

Supplementary Information:

**Flexible humidity-tolerant γ -Fe₂O₃-rGO-based nanohybrids for energy
efficient selective NO₂ gas sensing**

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1. Experimental Section

1.1 Reagents

Ferric sulfate, ferrous sulfate, ammonium hydroxide (25%), natural graphite flakes (75 + mesh) (Aldrich); hydrochloric acid, hydrogen peroxide (30%), potassium permanganate and phosphorus pentoxide (SD Fine Chemicals Ltd.); potassium persulfate (Merck); sulphuric acid (Thomas Baker); dimethyl sulfoxide (Sisco Research Laboratories Pvt. Ltd.) were used as received without any further purification.

1.2 Synthesis of GO

GO was synthesized from natural graphite flakes following the modified Hummers method [1] and is described briefly here. Graphite flakes (1.5 g) were added into the solution containing the preheated mixture of concentrated H_2SO_4 (6 mL), $\text{K}_2\text{S}_2\text{O}_8$ (1.25 g) and P_2O_5 (1.25 g) at 80 °C. The resulting mixture was stirred at 80 °C on an oil bath for about 4.5 h followed by its cooling down to room temperature. Thereafter, it was diluted with deionized water (DIW) and left overnight. Subsequently, it was filtered and washed repeatedly with DIW using a 2–20-micron filter to remove any residue. The product thus obtained was dried overnight under ambient conditions in a vacuum desiccator. The pre-treated graphite flakes were then put into ice-cold conc. H_2SO_4 (60 mL) at 0 °C. To this, solution KMnO_4 (7.5 g) was added gradually under stirring by maintaining the temperature below 20°C. The resulting mixture was stirred for about 2 h on an oil bath at 35 °C. It was followed by the addition of 125 mL DIW and kept the temperature at <50 °C. To this solution an additional 350 mL of DIW and a 10 mL of 30% H_2O_2 were added sequentially. It resulted in a change in the colour of the mixture from greenish-black to brilliant yellow. This mixture was left undisturbed for 24 h. Thereafter, it was centrifuged and washed with 10% aqueous HCl (1 L) followed by 1 L of DIW to remove any remaining acid. The brown product thus obtained was dried overnight at 50°C in the vacuum oven.

1.3 Synthesis of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles

The $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (NPs) were synthesized by using an earlier reported co-precipitation method [2]. A reaction of ferric sulfate (4.6 g) and ferrous sulfate (7.5 g) in 1 L of DIW was carried out at 40 °C by maintaining the pH at 3 by using ammonium hydroxide (25%) solution and stirred for 30 min. After that, the pH value was further increased to 10.5 and stirred this solution for 30 min and left opened to the environment, which resulted in the formation of $\gamma\text{-Fe}_2\text{O}_3$ NPs. These NPs were collected by using magnet and washed several times to remove unreacted reagents till the pH of the solution reached to around 7.

1.4 Gas sensor fabrication

The process for the fabrication of the sensor is described in Fig. S1(a). The prepared hybrid sample was sonicated for 10-15 min. The silver interdigitated electrodes (IDE) were fabricated on a flexible tempered glass substrate by using the vacuum coating unit. The thickness of silver interdigitated electrodes was kept in μm range, and the width of each of the electrodes and the distance between them were kept at 300 and 400 micrometres, respectively. The colloidal nanohybrid solution was then deposited on the interdigitated electrodes by using a drop-casting method. Then film was dried at 150°C on which the silver paste was applied to make the electrical contacts.

Table S1. Fitting results of O 1s XPS spectra of undoped γ -Fe₂O₃ and IO-rGO (0.1) composite.

| Materials | Binding-energy (eV) | Relative percentage (%) Of Oxygen species |
|---|--------------------------------|--|
| bare γ-Fe₂O₃ | 529.64 | 54.72 O _L (Lattice) |
| | 531.18 | 36.50 O _V (vacancy) |
| | 533.53 | 7.76 O _C (chemisorbed) |
| IO-rGO (0.1) | 529.84 | 33.24 O _L (Lattice) |
| | 531.09 | 60.54 O _V (vacancy) |
| | 533.03 | 6.21 O _C (chemisorbed) |

