Supporting Information

Synthesis of a metal-organic framework by plasma in liquid to increase reduced metal ions and enhance water stability

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1. Synthesis

1.1. Materials

All materials were purchased from FUJIFILM Wako Pure Chemical Industries, Ltd. (Japan) and used without any purification.

1.2. Plasma-in-liquid method

$Cu(NO_3)_2 \cdot 3H_2O$ (0.34 g) and 0.2 g of 1,3,5-benzenetricarboxylic acid were dissolved in 10 mL water and 30 mL ethanol, respectively. The solutions were mixed sufficiently with stirring. Plasma was generated in the solution by applying bipolar pulse voltage with an amplitude of 1.2–1.5 kV, frequency of 80 kHz, and pulse width of 1.0 μs (power supply; Kurita MPP-HV04–300 kHz) between tungsten electrodes inserted into the solution. The experimental setup and current and voltage waveforms are shown in Figs. S1 and S2. To prevent overheating of the solution, the glass container was placed in a water bath, and the temperature of the solution was maintained below 50ºC. Thereafter, the mixture was filtered and dried at 60 ºC overnight.

1.3. Conventional heating method

$Cu(NO_3)_2 \cdot 3H_2O$ (0.34 g) and 0.2 g of 1,3,5-benzenetricarboxylic acid were dissolved in 10 mL water and 30 mL ethanol, respectively. The solutions were mixed sufficiently with stirring. The solution was placed in a glass container and heated in an oil bath at 100 ºC for 3 h. Thereafter, the mixture was filtered and dried at 60 ºC overnight.

1.4. Triethylamine addition at room temperature

$Cu(NO_3)_2 \cdot 3H_2O$ (0.34 g) and 0.2 g of 1,3,5-benzenetricarboxylic acid were dissolved in 10 mL water and 30 mL ethanol, respectively. The solutions were mixed sufficiently with stirring. Triethylamine (0.2 mL) was added to the solution and stirred for 12 h at room temperature. Thereafter, the mixture was filtered and dried at 60 ºC overnight.

2. Water stability test

HKUST-1 (20 mg) synthesized using each method was placed into 5 mL of purified water and left for 12 h at room temperature. Following this, each sample was filtered and dried at 60 °C overnight.

3. Characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku Smartlab BBKC using Cu Kα radiation operating at 40 kV and 30 mA. The scanning electron microscopy (SEM) images were recorded on JEOL JSM-6060LV scanning electron microscope at an acceleration voltage of 15 kV. Fourier transform infrared (FTIR) spectroscopy was carried out using JASCO FT/IR-6700 spectrophotometer with attenuated total reflectance (ATR). Raman spectra were obtained using JASCO NRS-3100 spectrophotometer. Nitrogen (N_2) adsorption-desorption isotherms were obtained using a BELSORP-mini equipment at 77 K. Before the adsorption measurements, the sample was treated under reduced pressure ($<10^{-2}$ Pa) at 373 K for 12 h. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Kratos AXIS-NOVA spectrometer using Al Kα radiation operating at 15 kV and 10 mA. The XPS measurement conditions are listed in Table S1. Because of the insulating nature of the HKUST-1 samples, a charge neutralizer was used to compensate for sample charging by bombarding the samples with low-energy electrons. The background was subtracted using the Shirley method, and Gaussian curves were fitted. Fluorescence (FL) emission spectra were collected on a JASCO FP-8500 spectrophotometer. Thermogravimetric (TG) measurements were conducted from room temperature to 500 ºC at 10 K min^{-1} on a Rigaku Instrument, Thermo plus TG 8120, in a N_2 atmosphere.

