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**Amorphous Covalent Triazine Frameworks for High Performance Room
Temperature Ammonia Gas Sensing**

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Experimental

Materials

Zinc chloride (anhydrous, 98%) was purchased from J&K Scientific Ltd. (Beijing) and stored in a glove box and used as received. 1,4-dicyanobenzene (DCB) was purchased from J&K Scientific Ltd. (Beijing) and used without further purification.

Synthesis of the CTFs

The CTFs materials were synthesized according to a reported literature. The synthesis of CTF-1-A (where A means amorphous) was given as an example (Scheme S1). The DCB monomer (384.4 mg, 3 mmol) and ZnCl₂ (817.9 mg, 6 mmol) were transferred into a pyrex ampoule (3 × 18 cm) in glove box. The ampoules were evacuated, sealed and heated to 400 °C for 72h. The ampoule was then cooled down to room temperature and opened. No pressure was detected. The black reaction mixture was subsequently grounded in agate mortar and then washed thoroughly with diluted HCl to remove most of the ZnCl₂. Further purification including extracting in Soxhlet extractor by deionized water and THF for 24 hrs each and drying in vacuum at 150 °C. The yield was about 90%. The CTF-1-C (where C means crystalline) was synthesized similarly, while the molar ratio of DCB to ZnCl₂ was 1:1 and the reaction time was 40 hrs.

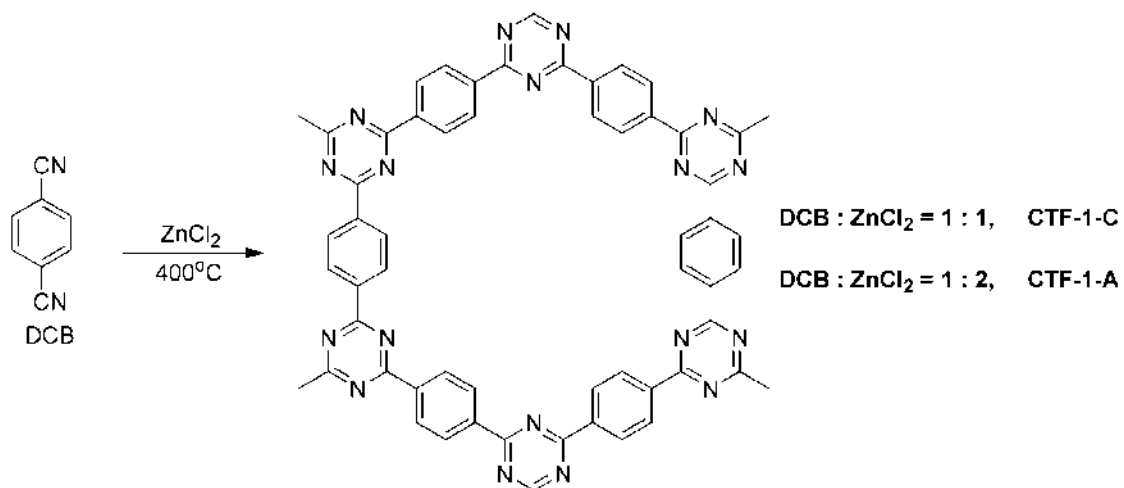
Characterization

The as-prepared CTF samples were characterized by X-ray diffraction (XRD, PANalytical, X'Pert PRO), X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, ESCALAB 250Xi), Fourier Transform Infrared spectroscopy (FT-IR, BRUKER, IFS 66v/s), and Laser Raman spectroscopy (Raman, HORIBA Jobin Yvon LabRAM HR800). Combustion elemental analysis was conducted on Vario EL III Elementar Analyser Systeme. Before testing, the samples were dried at 150 °C for 4 hrs to remove the absorbed moisture. SEM images were obtained with a field

emission scanning electron microscope (JSM-5600LV, JEOL, Japan). The powder samples were coated with gold by sputtering prior to observation. TEM images were obtained with a JEM-2010 transmission electron microscopy, operating at an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA) were recorded on a Netzsch thermal analysis system (STA 449C) in nitrogen at a heating rate of 10 °C/min. Nitrogen sorption experiments and micropore analysis were conducted at 77 K using Micromeritics ASAP 2020. Before sorption measurements, the samples were degassed in vacuum overnight at 150 °C. The surface area was calculated from multipoint BET plot, and the pore volume was determined by nonlocal density functional theory (NL-DFT). A CHI 660E electrochemical workstation was used to measure the resistance of the CTF layer between the Pd electrodes during NH₃ gas sensing process.

Gas sensing test

The as-prepared sensor was then introduced in an airtight chamber for the sensing test and the introduced sensor was allowed to carry out electric measurement in controlled atmosphere. Electrical measurements were carried out at room temperature under a specific NH₃ concentration, measuring the sensor resistance by a CHI 660E electrochemical workstation in chronoamperometry with a constant voltage of 1.0 V. The sensor response to NH₃ is defined as $\text{Response} = (R_{\text{NH}_3} - R_{\text{air}}) / R_{\text{air}} \times 100\%$, where R_{air} is the baseline electrical resistance of the sensor in dry air and R_{NH_3} is the resistance in NH₃ with different concentrations.



Scheme S1. Covalent triazine frameworks (CTFs) prepared by ionothermal polymerization of 1,4-dicyanobenzene (DCB) in molten ZnCl_2 .

Table S1. Elemental analysis of CTF samples.

Sample Name	XPS Survey			Found (%)					Calculated (%)				
	C	N	C/N	C	N	H	C/N	C/H	C	N	H	C/N	C/H
CTF-1-A	82.57	9.06	9.11	69.23	12.02	1.44	6.7	4.04	74.99	21.86	3.15	4.0	2.00
CTF-1-C	75.52	12.24	6.17	64.41	15.18	2.40	4.9	2.26	74.99	21.86	3.15	4.0	2.00

The probably incomplete combustion of the samples might be made responsible for deviations from the calculated values.