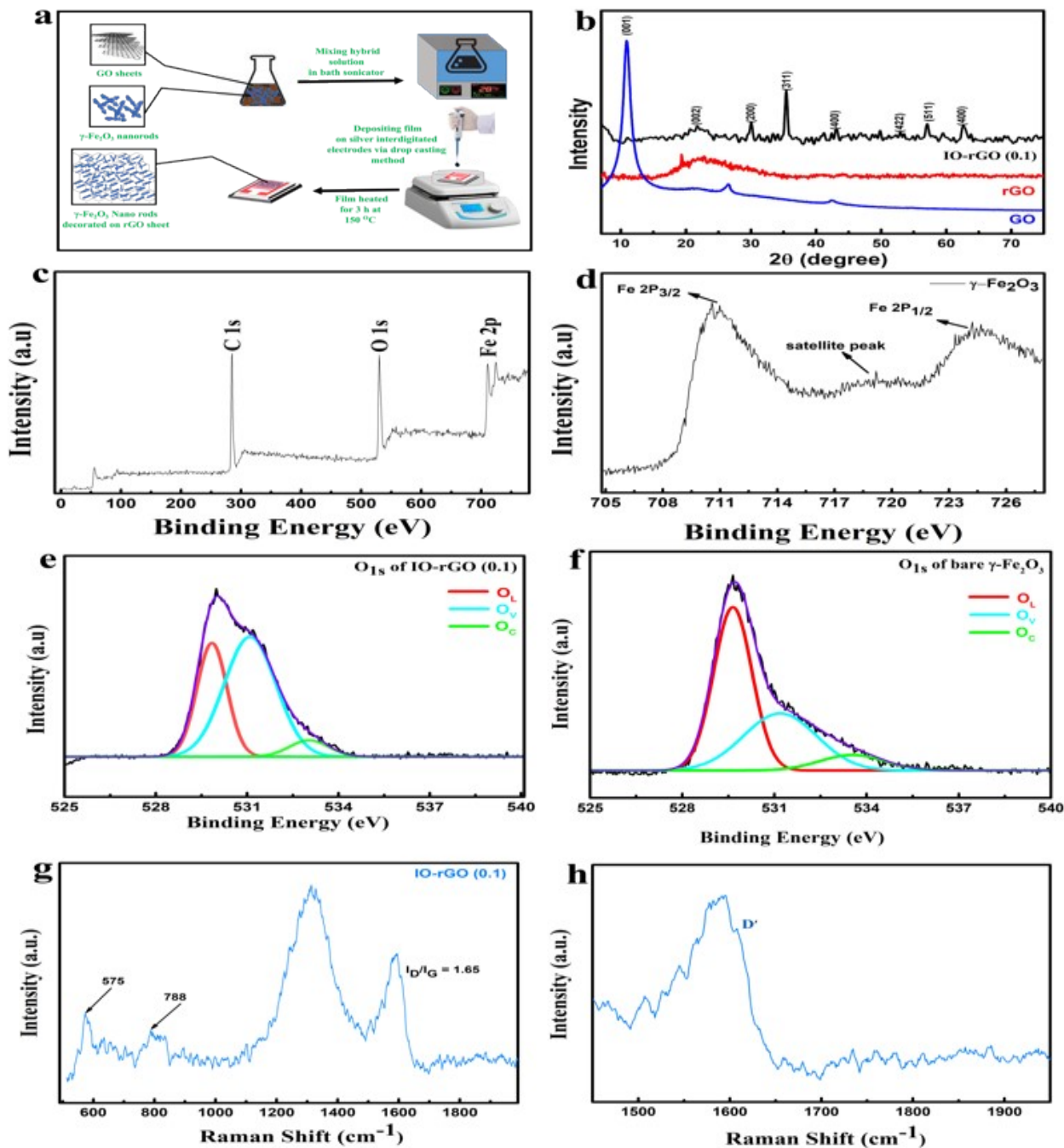


Fig. S1. Schematic of the formation of composite sensor thin film (a), XRD patterns of IO-rGO (0.1), rGO and GO (b), Wide scan XPS spectrum of IO-rGO (0.1) hybrid sensor (c), the high-resolution spectrum of Fe 2p peak in hybrid sensor (d), XPS O 1s core level spectra of IO-rGO (0.1) hybrid sensor and bare $\gamma\text{-Fe}_2\text{O}_3$ (e, f), Raman spectra of IO-rGO (0.1) (g, h).