Table S1. XPS measurement conditions

Orbit	Dwell [ms]	Sweep	Total time [s]
Survey	100	5	733
Cu 2p	200	10	1202
O 1s	200	10	802
C 1s	200	10	802

4. Supplementary figures

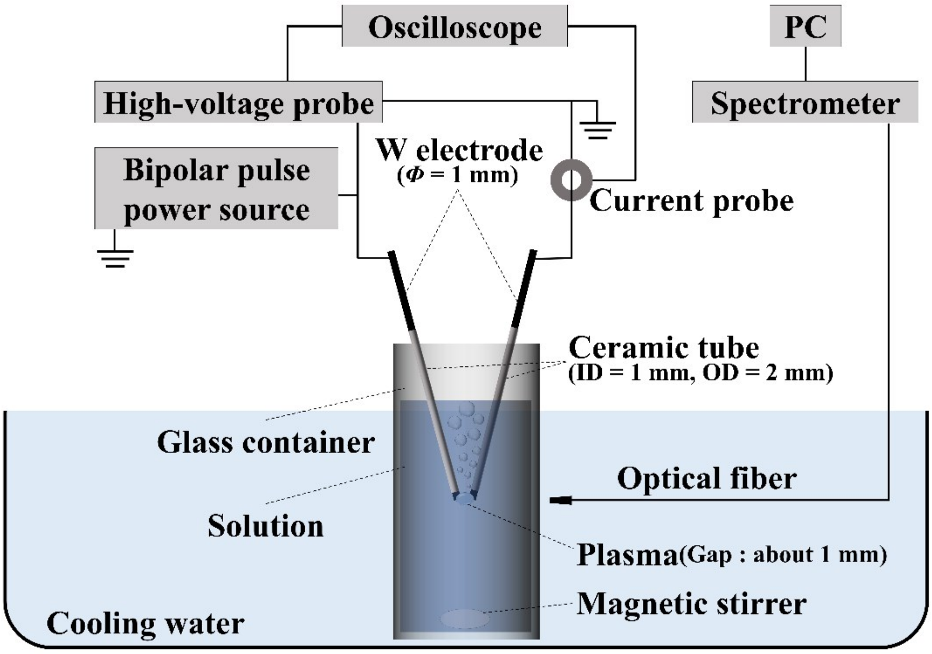


Figure S1. Experimental setup for synthesis by plasma in liquid.

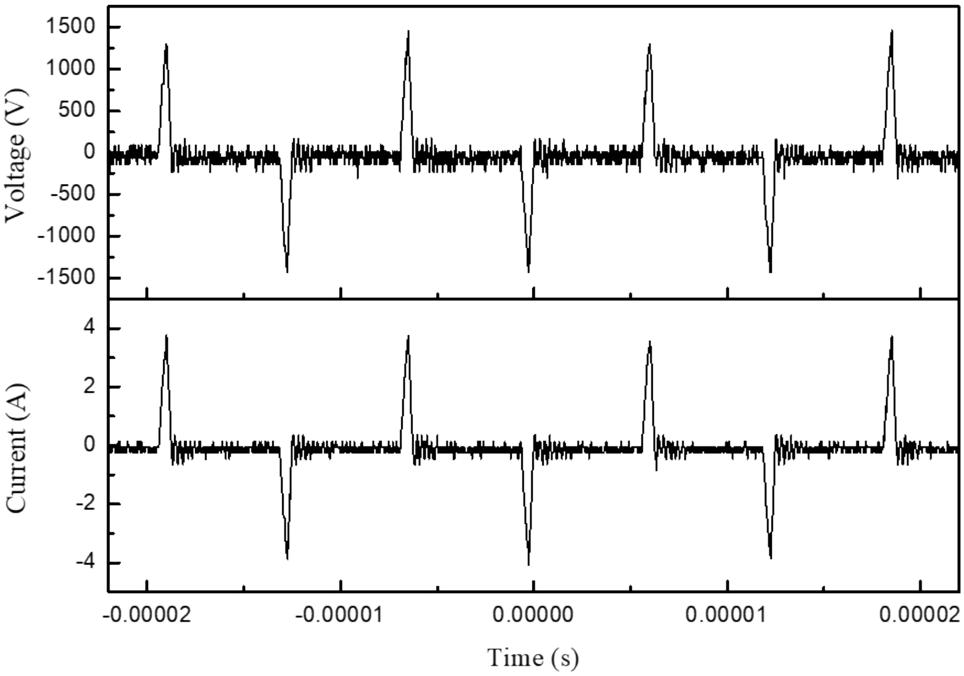


Figure S2. Current and voltage waveforms.

