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# Supplementary Information

# For

# “Hierarchical Nanohybrids of B- and N- Codoped Graphene/Mesoporous NiO Nanodisks: An Exciting New Material for Selective Sensing of $H_2S$ at Near Ambient Temperature”

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**KEYWORDS:** NiO, boron-nitrogen-rGO, hybrid composite, ambient temperature $H_2S$ sensing, excellent sensitivity, high selectivity.

## Preparation of Graphene oxide (GO)

GO was prepared by the oxidation of natural graphite powder according to Hummer's method. Typically, graphite powder (3.0 g) was added to concentrated $H_2SO_4$ solution under stirring in an ice bath. Then $KMnO_4$ slowly added slowly to the above suspension. Successively, the total solution transferred to 40 °C oil bath and vigorously stirred for 0.5 h. After that, 150 mL water was added, and the resultant solution stirred for 15 min at 95 °C. Additional 500 mL water added followed by a slow addition of 15 mL $H_2O_2$, turning the color of the solution from dark brown to yellow. The mixture was filtered and washed with 1:10 HCl aqueous solution to remove metal ions. The resulting solid was dried in air and diluted to 600 mL, making a graphite oxide aqueous dispersion. Finally, graphite oxide was purified through the dialysis process. The resultant graphite oxide aqueous dispersion was then diluted to 1.2 L, stirred overnight and sonicated for 30 min to exfoliate it to GO. The GO dispersion was then centrifuged at 3000 rpm for 40 min to remove the un exfoliated graphite.

**Preparation of boron-doped rGO incorporated NiO nanodisks ($NiO_{BG}$) composite:** In a typical synthesis process of $NiO_{BG}$ composite, the calculated amount of as-prepared NiO nanodisks and GO were ultrasonically dispersed in 70 mL of deionized water for 5 h. To this solution, 0.5 g of boric acid was added under constant magnetic stirring. Finally, the resultant solution was transferred to the Teflon lined autoclave, heated to 180 ºC at the heating rate of 10 ºC · $min^{-1}$ and maintained at that temperature for 12 hrs. After the completion of the reaction, the autoclave was naturally cooled to RT. The isolated material was purified through centrifugation process by several times washing with water and ethanol, then dried at 90 ºC for 12 h.

**Preparation of nitrogen-doped rGO incorporated NiO nanodisks ($NiO_{NG}$) composite:** In a typical synthesis process of $NiO_{NG}$ composites, the calculated amount of as-prepared NiO nanodisks and GO were ultrasonically dispersed in 70 mL of deionized water for 5 h. To this solution 2 mL of 1:1 aqueous ammonia/ hydrazine hydrate were added. Finally, the resultant solution was transferred to the Teflon lined autoclave, heated to 180 ºC at the heating rate of 10 ºC · $\text{min}^{-1}$ and maintained at that temperature for 12 hrs. After the completion of the reaction, the autoclave was naturally cooled to RT. The isolated material was purified through centrifugation process by several times washing with water and ethanol, then dried at 90 ºC for 12 h.

## Details of the experimental methods and characterization techniques

The morphologies of the as-synthesized products were analysed by the field emission scanning electron microscopy (JEOL JSM-7500F), Energy dispersive X-ray analysis (EDAX) performed with OXFORD Inca detector interfaced at 15 kV without sample sputtering, and transmission electron microscopy (TEM, HR-TEM, JEM-2100F, JEOL). The crystal structure identified by powder X-ray diffraction (XRD) measurements were carried out on X -Pert-pro using CuKα ($\lambda = 0.15406$ nm) radiation over a 2θ range of 2–70°. The Raman spectroscopy was performed using an NRS-5100, JASCO spectrometer. The X-ray photoelectron spectroscopy studies were carried out using an XPS, ESCALAB-MKII with AlKα X-ray ($h\nu = 1486.6$eV) as the emission source. The specific area was determined by the surface area and pore size distribution measurements using a BET (Micromeritics (ASAP2010)), surface area and pore size analyser at liquid nitrogen temperature.

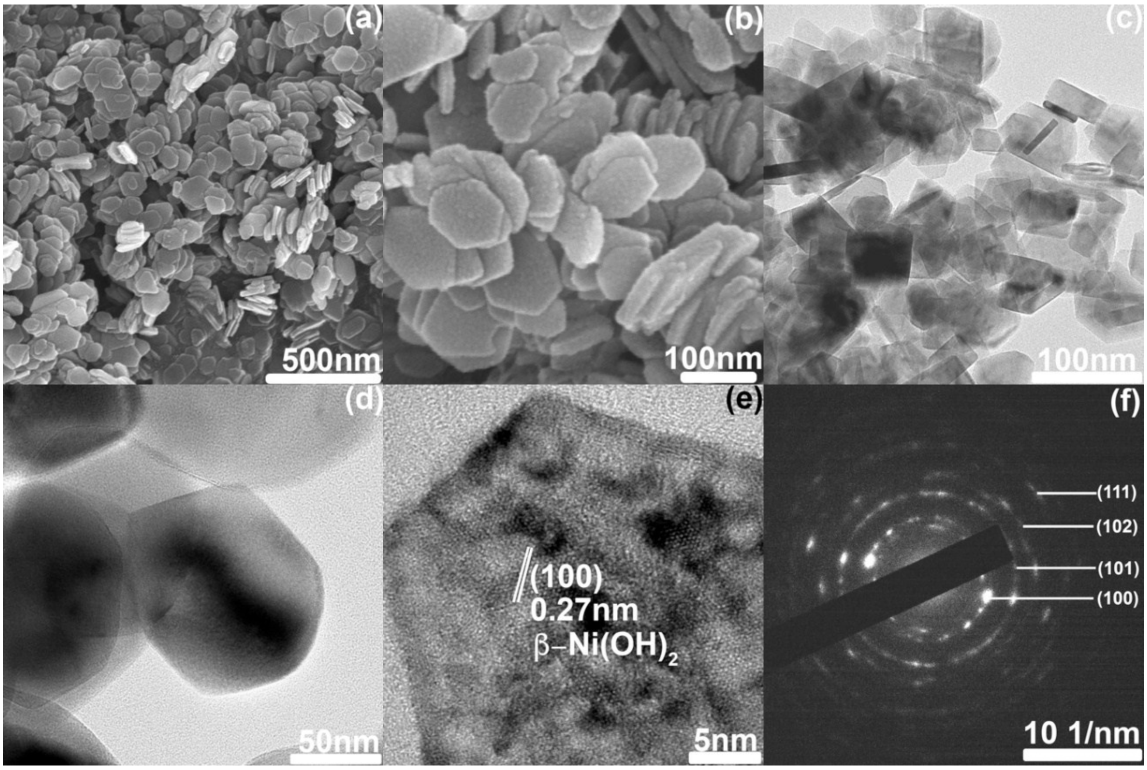


**Fig. S1**. Morphology of the as-prepared β-Ni$(OH)_2$ nanodisks in scanning and transmission mode. **(a, b)** FE-SEM images of the β-Ni$(OH)_2$ nanodisks at two different magnifications; TEM images of the as-prepared β-Ni$(OH)_2$ nanodisks at **(c)** low and **(d)** high magnifications; **(e)** HR-TEM and **(f)** SAED pattern of the as-prepared β-Ni$(OH)_2$ nanodisks.

