Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Oxygen plasma treatment of HKUST-1 for upkeep of its porosity upon moisture exposure

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Contents

Part S1. General information

1. Materials

Copper (II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$), zinc (II) acetate dehydrate ($Zn(acetate)_2{\cdot}2H_2O$) and trimesic acid were bought from Sigma-Aldrich. *N,N*-dimethylformamide (DMF), terephthalic acid, triethylamine (TEA) and Tetrafluoroboric acid (HBF_4) were purchased from Alfa Aesar. Ethyl alcohol (EtOH), chloroform ($CHCl_3$) and dicloromethane (DCM) were purchased from Daejung Chemicals. Methyl alcohol (MeOH) was bought from B&J Chemical.

2. Measurements

Plasma cleaner from Femto science (CUTE) was used for O_2 plasma treatment. N_2 sorption isotherms were collected by Brunauer-Emmett-Teller (BET) analyzer from Soletek (BELSORP-max). Thermogravimetric analysis (TGA) data were obtained by Auto Q500 from TA Instruments with a heating rate of 3 °C/min from 25 °C to 400 °C. The mass spectrometer (MS) coupled with a TGA instrument (MS) was employed for the quantitative analyses of released gas molecules during TGA. The mass spectrometric data were analyzed by Hiden QGA (Hiden Analytical Ltd.). Powder X-ray diffraction (PXRD) data were obtained by the Empyrean X-ray diffractometer (Panalytical). Raman spectra were collected by Almega XR from Thermo Scientific. Fourier transform-infrared (FT-IR) spectra were collected by Nicolet-6700 from Thermo Scientific.

Part S2. Preparation process of HKUST-1

$Cu(NO_3)_2{\cdot}3H_2O$ (4.35 g, 18 mmol), trimesic acid (2.52 g, 12 mmol) and HBF_4 (3.60 g, 125 mmol) in 180 mL mixture of DMF, EtOH and water (1:1:1) were sonicated for 30 minutes to make a blue clean solution. The solution was heated at 85 °C for 48 hours. The blue crystals were washed with DMF by 6 times for 2 days, MeOH by 9 times for 3 days and then DCM by 9 times for 3 days. The dark blue power was activated at 100 °C for 24 hours under vacuum (10^{-2} KPa).

Part S3. Air and moisture exposure process

About 0.50 g of HKUST-1 was exposed to air for 10 min. Among them 0.05 g of HKUST-1 (about 0.05 g) was sampled for various analyses including N_2 sorption, FT-IR, Raman spectroscopy, and PXRD analyses. The rest of HKUST-1 was exposed to moisture in the moisture chamber (Figure S2). Approximately 0.05 g of HKUST-1 was sampled after moisture exposure for 1 h, 5 h, and 10 h for the above-mentioned analyses.

Part S4. Experimental setup of oxygen plasma treatment and moisture exposure

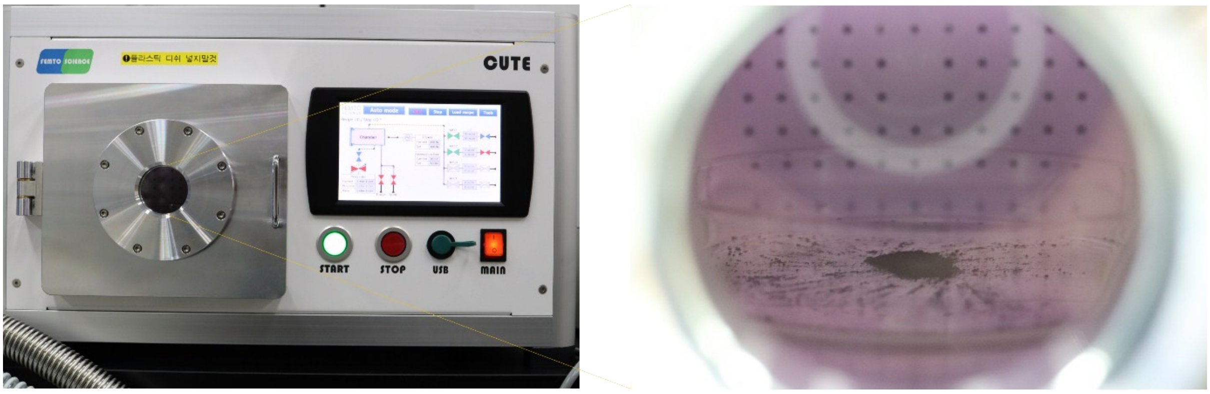

Figure S1. Experimental setup for O_2 plasma treatment. O_2 plasma exposure condition: Pressure (0.7-0.8 torr) and power (100 W).

