# **Supporting Information**

# Exfoliated Redox Active Imide Covalent-Organic Framework for Metal Free

# Hydrogen Gas Sensing

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## S1. Table S1- Summary of literature on COF-based chemiresistive gas sensors

COF Material	Response %	Response time (s)	recovery time (s)	T (°C)	Target gas	Conc. (%)	Ref
TAPB-BPDA COF	23.0 %	8-40	100-120	120	NH <sub>3</sub>	0.01	1
TAPB = 1,3,5-tris(4-aminophenyl) benzene and BPDA = 4,4`-							
biphenyldicarboxaldehyde							
CON -10	73.7 %	-	-	RT	NO <sub>2</sub>	0.001	2
(2,4,6-tris(5-bromothiophen-2-yl)-1,3,5-triazine and 2,5-							
bis(trimethylstannyl)thieno-(3,2-b) thiophene							
pCTF	0.34 %	100	400	RT	NH <sub>3</sub>	0.01	3
P <sub>2</sub> O <sub>5</sub> catalyzed covalent triazine-based framework							
T-2DP	87 %	47	56 to 140	-	NO <sub>2</sub>	0.015	4
triazine-based 2D polymer							
COF-DC-8	39%			RT	NH₃		5
COF based Nickelphthalocyanine and pyrenetetraone							
HMP-TAPB-1	16.6 %	65	100 –9	-	NH₃	0.05	6
(HMP- trichloroheptazine ;TABP- tris (4-aminophenyl) benzene)							
COF-TXDBA	-	37	42	RT	humidity		7
Truxene (10, 15-dihydro-5H-diindeno[1,2-a;1',2'-c]fluorene)							
(TX) and 1,4-phenylenediboronic acid (DBA))							
CTF-1-A	17.2 %	100	420	-	NH₃	0.01	8
Amorphous covalent triazine frameworks							
eNT COF	30.1 %	5.15	3.9	200	H <sub>2</sub>	1%	This work

"T" stands for temperature; "Conc." stands for Concentration; "RT" stands for Room temperature. "Ref." stands for reference.

Sensing Material	Sensor	Response	Recovery	Concentration	T °C	Ref
	Response <sup>#</sup>	time (s)	time (s)	of H <sub>2</sub> (%)		
SWNT SnO <sub>2</sub>	115 <sup>c</sup>	<5	<5	0.15	200	9
SnO <sub>2</sub> NWs	3.3 <sup>c</sup>	-	-	0.1	300	10
In <sub>2</sub> O <sub>3</sub> Np	18.5* <sup>C</sup>	35	60	0.15	250	11
In <sub>2</sub> O <sub>3</sub> NRs	23.5* <sup>C</sup>	48	176	0.1	250	12
ZnO NWs	225* <sup>C</sup>	65	148	0.05	200	13
CuO NWs	41.7 <sup>C</sup>	60	60	6	200	14
SnO <sub>2</sub> thin film	50	2	20	0.1	150	15
ZnO wire	2.83	90	-	0.1	200	16
TiO <sub>2</sub> thin film	10 <sup>a</sup>	10	≤5	0.05	500	17
TiO <sub>2</sub> thin film	1.24 <sup>a</sup>	-	-	1	225	18
In <sub>2</sub> O <sub>3</sub> NWs	10.6* <sup>C</sup>	31	80	0.05	200	19
ZnO NWs	5.3 <sup>a</sup>	60	-	0.01	200	20
ZnO	4000	1000		0.02	400	21
CuO	3.72ª	300	300	6	250	22
NiO	96.6 <sup>b</sup>	547	-	0.5	600	23
In <sub>2</sub> O <sub>3</sub> -ZnO NWs	7.0 <sup>a</sup>	-	-	0.2	300	24
ZnO NRs	2.0 <sup>a</sup>	11	15	0.005	350	25
ZnO nanotubes	3.6 <sup>a</sup>	900	900	0.01	400	26
Mg ZnO	50 <sup>a</sup>	300		0.5	300	27
ZnO NWs	11.2 <sup>a</sup>	8	12	0.05	280	28
Honeycombed SnO	8.4 <sup>a</sup>	4	10	0.0001	340	29
ZnO nano array	1370 <sup>c</sup>	20	25	0.1	250	30
p-TiO <sub>2</sub> thin film	28.5 <sup>c</sup>	2.4	34.6	0.1	150	31
2D ZnO	5.37 <sup>a</sup>	17.5	17.5	0.05	175	32
SnO <sub>2</sub> /ZnO	168.6 <sup>a</sup>	172	530	0.001	300	33
NiO nanowire	91 <sup>c</sup>	88	39	0.1	300	34