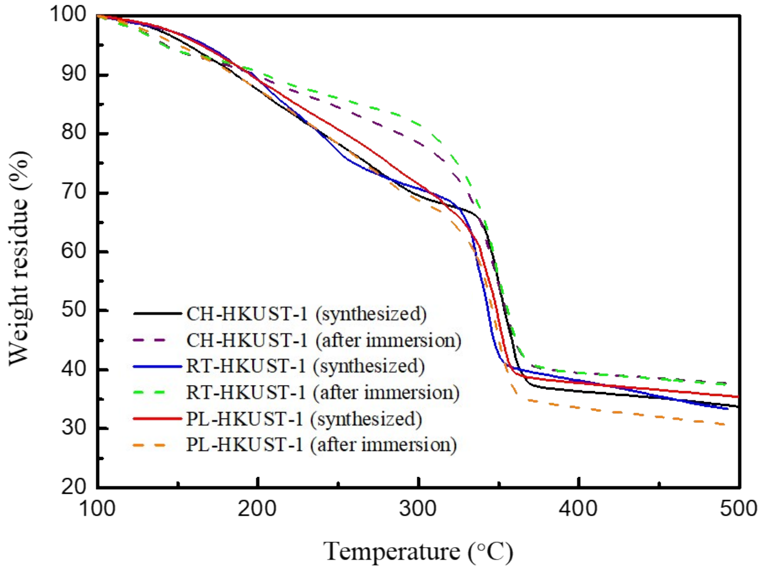
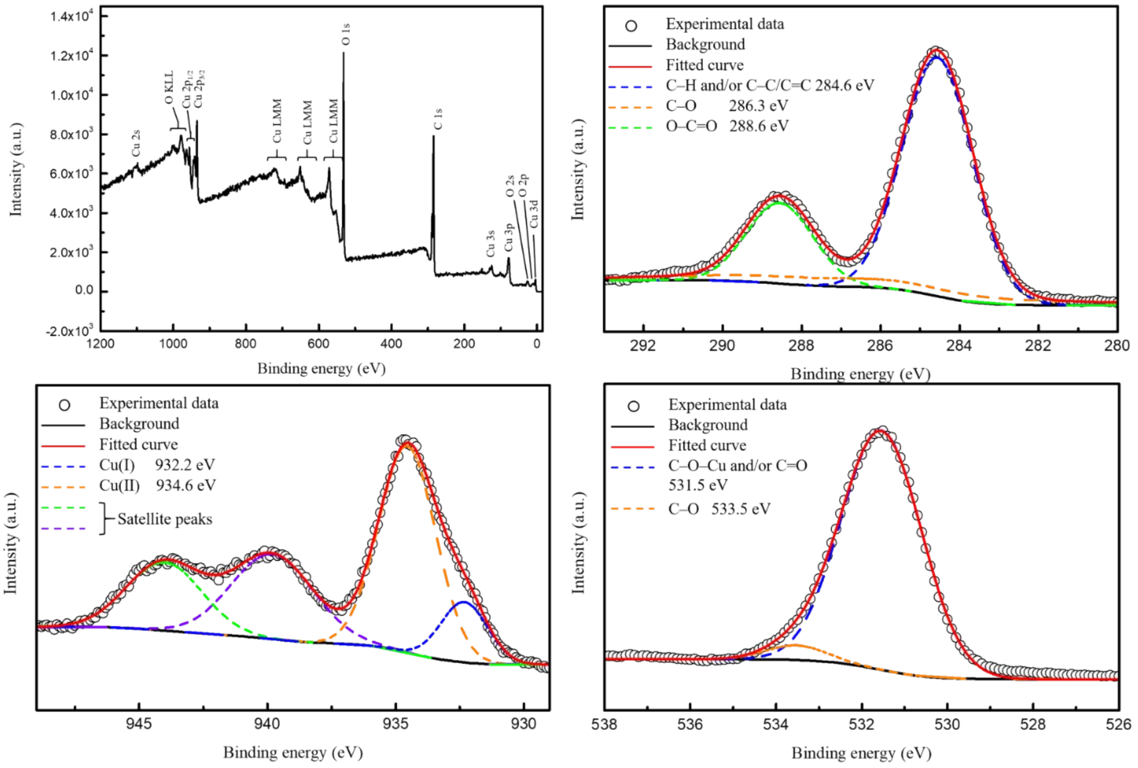