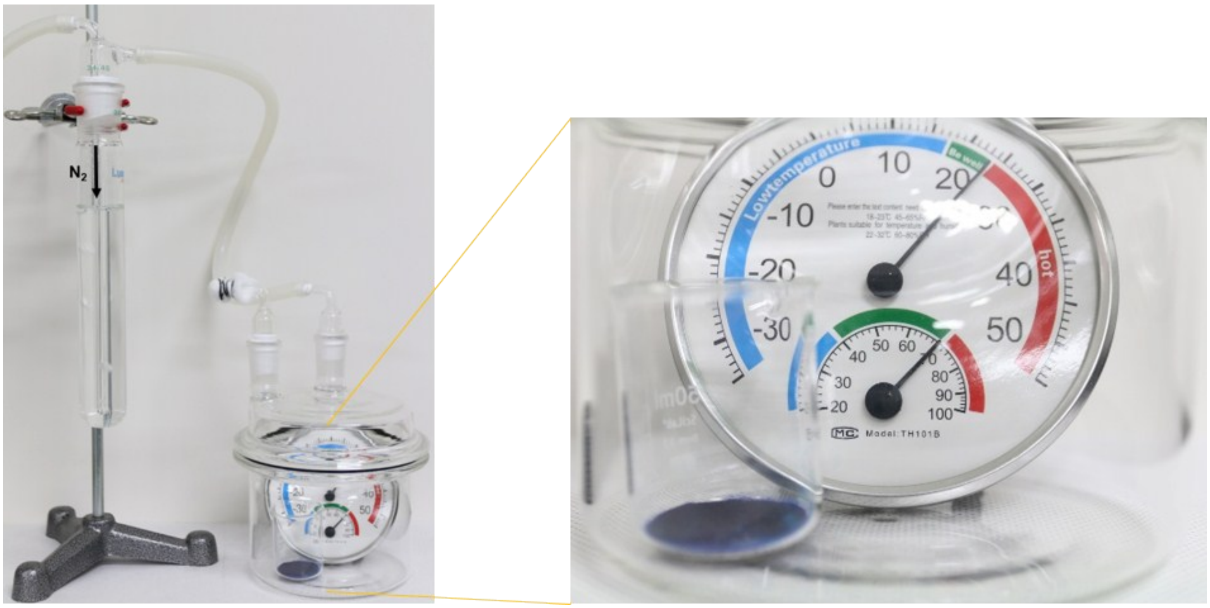

Figure S2. Experimental setup for 70% humidity exposure.

Part S5. Additional N_2 adsorption and desorption isotherms

Table S1. SPR (sorption performance retention) table.

			O_2-0-HKUST-1			
	activated HKUST-1	air exposure 10 m	moisture exposure 1 h	moisture exposure 5 h	moisture exposure 10 h	
V_m (cm^3/g)	484.84	268.04	235.99	0.73600	0.10750	**P/P_0= 0.1**
S_{BET} (m^2/g)	1913.5	1094.7	967.51	2.9296		
SPR$_1$ (%)		55.284	48.674	0.15180	0.02217	**From V_m**
SPR$_2$ (%)		52.209	50.562	0.15310		**From S_{BET}**
			O_2-10-HKUST-1			
	activated HKUST-1	air exposure 10 m	moisture exposure 1 h	moisture exposure 5 h	moisture exposure 10 h	
V_m (cm^3/g)	484.84	492.43	372.92	0.98520	0.21790	**P/P_0= 0.1**
S_{BET} (m^2/g)	1913.5	1990.5	1502.5	3.9323		
SPR$_1$		101.57	76.916	0.20320	0.044943	**From V_m**
SPR$_2$		104.02	78.521	0.20550		**From S_{BET}**
			O_2-40-HKUST-1			
	activated HKUST-1	air exposure 10 m	moisture exposure 1 h	moisture exposure 5 h	moisture exposure 10 h	
V_m (cm^3/g)	484.84	490.46	427.23	229.53	0.41960	**P/P_0= 0.1**
S_{BET} (m^2/g)	1913.5	1963.6	1702.6	938.24		
SPR$_1$		101.16	88.118	47.341	0.086544	**From V_m**
SPR$_2$		102.62	88.978	49.033		**From S_{BET}**
			O_2-60-HKUST-1			
	activated HKUST-1	air exposure 10 m	moisture exposure 1 h	moisture exposure 5 h	moisture exposure 10 h	
V_m (cm^3/g)	484.84	413.65	258.55	0.32430	0.22780	**P/P_0= 0.1**
S_{BET} (m^2/g)	1913.5	1658.9	1702.6	0.93083		
SPR$_1$		85.317	53.327	0.066888	0.046985	**From V_m**
SPR$_2$		86.695	88.978	0.048645		**From S_{BET}**