# S2. Table S2- Summary of literature on metal oxide based chemiresistive hydrogen gas sensors

eNT COF	30.1	5.15	3.9	1	200	This work
NiO nanosheet	191 <sup>c</sup>	150	-	0.015	250	37
In <sub>2</sub> O <sub>3</sub> nanocluster	18 <sup>b</sup>	1.7	1.5	0.05	260	36
WO <sub>3</sub> nanosheets	80 <sup>c</sup>	120	235	1	250	35

Note: \* Calculated from response and recovery curves; # sensor response calculation formulae, a =  $R_a/R_g$ ; b =( $R_a-R_g$ )/ $R_a$ ); c = ( $R_a-R_g$ ) / $R_a$  x100; "Ref." stands for reference; "SWNT" is single wall carbon nanotubes; "NWs" is nanowires; "Np" is Nano pushpins "NRs" is nanorods.

#### **S3.** General information

Naphthalene-1,4,5,8-tetracarboxylic dianhydride (NTCDA or NDA) is purchased from Merck Life Science Pvt. Ltd., Tris(4 aminophenyl)amine (TAPA or TPA) purchased from BLD pharma Pvt. Ltd ,N, N Dimethylformamide (DMF, HCON(CH<sub>3</sub>)<sub>2</sub>) is purchased from Merck Life Science Pvt. Ltd. Tetrahydrofuran ( $\geq$ 99.5%) (THF) is purchased from Merck Life Science Pvt. Ltd. Acetonitrile ( $\geq$ 99%) is purchased from Fischer scientific Pvt. Ltd. Trifloroacetic acid (TFA) ( $\geq$ 99%) is purchased from Chemical center Pvt. Ltd.

#### S4. Synthesis of materials

### 4.1. Synthesis of NDA -TAPA COF (NT COF)

Synthesis of NT COF was carried out following previous literature.<sup>38</sup> In a typical synthesis, NT COF was synthesized in Pyrex tube. NDA (0.15 mmol), TAPA linker (0.1 mmol) with 2 mL of DMF were discharged in 10 mL of Pyrex tube. The mixture was flash frozen at 77 K using liquid N<sub>2</sub> and degassed via three freeze-pump-thaw cycles. The tube was sealed followed by heating at 180 °C for three days. The resulting brown colour product was immersed in 10 mL of DMF for 2 days and for 5 days in ethanol for solvent exchange under 80 °C in isothermal oven. During the exchange process, DMF is changed six times a day and EtOH is changed four times a day. Finally, the EtOH exchanged

sample of NT COF was activated under high vacuum at room temperature for 24 h. thus forming the activated NT COF powder.

#### 4.2. Exfoliation of NT COF

The as synthesized NT COF was exfoliated by adopting acid exfoliation method as reported earlier for amines<sup>39</sup>. In this exfoliation method, 0.005 g of NT COF was added to 5 mL of exfoliating solvent containing anhydrous acetonitrile, anhydrous tetrahydrofuran and trifloroacetic acid in 7:3:2 ratio in a 15 mL glass vial. This reaction solution was allowed to stir vigorously at room temperature (25 °C) for 72 h. After stirring for 3 days, the reaction mixture was centrifuged in order to precipitate out the un-exfoliated bulk COF particles. The supernatant was considered as a colloidal dispersion containing the exfoliated NT COF (eNT COF). This colloidal dispersion was further characterized and subsequently used for gas sensing studies.