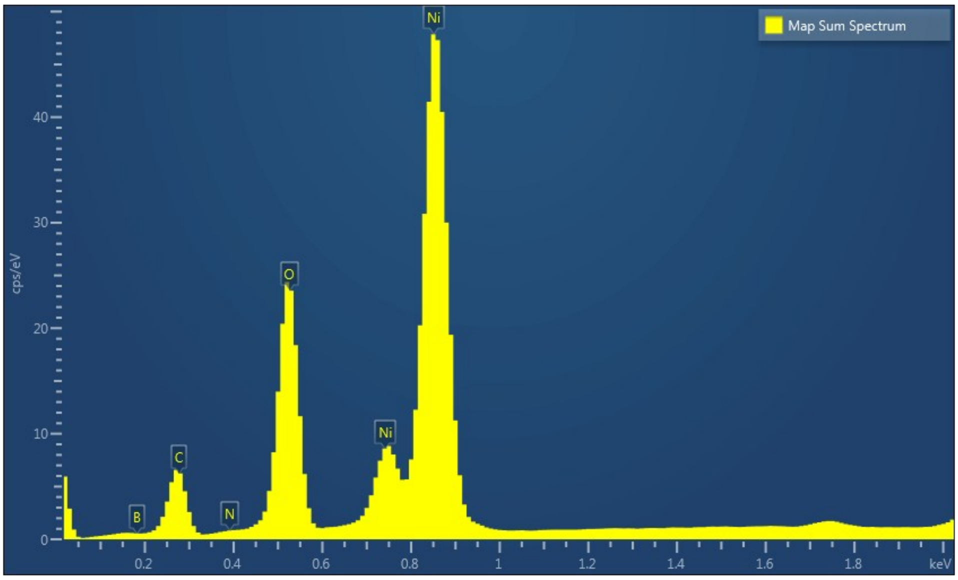


**Fig. S2**. Energy dispersive spectrum of the as-prepared $NiO_{BNG}$ hybrid nanocomposite.

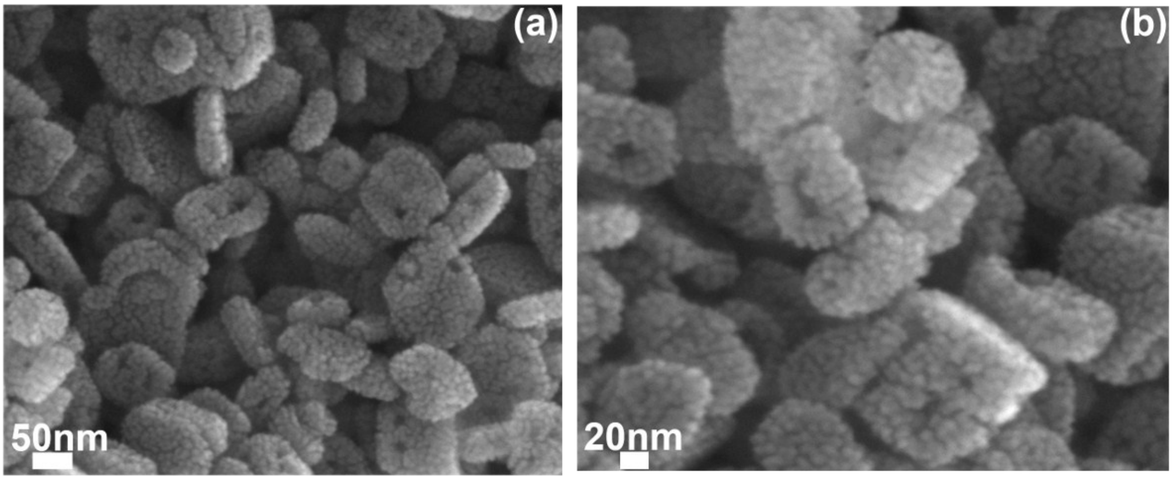


**Fig. S3**. FE-SEM images of the as-prepared $NiO_{BNG}$ hybrid nanocomposite.

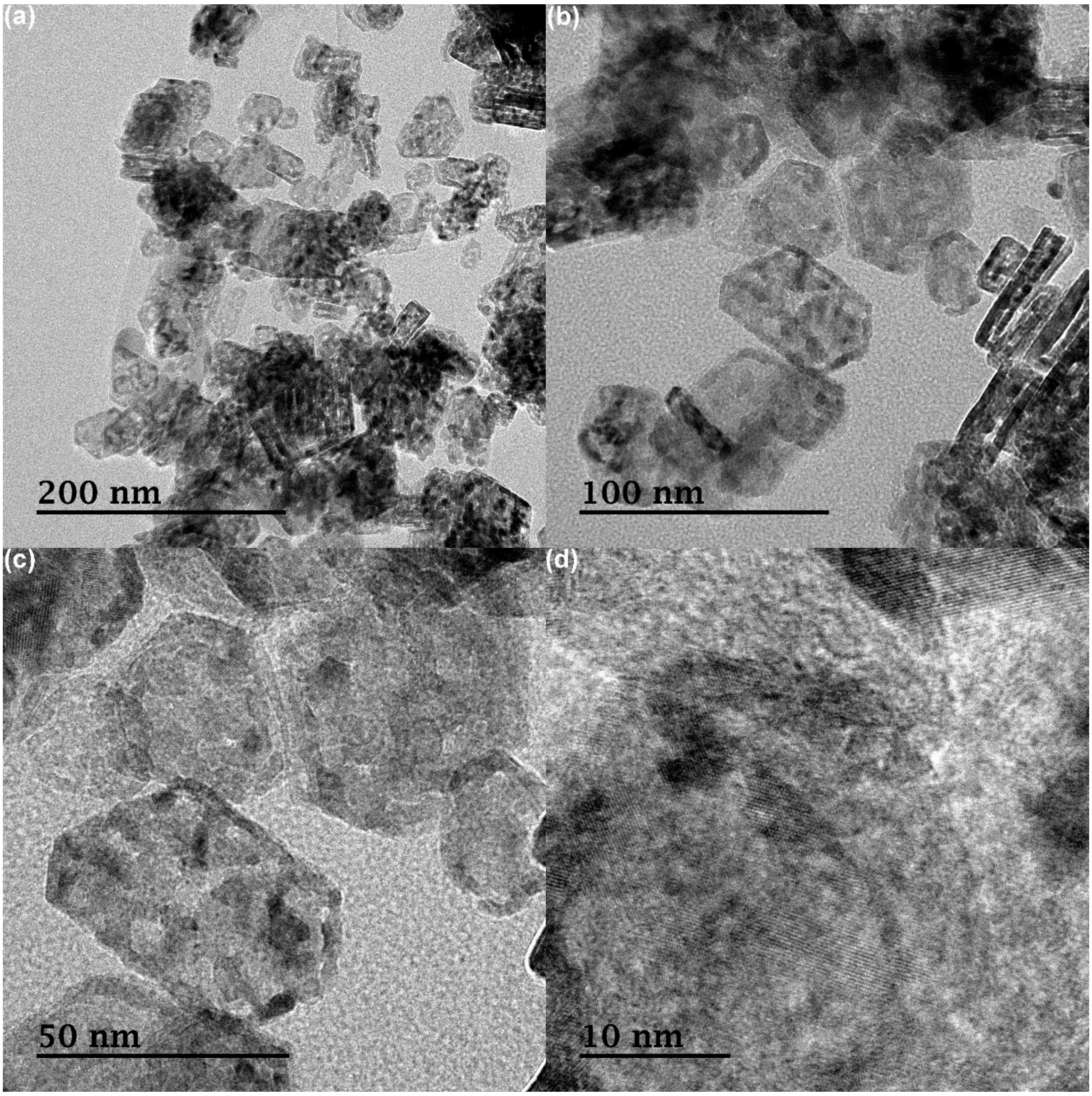


**Fig. S4**. Morphology of the as-prepared reduced graphene oxide incorporated NiO nanodisks ($NiO_{PG}$). **(a-d)** TEM images of the $NiO_{PG}$ composite at different magnifications.

