

Supplementary Information

Sheet-on-Sheet Architectural Assembly of MOF/Graphene for High-Stability Room Temperature NO Sensing

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1. FTIR spectra

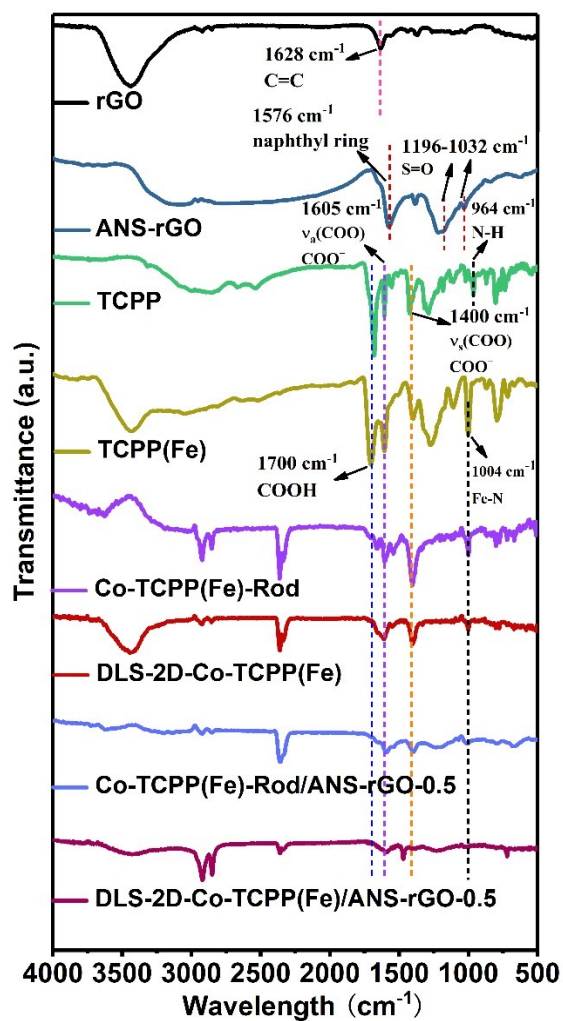


Fig. S1. FTIR spectra of rGO, ANS-rGO, TCPP, TCPP(Fe), Co-TCPP(Fe)-Rod, DLS-2D-Co-TCPP(Fe), Co-TCPP(Fe)-Rod/ANS-rGO-0.5, and DLS-2D-Co-TCPP(Fe)/ANS-rGO-0.5.

2. XRD

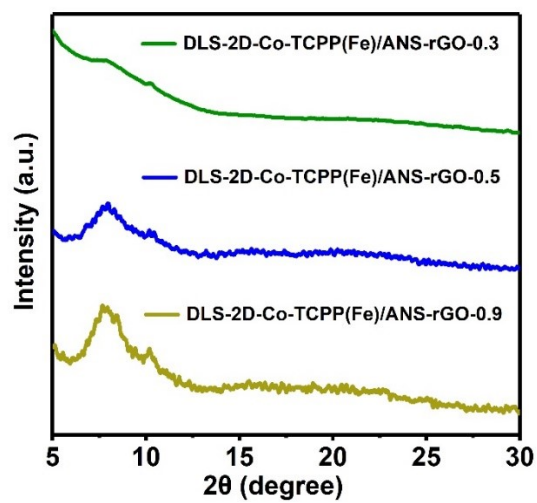


Fig. S2. XRD of DLS-2D-Co-TCPP(Fe)/ANS-rGO-0.3, DLS-2D-Co-TCPP(Fe)/ANS-rGO-0.5, and DLS-2D-Co-TCPP(Fe)/ANS-rGO-0.9.

3. BET

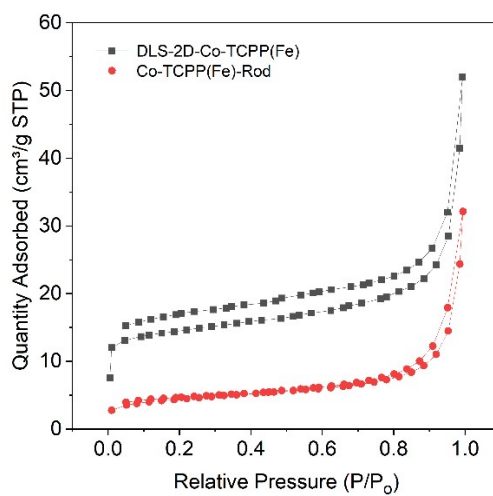


Fig. S3. Nitrogen adsorption-desorption isotherm of DLS-2D-Co-TCPP(Fe) and Co-TCPP(Fe)-Rod.

