Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Materials:

All water in the forthcoming synthetic steps was distilled and deionized. Styrene, methacrylic acid, copper acetate monohydrate (98+%), 1,3,5-benzenetricarboxylic acid (98+%) were obtained from Alfa Aesar. Sodium hydroxide, sodium bicarbonate, potassium persulfate and all solvents were supplied by Beijing Chemical Company. All solvents and chemicals are of reagent quality and were used without further purification. Common glass slides were cut to be 50×20 mm and immerged in H_2SO_4/H_2O_2 mixture for 12 hours, following rinsing with deionized water in ultrasonic bath for three times and then dried for use. All 7 ml vials for colloidal crystals growth and a reactive flask must be cleaned by rinsing with H_2SO_4/H_2O_2 mixture and deionized water.

Synthesis of COOH-terminated polystyrene colloidal crystal templates:

Non-crosslinked, monodisperse polystyrene spheres were synthesized using an emulsifier-free emulsion polymerization technique. In a typical preparation, a three-necked, 200-mL round-bottomed flask was filled with 80 ml of water and heated to 75^{o}C before 7.0 g of styrene and 0.35 g methacrylic acid were added under intensively stirring with a magnetic beater. Pure nitrogen was bubbled to deaerate the mixture for 30 min. In a separate 25-mL polyethylene bottle, 0.024 g of sodium hydroxide and 0.024 g sodium carbonate was dissolved to 5 ml water, added to the former solutions and reheated to 75 ^{o}C. 0.03 g potassium persulfate initiator was added to 5 ml of water and deaerated for 10 min. After adding the initiator to the total solution, nitrogen was passed through the flask for 10 min then stopped. The temperature was kept at 75 ^{o}C for 12 h. After alternative centrifugation and dispersion using water for 4 or 5 times to expunge residues, the monodispersed COOH-terminated polystyrene particles (330 nm) were obtained and fully dispersed in water with weight concentration of about 0.1%, which were allotted into 7 ml clean vials for the formation of colloidal crystal templates. A clean glass slide was put into each vial in vertically for colloidal crystal growth. After complete volatilization of water, COOH-terminated polystyrene colloidal crystal templates were formed on both sides of each glass slide.

Preparation and growth of HKUST-1 [$Cu_3(BTC)_2$] MOFs layer on COOH-terminated polystyrene photonic crystals film:

The freshly prepared COOH-terminated polystyrene photonic crystals film on glass substrates were immersed subsequently in a 50 mM of $Cu(CH_3COO)_2 \cdot H_2O$ ethanol solution for 1 hour and in a 5 mM of 1,3,5-benzenetricarboxylic acid ethanol solution for 1 hour at 40 ^{o}C. Between each step the substrates were rinsed with ethanol and dried in air at 60 ^{o}C. After 5-cycle growth, the substrates were rinsed with ethanol, dried and well kept at room temperature. In our work, we optimized the growth procedure. With the repeated cyclic growth, more HKUST-1 materials were coated onto the surface of PS arrays. After 5-cycle growth, the intracavities of colloidal array were almost fulfilled with MOF, but still some pores exist in PS arrays. To achieve good sensing performance of the prepared photonic films, more MOF sensing materials and at the same time some pore structure, which is favorable for molecule transport, are required. Thus, we found that 5-cycle growth for the MOF film preparation is a good one to reach our goal.

Organic vapor testing:

All organic vapor exposure experiments were conducted under a saturated vapor condition. A 5-cycle growth of HKUST-1 film was placed in the glass vial without contacting the solvent. In typical test, 0.1 ml of ethanol was added into a glass vial (22 ml in volume), kept by a stopper and then placed at 60 ^{o}C. After 2 hours vapor exposure, and cooling at room temperature, the stopbands peak of the HKUST-1 film was monitored via UV-vis spectrometer. After each vapor testing, the HKUST-1 film was degassed at 80 ^{o}C for 2 hours in high-vacuum drying oven.

Characterization:

XRD measurements were performed on Bruker D8 Advance X-Ray powder diffractometer. In our case, the used PS spheres were removed from the prepared photonic MOF films by using tetrahydrofuran (THF). In order to obtain pure HKUST-1 powder for PXRD studies, the obtained MOF sample was washed thoroughly with THF and dired at 80 ^{o}C under vacuum for two days.TEM images were obtained using JEM 2010 high-resolution transmission electronic microscope at an acceleration voltage of 120 kV. SEM images were obtained using a field emission scanning electron microscopy (FESEM) on a JEOL JSM-5400 system at an accelerating voltage of 8 kV. UV-Vis spectra were collected on PerkinElmer Lambda35 spectrometer. Simultaneous TGA-IR was performed on a NETZSCH STA 409C TGA analyzer under flowing nitrogen coupled with a Nicolet Nexus 670 IR instrument.