Table S2. Porosity data for CTFs from N₂ isotherms collected at 77K

code	S_{BET} [m ² g ⁻¹] ^(a)	S_{Lang} [m ² g ⁻¹] ^(b)	$V_{0.1}$ [cm ³ g ⁻¹] ^(c)	V_{tot} [cm ³ g ⁻¹] ^(d)	$V_{0.1}/V_{\text{tot}}$
CTF-1-A	1475	2020	0.407	0.767	0.53
CTF-1-C	1104	1510	0.330	0.559	0.59

^(a) BET surface area calculated over the pressure range 0.01-0.30 P/P_0 at 77 K, ^(b)

Langmuir specific surface area calculated from the nitrogen adsorption isotherm by

application of the Langmuir equation, ^(c) $V_{0.1}$, pore volume at $P/P_0 = 0.1$ at 77 K, ^(d)

V_{tot} , total pore volume calculated at $P/P_0 = 0.98$.

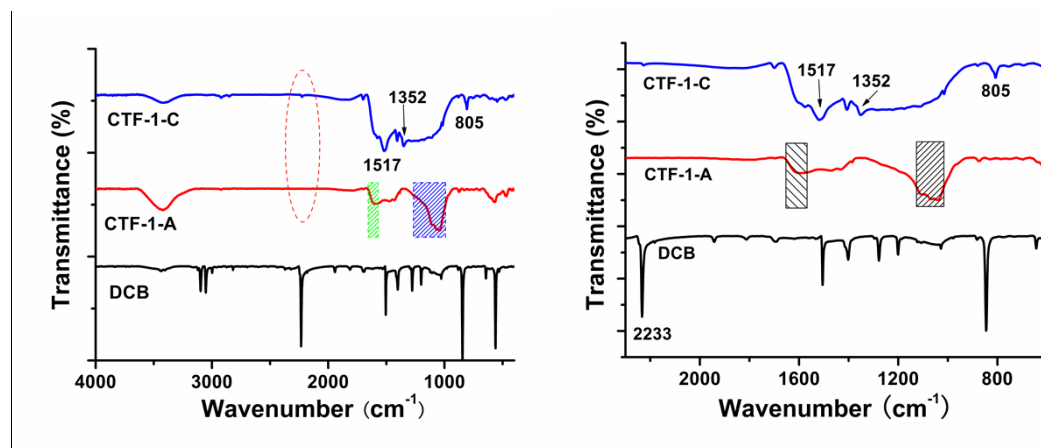


Figure S1. Magnified FT-IR spectrum of the CTFs. CTF-1-A shows strong absorption peaks indicate the C-N stretch (1050 cm^{-1} – 1270 cm^{-1}) and open-chain imino (1690 cm^{-1} – 1560 cm^{-1}) because of ring fragmentation. On the other hand, CTF-1-C shows absorption band at around 1517 cm^{-1} , 1352 cm^{-1} and 805 cm^{-1} pointing to the characteristic of the triazine units. For both CTF, the disappearance of carbonitrile stretching band at 2233 cm^{-1} indicate the completion of the trimerization reaction.

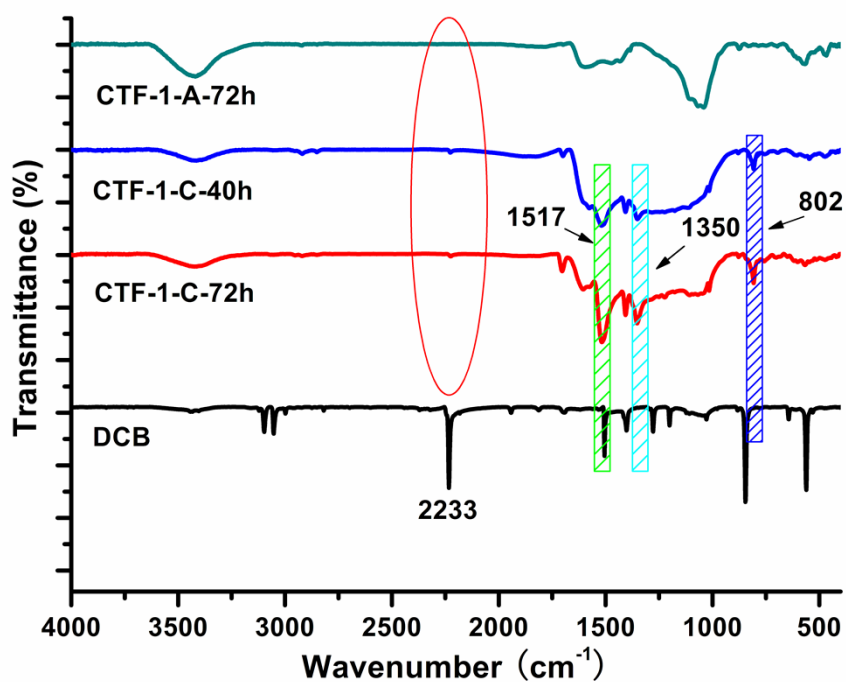


Figure S2. FT-IR spectrum of CTFs prepared with different reaction time. It was conformed again that by tuning the ratio of ZnCl_2 to DCB, the morphology can be controlled well. Compared with the amorphous CTF-1-A (72hrs), the crystalline samples show obvious adsorption bands at around 1517 cm^{-1} , 1352 cm^{-1} and 805 cm^{-1} pointing to the characteristic of the triazine units, for all CTF-1-Cs with different reaction time.