4. XPS spectra

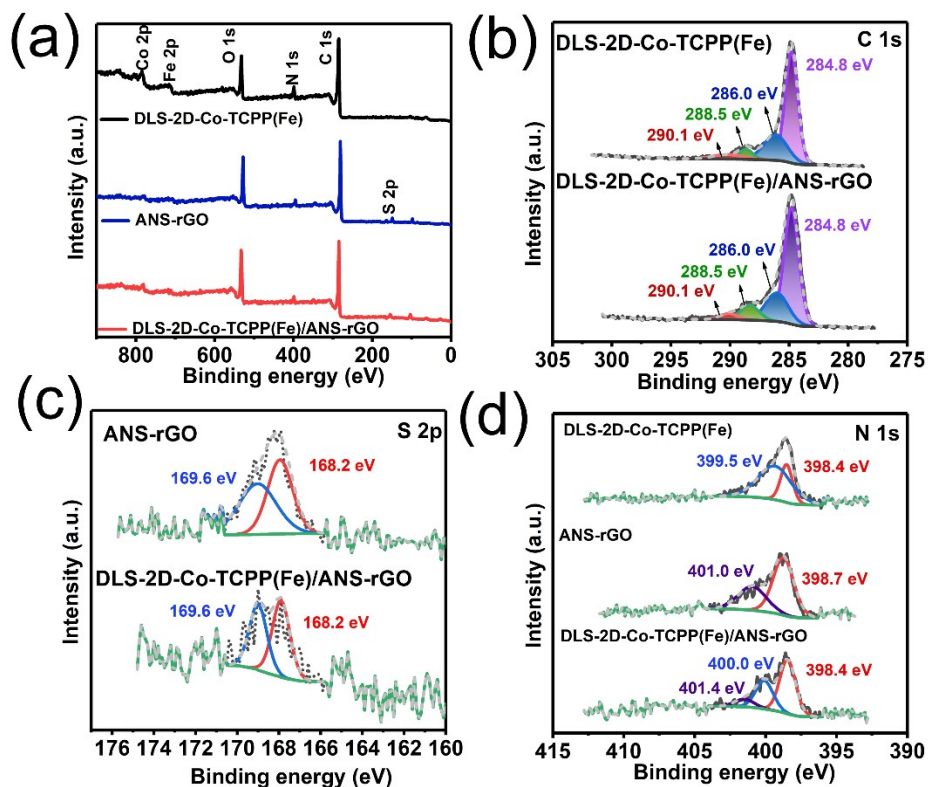


Fig. S4. XPS spectra (a) and high-resolution spectra of (b) C 1s, (c) S 1s, (d) N 1s of Co-TCPP(Fe)-S, ANS-rGO, and DLS-2D-Co-TCPP(Fe)/ANS-rGO-0.5.

5. Humidity response test

The gas sensing response curves of DLS-2D-Co-TCPP(Fe)/ANS-rGO-0.5-based sensor in the different R.H. of 0% N₂, 30% N₂, 50% N₂, and 70% N₂ were shown in Fig. S3. It was found that DLS-2D-Co-TCPP(Fe)/ANS-rGO-0.5-based sensor exhibited response decreasing along with the increase of R.H., which was attributed to the competition between the H₂O and NO molecules adsorbed on the surface of the sensing layer. It is indicated that the obtained sensor is not resistant to humidity. This issue could be addressed by the matured technology of pre-drying the injected exhaled breath.

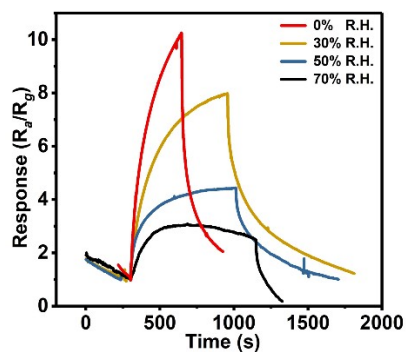


Fig. S5 Gas sensing response curves of DLS-2D-Co-TCPP(Fe)/ANS-rGO-0.5-based sensor toward 10 ppm NO under different relative humidity at room temperature.