#### **S5.** Characterization

The powder X-ray diffraction (PXRD) of the COFs based materials was recorded on Bruker D8 advance with Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å). The PXRD of bulk NT COF was carried out as such in its powder form while to measure the PXRD of eNT COF, the colloidal dispersion of the exfoliated COF was first drop casted on a pre-heated glass slide (dimensions of 1 cm x 1 cm) maintained at a temperature of 80 °C on a hot plate. The drop-cast was continued till a uniform visible film on the glass slide was obtained. Reagent alcohol (90% ethanol, 5% methanol, 5% isopropanol) was added after the film has dried for further deprotonation of the eNT COF film. The glass slide with the film on it was dried and analyzed for XRD.

Fourier-transform infrared (FT-IR) spectra was recorded on Alfa Bruker model (400-4000 cm<sup>-1</sup>) using KBr pellet, to confirm the presence of characteristic functional groups in the COF structure. Raman spectra were obtained using Horiba Jobin Yvon LabRAM Raman microscope using 50x long working distance (LWD) objective with 532 nm laser as excitation source. The spectra were obtained with 20 s spectral acquisition time. Prior to the measurements, calibration is performed using standard Si sample. UV–visible spectra of dispersions and monomer solutions were recorded on Shimadzu UV-2600 spectrophotometer. UV-Vis diffuse reflectance spectra (UV-Vis DRS) were recorded using Jasco V770 equipped with integrating sphere setup.

Field emission scanning electronic microscopy (FESEM) of as synthesized materials is measured using a Tescan Mira3/Quanta FEG 250 instrument. The samples for FESEM were prepared as follows: For bulk COF, the sample was ultra-sonicated in isopropyl alcohol (IPA) for 5 min and drop casted on a silicon substrate preheated at 100 °C; in case of exfoliated COF the colloidal dispersion was diluted with IPA and further drop casted on a silicon substrate at 100 °C.

Transmission electron microscopy (TEM) was performed using JEOL JEM 2100 plus operating at 200 kV. For TEM analysis the dilute colloidal dispersion was drop casted on Cu grid and vacuum dried and then electron microscopy analysis was carried out. Further from high-resolution transmission electron microscopy (HRTEM) images, fast Fourier transform (FFT) of the eNT COF sample were generated.

Atomic force microscopy (AFM) images were collected by using Bruker Nanoscope multimode 8 AFM 5500 in Scanasyst mode. The samples for AFM analysis are prepared by similar procedure followed for FESEM.

To study the surface area of the bulk COF, N<sub>2</sub> adsorption isotherms were measured at 77 K. Prior to measurements, the sample was degassed under vacuum overnight at 150 °C. The Brunauer–Emmett–Teller (BET) surface area of the COF was calculated as 888.04 m<sup>2</sup>/g<sup>-1</sup> (fig. S1). Based on sorption data, the pore size was calculated to be 0.45 nm (fig. S2).

Solid-state <sup>13</sup>C CP-MAS (Cross-Polarization with Magic Angle Spinning) spectra were recorded on a JEOL (model ECX-400 MHz) spectrometer operating at 100.52 MHz with a contact time of 1.1 ms and a relaxation delay of 5.0 s (fig.S9).



Fig. S1. N<sub>2</sub> sorption isotherms of Bulk NT COF



Fig. S2. pore size distribution of bulk NT COF



Fig. S3. TEM image of Bulk NT COF, inset reflects the FFT



Fig. S4. Field emission scanning electron microscopy (FESEM) image of bulk NT COF



Fig. S5. Field emission scanning electron microscopy (FESEM) image of eNT COF



**Fig. S6**. Fourier transform infra-red (FT-IR) spectra of **e**NT COF showing the amic acid functionalities.



Fig. S7. Raman spectra of bulk NT COF and eNT COF

![](_page_11_Figure_0.jpeg)

**Fig. S8**. UV-Visible diffuse reflectance spectra (UV-Vis DRS) of bulk NT COF

![](_page_12_Figure_0.jpeg)

Fig. S9. Solid-state <sup>13</sup>C CP/MAS NMR spectra for eNT COF

### Characterization data after H<sub>2</sub> sensing

![](_page_13_Figure_1.jpeg)

**Fig. S10.** shows the data of eNT COF before and after sensing a) PXRD, b) FT-IR, c) Raman spectra, d) UV-Visible spectra of eNT COF dispersions before and after sensing.