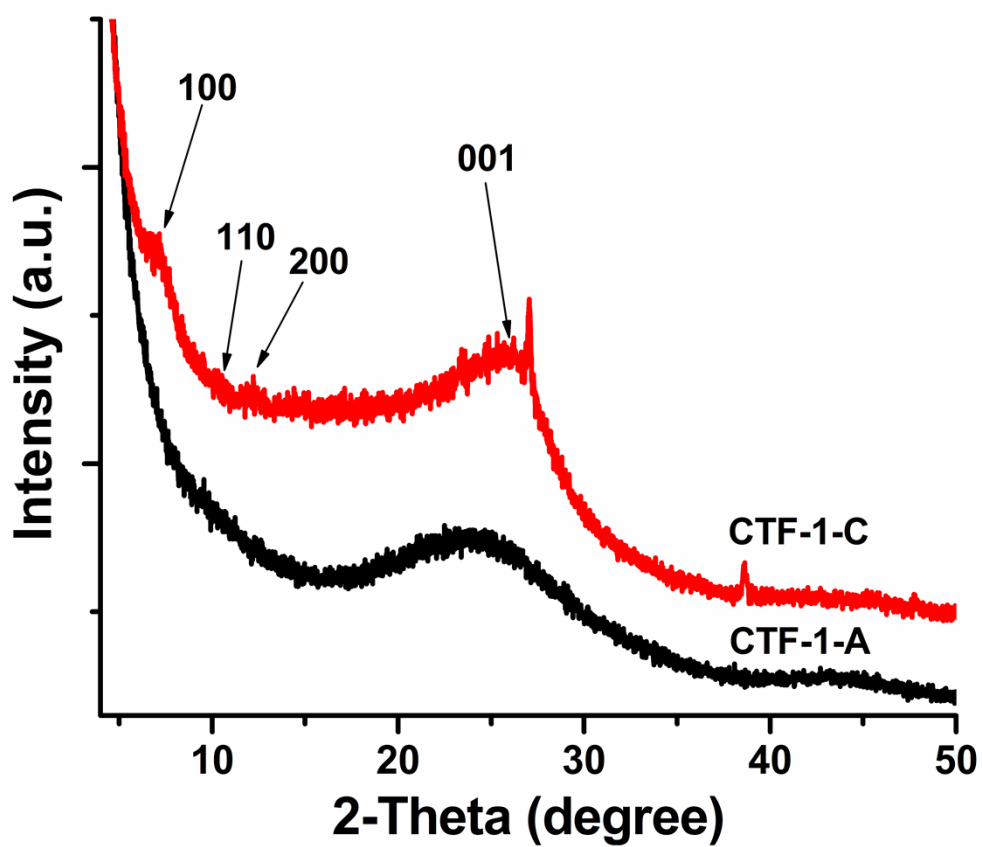


Figure S3. PXRD patterns of the CTFs.

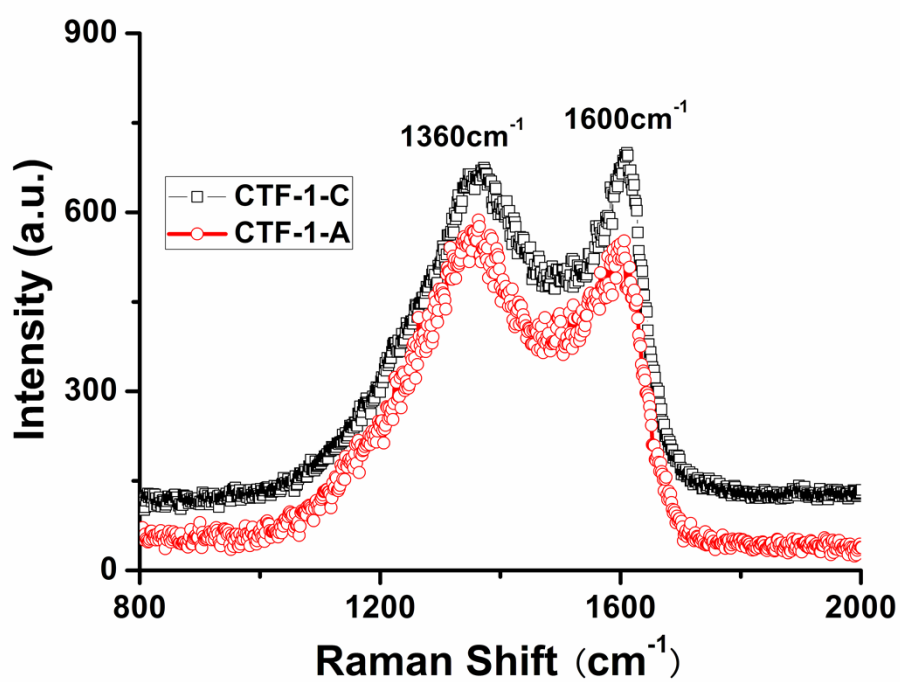


Figure S4. Raman spectrum of the CTFs at a laser excitation of 532 nm. In order to reveal the electronic structure of CTFs, Raman spectroscopy was conducted on the CTFs powders. For both CTFs, the G band at about 1600 cm⁻¹ reveals the existence of a 2D porous-honeycomb structure, which is constituted by benzene rings and triazine rings.