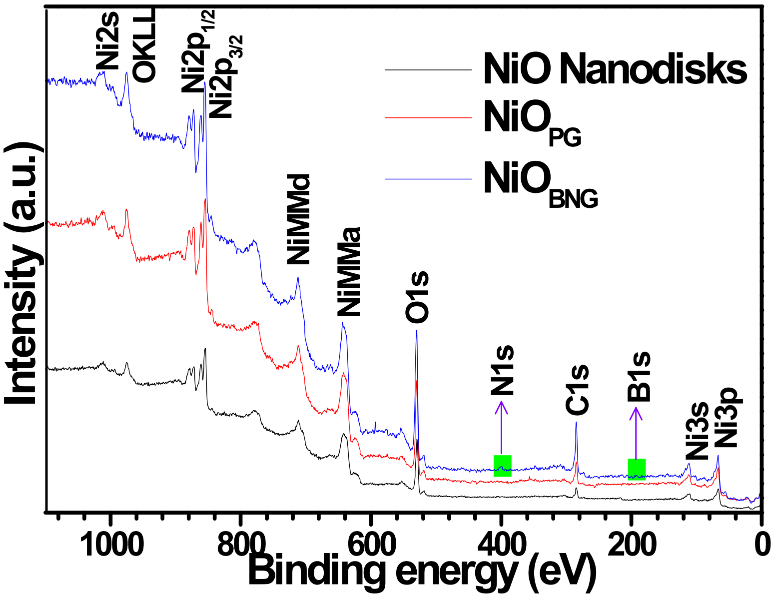


**Fig. S5.** X-ray photoelectron spectra of the as-prepared NiO, $NiO_{PG}$ and $NiO_{BNG}$ hybrids.

**Table S1.** Atomic percentage (at. %) of carbon, oxygen, nitrogen, boron, and nickel in the $NiO_{BNG}$ hybrids, derived from the XPS analysis.

| Name | Peak BE | FWHM eV | Area (N) | At. % |
|---|---|---|---|---|
| C1s | 284.6 | 3.19 | 9833.46 | 32.65 |
| O1s | 530.23 | 4.5 | 11314.52 | 37.96 |
| N1s | 399.5 | 4.45 | 698.66 | 2.18 |
| B1s | 190.86 | 2.01 | 1510.19 | 4.71 |
| Ni2p3 | 855.02 | 4.53 | 3571.65 | 11.13 |
| Ni2p1 | 874.17 | 7.24 | 3936.71 | 12.27 |

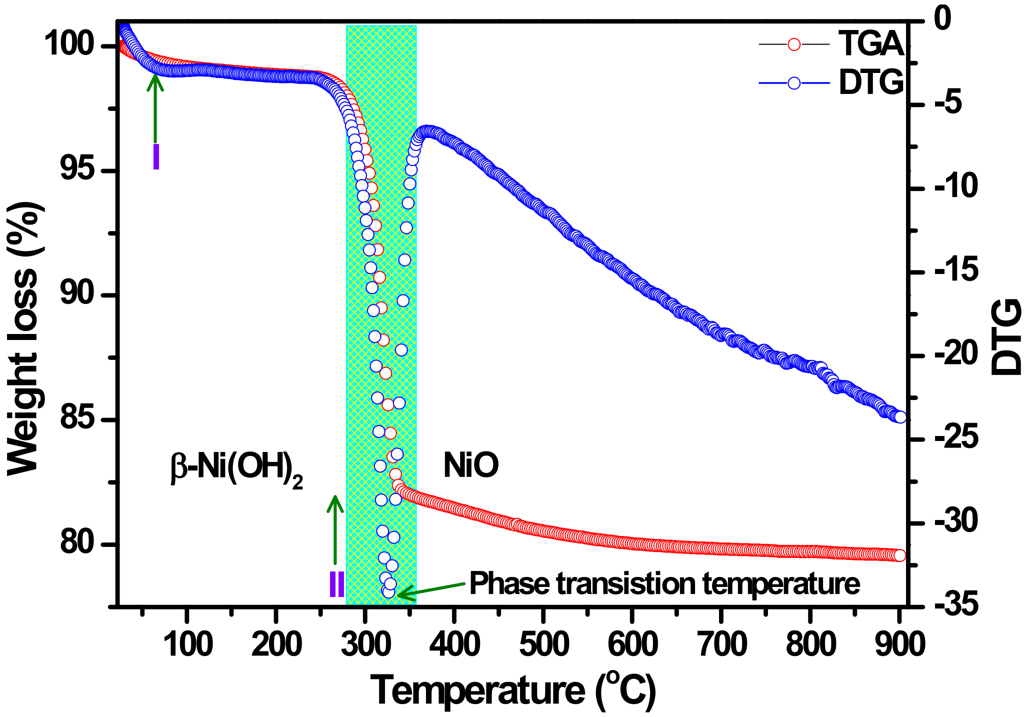


**Fig. S6**. Thermogravimetric-differential thermal profile of the as-prepared β-Ni(OH)$_2$ nanodisks carried out at an oxygen environment from room temperature to 900 °C at the heating rate of 10 °C · min$^{-1}$.