#### S6. Computational method for DFT calculation

All the calculations were performed using Density Functional Theoretical (DFT) method with M06-HF hybrid functional and 6-31+G(d) all electron basis set as implemented in the Gaussian 09 package<sup>40</sup>. No symmetry constraints were imposed during structure optimization. The binding energy (BE) was calculated using the following formula

#### $BE = E_{(NDI_TPA/H2)} - [E_{(NDI_TPA)} + E_{(H2)}]$ (1)

where  $E_{(NDI_TPA/H2)}$  denotes energy of H<sub>2</sub> bounded NDI\_TPA,  $E_{(NDI_TPA)}$  and  $E_{(H2)}$  denotes energy of NDI\_TPA and H<sub>2</sub> molecule respectively. The electric field calculations were performed for the optimized models at 0.001 V/Å uniform electric field using the same functional and basis set included in the Gaussian 09. The molecule in figure S7 was considered as structural model for the computations as proposed by Zhu et al.<sup>41</sup> The optimization of NDI lead to planar core geometry with HOMO-LUMO gap of 1.016 eV, where the orbitals are localized at both the terminal phenyl rings. The four oxygen atom in the core rings were characterized as equivalent oxygens. Hence, the H<sub>2</sub> binding modes are calculated at one oxygen center by generating various possible structures, which are

- (i) near electronegative oxygen atom parallel to core ring
- (ii) near electronegative oxygen atom perpendicular to the core ring
- (iii) above the core ring to check the possibility of stacking.

Irrespective of the initial geometries (Figure S11), calculations predict that guest binding occurs primarily via electrostatic interactions between one of the hydrogen atom in the hydrogen molecule and the carbonyl oxygen atoms (2.710 Å distance) of NDI, with associated binding energies of −2.177 kcal mol<sup>-1</sup>. To understand the interaction of H<sub>2</sub> molecule in presence of electric field, the molecules were subjected to uniform electric field of 0.001 V/Å. The computational results suggest that, the presence of electric field does not alter the structure. However, the electric field polarizes the orbital as a result HOMO and LUMO delocalized at the both end. As a consequence, two binding orientation were observed as shown in figure S11

towards the same oxygen atom within the relative energy of 0.186 kcal mol<sup>-1</sup>. The presence of electric field polarizes the oxygen atom of NDI with relatively high negative charge. As a result, the electrostatic interaction between NDI and H<sub>2</sub> increased, which is reflected in the binding energy by -2.5 - 2.7 kcal mol<sup>-1</sup>. Note that the presence of electric filed increases the electrostatic interaction between NDI and H<sub>2</sub> by 0.02 - 0.28 Å.

![](_page_15_Figure_1.jpeg)

**Fig. S11.** (a) Optimized structures of NDI-TPA layer, (b) optimized binding site of  $H_2$  within NDI-TPA, (c) optimized conformer 1 of  $H_2$ - NDI-TPA layer with electric field, E and (d) optimized conformer 2 of  $H_2$ - NDI-TPA layer with electric field. The distance between  $H_2$  and O atom and the dihedral angle between the NDI and the TPA planes are shown. The magnitude of charge transfer is also given.

![](_page_16_Figure_0.jpeg)

**Fig. S12.** Optimized binding sites and relative energies ( $\Delta E$ ) of H<sub>2</sub> within NDI-TPA in presence of electric field. The distance between H<sub>2</sub> and O atom is given in Å.

![](_page_17_Figure_0.jpeg)

**Fig. S13.** HOMO-LUMO pictures and their energy gaps ( $\Delta$ ) of (a) Optimized structures of NDI-TPA layer, (b) Optimized binding site of H<sub>2</sub> within NDI-TPA, (c) Optimized conformer 1 of H<sub>2</sub>- NDI-TPA layer with electric field, E and (d) Optimized conformer 2 of H<sub>2</sub>- NDI-TPA layer with electric field.

**Table S3**. Computed Partial Mulliken Charges in eNT COF for atoms involved in binding for NDI-H2 with and without an electric field.