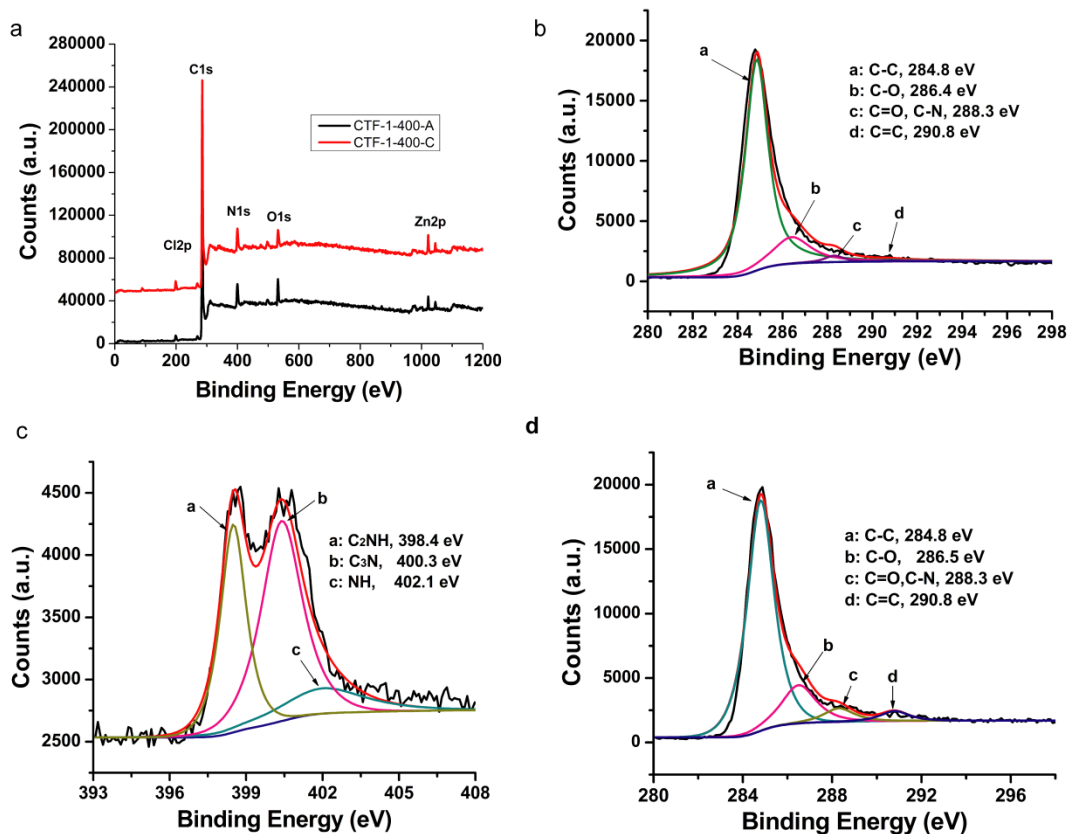


Figure S5. XPS spectrum of CTF-1-A. a) the survey of CTF-1-A and CTF-1-C in which we can see some intensity for the residual Zn and Cl; b) C1s spectrum, shows the presence of a high concentration of C-C and C-H species (~ 284.8 eV) and smaller concentrations of C-O at about 286.5 eV, C=O and C-N at about 288.3 eV, and C=C species at about 290.8 eV; c) N1s spectrum, shows the presence of C₂NH (~ 398.4 eV), C₃N (~ 400.3 eV), and NH (~ 402.1 eV) species; and d) C1s spectrum of CTF-1-C for comparison with that of CTF-1-A. The C-N species in CTF-1-C was about 5.04%, while the value of CTF-1-A was only 2.04%.

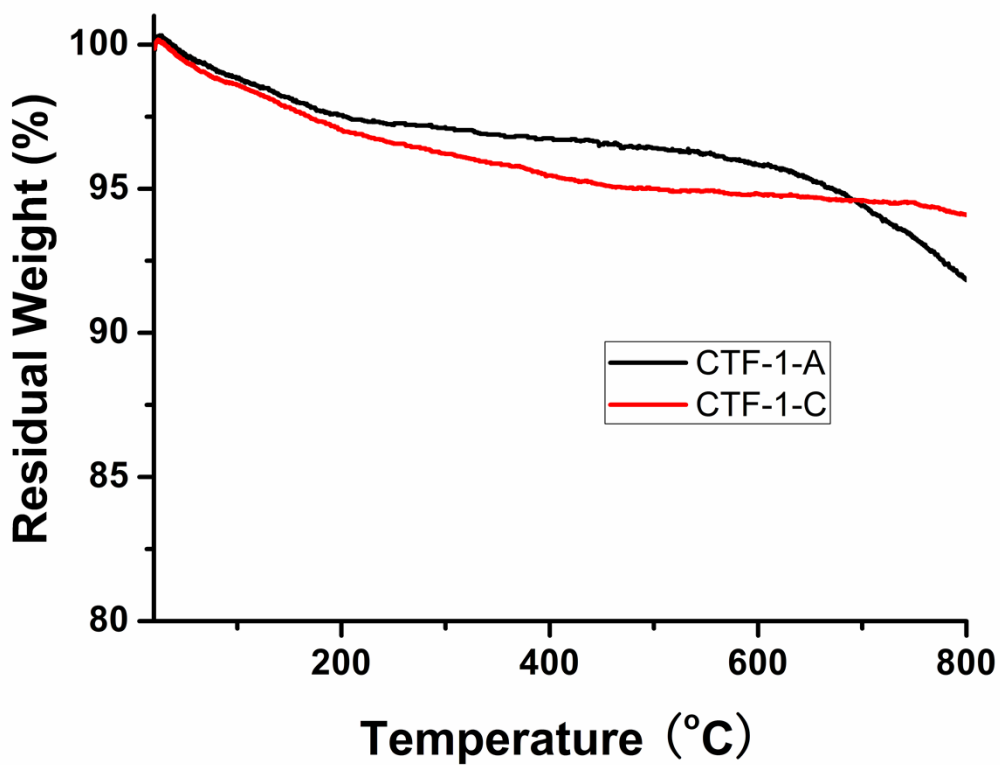


Figure S6. TGA curves of the CTF-1 networks indicated their excellent thermal stability above 600 °C. (Test conditions: room temperature to 800 °C, N₂, 10 °C/min)

