

Electronic Supplementary Information for

Highly energy- and time-efficient synthesis of porous triazine-based framework: Microwave-enhanced ionothermal polymerization and hydrogen uptake

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Experimental

Materials: Anhydrous Zinc chloride was purchased from Sinopharm (Shanghai) Chemical Reagent Co., Ltd. 1,4-dicyanobenzene (DCB) was purchased from Aldrich. Other chemical reagents and organic solvents were commercially purchased and used as received.

Characterization: Powder X-ray diffraction (XRD) data were recorded using a step scan with a range of 5-60 degrees 2θ on a Philips-1700X diffractometer (Cu- $K\alpha$ radiation, $\lambda = 0.154178$ nm), and FT-IR spectra (KBr pellets) were recorded in the 400-4000 cm^{-1} range using a Nicolet Nexus 870 FTIR spectrometer. TEM studies were carried out on a JEOL JSM-2100 electron microscope operating at 200 kV, and SEM images were obtained at 5 kV from a Hitachi S4800 scanning electron microscope. Nitrogen adsorption and desorption isotherms, as well as hydrogen adsorption at low pressure (1 bar) were measured at 77 K using a Micromeritics 2020M+C system after the samples were first degassed at 180 °C overnight. Surface areas were determined by the BET method and the pore size distribution was determined by the Barrett–Joyner–Halenda (BJH) method. For the BJH analysis, the pore size distribution was obtained from the analysis of the adsorption branch of the isotherm. TGA measurements were carried out between 50 and 1000 °C in air or from 50 to 800 °C under N_2 atmosphere using a Pyris1 TGA-1.

Preparation: In a typical synthesis, 1,4-dicyanobenzene (2.0 g, 15.6 mmol) and ZnCl_2 (16 g, 117.6 mmol) were transferred into a 25 ml crucible. Then, the crucible was put in a microwave oven (Glanz P70D20SP-DF, Shenzhen, China). After microwave irradiation for various reaction times at different microwave power outputs, the reaction mixture was allowed to cool to room temperature. The resulting solid was then grounded and washed with a large amount of diluted HCl to remove most of the ZnCl_2 . To remove the residual ZnCl_2 the as-synthesized powder was magnetically stirred in diluted HCl overnight. Finally, the sample was filtered off, washed with water and THF, and then dried at 150 °C in vacuum (0.01 MPa). Although most of the ZnCl_2 could be extracted, in all cases some small amounts of zinc remained in CTF structures as reported previously. This was also confirmed by TGA results in the present work as shown in Fig. S9.

CAUTION: High-temperature of the crucible during and after the reaction may lead to the crack of the microwave oven salver. So thermal isolation between the crucible and the microwave oven salver should be guaranteed by using asbestine sheets.

Table S1. Synthetic conditions and porosity properties of CTF samples prepared by using MW-enhanced method.

| Sample | Reaction time | MW output (W) | S_{BET} ($\text{m}^2 \text{g}^{-1}$) | Pore vol ($\text{cm}^3 \text{g}^{-1}$) ^a | H ₂ uptake (mg g^{-1}) ^b |
|-------------|--------------------------------|---------------|---|---|---|
| S0-1 | 0.5 h | 120 | — | — | — |
| S0-2 | 1 h | 120 | — | — | — |
| S1 | 1.5 | 120 | 1049 | 0.74 | 9.1 |
| S2 | 4 h | 120 | 997 | 0.71 | 8.9 |
| S3 | 5 h | 120 | 935 | 0.55 | 10.0 |
| S4 | 6 h | 120 | 901 | 0.49 | 7.7 |
| S5 | 8 h | 120 | 809 | 0.51 | 8.1 |
| S6 | 1 h | 210 | 1227 | 1.52 | — |
| S7 | 2 h | 210 | 1217 | 1.55 | 10.0 |
| S8 | 1 h (120 W) + 0.5 h (460 W) | 120/460 | 1246 | 1.07 | 10.2 |
| S9 | 1 h (210 W) + 0.5 h (460 W) | 210/460 | 1228 | 0.84 | 7.6 |

^a Determined at P/P₀ = 0.97. ^b Measured at 77 K and 1 bar.