6. Gas sample preparation

In this work, the volatile organic compounds (ethanol, methanol, acetic acid, and acetone) for injection can be generated by heating the corresponding compound liquids on a heating plate in the chamber. Other gas samples (NO, H₂S, BTEX, NH₃, CO₂) were prepared by using a drying tube to dry before it enters the test chamber.

7. Gas response test

As shown in Fig. S6, an array of DLS-2D-Co-TCPP(Fe)/ANS-rGO hybrid

materials with different feed mass ratios of 0.05:1, 0.1:1, 0.3:1, 0.5:1, and 0.9:1 (DLS-2D-Co-TCPP(Fe): ANS-rGO) were obtained and named as DLS-2D-Co-TCPP(Fe)/ANS-rGO-0.05, DLS-2D-Co-TCPP(Fe)/ANS-rGO-0.1, DLS-2D-Co-TCPP(Fe)/ANS-rGO-0.3, DLS-2D-Co-TCPP(Fe)/ANS-rGO-0.5, and DLS-2D-Co-TCPP(Fe)/ANS-rGO-0.9, respectively. Among them, DLS-2D-Co-TCPP(Fe)/ANS-rGO-0.5-based sensor demonstrated superior sensitivity to 10 ppm NO at room temperature, indicating the mass ratio of MOF and graphene was an unignore factor for NO sensing.

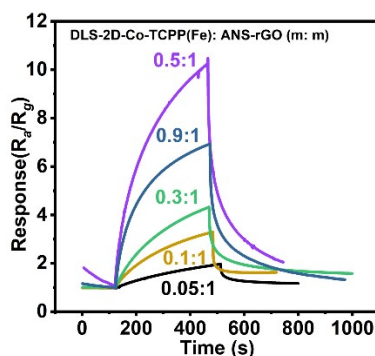


Fig. S6 Response curve after exposure to 10 ppm NO of DLS-2D-Co-TCPP(Fe)/ANS-rGO with different mass ratio of 0.05:1, 0.1:1, 0.3:1, 0.5:1, and 0.9:1 (DLS-2D-Co-TCPP(Fe) : ANS-rGO).

8. Gas sensing measurements

Gas sensors were fabricated using the drop-dry method, wherein 10 μ L of a well-dispersed gas sensing material dispersion (10 mg/mL) was uniformly applied onto the interdigital electrodes (IDEs) of the ceramic substrate. Subsequently, the sensors were dried at 50 $^{\circ}$ C on a heating holder for 5 minutes to facilitate the preparation of gas sensors for subsequent gas-sensitive testing. The alterations in sensor resistance were tracked using a Keithley 2450 electrometer.

Since the reaction of the target gas with the sensing material causes a change in

sensor resistance, the changes in current shown on the electrometer can be observed before and after the injection of the target gas under an excitation voltage of 0.1 VDC. In the work, gas sensing tests of all materials were performed at room temperature (25 ± 2 °C) in the dry N₂ background.

Typically, the response (S) to gas is represented as R_a/R_g , where R_a and R_g denote the resistance of the gas sensor in nitrogen and target gases, respectively. In this study, the response S to NO is specifically defined as R_a/R_g due to its pronounced oxidizing nature. The response/recovery time is conventionally characterized as the duration to attain 90% response from the moment the gas sensor is exposed/removed from the gas. The pLOD is commonly defined as the minimal concentration of the target gas detectable practically by the gas sensor.

9. Structure characterization

The structural characteristics of the prepared samples were assessed through Fourier Transform Infrared Spectroscopy (FTIR) using a Vertex 70 instrument (Bruker, Germany), and their X-ray diffraction (XRD) patterns were acquired via a D8 Advance diffractometer (Bruker, Germany) utilizing Cu K α radiation. UV–Vis absorption spectra were captured employing a UV–Vis spectrophotometer (UV–1900, Shimadzu, Japan). Raman spectra were acquired using Raman-scattering spectroscopy (Renishaw, UK) equipped with a 532 nm laser as the excitation source. The C 1s at 284.8 eV of X–ray photoelectron spectroscopy (XPS, Axis Supra, Shimadzu, Japan) was used as a reference. The morphologies of as–prepared samples were characterized by Field

emission scanning electron microscopy (FESEM, ZEISS Ultra 55, Germany). The TEM images were obtained by Transmission electron microscopy (TEM, Talos F200X, FEI). Electrochemical impedance spectroscopy (EIS) measurements were carried out in 5.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1, mol: mol) containing 0.1 M KCl, while the applied perturbation amplitude was 0.005 V, the frequencies swept from 105 to 10⁻² Hz, the initial potential of 0.20 V and quiet time of 2 s. Mott–Schottky plot measurements were carried out in 1 M Na_2SO_4 solution with a frequency of 100 Hz which recorded by electrochemical workstation (CIMPS-2, ZAHNER, Germany).