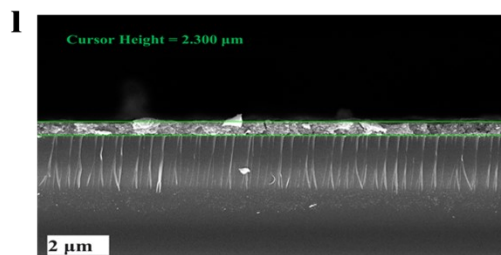
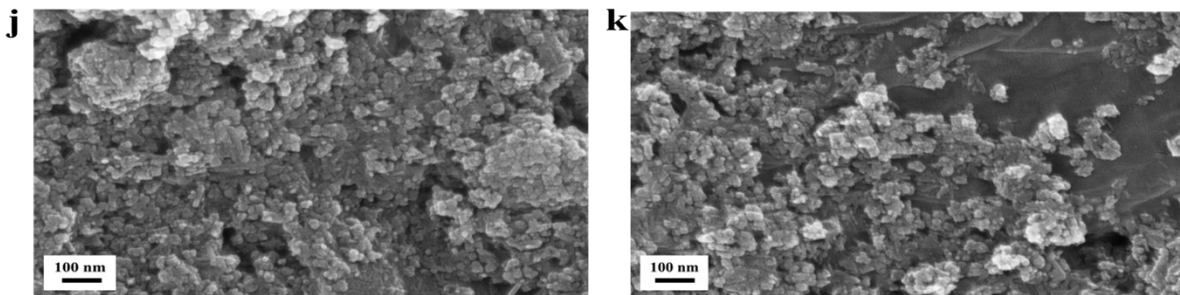
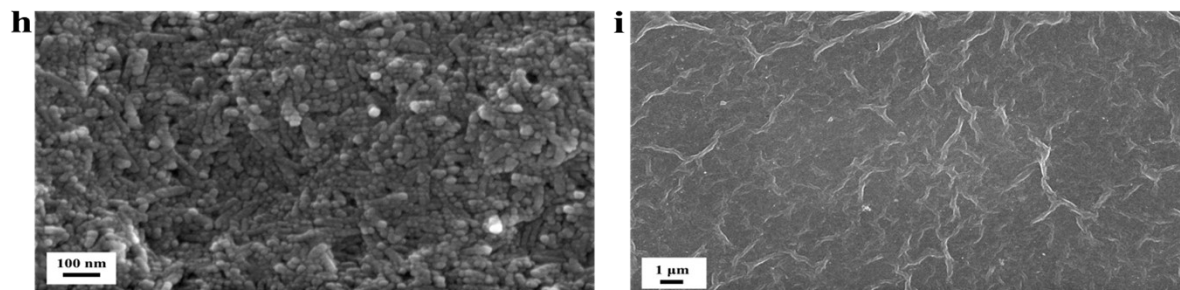
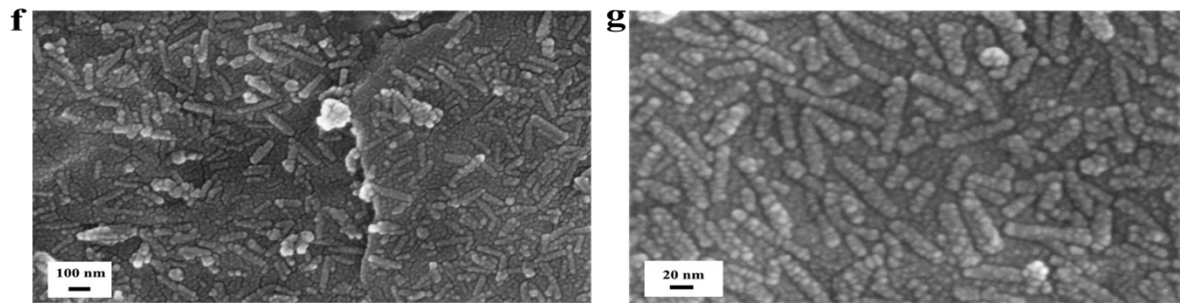
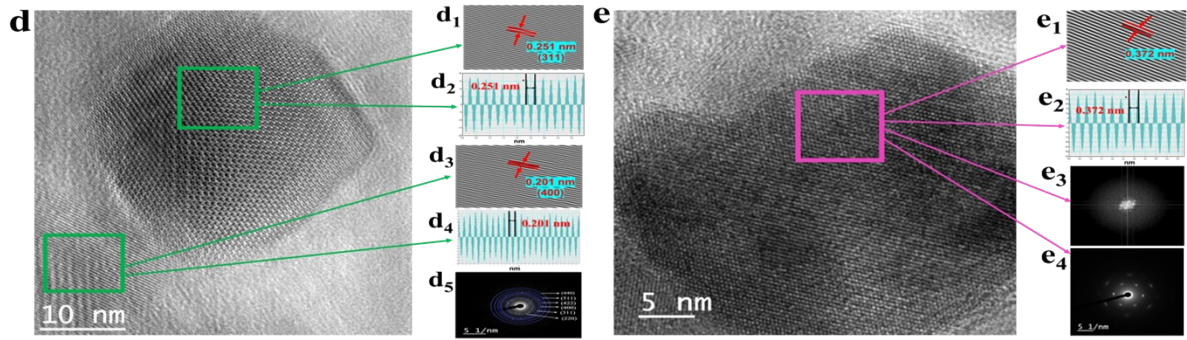
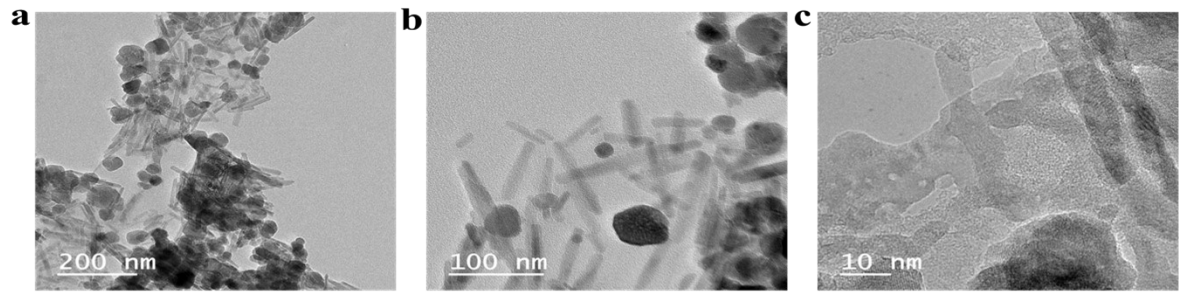


