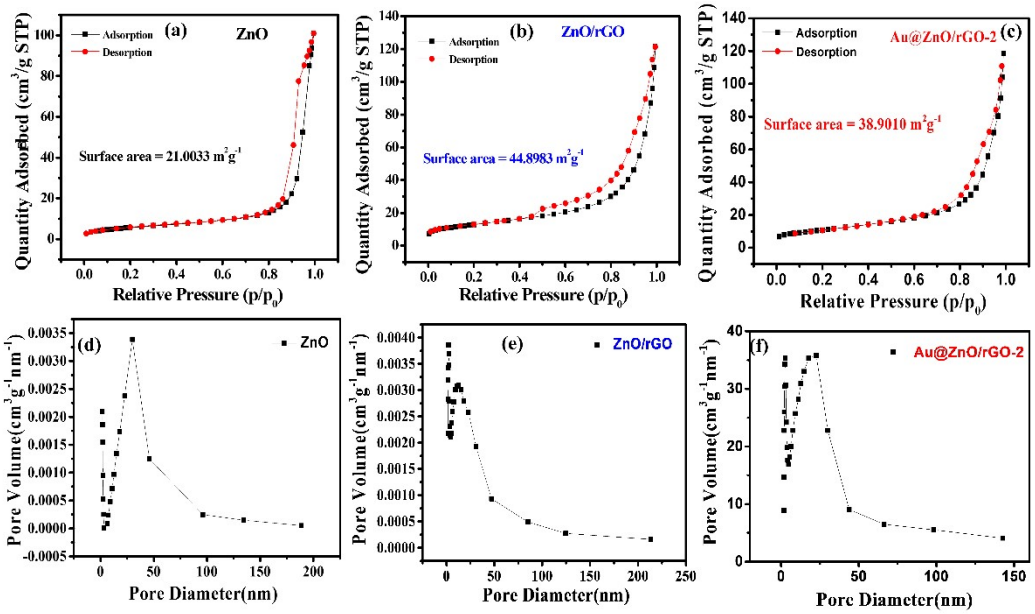


(h)

Element (wt %)	Au-1	Au-2	Au-3
Zn	51.20	58.71	61.25
O	20.83	18.93	16.92
C	25.84	17.94	16.61
Au	2.13	4.42	7.22

Figure S4: (a-g) EDS pattern for elemental composition of Au@ZnO/rGO-2; (h) Table shows the elemental distribution in % for Au@ZnO/rGO-1, Au@ZnO/rGO-2, and Au@ZnO/rGO-3 materials, respectively.

Figure S5: N_2 adsorption/desorption curve and pore size distribution (a) (d) for ZnO; (b) (e)



for ZnO/rGO; (c) (f) for Au@ZnO/rGO-2.