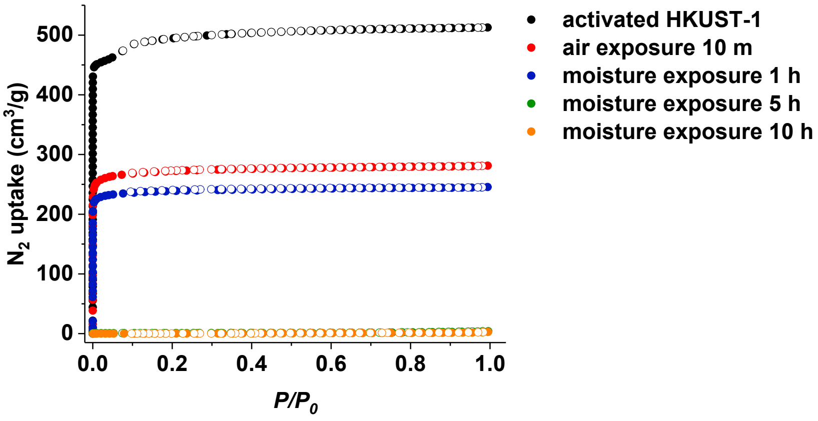

Figure S3. N_2 adsorption and desorption isotherms of activated HKUST-1 (black) and O_2-0-HKUST-1 upon air exposure for 10 min (red dots) and moisture exposure for 1 h (blue dots), 5 h (green dots), and 10 h (orange dots).

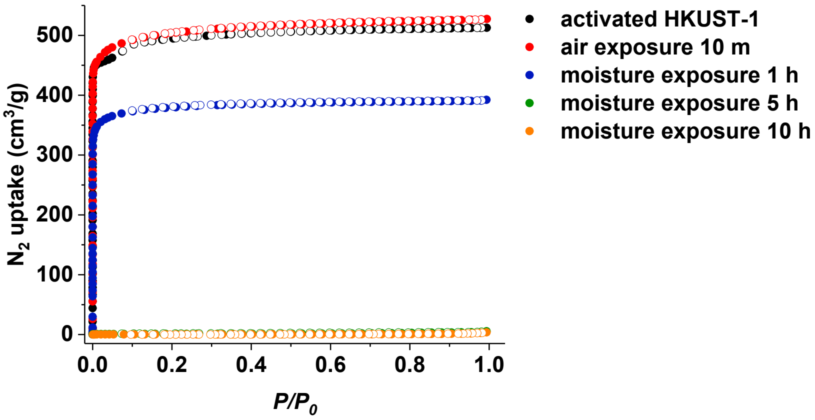

Figure S4. N$_2$ adsorption and desorption isotherms of activated HKUST-1 (black) and O$_2$-10-HKUST-1 upon air exposure for 10 min (red dots) and moisture exposure for 1 h (blue dots), 5 h (green dots), and 10 h (orange dots).