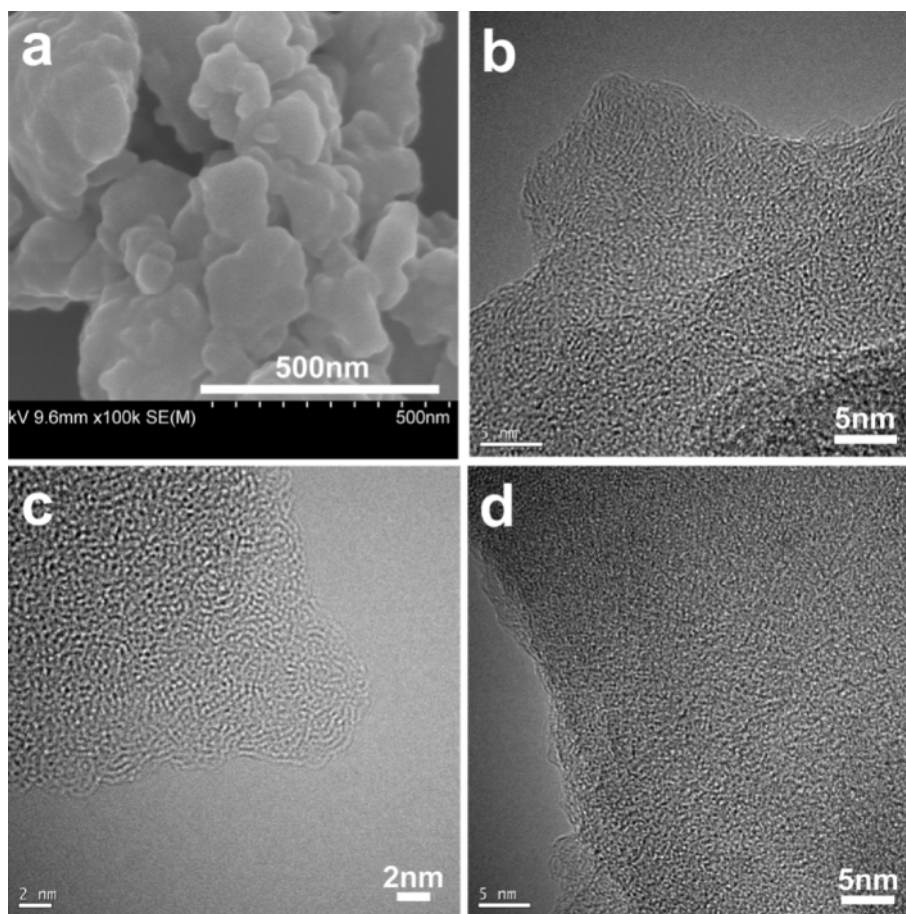


Figure S7. SEM (a) and HR-TEM (b-d) images of CTF-1-A.

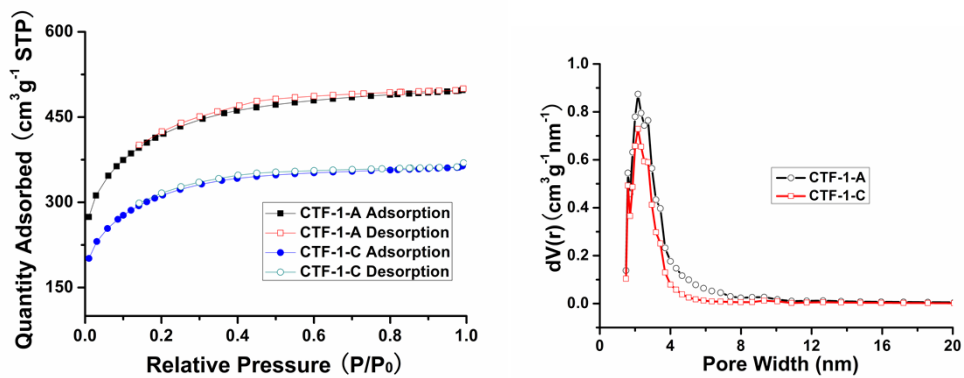


Figure S8. Nitrogen sorption-desorption isotherms of the CTFs at 77 K (left); NL-DFT pore size distribution of the CTFs (right).

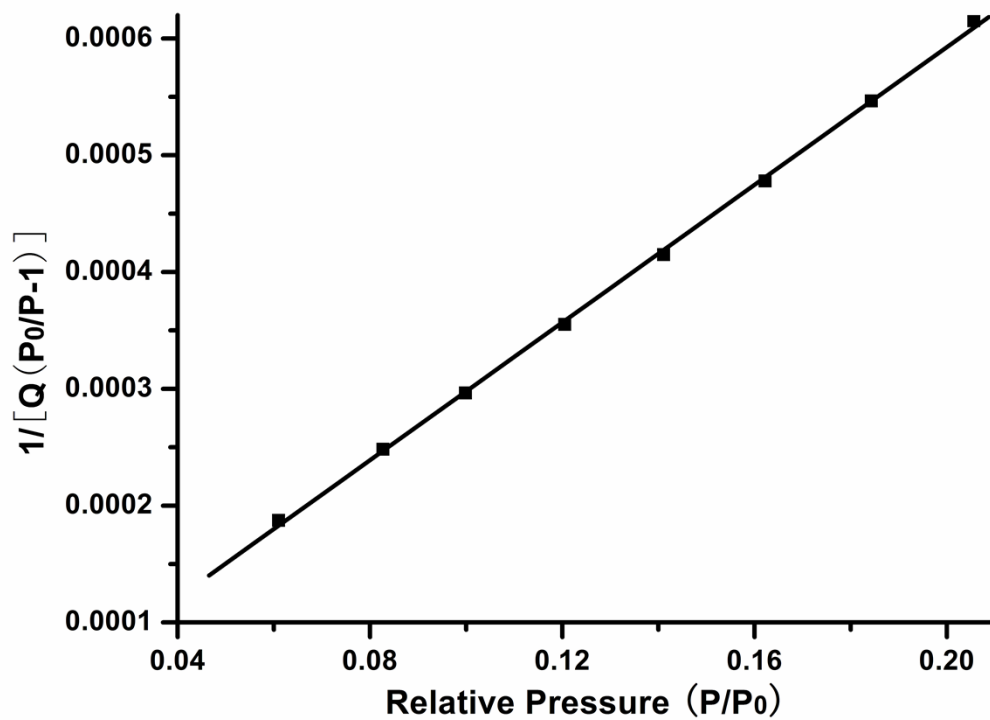


Figure S9. BET plot for the sample CTF-1-A.