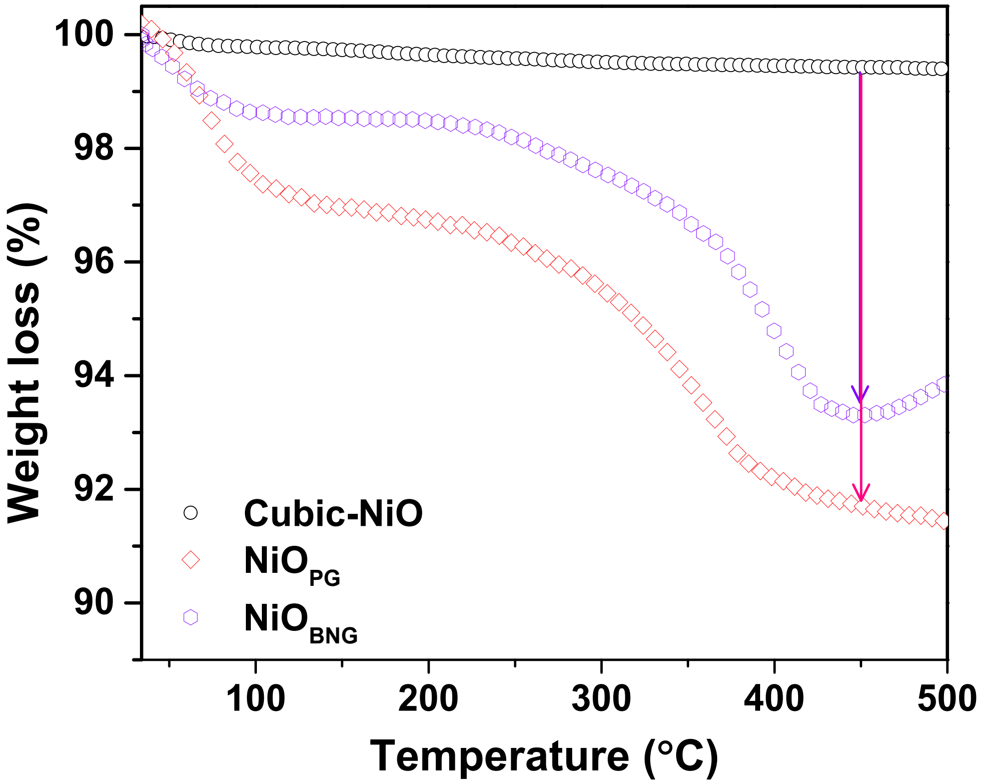


**Fig. S7**. Thermogravimetric-differential thermal profile of the as-prepared NiO nanodisks, NiO$_{PG}$ and NiO$_{BNG}$ hybrid nanocomposites carried out at an oxygen environment from room temperature to 500 °C at the heating rate of 10 °C · min$^{-1}$.

## Gas sensor fabrication.

For device fabrication, the as prepared materials were made into a thick homogeneous paste. The paste was coated on an alumina substrate on which a four-finger gold electrode is patterned for electrical contacts. The finger thickness and average spacing of the gold electrode is of ~200 µm and 30 µm, respectively. The effective sensing area of the sensor is ~3 $mm^2$. The control on operating temperature was achieved and monitored using a PDI controller equipped with a Chromel-Alumel K-type thermocouple positioned in proximity with the gas sensor surface. Prior to each experimentation the sensing element was pre-heated at 150 °C for 3 h in air to stabilize the sensor surface. All gas-sensing experiments were carried out in a dry air environment. at a gas flow rate of 300 $cm^3$/min. The resistance of the sensor was continuously monitored as a function of time by an Agilent digital multimeter and Keithley source measuring unit with the help of LabVIEW based data acquisition system. The recovery of the sensor was recorded by exposing it to dry air. The gas-sensing measurements were carried out by monitoring changes in resistance under a constant applied voltage during cyclic exposure to different concentrations of gas.

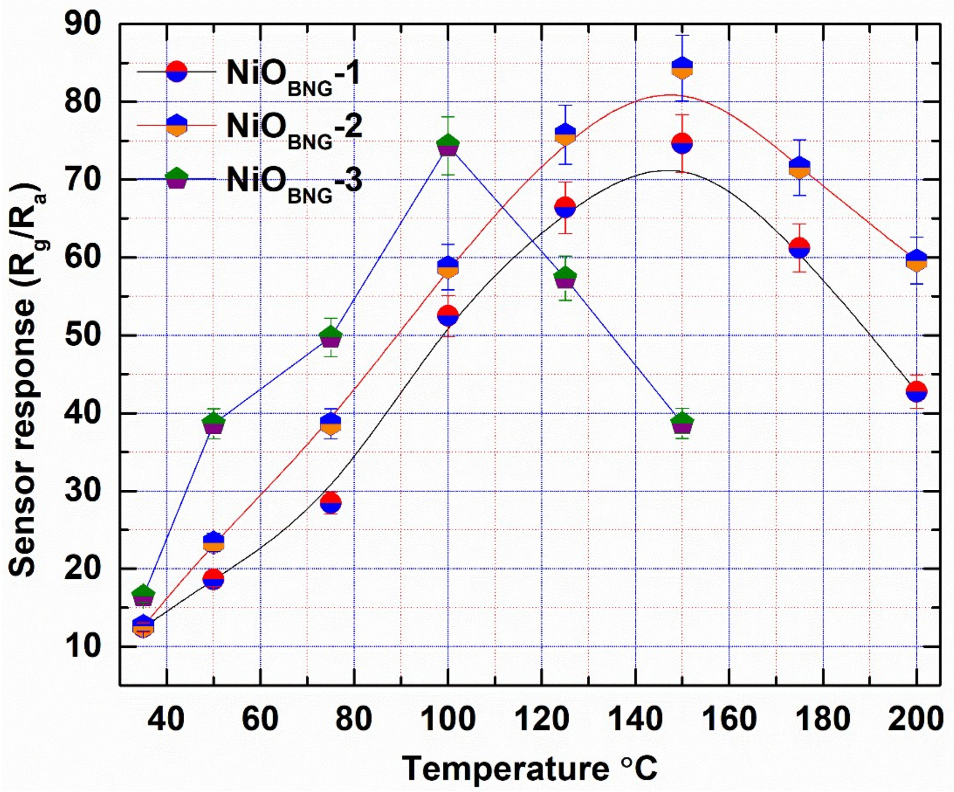


**Fig. S8.** Temperature dependent sensing response profile of the sensors based $NiO_{BNG-1}$, $NiO_{BNG-2}$, and $NiO_{BNG-3}$ to 100 ppm of $H_2S$.

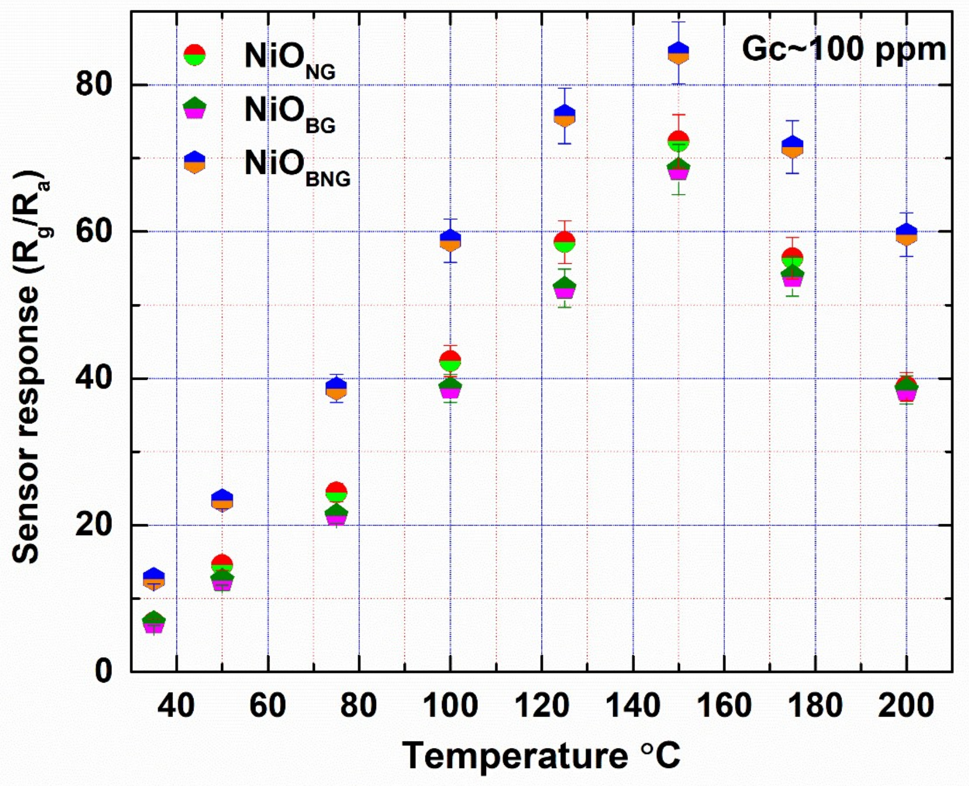


**Fig. S9.** Temperature dependent sensing response profile of the sensors based on the nitrogen doped rGO incorporated NiO nanodisks (NiO$_{NG}$), boron doped rGO incorporated NiO nanodisks (NiO$_{BG}$) and boron-nitrogen co-doped rGO incorporated NiO nanodisks (NiO$_{BNG}$) to 100 ppm of $H_2S$.