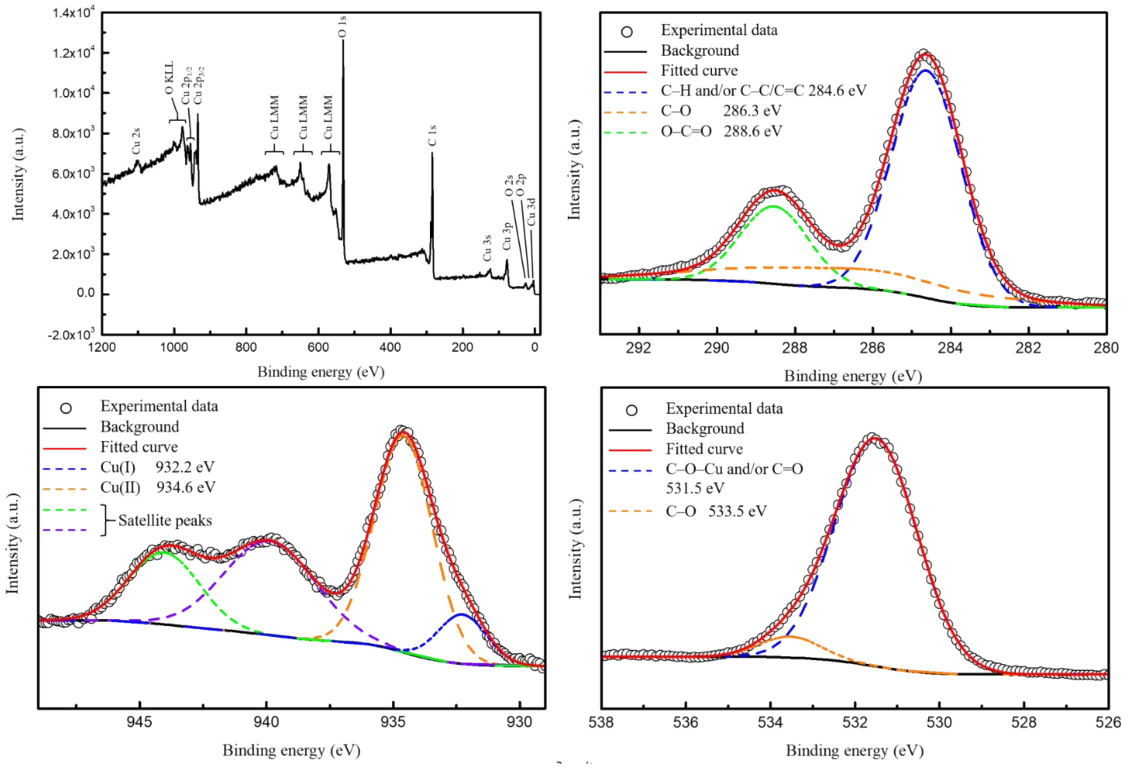