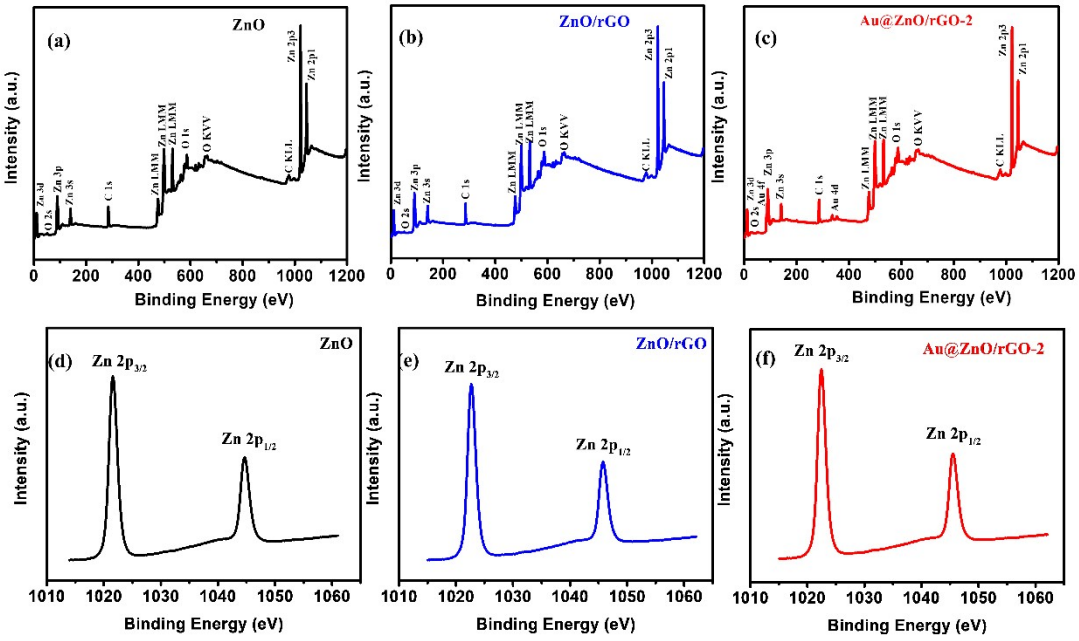


Figure S6: XPS survey and their corresponding Zn peak spectrums for (a) and (d) for ZnO; (b) and (e) for ZnO/rGO; (c) and (f) for Au@ZnO/rGO-2 materials.

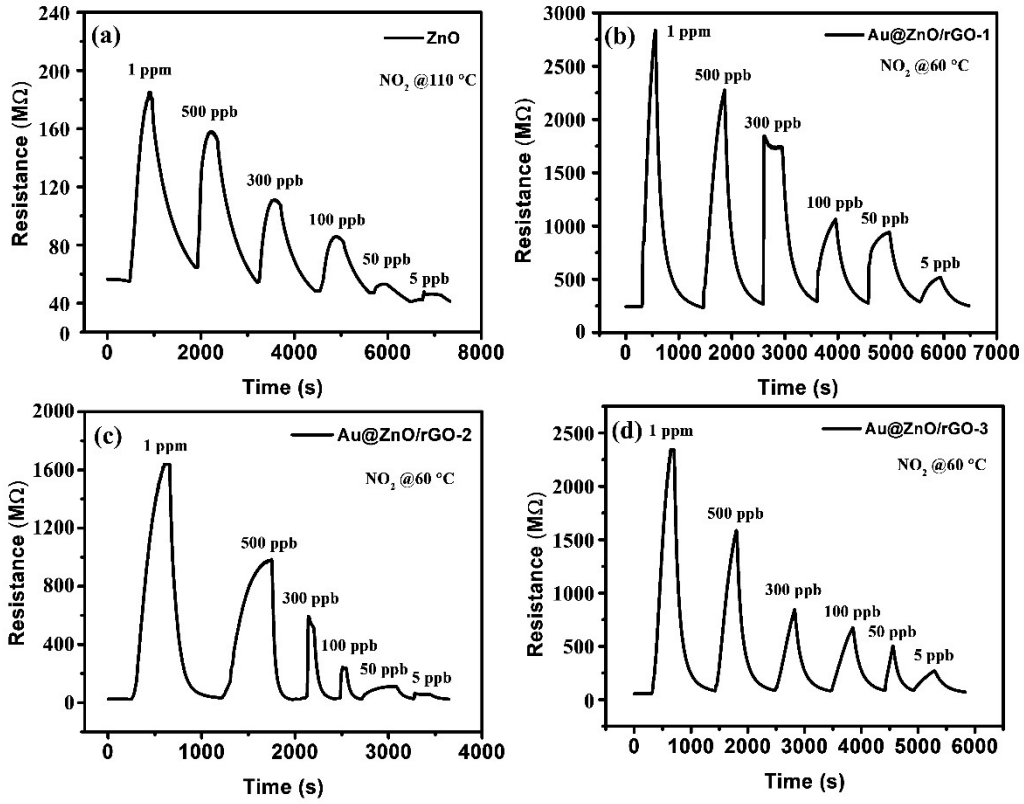


Figure S7: Temporal resistance curves for (a) ZnO; (b) Au@ZnO/rGO-1; (c) Au@ZnO/rGO-2; (d) Au@ZnO/rGO-3 sensors to NO_2 gas concentration in 5 ppb to 1 ppm.