Table S2. Elemental analysis results of CTF samples obtained in this work.

| Sample | C | N | H | C/N |
|-----------|-------|-------|-------|-------|
| 1 | 73.82 | 10.97 | 1.795 | 6.729 |
| 2 | 65.27 | 10.67 | 1.813 | 6.117 |
| 3 | 65.99 | 8.841 | 2.85 | 7.464 |
| 4 | 69.79 | 12.19 | 2.088 | 5.724 |
| 5 | 73.77 | 9.835 | 2.16 | 7.501 |
| S1 | 75.48 | 10.21 | 2.527 | 7.394 |
| S2 | 72.14 | 11.95 | 2.454 | 6.035 |
| S3 | 74.49 | 15.47 | 3.02 | 4.814 |
| S4 | 62.8 | 11.98 | 3.052 | 5.242 |
| S5 | 68.52 | 13.61 | 2.019 | 5.035 |
| S6 | 74.88 | 7.884 | 2.516 | 9.498 |
| S7 | 74.28 | 9.447 | 2.25 | 7.862 |

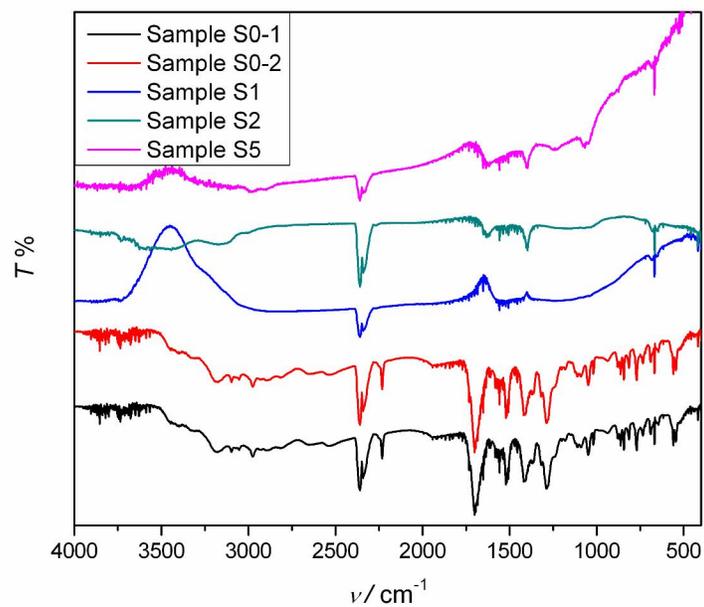


Figure S1. FT-IR spectra of CTF samples S0-1, S0-2, S1, S2, and S5.

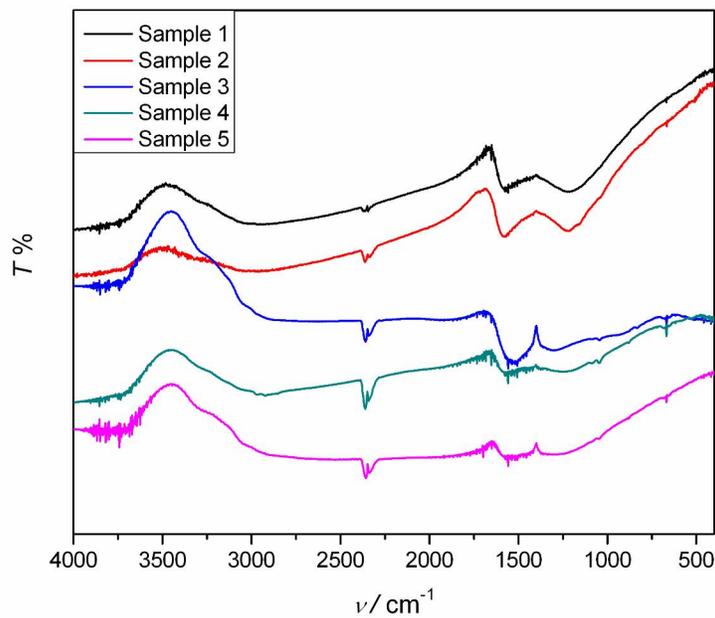


Figure S2. FT-IR spectra of CTF samples 1-5.