BET Surface Area Report

BET Surface Area: $1475.1854 \pm 15.1778 \text{ m}^2/\text{g}$

Slope: $0.002948 \pm 0.000030 \text{ g}/\text{cm}^3 \text{ STP}$

Y-Intercept: $0.000003 \pm 0.000004 \text{ g}/\text{cm}^3 \text{ STP}$

C: 969.346303

Qm: $338.8739 \text{ cm}^3/\text{g STP}$

Correlation Coefficient: 0.9996881

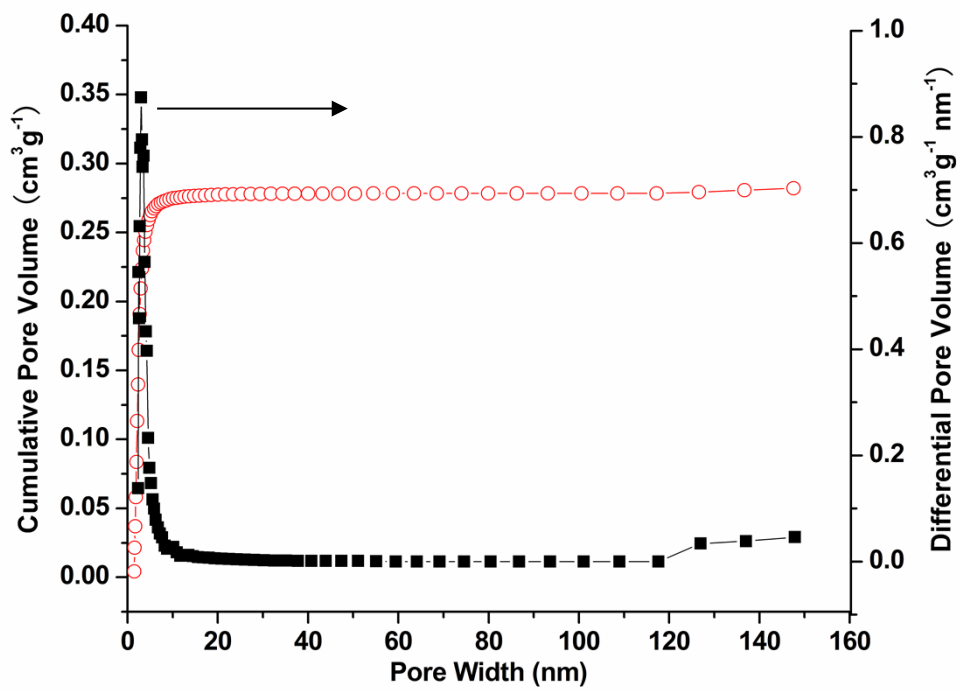


Figure S10. NL-DFT pore size distribution of the sample CTF-1-A.

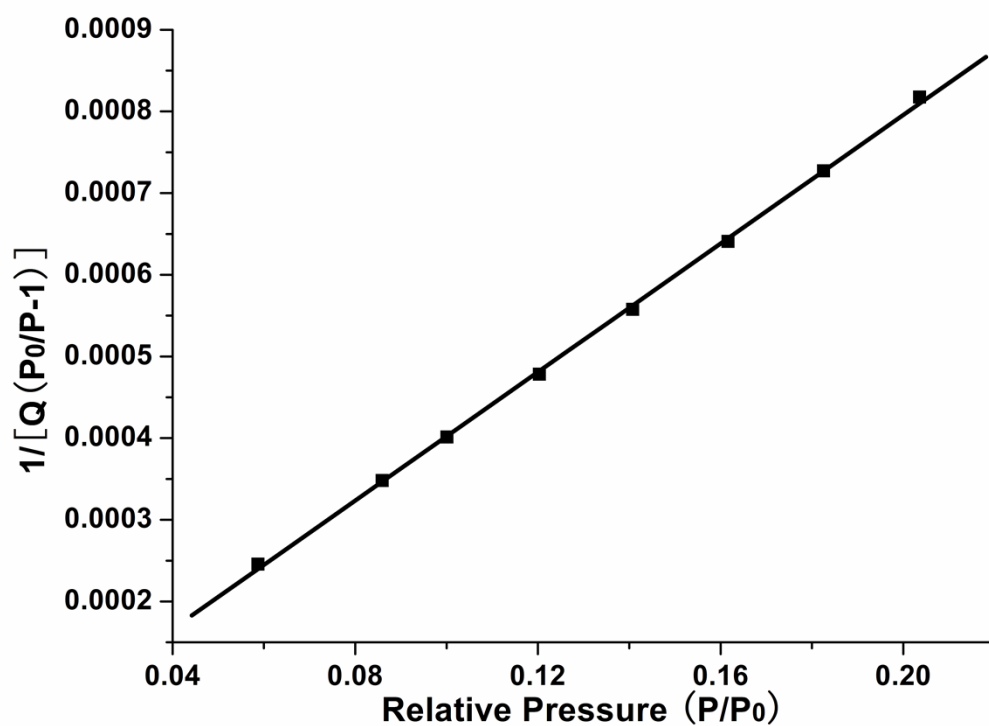


Figure S11. BET plot for the sample CTF-1-C.