Figure S3. Thermogravimetry curves of CH-HKUST-1, RT-HKUST-1, and PL-HKUST-1 before and after immersion in water.

(a) CH-HKUST-1



(b) RT-HKUST-1



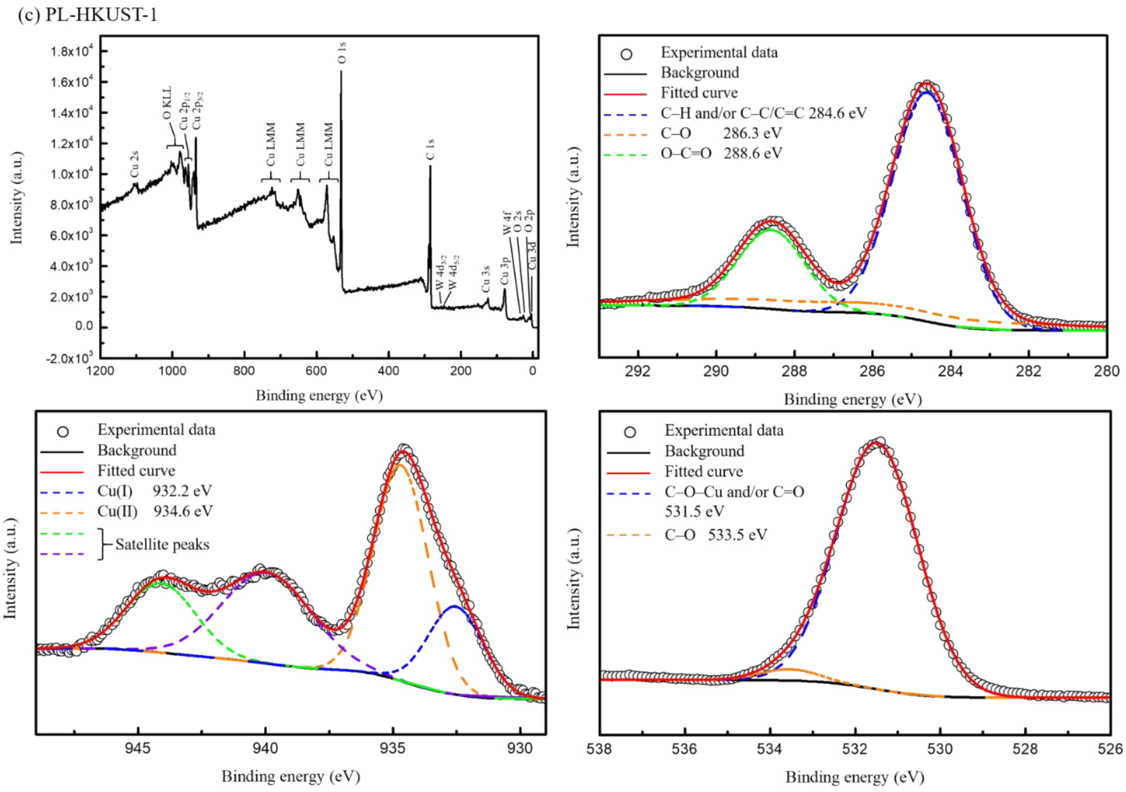


Figure S4. XPS spectra of HKUST-1: (a) CH-HKUST-1, (b) RT-HKUST-1, and (c) PL-HKUST-1.

Tungsten peaks in the wide scan of PL-HKUST-1 probably originate from the electrode used for plasma generation. The area ratios of Cu(Ⅰ) and Cu(Ⅱ) were estimated to be 29:71, 19:81, and 16:84 for PL-HKUST-1, CH-HKUST-1, and RT-HKUST-1, respectively. The fact that Cu(Ⅰ) is detected in CH-HKUST-1 and RT-HKUST-1 is probably due to the reduction of Cu(Ⅱ) by the X-ray source and charge neutralizer during the XPS measurement.[1] The reduction of Cu(Ⅱ) to Cu(Ⅰ) was also observed during the XPS data collection of HKUST-1, and the extent of reduction increased with increasing exposure time.[2] Since the XPS measurement times were identical for the three synthesized samples, the amount of Cu(Ⅰ)in the PL-HKUST-1 should be higher than those in CH-HKUST-1 and RT-HKUST-1. Assuming that the reduction ratio is the same, PL-HKUST-1 would have approximately 10% of the reduced copper ions.