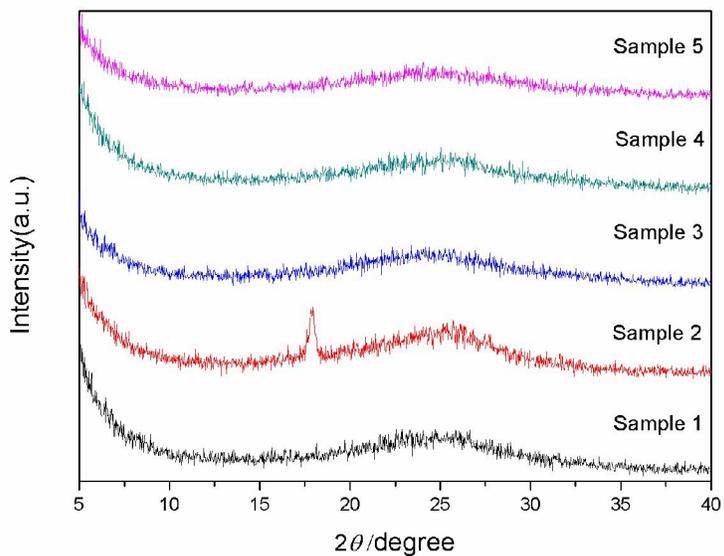


Figure S3. Powder XRD patterns of CTF samples **1-5**.

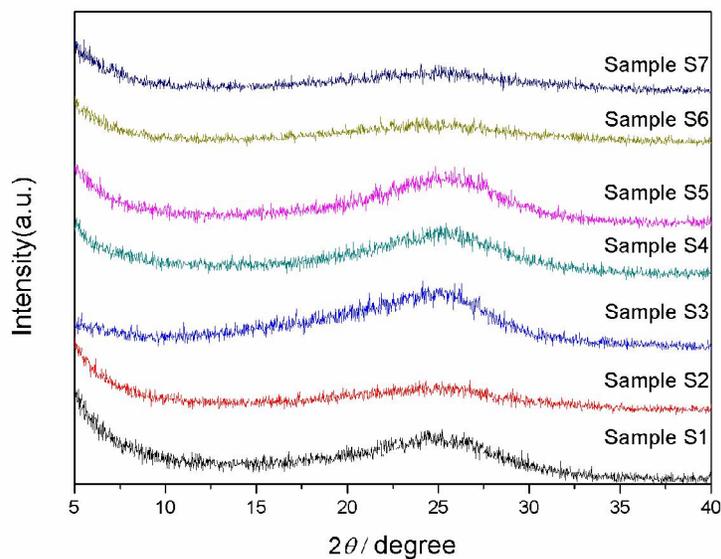


Figure S4. Powder XRD patterns of CTF samples **S1-S7**.