Conditions	Oxygen	Hydrogen molecule (H1/H2)
NDI and $H_2$ without any interactions	-0.324	0/0
NDI-H <sub>2</sub> No electric field	-0.240	0.039/-0.013
NDI-H <sub>2</sub> Conformer 1 with an electric field	-0.257	0.034/-0.009
NDI-H <sub>2</sub> Conformer 2 with an electric field	-0.273	0.042/-0.025

#### S7. Chemiresistive gas sensing measurements

The Hydrogen gas sensing studies of eNT COF were studied by a customized two probe chemiresistive sensing setup. The sensing setup includes Keithley source measure unit (SMU) (Model No. 2450) to measure change in the resistance of film in the presence and absence of analyte gas upon application of voltage bias. The probe station is provided with two Alicat Mass Flow Controllers (MFCs) which are connected to form a single output to allow mixing of gases and also to monitor the gas flow and concentration of balance and target gas. Further, the probe station is equipped with a heating chuck and micromanipulators with two tungsten probes/ tips placed inside the gas sensing chamber. The heating chuck is connected to a temperature control unit to control the temperature of the device during the experiment. The data processing is done via kickstart software that is used to remote keithley SMU, while flow vision software is used to control MFCs. The chemiresistive gas sensing station is schematically described in a scheme S1.

![](_page_19_Figure_2.jpeg)

Scheme S1: Schematic representation of chemiresistive gas sensing setup used in this work.

The fabrication of gas sensor device was done by drop cast method inside the probe chamber. The interdigitated electrode (IDE, 10 pairs of gold fingers with 100  $\mu$ m of finger width and gap width, based on a ceramic substrate) was placed on the heating chuck and temperature was maintained

at 80 °C under 500 sccm  $N_2$  flow. The dispersion of eNT COF was drop casted on IDE until a uniform film was formed.

The fabricated gas sensor was studied at different temperatures starting from 80 °C, 100 °C, 150 °C, 200 °C, and 250 °C, and by varying the concentration of H<sub>2</sub> gas from 0.2 % to 1 % range under a constant bias of 1 V. N<sub>2</sub> was used as a balance as well as diluting gas. The sensor was optimized under N<sub>2</sub> to obtain a stable baseline to study its behavior towards hydrogen gas. The H<sub>2</sub> flow was controlled by using the MFCs and dilution of H<sub>2</sub> was carried out with N<sub>2</sub> while measuring the H<sub>2</sub> concentration effect. Throughout the experiment the total flow rate of gases was fixed to 500 sccm.

The gas sensing characteristics of the sensor were calculated by using the formulae given below.

#### 7.1. Calculation of gas sensing parameters

The response of a chemiresistive sensor is calculated by the measuring the change in resistance (R) of the COF film before and after analyte exposure when placed between two electrodes (in this case: probes) upon application of potential bias (1 V). The parameters used to describe gas sensing performance include response %, response time (s), recovery time (s) and recovery percent.

i) Response %

The response % is defined as the change in the resistance of the chemiresistive material upon exposure to analyte gas.

The response % is calculated by

Response 
$$\% = \frac{Ra - Rg}{Ra} \times 100$$

Where, R<sub>a</sub> = Resistance of the chemiresistor in the presence of nitrogen (inert gas),

R<sub>g</sub> = Resistance of the chemiresistor in the presence of target gas (hydrogen gas).

#### ii) Response time

The response time is the speed of response. It is defined as the time required for eNT COF sensor to give maximum response of the signal such as change in resistance upon exposure to the target

gas The response time is defined as the time taken by eNT COF sensor to get maximum signal in the presence of target gas.

$$T_{res} = T_2 - T_1$$

Where,  $T_{res}$ = Sensor response time is calculated from  $T_2$  and  $T_1$ .

 $T_2$  = The total time required to achieve maximum response (90%) upon exposure to target gas.

 $T_1$  = The starting time is taken from the base line in the presence of balance gas.

iii) Recovery time

The recovery time is defined as the time taken by eNT sensor to come back to 90% of the original base line while removing the target gas.

$$T_{rec} = T_4 - T_3$$

Where,  $T_{rec}$  = Sensor response time is calculated from  $T_3$  and  $T_4$ .