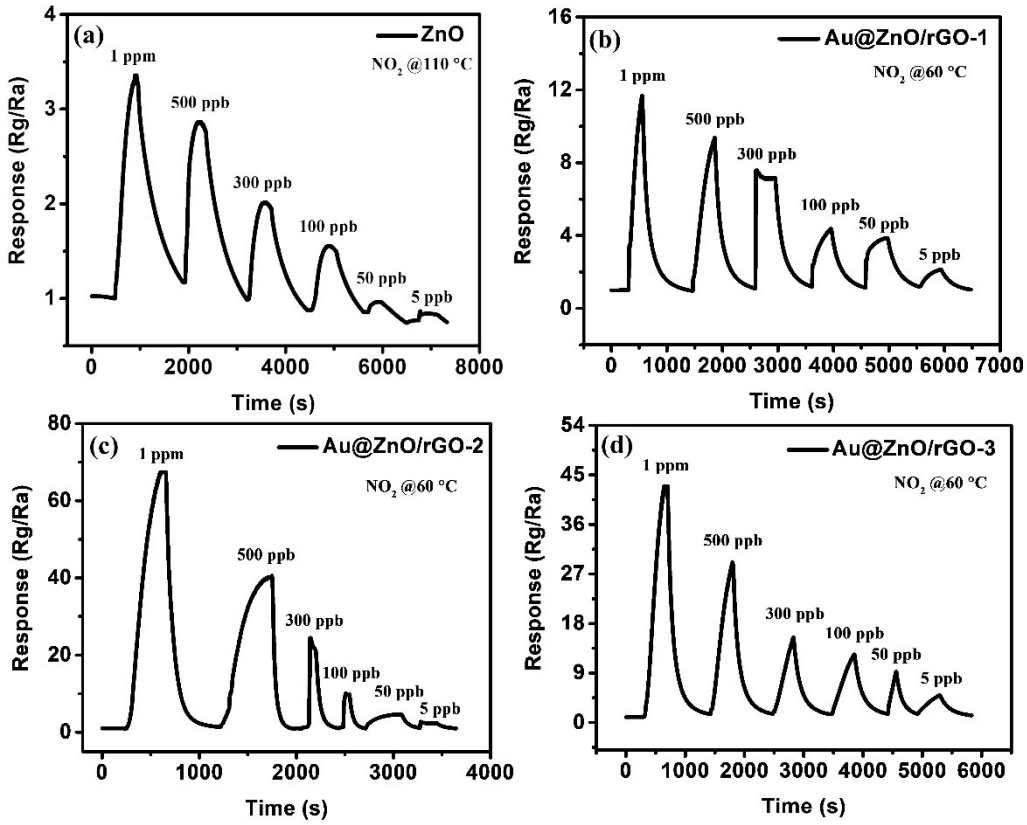
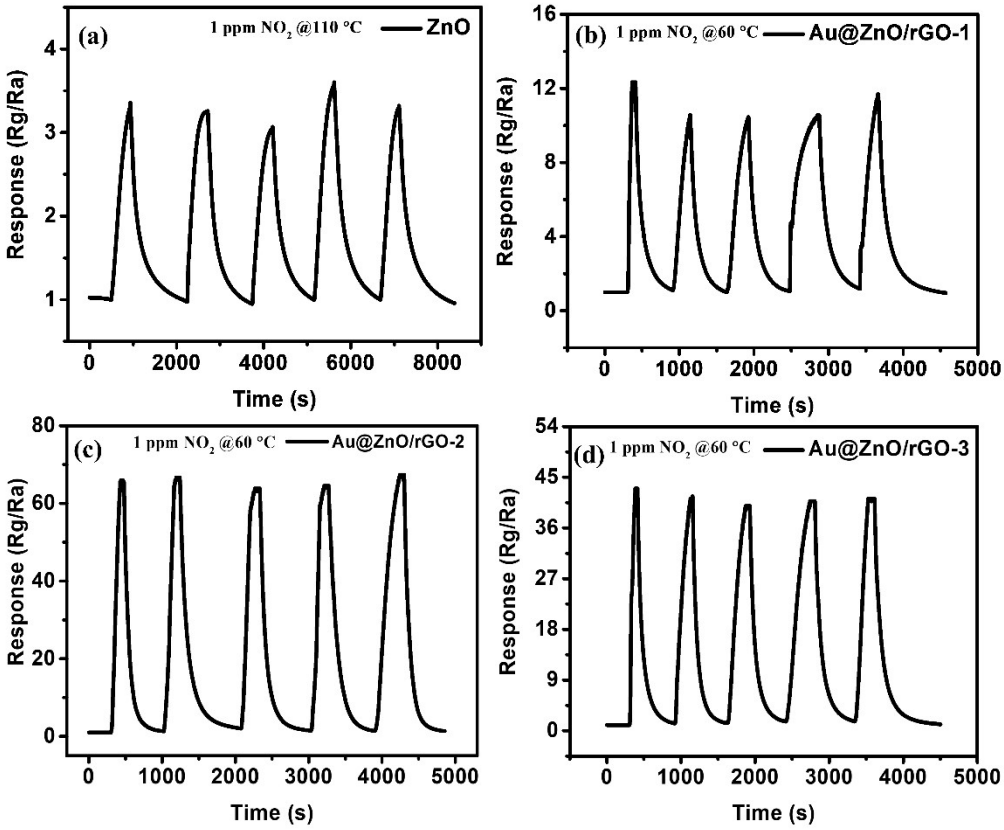