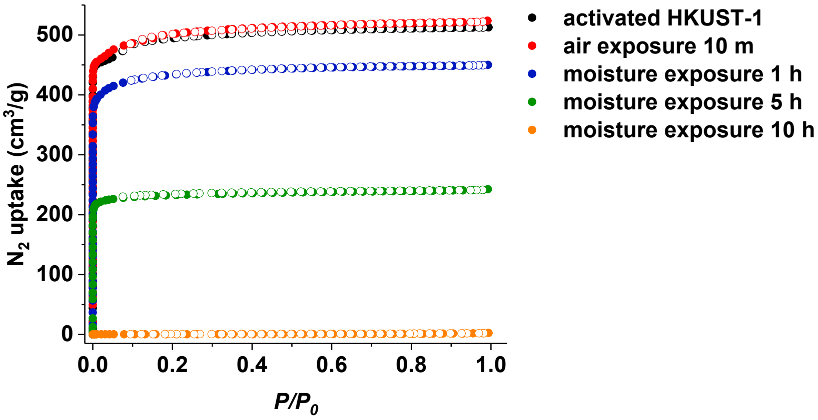

Figure S5. N$_2$ adsorption and desorption isotherms of activated HKUST-1 (black) and O$_2$-40-HKUST-1 upon air exposure for 10 min (red dots) and moisture exposure for 1 h (blue dots), 5 h (green dots), and 10 h (orange dots).

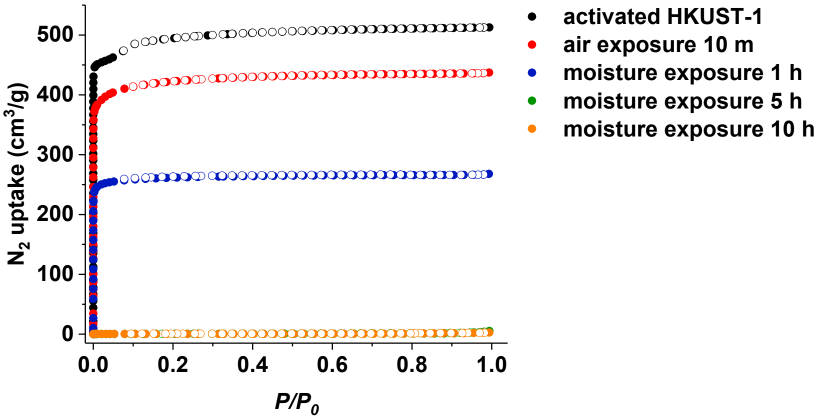

Figure S6. N$_2$ adsorption and desorption isotherms of activated HKUST-1 (black) and O$_2$-60-HKUST-1 upon air exposure for 10 min (red dots) and moisture exposure for 1 h (blue dots), 5 h (green dots), and 10 h (orange dots).

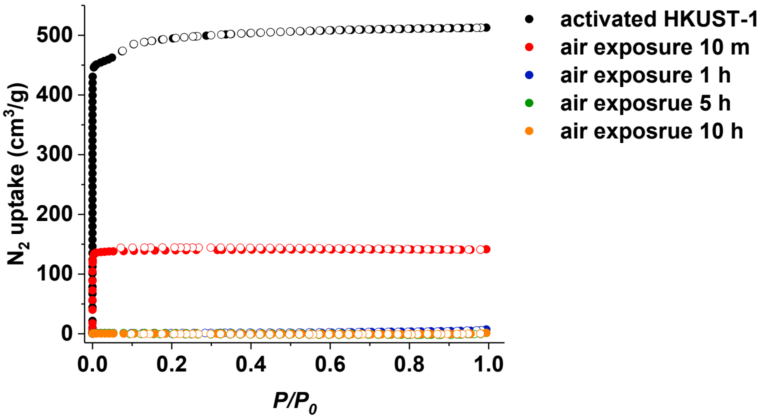

Figure S7. N_2 adsorption and desorption isotherms of activated HKUST-1 (black) and O_2-0-HKUST-1 upon air exposure for 10 min (red dots), 1 h (blue dots), 5 h (green dots), and 10 h (orange dots).

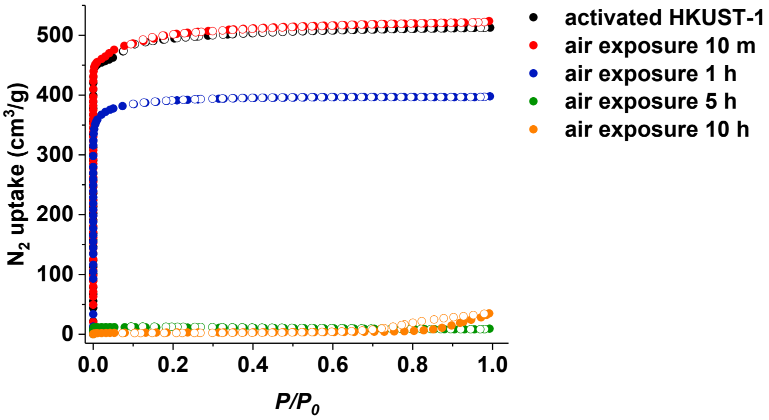

Figure S8. N_2 adsorption and desorption isotherms of activated HKUST-1 (black) and O_2-40-HKUST-1 upon air exposure for 10 min (red dots), 1 h (blue dots), 5 h (green dots), and 10 h (orange dots).

