Supporting Information

Infrared Laser Writing of MOFs

Kenji Hirai* and Kazuki Sada*

Department of Chemistry, Faculty of Science, Hokkaido University, North-10 West-8, Kita-ku, Sapporo, 060-0810, JAPAN

Experimental Sections

Synthesis of MOFs by IR laser:

The solution for MOF synthesis is prepared by following the condition.

• MIL-53(Fe): [Fe(OH)(bdc)]_n

FeCl₃•6H₂O (220.3 mg, 8.25×10^{-1} mmol) and 1,4-benzenedicarboxylic acid (H₂bdc: 68.6 mg, 4.13×10^{-1} mmol) were dissolved in *N*,*N*-dimethylformamide (5 mL).

- HKUST-1: [Cu₃(btc)₂(H₂O)₃]_n
 Cu(NO₃)•3H₂O (74.4 mg, 2.5 × 10⁻¹ mmol) and 1,3,5-benzenetricarboxylic acid (H₂btc: 27.6 mg, 1.67 × 10⁻¹ mmol) were dissolved in ethanol and water (5 mL).
- MOF-5: [Zn₄O(bdc)₃]_n

 $Zn(NO_3)_2$ •6H₂O (111.6 mg, 3.75 × 10⁻¹ mmol) and 1,4-benzenedicarboxylic acid (H₂bdc: 46.5 mg, 2.82 × 10⁻¹ mmol) were dissolved in *N*,*N*-dimethylformamide (5 mL).

- UIO-66: [Zr₆O₄(OH)₄(bdc)₆]_n
 ZrCl₄ (29.1 mg, 1.25 × 10⁻¹ mmol) and 1,4-benzenedicarboxylic acid (H₂bdc: 41.5 mg, 2.5 × 10⁻¹ mmol) were dissolved in *N*,*N*-dimethylformamide (5 mL).
- ZIF-8: [Zn(2-MeIm)₂]_n

Zn(NO₃)₂•6H₂O (59.5 mg, 2.0×10^{-1} mmol) and 2-methylimidazole (H₂bdc: 66.4 mg, 4.0 $\times 10^{-1}$ mmol) were dissolved in *N*,*N*-dimethylformamide (5 mL).

The glass substrate was washed with deionized water and dried completely. The prepared solutions were casted on a glass substrate which was place under the focus lens of infrared IR laser (Fabool Laser CO₂, smartDIYs Co.,Ltd.). The IR laser was swept on the solution (the laser setting for each experiment is described in the main text). After IR laser sweeping, the resulting powders were collected for SEM and XRD experiments.

Instrumentation: SEM observation was carried out with JEOL JIB-4600F/HKD and JEOL JSM-7100F. XRD data were collected by Bruker D8 Advance ECO.

IR Laser Machine



Fig. S1. Schematic illustration of IR laser machine: (a) a whole image the machine (top view), (b) a close up image of movable IR laser and target samples (side view).

Thermal Energy Provided by the IR Laser

Laser and Reaction Solution Laser: 12 W, 100 mm/min Specific Heat Capacity of DMF: 0.485 cal/g•°C Density of DMF: 0.944 g/cm³

Volume of Reaction Solution line width: 180 μ m (Fig. S4) line length swept by IR laser per second: 1667 μ m thickness of solution: 100 μ m volume of the solution: 180 × 1667 × 100 μ m³

Absorbance of IR Laser wavelength of IR laser: 9.2-10.8 μm absorbance rate: 39.2 % (Fig. S2)

The thermal energy provided to the solution enables to increase the temperature of DMF solution up to 192 °C. The actual temperature increase should be less than 192 °C because of the convection flow and thermal diffusion; however, the IR laser provides sufficient energy to heat up the solution to the temperature at which MOF crystals are formed (usually over 100 °C).



Fig. S2. IR spectra of DMF. The red box indicate the wavelength region of IR laser (9.2-10.8 μ m).

SEM Image of MOF Patterning



Fig. S3. SEM image of line patterning of MIL-53. The substrate was sliced and the ditch was observed from the side of substrate.

Line Resolution of IR Laser Sweeping



Fig. S4. (a) Photograph of a piece of card board after laser sweep. A red arrow indicates the line generated by laser sweeping. (b) SEM image of card board after laser sweeping. A line with width of $180 \mu m$ was observed.

Line Width of MOF Patterning



Fig. S5. SEM images of line patterning of MOFs: (a) MIL-53 and (b) HKUST-1. SEM images of line patterning of MOFs: (a) MIL-53 and (b) HKUST-1.

MOF Patterning crystals deposited in the ditch



Fig. S6. SEM images of line patterning of MIL-53 (a) after scratching by tweezers, and (b) after washing with DMF. The yellow arrow indicate the direction of scratching.

Laser Irradiation at Cotton with Metal Ions and Organic Ligands

FeCl₃•6H₂O (220.3 mg, 8.25×10^{-1} mmol) and 1,4-benzenedicarboxylic acid (H₂bdc: 68.6 mg, 4.13×10^{-1} mmol) were dissolved in *N*,*N*-dimethylformamide (5 mL). The reaction solution was adsorbed with cotton. The laser was swept on cotton (maximum laser intensity: 12 W, sweep rate: 100 mm/min).



Fig. S7. A photograph of the cotton after laser irradiation. The cotton was burned by laser sweep.





Fig. S8. SEM images of MIL-53(Fe) synthesized by IR laser. The sweep number of IR laser number was varied at (a) 1 time, (b) 2 times, (c) 3 times, (d) 4 times and (e) 5 times (same as Fig.2a).



Fig. S9. XRD patterns of MIL-53(Fe) synthesized by IR laser at various sweeping numbers: (a) 5 times, (b) 4 times, (c) 3 times, (d) 2 times and (e) 1 time. (f) simulated XRD patterns of MIL-53(Fe).



Fig. S10. Mean size of crystal domains of MIL-53(Fe) synthesized by IR laser irradiation. The crystallinity was improved with increasing the number of laser sweeping.

Effect of Laser Sweep on Crystal Size



Fig. S11. SEM images of MIL-53(Fe) synthesized by IR laser. The max intensity of IR laser was varied at (a) 6 W, (b) 12W (same as Fig.2a) and (c-d) 24W. The spindle-like crystal of MIL-88 was observed in Fig. S4d.



Fig. S12. XRD patterns of MIL-53(Fe) synthesized by IR laser at various laser intensity: (a) 24 W, (b) 12 W, (c) 6 W. (f) simulated XRD patterns of MIL-53(Fe).