Fig. S2. TEM, HRTEM images and corresponding SAED pattern of IO-rGO (0.1) (a-e), FESEM images of IO-rGO (0.1) nano hybrids at low and high resolution (f, g), FESEM images of bare γ -Fe₂O₃ and reduced graphene oxide (h, i), FESEM images of IO-rGO (0.05) and IO-rGO (0.2) nano hybrids respectively (j, k), sensor film thickness (l).

2. Gas sensing set up

A self-designed stainless-steel chamber was used for all gas sensing measurements.

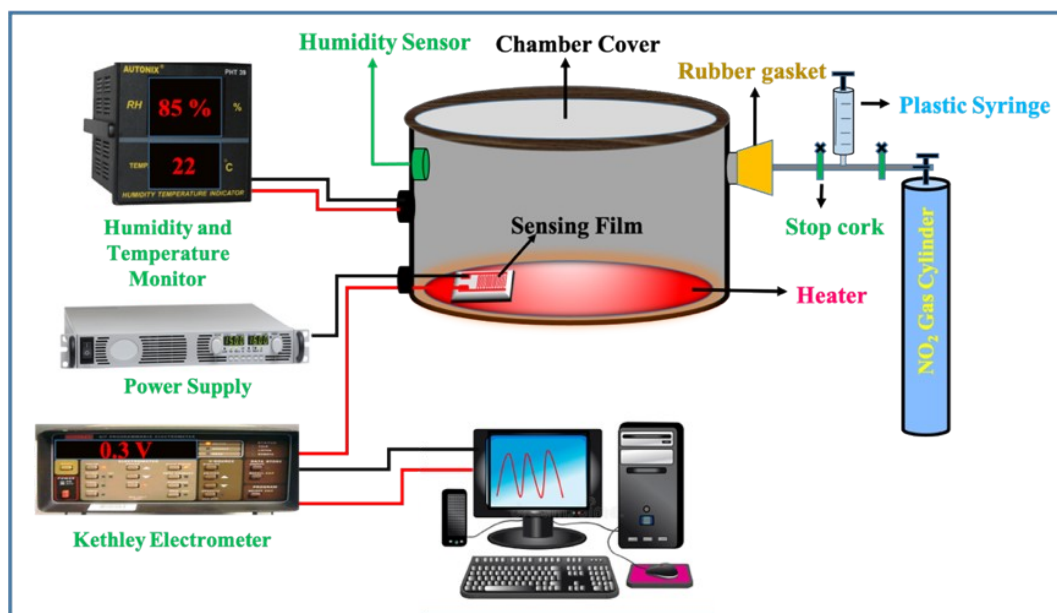


Fig. S3. Gas sensing setup.