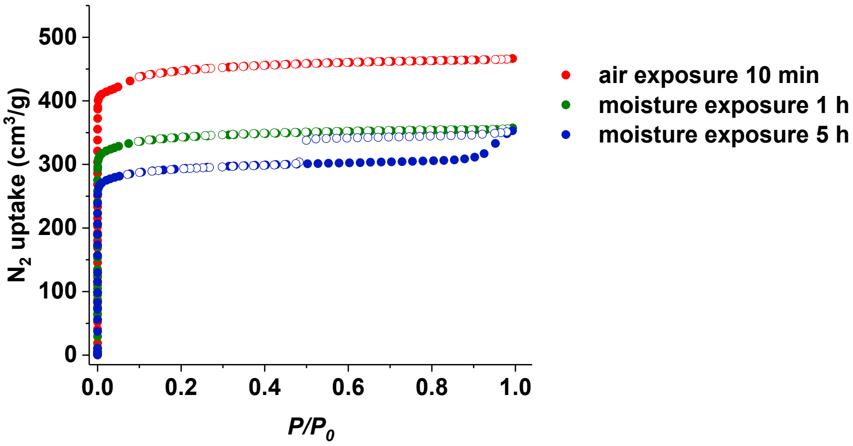

Figure S9. N_2 adsorption and desorption isotherms of O_2-60-HKUST-1 after reactivation process at 100 °C for 24 h. Red, green, and blue dots are for 10 min air exposed and 1 h and 5 h moisture exposed samples, respectively.

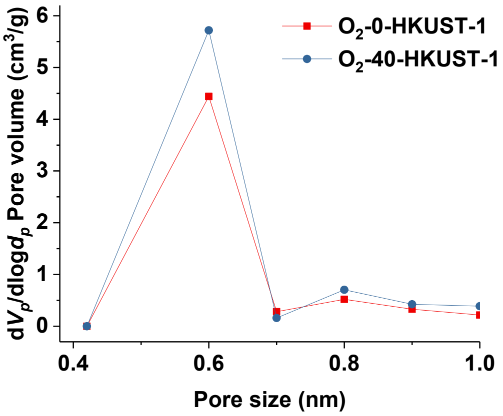

Figure S10. Micro-pore size distribution (MP plot) of reactivated O_2-0-HKUST-1 (red) and O_2-40-HKUST-1 (blue) after moisture exposure for 5 h. the samples were reactivated at 100 °C under vacuum for 24 h.

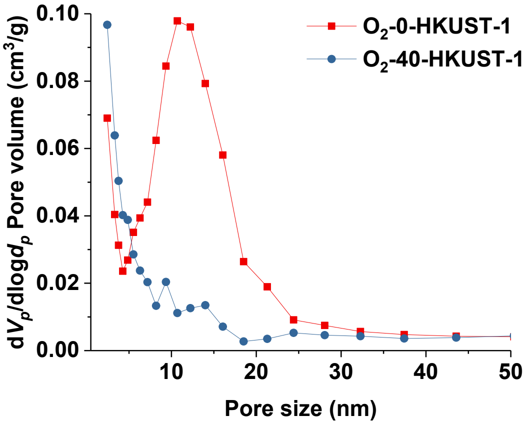

Figure S11. Meso-pore size distribution (BJH plot) of reactivated O_2-0-HKUST-1 (red) and O_2-40-HKUST-1 (blue) after moisture exposure for 5 h. the samples were reactivated at 100 °C under vacuum for 24 h.