T<sub>4</sub> = The total time required to achieve at maximum recovery (90%) upon exposure to

balance gas

 $T_3$  = The amount of time required to stabilize the baseline resistance with an analyte gas

![](_page_22_Figure_0.jpeg)

**Fig. S14.** The calculation of gas sensing parameters (response%, response and recovery times) in this work.

### iv) Recovery (%)

The recovery % was calculated by using the experimental values. The formulae are given below:

Recovery 
$$\% = \frac{R2-R3}{R1-R2} \times 100$$

Where,  $R_1$  is the resistance in  $N_2$  (absence of target gas),  $R_2$  is the maximum resistance value upon exposure to  $H_2$  (presence of target gas, and  $R_3$  is the recovered resistance after purging with  $N_2$ .

![](_page_23_Figure_4.jpeg)

Fig. S15. The recovery % of eNT COF sensor on exposure to different concentrations H<sub>2</sub> at 200 °C.

Temperature (°C)	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Recovery %
100	2.17978E9	1.37607E9	2.14884E9	96.1
150	1.95211E9	1.27014E9	1.93643E9	97.7
200	2.39874E8	1.61256E8	2.34335E8	99.3

Table S4. eNT sensor Recovery percent values at 100 °C, 150 °C, and 200 °C.

#### v) Signal-to-noise ratio (SNR)

The Signal-to-noise ratio (SNR) of eNT sensor was calculated by using the experimental values<sup>42</sup>,<sup>43</sup>,<sup>44</sup>. The formula is given below:

$$\frac{S}{N} = \frac{\mu \text{ (mean of signal)}}{\sigma \text{ (standard deviation of noise)}}$$

Where, the  $\mu$  is the mean of signal taken from the base line in the presence of hydrogen and the  $\sigma$  is the standard deviation of the noise taken from the noise of the base line.

At 80 °C mean of signal ( $\mu$ ) is 1.5 and the standard deviation of noise is 0.152. Similarly, the mean of signal ( $\mu$ ) at 100 °C, 150 °C, 200 °C, and 250 °C is obtained as 1.43 ,1.29, 1.3 and 6.5 respectively. The noise standard deviation at 100 °C, 150 °C, 200 °C and 250 °C is 0.096, 0.052, 0.020 ,0.146 respectively.

![](_page_25_Figure_1.jpeg)

**Fig.S16.** Behavior of bulk NT COF in the presence of 1 % of H<sub>2</sub> at 200 °C.

# 7.2. H<sub>2</sub> Sensing studies of eNT COF at 80 $^{\circ}\text{C}$

![](_page_26_Figure_1.jpeg)

Fig. S17. Response and recovery curve in the presence of 1 % of  $H_2$  at 80 °C.

### 7.4. H<sub>2</sub> Sensing studies of eNT COF at 100 °C

![](_page_27_Figure_1.jpeg)

**Fig. S18.**  $H_2$  gas sensing studies of eNT COF sensor at 100 °C. a) Response and recovery curves in the presence of 1 % of  $H_2$ , b) concentration effect and c) summary of gas sensing characteristic with respect to  $H_2$  concentration.

Concentration of H <sub>2</sub>	Response (%)	Response time (s)	Recovery time (s)
1	46.5±1.3	6.3 ± 1.5	5.9 ± 1.3
0.8	46 ± 1.2	6.3 ± 1.5	$2.1 \pm 0.8$
0.6	39.3 ± 1.7	4 ± 1.7	4.7 ± 1.1
0.4	23.6 ± 1.3	4.6 ± 1.5	5.5 ± 0.6
0.2	21.29 ± 1.4	4.2 ± 1.2	2 ± 0.9

 Table S5.
 The eNT COF sensor 100 °C sensing characteristics data

### 7.5. H<sub>2</sub> Sensing studies of eNT COF at 150 °C

![](_page_29_Figure_1.jpeg)

**Fig. S19.**  $H_2$  gas sensing studies of eNT COF sensor at 150 °C. a) Response and recovery curves in the presence of 1 % of  $H_2$ , b) concentration effect and c) summary of gas sensing characteristic with respect to  $H_2$  concentration.