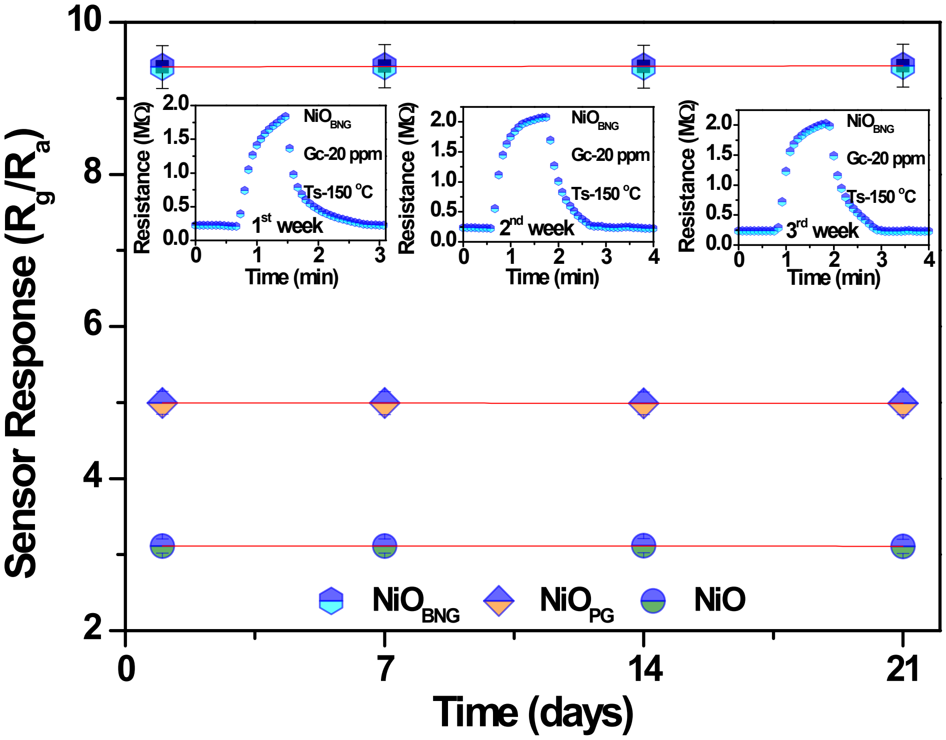


**Fig. S10.** Stability of the sensors based on bare NiO nanodisks, pristine NiO$_{PG}$ and NiO$_{BNG}$ to 20 ppm $H_2S$ at 150 °C for 21 days.

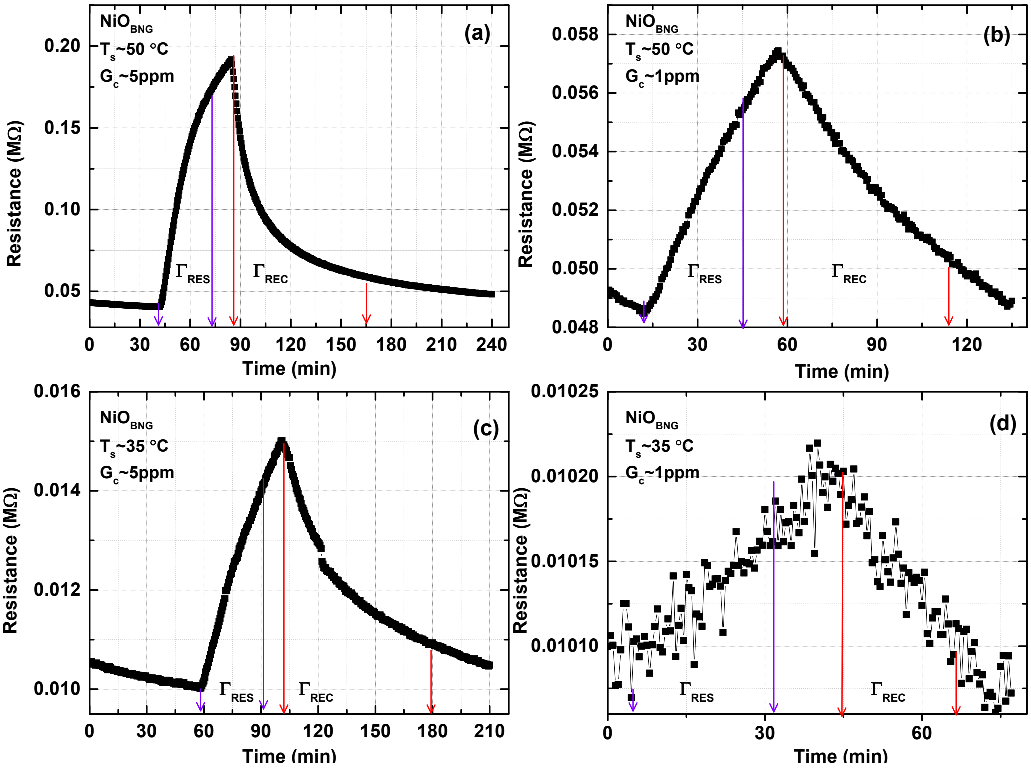


**Fig. S11.** Response/recovery characteristics of NiO$_{BNG}$ sensor towards (a) 5 ppm (b) 1 ppm of $H_2S$ at operating temperature of 50 °C and (c) 5 ppm (d) 1 ppm of $H_2S$ at operating temperature of 35 °C.