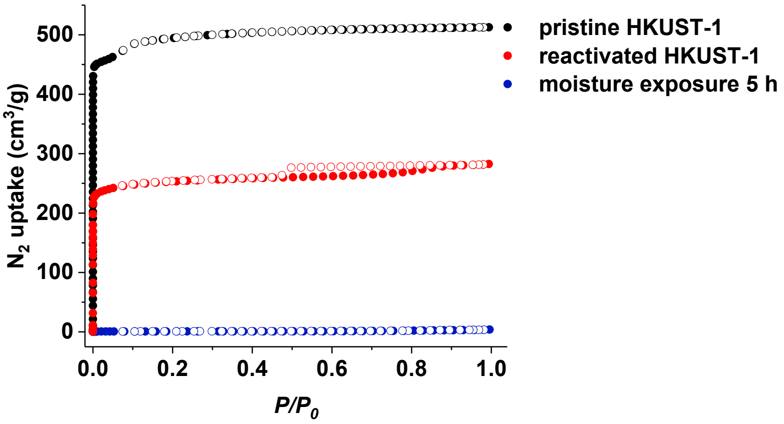

Figure S12. N$_2$ adsorption and desorption isotherms of pristine HKUST-1 (black dots), HKUST-1 after exposure to moisture for 5 h (blue dots), and reactivated HKUST-1 (red dots).

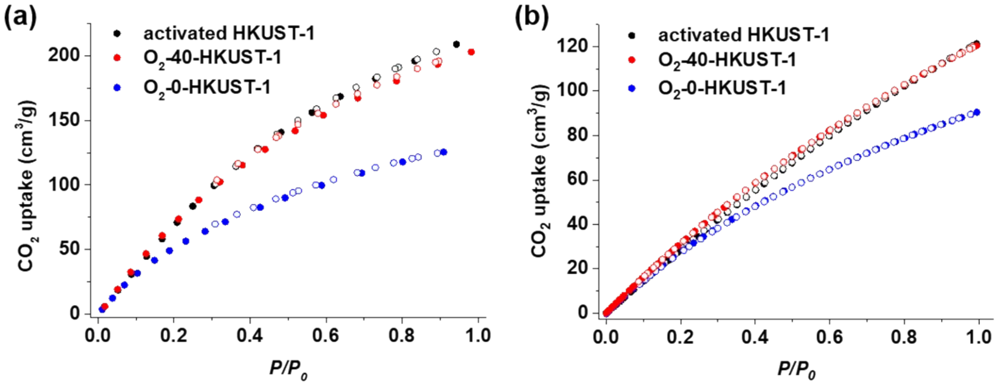

Figure S13. CO$_2$ adsorption and desorption isotherms of activated HKUST-1 (black dots), O$_2$-0-HKUST-1 (blue) and O$_2$-40-HKUST-1 (red). (a) 273 K and (b) 298 K.

Part S6. Additional analysis

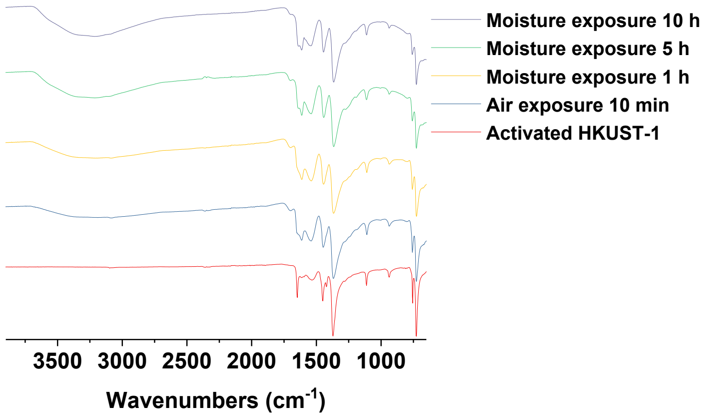

Figure S14. IR spectrum of activated HKUST-1 (red) and O_2-0-HKUST-1 upon air exposure for 10 min (blue) and moisture exposure for 1 h (yellow), 5 h (green), and 10 h (navy).