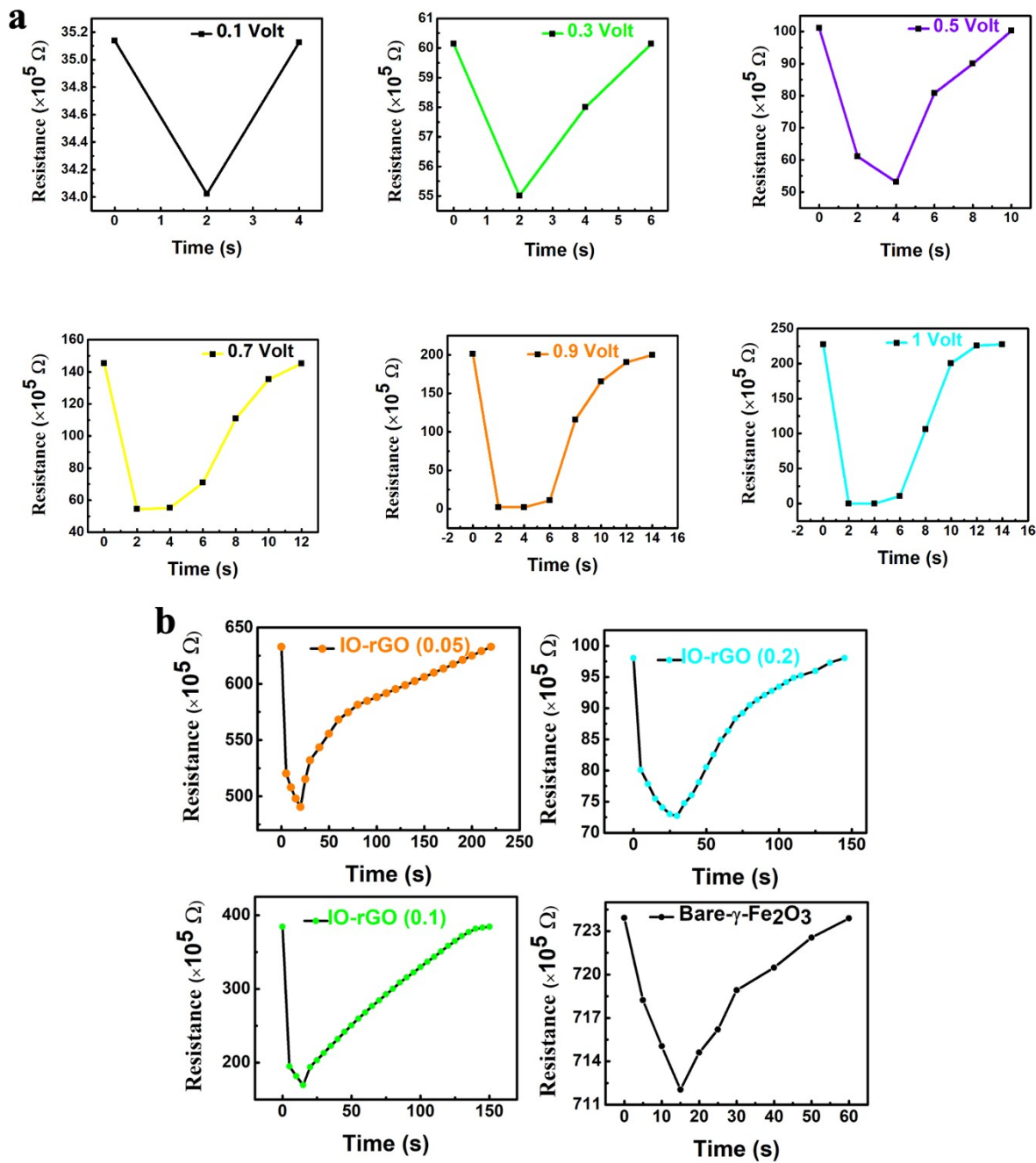


Fig. S4. Plots of the resistance versus time at different voltages in the presence of 97 % humidity for IO-rGO (0.1) nanohybrids(a), Plots of the resistance versus time upon exposure to 10 ppm NO_2 for all fabricated sensor samples along with that of bare IO (b).