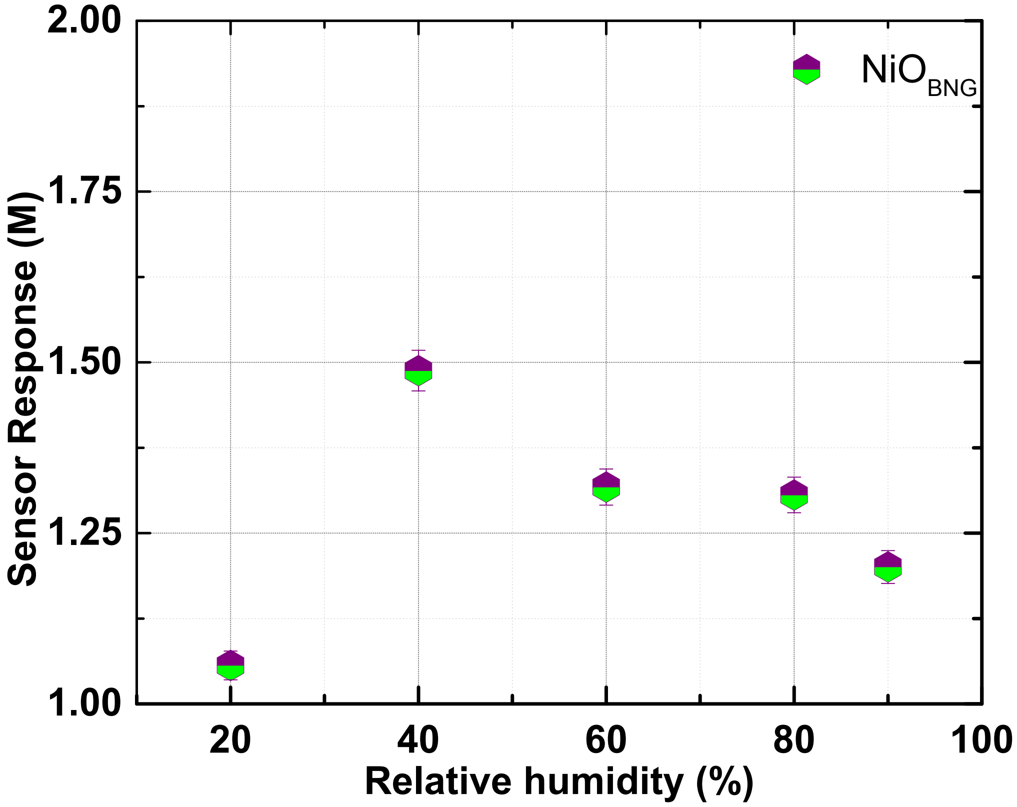
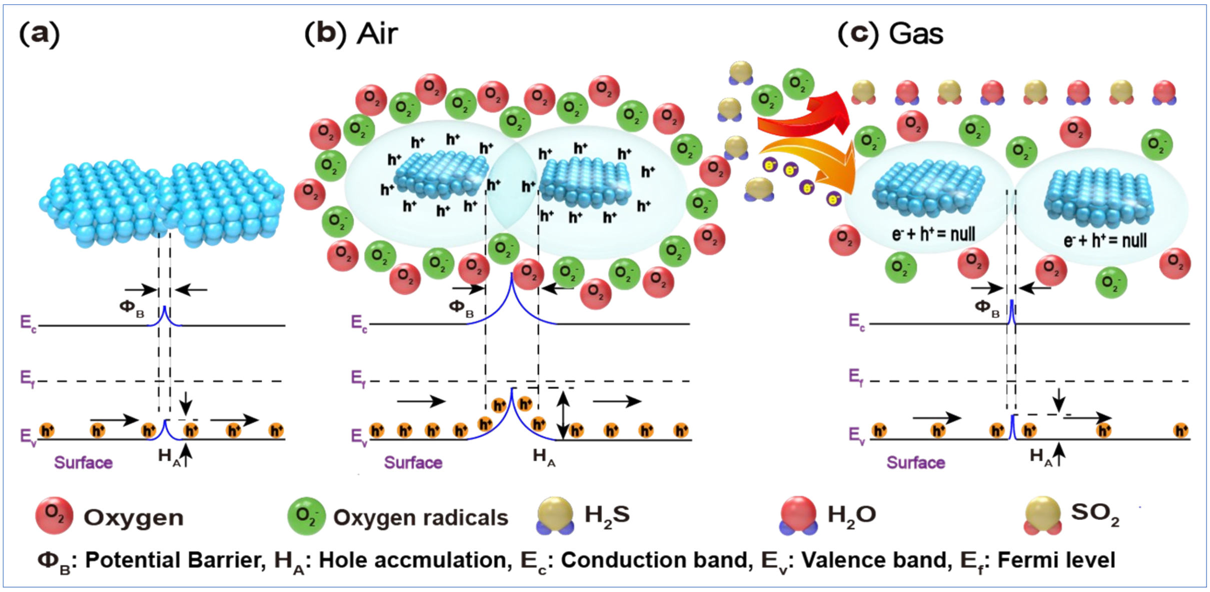


**Fig. S12.** Sensor response of NiOBNG at 35 °C to different relative humidity.



**Scheme S1.** Representative energy band diagrams and physical structures illustrating the $H_2S$-sensing mechanism in air and $H_2S$ atmosphere.

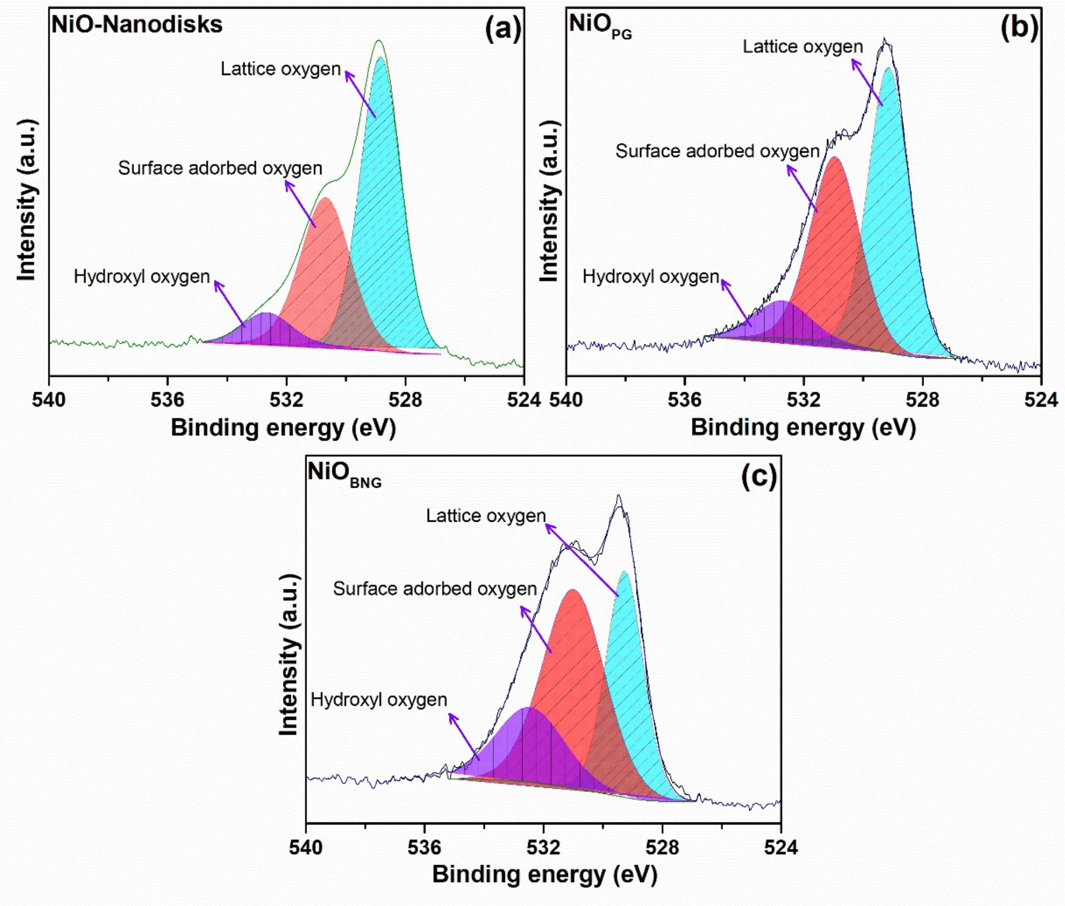


**Fig. S13.** High-resolution O1s core-level spectra of the as-prepared NiO nanodisks, NiO$_{PG}$ and NiO$_{BNG}$ composites.