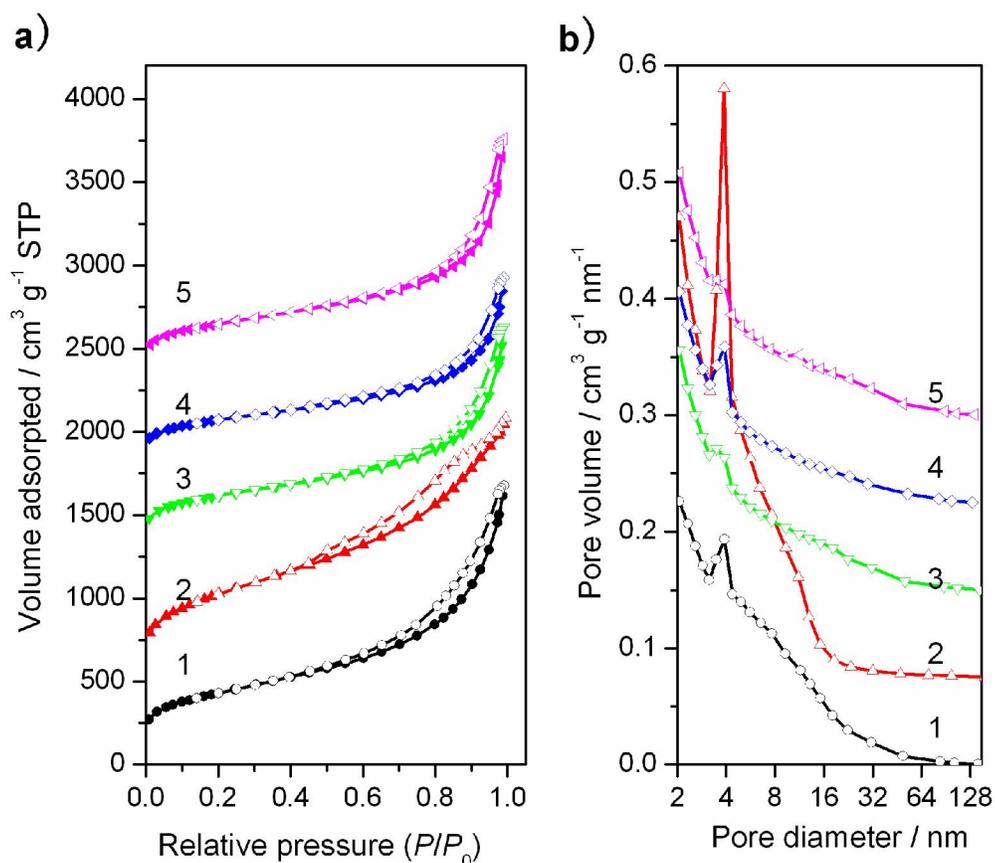


Figure S5. a) N_2 adsorption-desorption isotherms of CTF samples **1-5**, and b), distribution of mesopore diameters. The isotherms for samples **2-5** were vertically offset by 350, 700, 1250 and $1750 \text{ cm}^3 \text{ g}^{-1}$, respectively. Distribution of mesopore diameters were calculated via the Barrett-Joyner-Halenda (BJH) algorithm using the adsorption branch. The distribution of pore diameters for samples **2-5** were vertically offset by 0.075, 0.15, 0.225, and $0.3 \text{ cm}^3 \text{ g}^{-1} \text{ nm}^{-1}$, respectively.

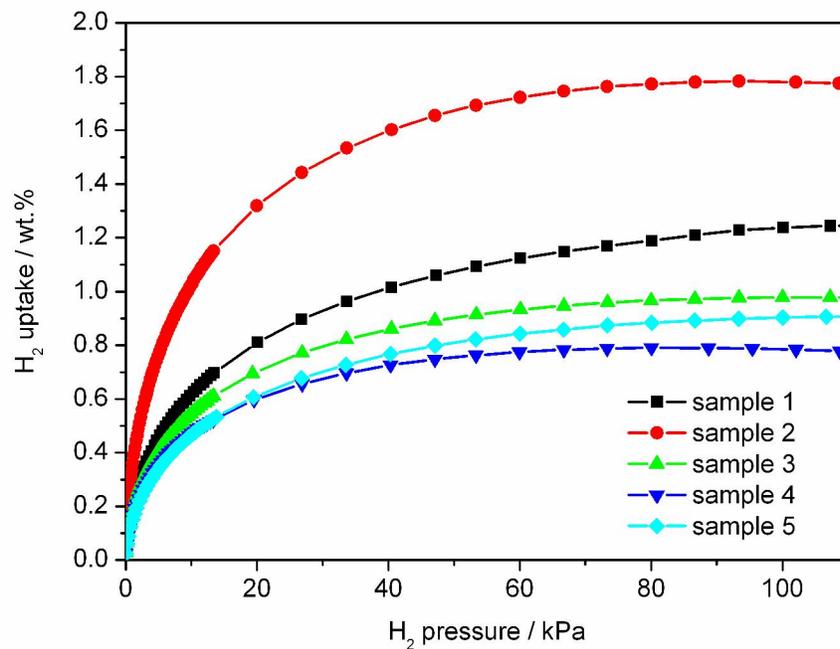


Figure S6. H₂ adsorption of CTF samples 1-5 at low pressure at 77 K.