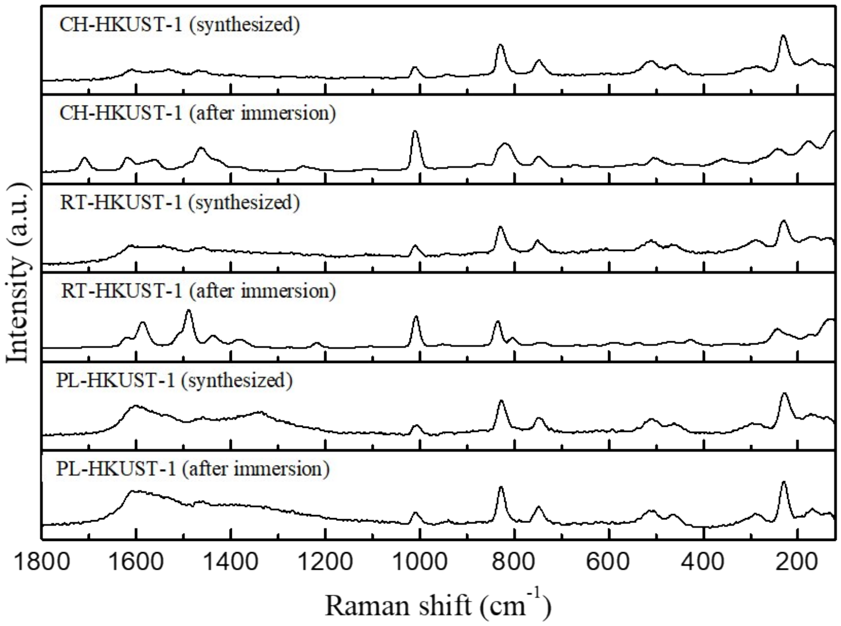


Figure S5. Raman spectra of CH-HKUST-1, RT-HKUST-1, and PL-HKUST-1 before and after immersion in water. The peaks detected for CH-HKUST-1, RT-HKUST-1, and PL-HKUST-1 as synthesized were similar to those observed previously for HKUST-1.[3] The change in the peaks of CH-HKUST-1 and RT-HKUST-1 at 1400–1800 cm^{-1} after immersion in water arises from the COO bond[4] owing to the structural change in HKUST-1; this is consistent with the FTIR analysis.

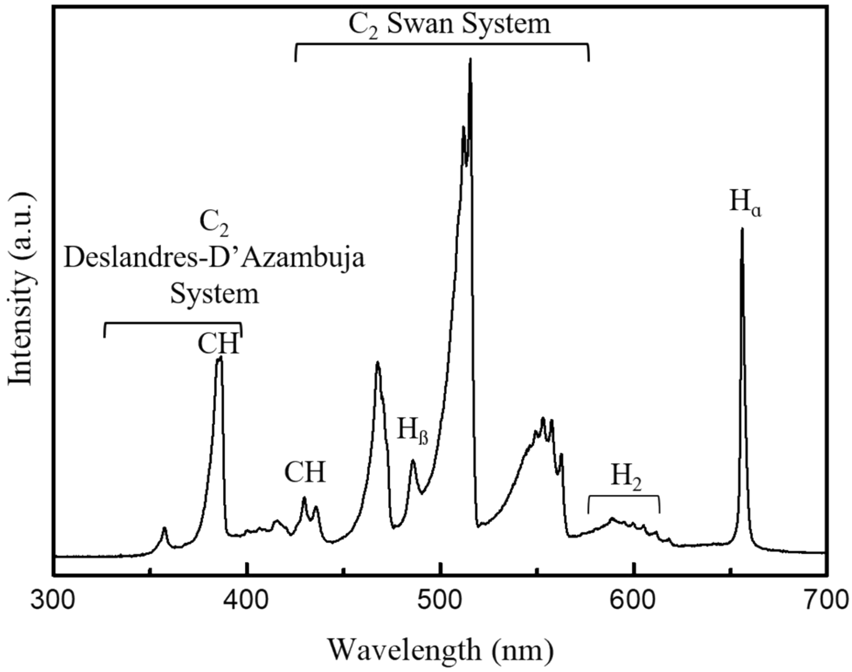


Figure S6. Optical emission spectrum of the plasma during the preparation of PL-HKUST-1.

References

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