BET Surface Area Report

BET Surface Area: $1104.0937 \pm 10.8982 \text{ m}^2/\text{g}$

Slope: $0.003934 \pm 0.000039 \text{ g}/\text{cm}^3 \text{ STP}$

Y-Intercept: $0.000009 \pm 0.000005 \text{ g}/\text{cm}^3 \text{ STP}$

C: 446.475184

Q_m: $253.6281 \text{ cm}^3/\text{g STP}$

Correlation Coefficient: 0.9997121

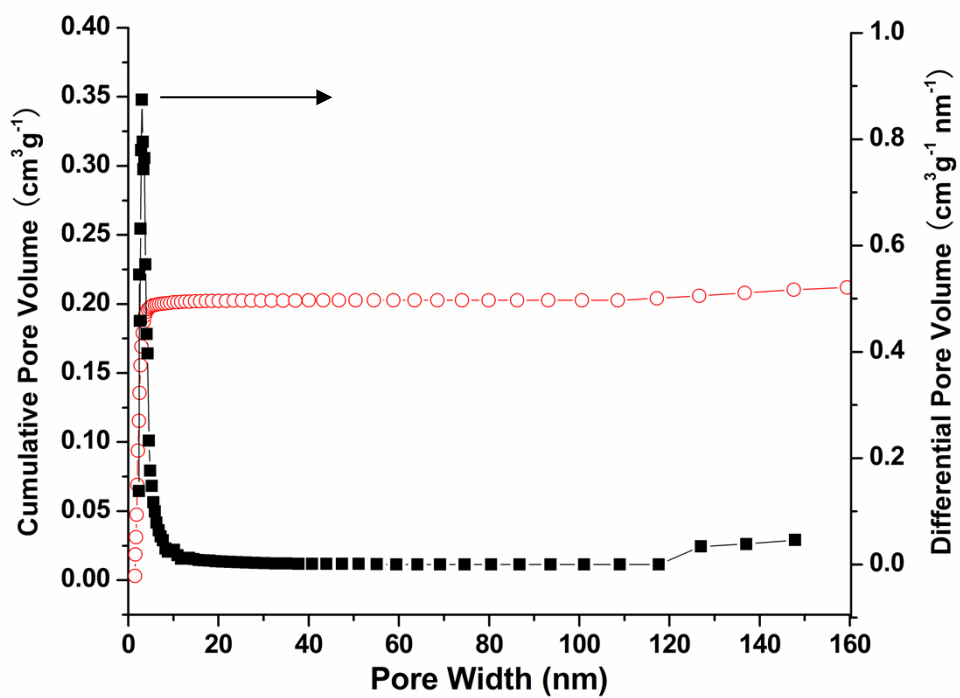


Figure S12. NL-DFT pore size distribution of the sample CTF-1-C.

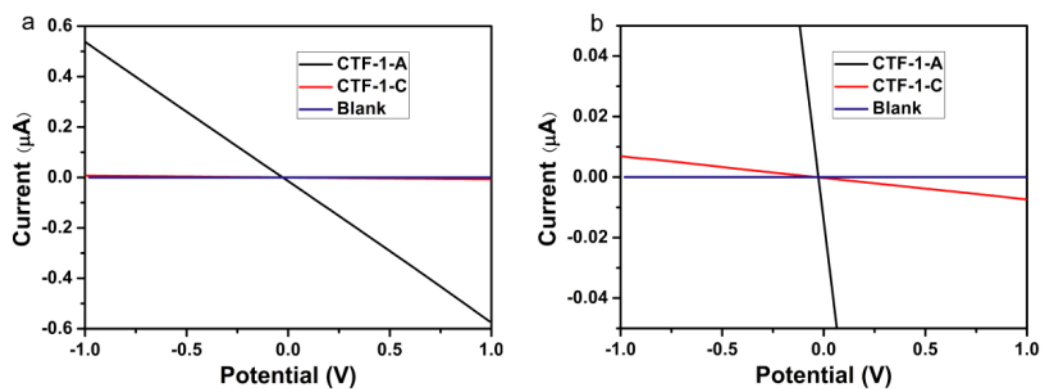


Figure S13. Current versus voltage (I - V) curves of the CTFs and the blank IE. The resistance of the as-prepared gas sensor based on CTF-1-A was in the order of $10^6 \Omega$.

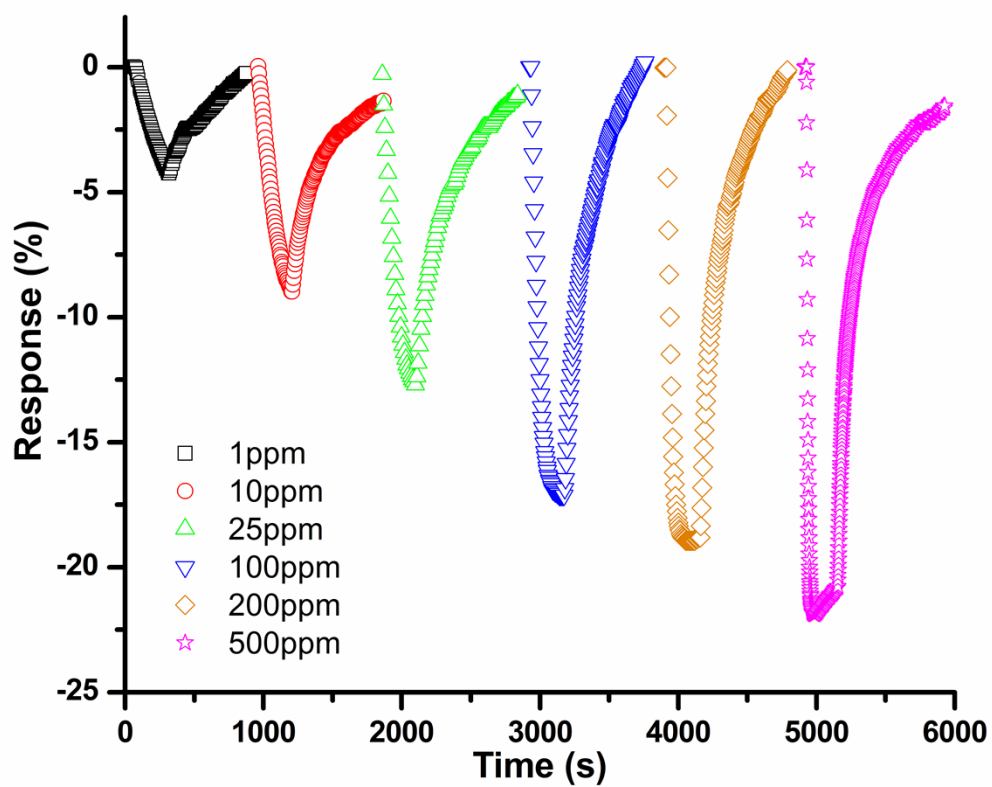


Figure S14. Representative dynamic response of CTF-1-A sensor for room temperature detection of NH₃ with concentration of 1 ppm to 150 ppm.