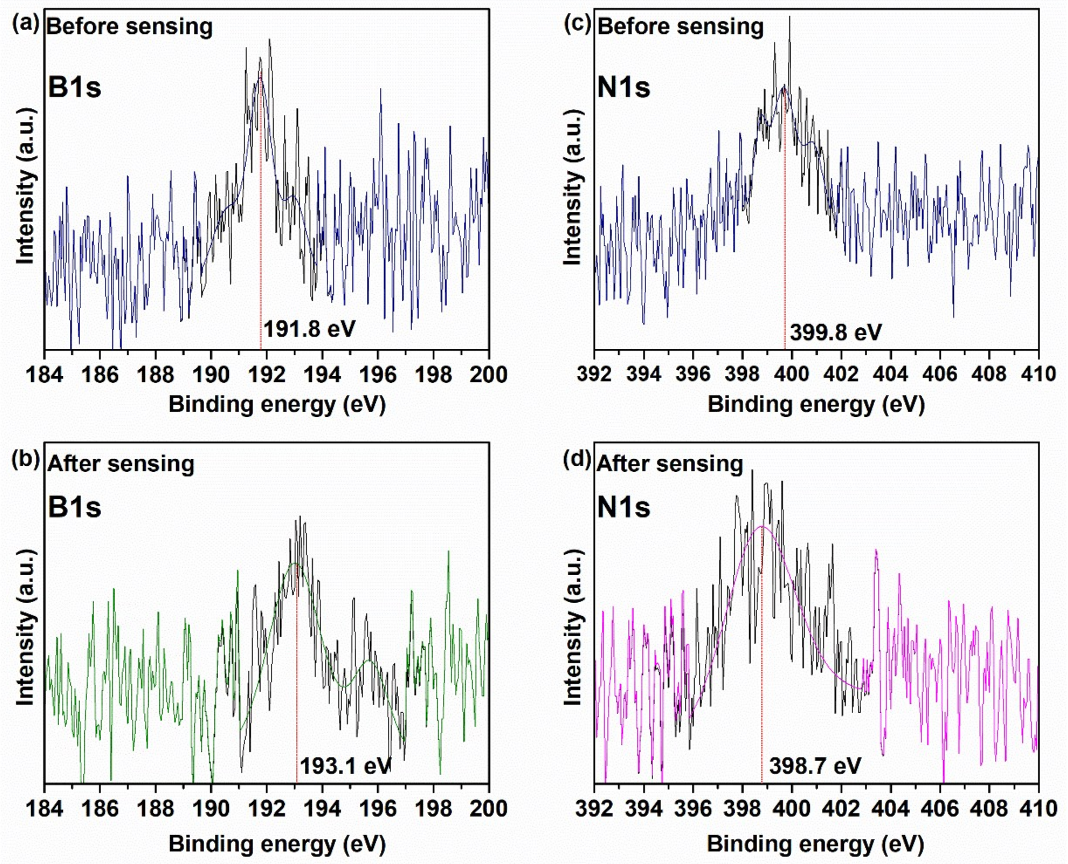


**Fig. S14.** High-resolution B1s and N1s core-level spectra of the NiO$_{BNG}$ hybrid nanocomposite before and after exposure to $H_2S$ at 50 ºC.

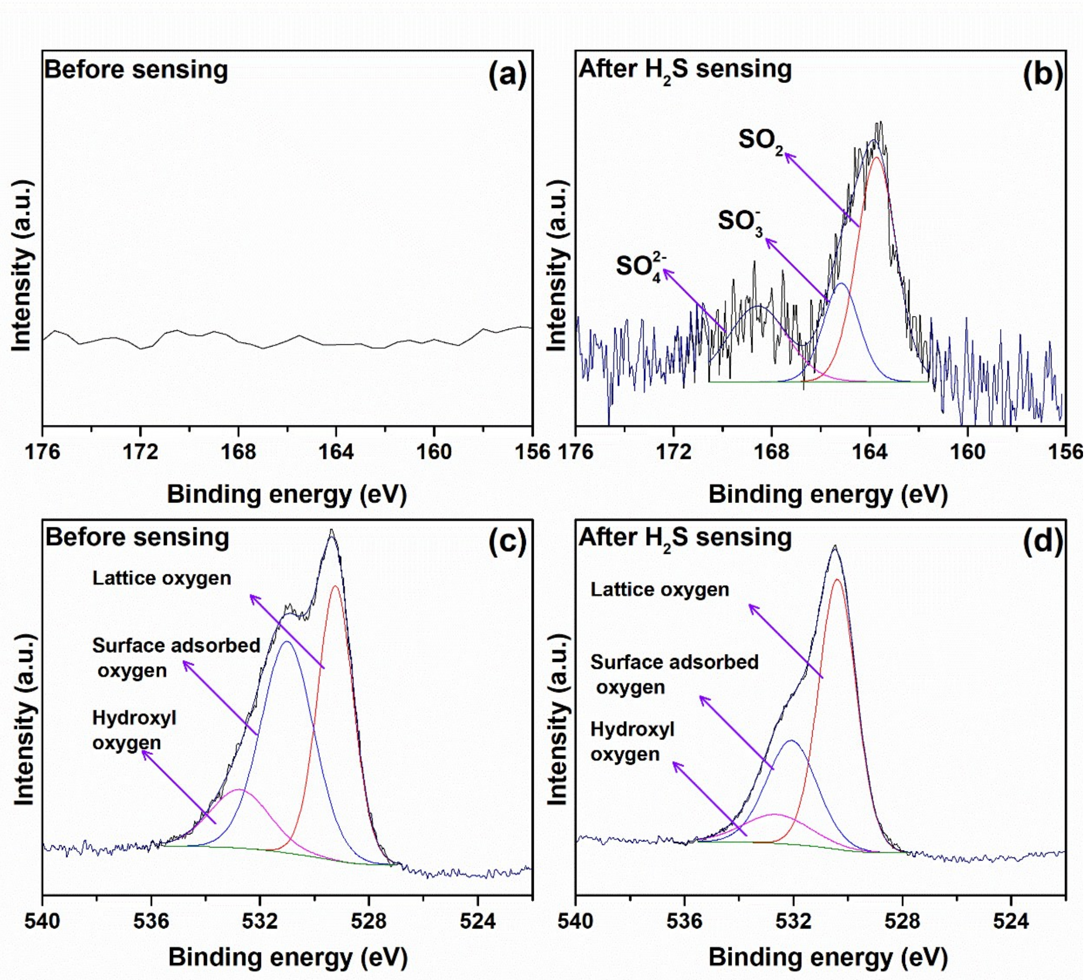


**Fig. S15.** (a, b) S 2p core-level spectra and (c, d) O 1s core-level spectra of the $NiO_{BNG}$ hybrid before and after exposure to $H_2S$ at 50 °C.