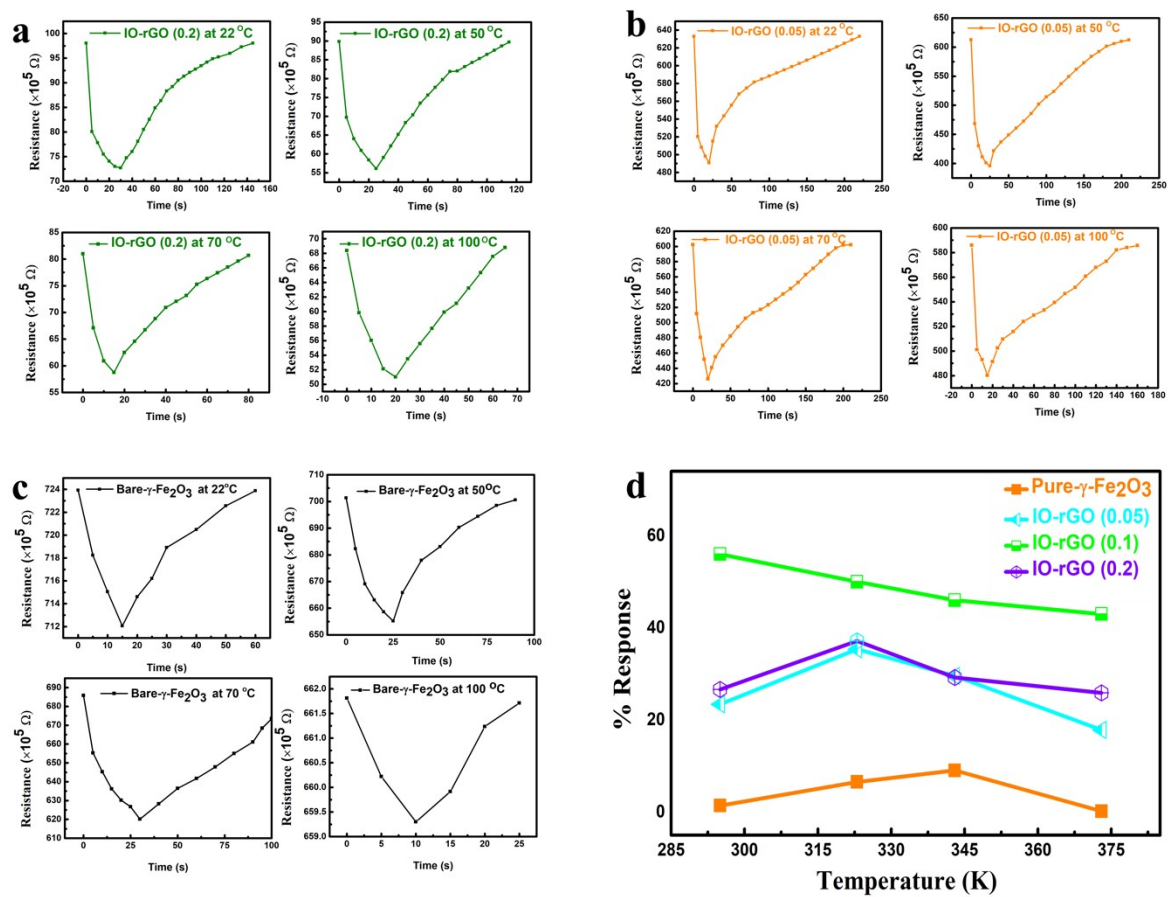


Fig. S5. The resistance versus operating temperature plots upon exposure to 10 ppm NO₂ IO-rGO (0.2), IO-rGO (0.05), and bare γ -Fe₂O₃ nanohybrids (a-c), The % response versus operating temperature plots open exposes of 10 ppm NO₂ for all fabricated sensor samples (d).

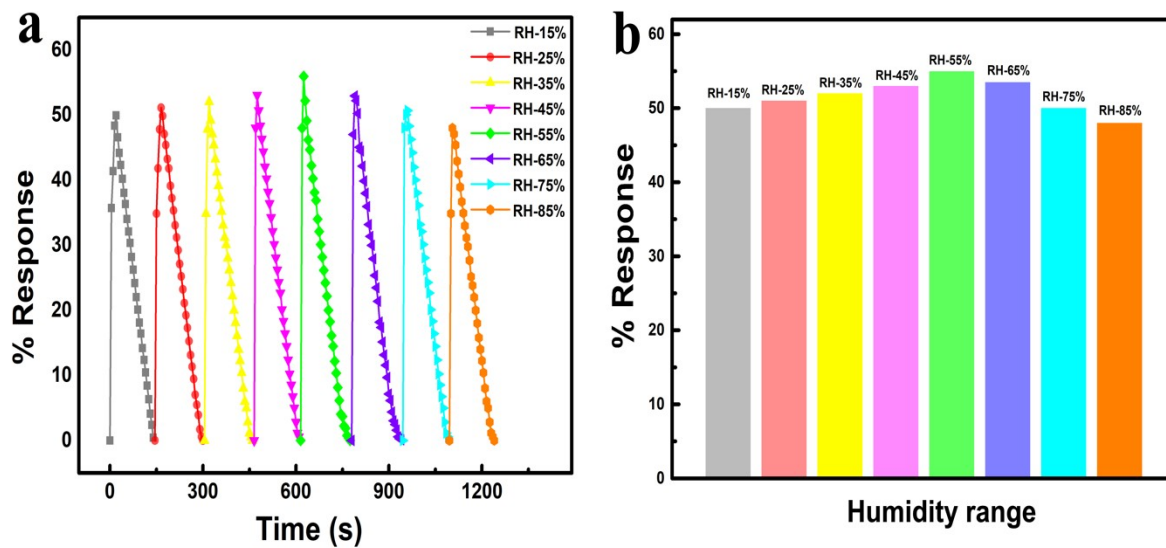


Fig. S6. The Effect of relative humidity levels (15-85 %) on %response value for a typical 10 ppm NO₂ gas. (a), %response bar diagram (b).

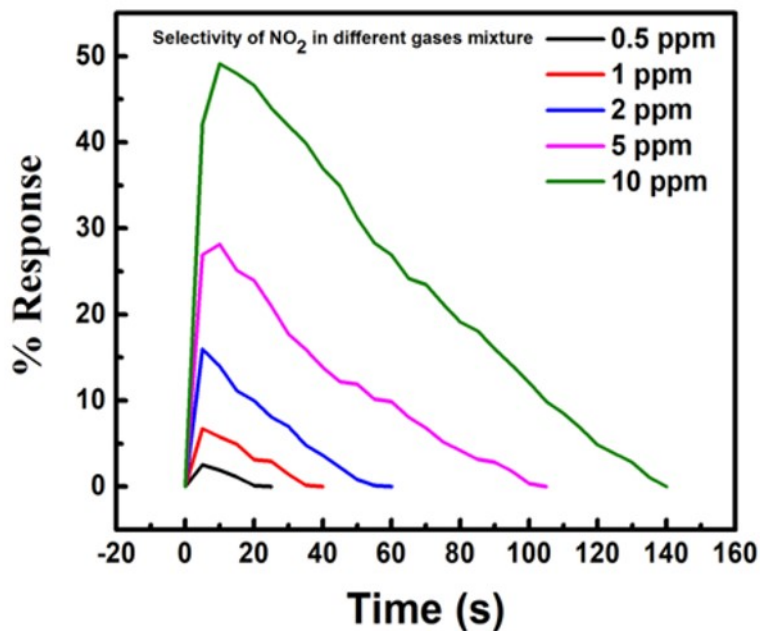


Fig. S7. The monitoring of % response of NO₂ upon varying its amount from 0.5 - 10 ppm in the mixture of gases,