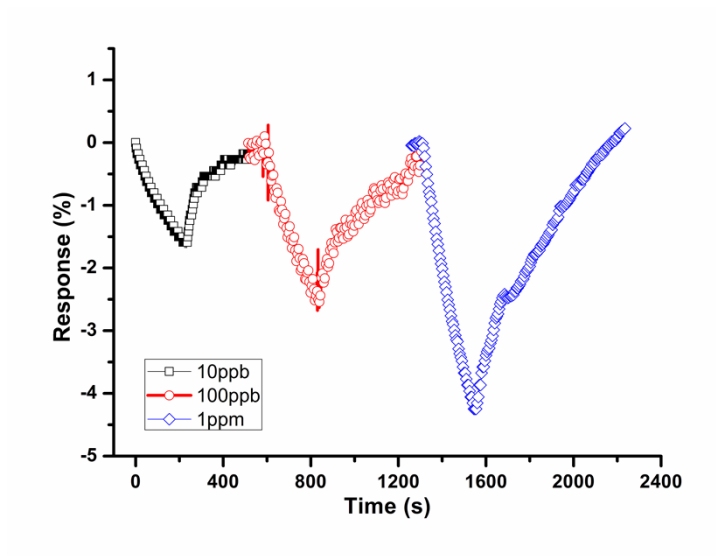


Figure S15. Response of CTF-1-A sensor to NH₃ with concentration of ppb level.

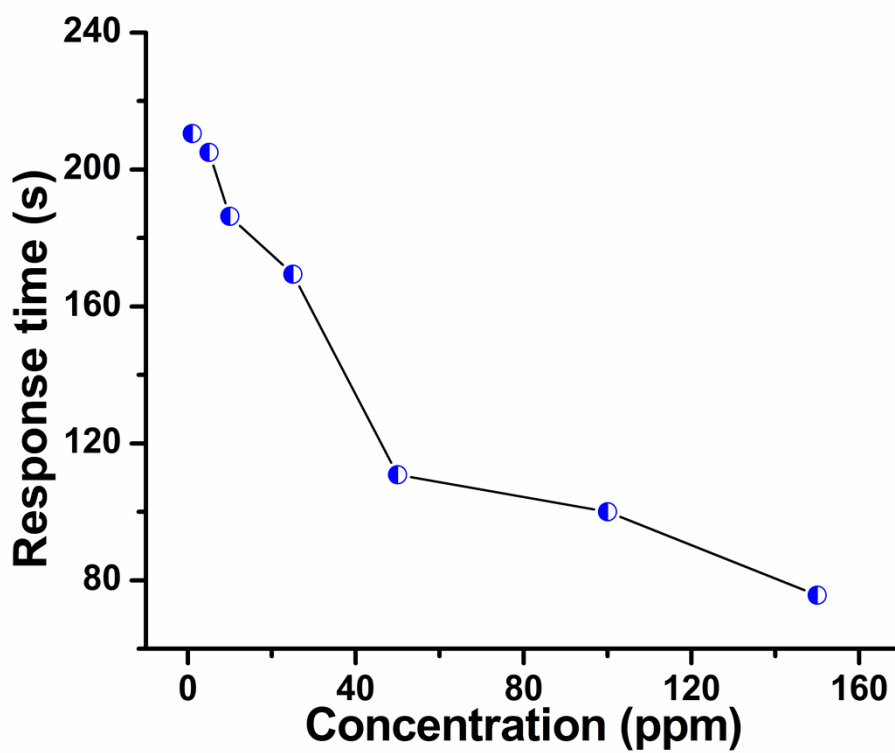


Figure S16. Plot of response time *versus* NH₃ concentration ranged from 1 to 150 ppm.

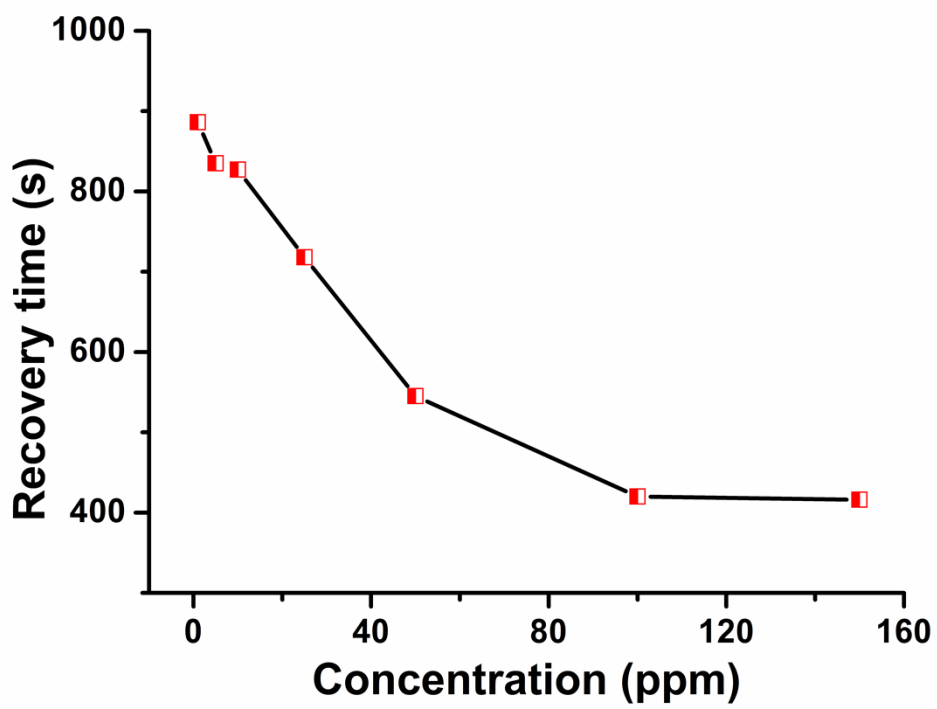


Figure S17. Plot of recovery time *versus* NH₃ concentrations ranged from 1 to 150 ppm.