Supporting Information

Plasmonics-enhanced metal-organic frameworks nanofilms for highly sensitive nearinfrared absorption

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Experimental details

Materials: Indium(III) acetate (In(Ac)₃, 99.99%) and copper nitrate hexahydrate (Cu(NO₃)₂·6H₂O, 98%) were purchased from Alfa Aesar. Tin(II) 2-ethylhexanoate (95%), copper acetate (Cu(Ac)₂, 98%), benzene-1,3,5-tricarboxylic acid (BTC, 95%), oleylamine (OLA, >70%), 1-octadecene (ODE, 90%), and 2-ethylhexanoic acid (99%) were delivered from Sigma-Aldrich. Ethyl acetate (99.9%) from Fisher Scientific, *n*-hexane (95%) from J.T. Baker, anhydrous tetrachloroethylene (TCE, 99%) from Cole-Parmer, ACS grade of ethanol (>99.5%) from Macron chemicals were used for solvents. All chemicals were used as purchased without further purification. Sapphire as substrates were purchased from Precision Micro-Optics with 430 µm thickness.

Sn-doped indium oxide nanocrystals (ITO NCs) synthesis: ITO NCs were synthesized by using a hot-injection method. A solution consisting of $In(Ac)_3$ (0.96 - 1.20 mmol), Tin(II) 2-ethylhexanoate (0.01 - 0.24 mmol), 2-ethylhexanoic acid (3.6 mmol), and octadecene (10 mL) in a three-neck flask was stirred under vacuum at 80 °C for 30 min, then purged with Ar gas at 150 °C for 60 min while stirring. In the meantime, a solution containing oleylamine (10 mmol) and

octadecene (5 mL) was purged with Ar gas at 100 °C for 60 min, and then was injected into a threeneck flask at 240 °C. The reaction mixture was held at 290 °C for 2 hrs. The reaction mixture was allowed to cool and 10 mL of ethyl acetate was added to precipitate the NCs followed by centrifuging at 6000 rpm for 10 min. The supernatant was discarded, and 5 mL of toluene and 5 mL of ethyl acetate were added to flocculate the NCs followed by an additional centrifuging at 6000 rpm for 10 min. The supernatant was decanted, and the final product was re-dispersed in non-polar solvent such as tetrachloroethylene, hexane, and toluene for further characterization.

ITO thin films: A spin-coating method was used to fabricate ITO thin films. Sapphire, as the substrate, was cleaned *via* sonication in a three step process: 15 min deionized water, 15 min acetone, 15 min isopropanol. Three rinses were performed between each sonication step. A total of 100 μ L of the ITO NCs dispersed in hexane were spin-coated onto a sapphire substrate (2.5 cm x 2.5 cm) at 5000 rpm for 30 s. Finally, the ITO NCs-coated sapphire substrate was treated by O₂ plasma at 20 W for 10 minutes.

Cu-BTC films and bulk powder: A stepwise layer-by-layer (LBL) method was used to grow the Cu-BTC MOF thin films onto the ITO-coated sapphire substrate. In a typical method, the ITOcoated sapphire substrate after O_2 plasma treatment was immersed in a 2 mM solution of the metal precursor (Cu(Ac)₂) in 60 mL of ethanol for 20 min. Subsequently, the ITO-coated sapphire substrate was immersed in a 0.2 mM solution of the organic ligand (BTC) in 60 mL of ethanol for 40 min. Between each step the substrates were rinsed with ethanol to remove unreacted precursor ions or molecules and to ensure uniform film growth and then dried in a N₂ stream. Powder-typed bulk Cu-BTC synthesized *via* a typical solvothermal method in the batch reactor was also prepared. A solution of Cu(NO₃)₂·6H₂O (3.6 mmol) in 60 mL of ethanol and BTC (8.1 mmol) in 60 mL of ethanol were both stirred separately for 10 min in 250 mL beakers. A 50/50 mixture of Cu(NO₃)₂ and BTC solution was stirred for 10 min, then was placed in a Teflon autoclave. The sealed autoclave was heated to 120 °C, held for 18 h in a convective oven, and cooled to room temperature naturally. The collected reaction products were washed with ethanol 3 times and were dried under vacuum for 24 h at 70 °C. The detailed information of materials and characterization can be found in the supporting information.

Sensor performance: The flow gas-cell designed for the NIR absorption measurements using plasmonic-enhanced nano-composite MOF//ITO/Sapphire is shown in Fig. S4. Before measuring transmittance (%T), the gas-cell was purged with ultra-high purity Ar gas for 24 hrs at room temperature to establish a baseline spectrum. A high (100%) or low (0.1% in N₂) concentration of CO₂ gas was then passed through the flow-cell at atmospheric pressure. The flow rates of the gases were set at 10 mL min⁻¹ using mass-flow-controllers.

Characterizations: X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima IV Diffractometer, operating at 40 kV and 40 mA with Cu k α radiation (0.154 nm) in the 20 scan range from 5° to 30° with a step size of 0.01. Field emission-scanning electron microscope (FE-SEM) analysis was conducted with an FEI Quanta 600 and FEI Nova NanoSEM 230 using 10 kV accelerating voltage. A thin gold/palladium layer was coated on the samples to increase their electrical conductivity. The gas sensing properties were measured with a Thermo Scientific Nicolet 6700 Fourier transform infrared (FT-IR) spectrometer. High resolution transmission electron microscopy (HRTEM) images were obtained using FEI Titan 80-300 operating at 300 kV. X-ray photoelectron spectroscopy (XPS) was carried out with a PHI 5600ci instrument using a monochromatized Al Ka X-ray source (1486.6 eV). The pass energy of the analyzer was 23.5 eV. Binding energies were calibrated using the C 1s signal located at 285.0 eV. Samples were lightly sputtered (~30 sec) to remove the very-top surface contamination. The O₂ plasma treatments were performed using a Harrick Plasma system, operating at 50 W for 20 min.



Fig. S1. Top and cross-sectional SEM images of the Cu-BTC MOF on ITO film grown by (A) 10 cycles and (B) 30 cycles LBL method.



Fig. S2. UV-Vis-NIR spectra of the ITO NCs dispersed in TCE and as-deposited ITO NCs on sapphire by spin-coat.



Fig. S3. XPS analysis of the ITO NCs with the 10%-Sn. (A) In 3d, (B) Sn 3d, and (C) O 1s spectra.



Fig. S4. Schematic diagram of flow-cell designed in this study with dimension of 6 mm, width of 4 mm, and height of 1.5 mm.



Fig. S5. (Left) Schematic diagram of flow-cell without MOF and ITO films. (Right) general absorption spectrum of CO_2 measured by FT-IR at (upper) 100% and (lower) 0.1% CO_2 flowing in gas-cell without the ITO//MOF thin films designed in this study. No absorption signal is observed in the NIR range at the low concentration of CO_2 .



Fig. S6. Recovery test of the flow cell designed in this study. The flow cell was first passed with 100% CO₂ gas for 5 min, and then was purged with ultra-high purity Ar gas. The absorption spectrum of CO₂ at (A) ~2700 nm and (B) ~4200 nm were measured at room temperature, atmospheric pressure, and 10 mL min⁻¹ of Ar. Right images show magnified spectra of the dotted square inset area as a function of elapsed time.