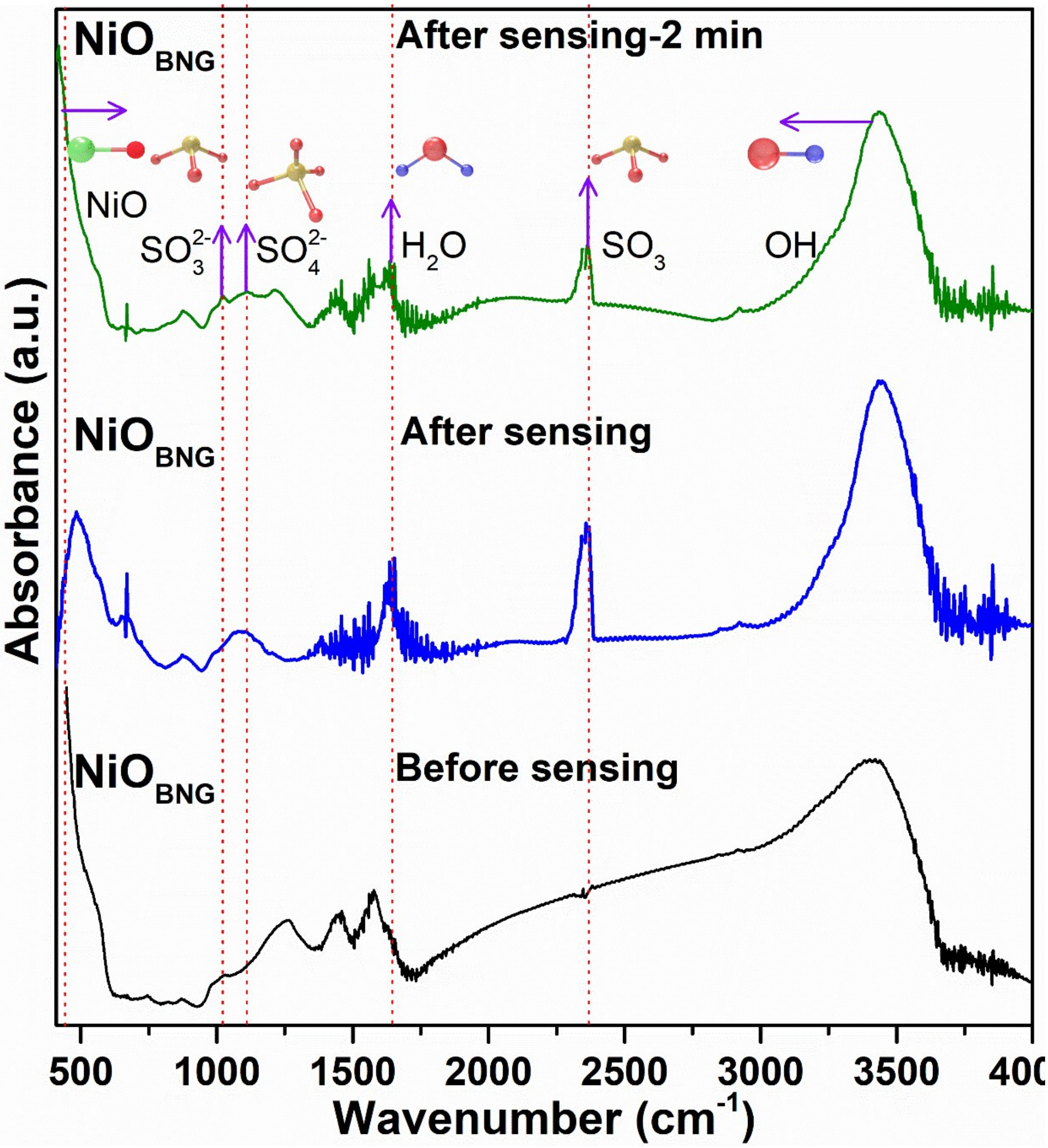
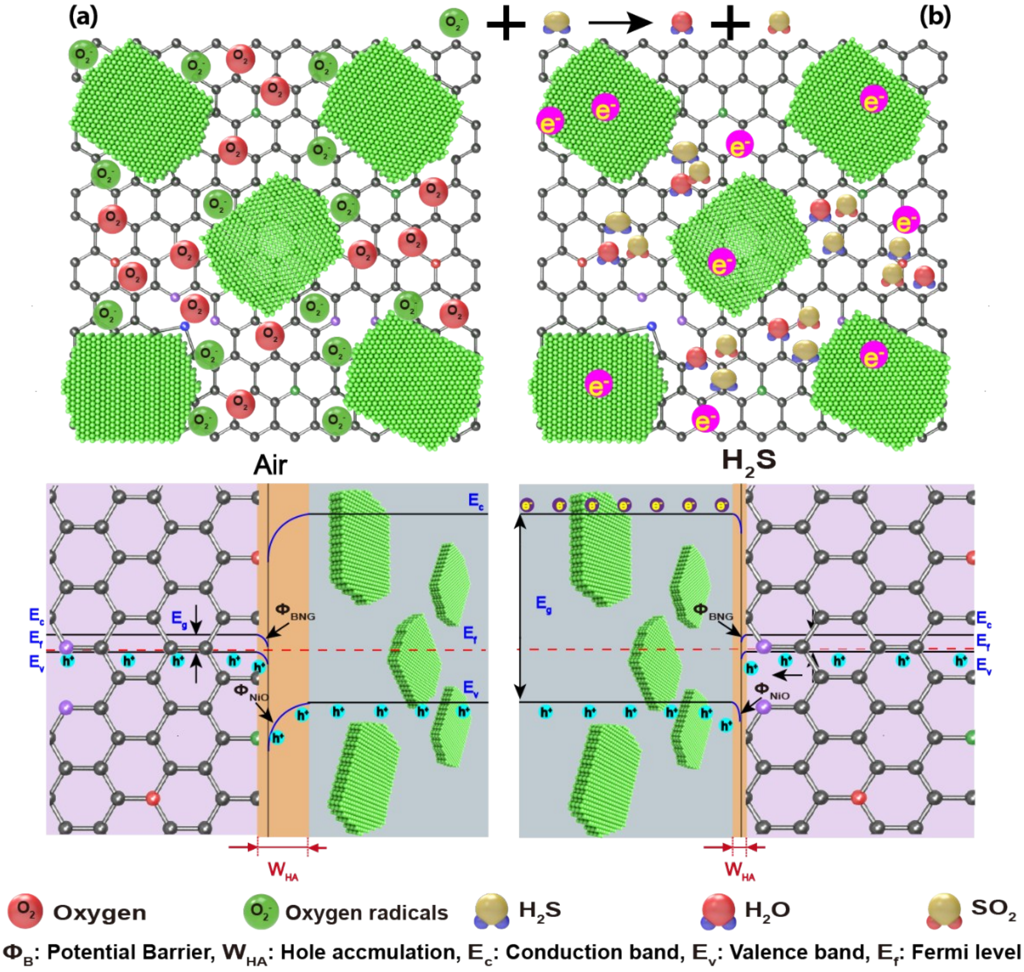


**Fig. S16.** FTIR spectra of the NiO$_{BNG}$ hybrid nanocomposite before and after exposure to 500 ppm of $H_2S$ at 50 °C.



**Scheme S2.** Representative energy band diagrams and physical structures illustrating the $H_2S$-sensing mechanism of $NiO_{BNG}$ hybrid nanocomposite sensor in air and $H_2S$ atmosphere.