

Supporting Information

Green, Scalable and Morphology Controlled Synthesis of Nanofibrous Covalent Organic Frameworks and Their Nanohybrids through Vapor-Assisted Solid-State Approach

Yi Jiang, Wei Huang, Jianying Wang, Qi Wu, Haijiang Wang, Lili Pan and Xikui Liu*

College of Polymer Science and Engineering, Sichuan University, Chengdu610065, People's Republic of China.

E-mail: xkliu@scu.edu.cn.

1. Experimental Section:

Monomer Synthesis

2,6-dihydroxynaphthalene-1,5-dicarbaldehyde (DHNDA) and 2,4,6-tris(4-aminophenyl) pyridine (TAPP) were prepared as previous reported.^{s1,s2} Graphene oxide (GO) was prepared by a well-established modified hummer's method through natural flake graphite. Other chemicals and solvent were purchased and purified according to standard procedures.

Vapor-assisted solid-state synthesis of nanofibrous COFs

Typically, a mixture of DHNDA (648mg, 3 mmol and TAPP (700.4 mg, 2 mmol) was grinded in a mortar within 1hr at room temperature and then put in a tiny glass beaker, the glass beaker and another glass vial containing 2ml solvent mixture were transferred into a Teflon-lined autoclave, and treated at 120°C for 48 h to finish the solid-state condensation. The resulted red-brown material was collected and washed with THF, and dried at 80° C under vacuum for 24 h, yield ca. 85%.

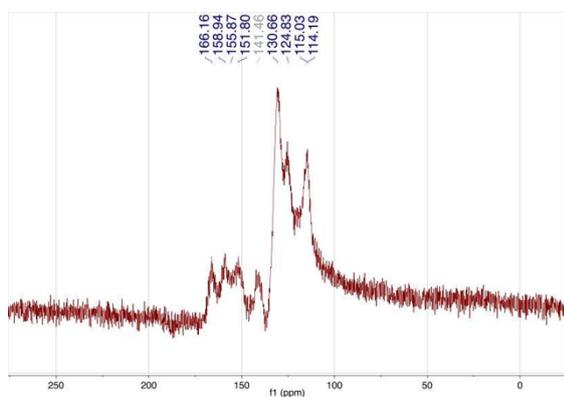
Vapor-assisted solid-state synthesis of nanofibrous COFs/graphene oxide nanohybrids

DHNDA and TAPP are first dissolved in THF, graphene oxide was immersing in the solution for 10 min. After filtered out and drying, it was transferred into a Teflon-lined autoclave and treated by a vapor-assisted solid-state process as mentioned above. Microwaving carbonization is carried out in a Panasonic Microwave at 1KW for 5min.

Characterization

FT-IR spectra were measured with a Nicolet 560 spectrometer. ¹H-NMR spectra were recorded on a BrukerAvance 400 NMR spectrometer. Powder X-ray diffraction (PXRD) data were collected with an X'Pert Pro MPD diffractometer operated at 30 KV and 15 mA with Cu K α radiation, from 2 θ =1.5 to 40° with a scanning rate of 1°/min. SEM was conducted with an Inspect F SEM at an accelerating voltage of 20KV. TEM observations were performed with a JEM 100CX II transmission electron microscope at an accelerating voltage 80 KV. The nitrogen absorption and desorption isotherms were measured at 77 K using a Tristar system, the samples were degassed at 150°C for 10 hours before the measurement. Surface area was calculated from the adsorption data using Brunauer-Emmett-Teller (BET) method. The pore width distribution curves were obtained from the adsorption branch using non-local density functional theory (NLDFT) method. The thermal property was measured using a TGA instrument (SDT Q600) heating to 800°C at 10°C/min.

2. ¹³C-NMR of COFs



REFERENCE

- S1: Huang, W.; Jiang, Y.; Li, X.; Li, X. J.; Wang, J. Y.; Wu, Q.; Liu, X. K. *ACS Appl. Mater. Interfaces* **2013**, 5, 8845-8849
- S2: Chen, Z. H.; Jiang, Y.; Chen, L.; Huang, W.; Li, X.; Li, X. J.; Liu, X. K. *Polym. J.* **2013**, 45, 1087-1093