Table S2. Optimization of temperature for the highest % response for bare γ -Fe₂O₃, IO-rGO (0.05), IO-rGO (0.1) and IO-rGO (0.2) nano hybrids.

| Materials | Temperature (K) | Highest %Response |
|---|-----------------|-------------------|
| bare γ -Fe ₂ O ₃ | 295K | 9 |
| IO-rGO (0.05) | 323K | 35 |
| IO-rGO (0.1) | 343K | 56 |
| IO-rGO (0.2) | 273K | 37 |

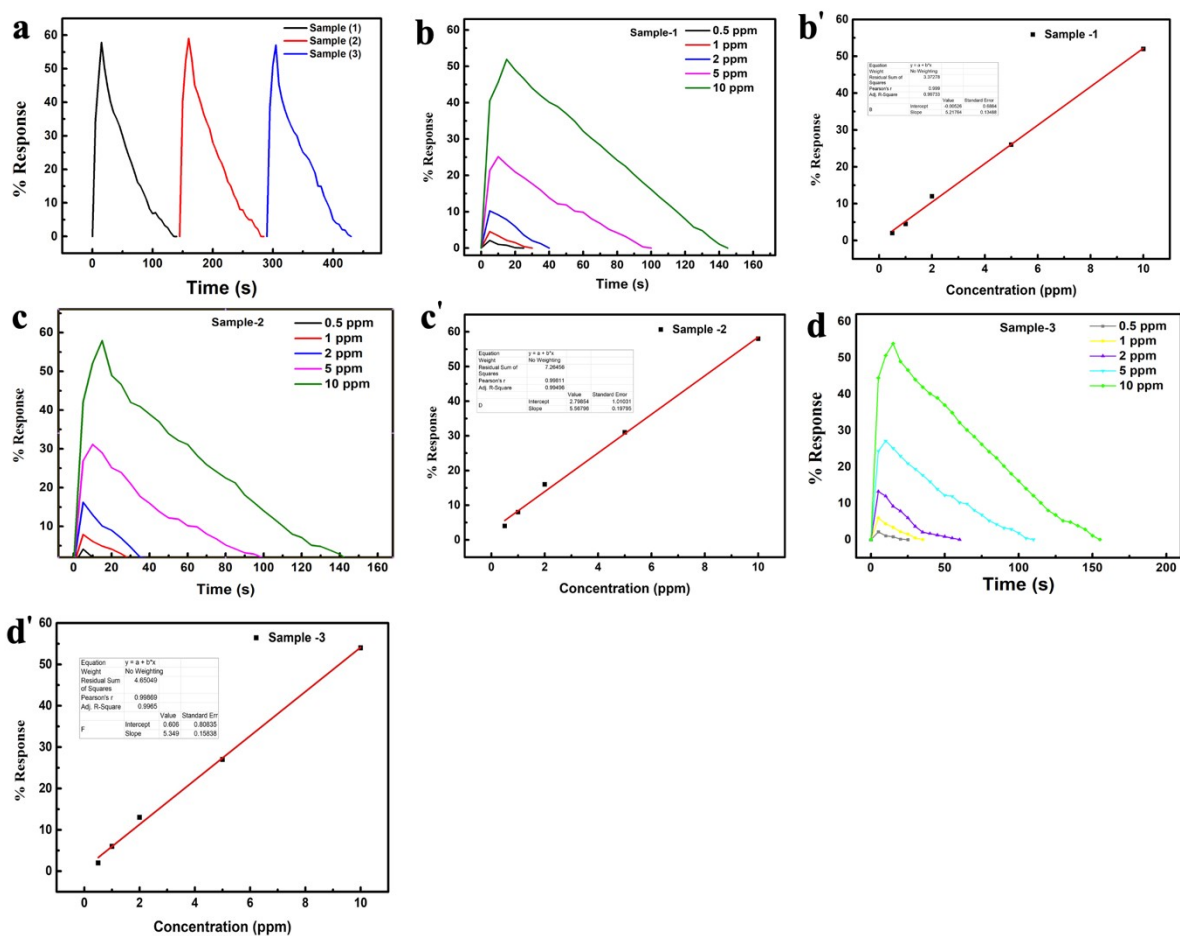
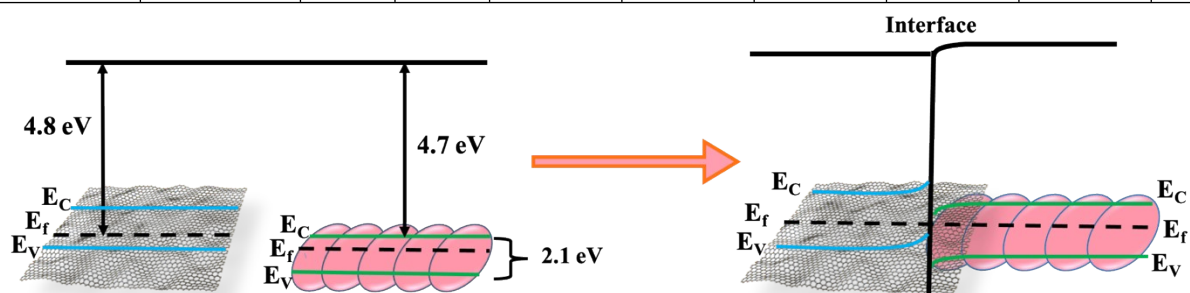