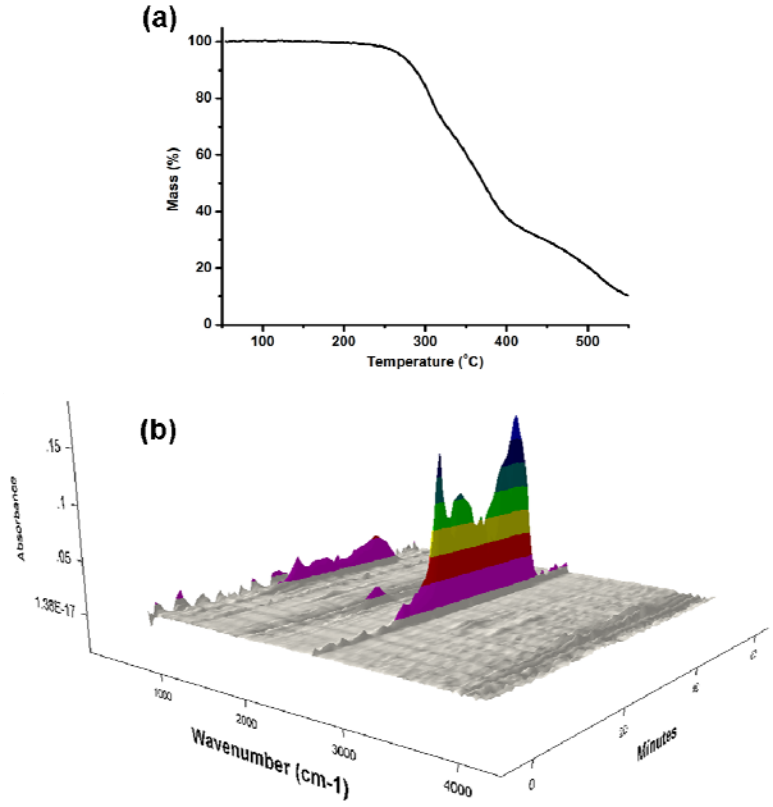

Figure S1 TGA-IR investigation on the activated HKUST-1 films: (a) TGA curve, heating rate: 10^{o}C/min; (b) Three-dimensional IR spectrum showing the evolution of components

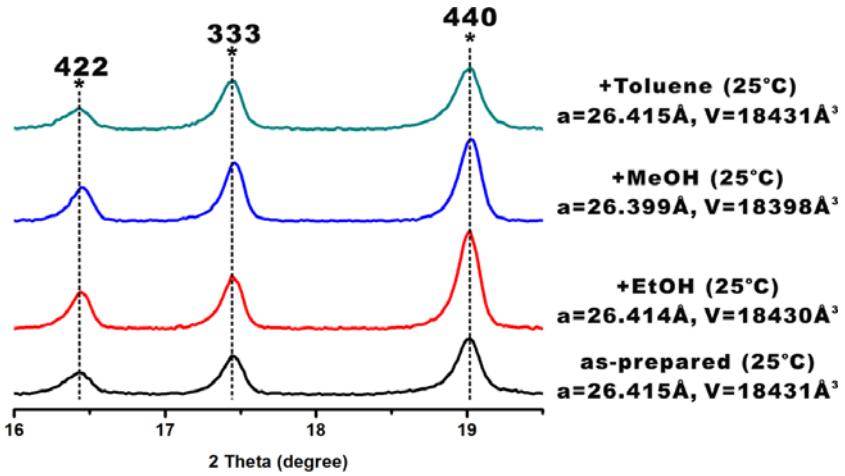

Figure S2. XRD patterns of the bulk HKUST crystal and the HKUST samples after the exposure to different organic vapors (Ethanol, Methanol, and Toluene)

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References:

1. Shekhah, H. Wang, D. Zacher, R. A. Fischer and C. Wöll, *Angew. Chem. Int. Ed.*, 2009, **48**, 5038.
2. C. Shekhah, H. Wang, S. Kowarik, F. Schreiber, M. Paulus, M. Tolan, C. Sternemann, F. Evers, D. Zacher, R. A. Fischer and C. Wöll, *J. Am. Chem. Soc.*, 2007, **129**, 15118.
3. R. Ameloot, E. Gobechiya, H. Uji-i, J. A. Martens, J. Hofkens, L. Alaerts, B. F. Sels and D. E. De Vos, *Adv. Mater.*, 2010, **22**, 2685