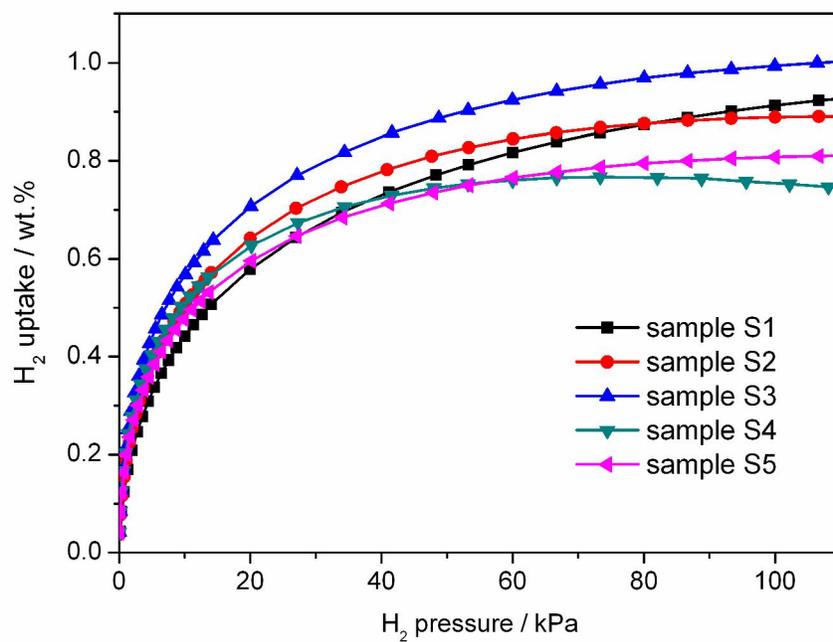


Figure S7. H₂ adsorption of CTF samples S1-S5 at low pressure at 77K.

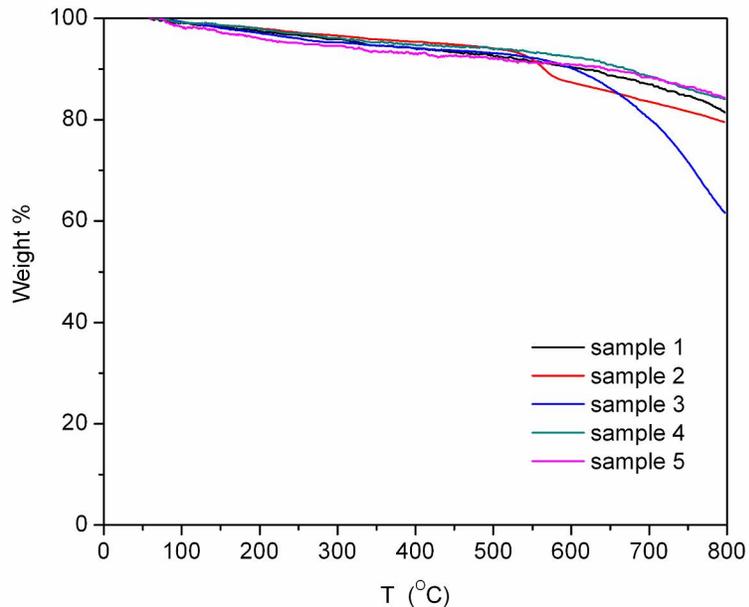


Figure S8. Thermogravimetric analysis curves of CTF samples **1-5** under nitrogen atmosphere.

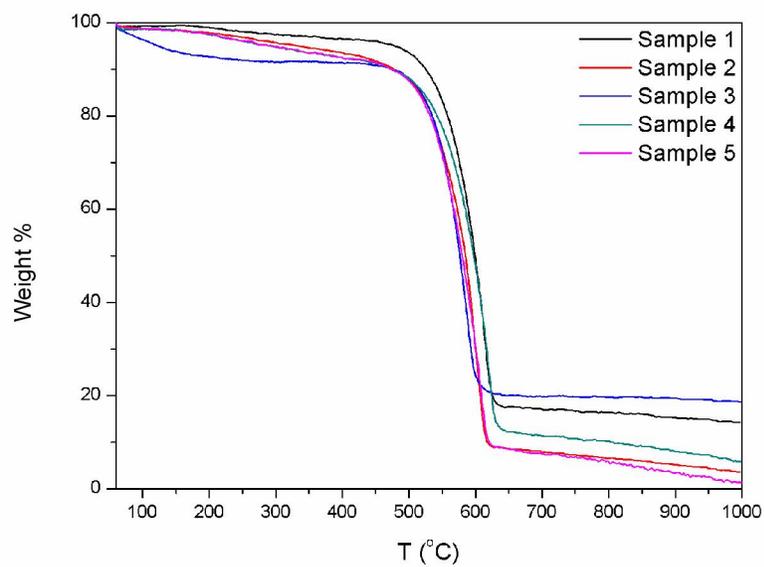


Figure S9. TGA curves of CTF samples **1-5** in air.