Figure S8: Time response curve for (a) ZnO; (b) Au@ZnO/rGO-1; (c) Au@ZnO/rGO-2; (d) Au@ZnO/rGO-3 sensors to NO_2 gas concentration in 5 ppb to 1 ppm.

Figure S9: Repeatability test for (a) ZnO; (b) Au@ZnO/rGO-1; (c) Au@ZnO/rGO-2; (d)



Au@ZnO/rGO-3, respectively.

Table S1: Sample description and parameters calculated from XRD patterns of ZnO, Au@ZnO/rGO-1, Au@ZnO/rGO-2 and Au@ZnO/rGO-3.

Samples	**2θ (hkl)**	**FWHM (radian)**	**Crystallite size (nm)**
ZnO	36.23 (101)	0.013788	11.04
Au-ZnO/rGO-1	36.25 (101)	0.010995	13.85
Au-ZnO/rGO-2	36.27 (101)	0.010821	14.07
Au-ZnO/rGO-3	36.26 (101)	0.010995	13.85

Table S2: The XPS peak intensity values for ZnO, ZnO/rGO, Au@ZnO/rGO-2, respectively.

Samples	O_L		O_V		O_C	
	Peak (eV)	**Percentage (%)**	**Peak (eV)**	**Percentage (%)**	**Peak (eV)**	**Percentage (%)**
ZnO	530.1	47.4	530.9	36.8	532.3	15.8
ZnO/rGO	530.4	57.1	531.4	21.0	532.3	21.9
Au@ZnO/rGO-2	530.8	72.0	531.9	15.5	532.8	12.5

Table S3: Response values of ZnO, Au@ZnO/rGO-1, Au@ZnO/rGO-2, and Au@ZnO/rGO-3 sensors to NO_2 gas concentration ranging from 5 ppb to 1 ppm.

Concentration	ZnO	Au@ZnO/rGO-1	Au@ZnO/rGO-2	Au@ZnO/rGO-3
5 ppb	0.839	2.095	2.314	4.843
50 ppb	0.964	3.864	4.637	9.235
100 ppb	1.55	4.353	9.711	12.39
300 ppb	2.014	7.169	24.417	15.506
500 ppb	2.865	9.368	40.534	29.094
1 ppm	3.356	11.686	67.386	42.982