10. Synthesis of TCPP(Fe)

Preparation of TCPP(Fe) (Fe(III) meso-tetrakis (4-carboxylphenyl)): TCPP was prepared by modifying literature methods.¹ TCPP ((0.983 g, 1.24 mmol) and $FeCl_3 \cdot 6H_2O$ (2 g, 7.39 mmol) were dissolved in 150 mL of DMF in a 500 mL capped vial. After that, the solution was heated to 150 °C under stirring and kept the reaction for 12 h. After the reaction was cooled to room temperature, deionized water (250 mL) was added to aid precipitation. The precipitate was collected by filtration and washed with deionized water. Then, the solid was dissolved in NaOH aqueous solution (0.1 M, 300 mL) and HCl (1.0 M, 300 mL) respectively. The precipitate was filtered, washed with deionized water (3 × 300 mL), and dried in vacuo to give the title compound as a dark purple powder.

11. Synthesis of Co–TCPP(Fe)–Rod MOF

Preparation of Co–TCPP(Fe)–Rod: TCPP(Fe) (9.6 mg, 0.011 mmol),

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (16.0 mg, 0.055 mmol) and 0.5 g benzoic acid in 78 mL of the mixture of DMF and deionized water (V: V=12:1) were dissolved in a 100 mL capped vial. After that, the solution was sonicated for 10 min. The vial was heated to 90 °C and kept the reaction for 6 h. The resulting powders were washed twice with anhydrous ethanol and collected by vacuum filtration. Finally, the obtained Co–TCPP(Fe)–Rod MOF powders were redispersed in 10 mL of ethanol.

12. Synthesis of ANS–rGO

Preparation of ANS–rGO: ANS–rGO was prepared by hydrothermal reduction method, referring to the previously reported work.² Typically, 90 mg of ANS (5–aminonaphthalene–1–sulfonic acid) was added in 10 mL of DI water, 4 mL of GO dispersion, 5 mL of NaOH solution (4 mg /mL) and the mixture was kept at 80°C for 1 h under stirring after the addition of 10 mL hydrazine hydrate. The resultant dispersion was then rinsed thrice by vacuum filtration with DI water. Finally, above–mentioned solution were re–dispersed in 20 mL of water under mild sonication.

13. Synthesis of Co–TCPP(Fe)-Rod/ANS–rGO

Fabrication of Co–TCPP(Fe)-Rod/ANS–rGO: Co–TCPP(Fe)-Rod/ANS–rGO hybrid was prepared through supramolecular self-assembly. First, a certain volume of Co–TCPP(Fe)-Rod ethanol suspension and ANS–rGO deionized water suspension was added into a 20 ml capped vial. Then, the mixture was sonicated for 20 min at 50 °C. The obtained products were heated under a vacuum at 30 °C for 30 minutes and then stored under nitrogen conditions. The Co–TCPP(Fe)-Rod/ANS–rGO hybrid with

different feed mass ratios from 0.05:1 to 0.9:1 (Co-TCPP(Fe)-Rod: ANS-rGO, m:m) named Co-TCPP(Fe)-Rod/ANS-rGO-0.05, Co-TCPP(Fe)-Rod/ANS-rGO-0.1, Co-TCPP(Fe)-Rod/ANS-rGO-0.3, Co-TCPP(Fe)-Rod/ANS-rGO-0.5, and Co-TCPP(Fe)-Rod/ANS-rGO-0.9 were fabricated through changing the relative mass of suspension.

1 A. D. Cardenal, H. J. Park, C. J. Chalker, K. G. Ortiz and D. C. Powers, *Chemical Communications*, 2017, **53**, 7377-7380.

2 W. Pei, T. Zhang, Y. Wang, Z. Chen, A. Umar, H. Li and W. Guo, *Nanoscale*, 2017, **9**, 16273-16280.