Fig. S8. Batch-to-batch reproducibility for sensing of NO₂ gas at varied concentrations using different samples of IO-rGO (0.1) (a-d').

| Materials | Humidity tolerance | [NO ₂] (ppm) | Temp. (°C) | Operating Voltage (V) | Response (%) | Detection limit (ppm) | Response /recovery time (min) | Stability Period Reported in MS | Ref. |
|---|--|--------------------------|---------------|-----------------------|---------------|-----------------------|-------------------------------|---------------------------------|----------------|
| In ₂ O ₃ NR/rGO | NR | 29 | RT | NR | 50 | 0.97 | 1.45/25 s | NR | [2] |
| NGr | NR | 10 | RT | NR | 7.74 | NR | 0.12/18.11 | NR | [3] |
| Au@ZnO/rGO | RH (30-75)% | 1 | 60° | NR* | 67.38 | 0.005 | 4.1/2.8 | 10 days | [4] |
| Pd-CuO/rGO | RH (25-90)% | 100 | RT | 0.1 | 64.2 | 0.05 | 0.16/0.15 (90% recovery) | NR | [5] |
| Fig. S9. The energy band diagram for γ-Fe₂O₃-rGO nano hybrids. α-Fe₂O₃/rGO | RH-(25-54)% | 5 | RT | NR | 38 | 0.1 | 1.26/16 | NR | [6] |
| Fe ₃ O ₄ /rGO | NR | 400 | RT | NR | 24.2 | 30 | 4.6/12.3 | NR | [7] |
| WO ₃ /rGO | NR | 56 | RT | NR | 40.8 | 7 | -/- | 7 days | [8] |
| In ₂ O ₃ /rGO | NR | 30 | RT | NR | 8.25 | 5 | 4/24 | NR | [9] |
| ZnO/rGO/0.5 | NR | 50 | 130° | 5 | 62.0 | 0.1 | 0.05/0.16 | NR | [10] |
| Co ₃ O ₄ /rGO | NR | 60 | RT | NR | 80 | - | - | NR | [11] |
| SnO ₂ /rGO | NR | 50 | RT | NR | 6.5 | 10 | 3.17/3.73 | NR | [12] |
| SnO ₂ /RGOH | Unstable response at High RH RH-(30-100)% | 4 | RT | 0.1 | 15 | 0.5 | 3/4.3 | NR | [13] |
| AgNPs-SnO ₂ - rGO | NR | 5 | RT | NR | 2.17 | 1 | 0.81/5.65 | NR | [14] |
| SnO ₂ /N-RGO | NR | 5 | RT | NR | 1.38 | 1 | 0.75/2.8 | 15 days | [15] |
| rGO/SnO ₂ | RH (0-54)% | 25 | RT | NR | 25 | 1 | NR | NR | [16] |
| Zn-doped CuO/rGO | RH-(15-85)% | 40 | RT | NR | 54.5 | 2 | 1/NR | 35 days | [17] |



| | | | | | | | | |
|---|-----|----|-----|-----|-----|------------------------|------------|--------------|
| γ -Fe ₂ O ₃ /rGO nanohybrids stable response RH-(15-97)% | 10 | RT | 0.3 | 56 | 0.5 | 0.25/2.08 | > 365 days | This work |
| | 0.5 | RT | 0.3 | 3.5 | 0.5 | 0.08/0.25 (0.5 ppm) | | |

Table S3. A comparison of NO₂ sensing performance of the current work with reported results of other groups.

References

- [1] Kumar, A., & Khandelwal, M. (2014). A novel synthesis of ultrathin graphene sheets for energy storage applications using malonic acid as a reducing agent. *J. Mater. Chem. A*, 2(47), 20345-20357.
- [2] Kaloti, M., & Kumar, A. (2016). Synthesis of chitosan-mediated silver coated γ -Fe₂O₃ (Ag- γ -Fe₂O₃@ Cs) superparamagnetic binary nanohybrids for multifunctional applications. *J. Phys. Chem. C*, 120(31), 17627-17644.