Concentration of H <sub>2</sub>	Response time (s)	Recovery time (s)	Response (%)
1	6.93 ± 1.4	6.7 ± 1.9	38.9 ± 1.46
0.8	4.6 ± 1.4	$4.2 \pm 1.4$	28.66 ± 1.9
0.6	5.3 ± 1.4	4.3 ± 1.5	27 ± 1.9
0.4	5.5 ± 1.4	4.5 ± 1.35	18.33 ± 1.6
0.2	4.8 ± 1.03	4.3 ± 1.43	15.31 ± 0.3

Table S6. The eNT sensor 150 °C sensing characteristics data

# 7.6. H<sub>2</sub> Sensing studies of eNT COF at 200 $^{\circ}\text{C}$

![](_page_31_Figure_1.jpeg)

Fig. S20. Summary of  $H_2$  gas sensing characteristics of eNT COF sensor at 200 °C.

Concentration of H <sub>2</sub>	Response time (s)	Recovery time (s)	Response (%)
1	4.5 ± 0.6	3.9 ± 0.3	30.7 ± 0.26
0.8	5.4± 0.9	3.8 ± 0.8	23 ± 0.2
0.6	4.7 ± 1	5.0±1	18.5 ± 0.25
0.4	3.2 ±0.8	3.1±0.6	13.5 ± 0.2
0.2	3.2 ±0.8	3.7± 1.5	7.4 ± 0.25

Table S7. Summary of sensing characteristics of eNT COF sensor at 200 °C.

#### 7.7. H<sub>2</sub> Sensing studies of eNT COF at 250 °C

![](_page_32_Figure_1.jpeg)

Fig. S21. Response and recovery curve in the presence of 1 % of H<sub>2</sub> at 250 °C.

### S8. Limit of detection (LOD) calculation

LOD has been calculated using the formula

LOD (ppm) = 
$$\frac{3 \text{ X RMS (noise)}}{\text{S}}$$
  
RMS (ppm <sup>-1</sup>) =  $\sqrt{V_x^2/N}$ 

Where, RMS (noise) = root mean square (RMS) noise of baseline which is calculated using variation method, where,  $V_x^2 = \sum (Yi - Y)^2$  values are the experimental data points of baseline from ( $\Delta R/R_a$ ) vs time (s) plot, Y<sub>i</sub> and Y are the measured data point and fitted curve values, respectively. S = Slope of linear fitted data from ( $\Delta R/R_a$ ) of the sensor to the H<sub>2</sub> concentration (ppm). N is number of data points.<sup>45</sup>, <sup>46</sup>

The limit of detection (LOD) of the sensors calculation is as follows

Step 1: Linear fit the  $(\Delta R/R_a)$  of the sensor to the H<sub>2</sub> concentration (ppm) as shown in fig. S22a and extract the slope value.

Step 2: Perform a 5<sup>th</sup> order polynomial fit for the response ( $\Delta R/R_a$ ) versus time (s) curves at the baseline before exposure to H<sub>2</sub> (fig. S22b).

Step 3: Select a set of N=8 data points from the baseline before H<sub>2</sub> exposure.

Step 4: Calculate the regular residual ( $Y_i - Y$ ) for each data point, where  $Y_i$  is the measured data point, and Y is the corresponding value from the fitted curve. The values for these parameters are given in table S8.

Step 5: Calculate RMS (noise) and LOD using equation, RMS (ppm<sup>-1</sup>) =  $\sqrt{V_x^2 / N}$  and LOD (ppm) =  $\frac{3 \text{ X RMS (noise)}}{S}$  respectively. The results of these calculations are presented in table S8.

![](_page_34_Figure_0.jpeg)

**Fig. S22.** a) Linear fit plot between  $\Delta R/R_a$  and concentration of  $H_2$  (ppm), b) Plot of 5<sup>th</sup> order polynomial fitted normalized resistance eNT COF sensor as a function of time at the baseline before target gas exposure

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