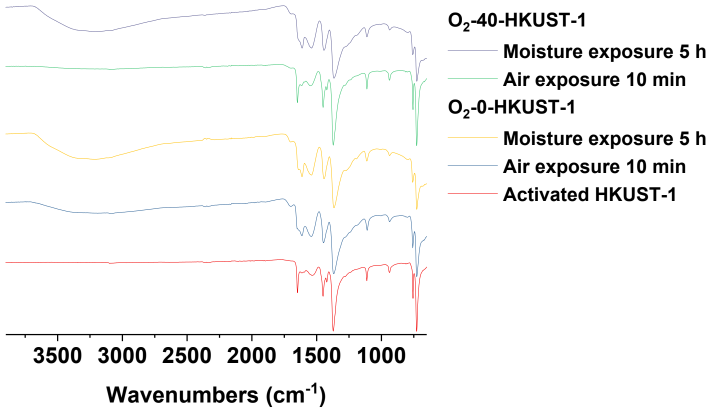

Figure S15. IR spectrum of activated HKUST-1 (red), O_2-0-HKUST-1 upon air exposure for 10 min (blue) and moisture exposure for 5 h (yellow), and O_2-40-HKUST-1 upon air exposure for 10 min (green) and moisture exposure for 5 h (navy).

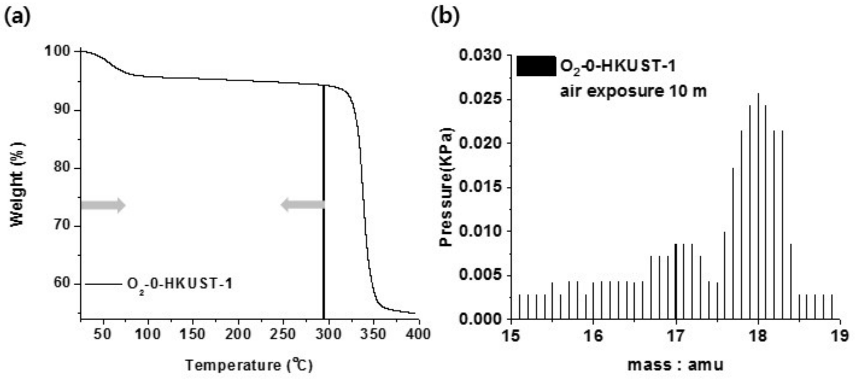

Figure S16. (a) TGA thermograph of O_2-0-HKUST-1 after air exposure for 10 min. (b) The TGA-MS data. The displayed MS histogram was recorded during the temperature increment from RT to 280 °C.

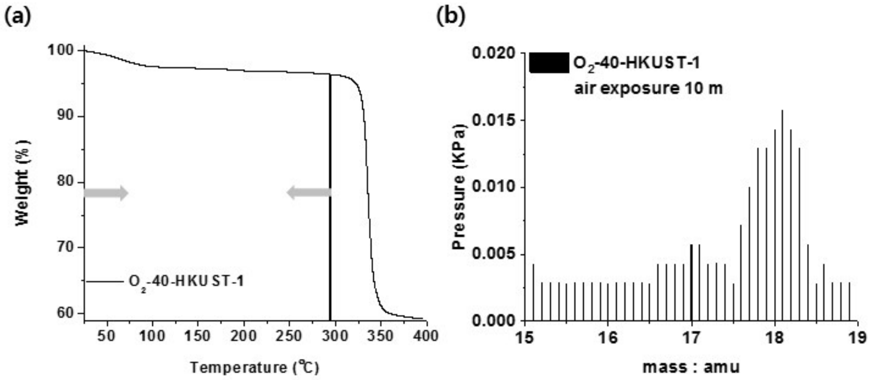

Figure S17. (a) TGA thermograph of O_2-40-HKUST-1 after air exposure for 10 min. (b) The TGA-MS data. The displayed MS histogram was recorded during the temperature increment from RT to 280 °C.

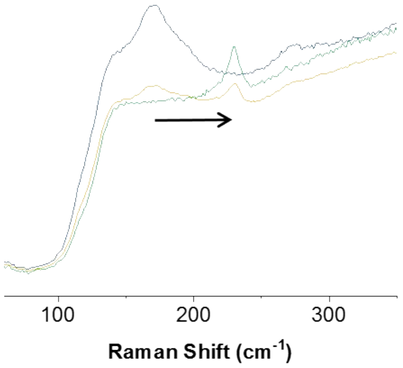

Figure S18. Raman spectra of O_2-0-HKUST-1 (moisture exposure for 5 h). The peak at 172 cm^{-1} was blue-shifted back to 229 cm^{-1} after exposure of laser light (532 nm). Raman spectroscopy was performed under inert conditions to prevent the coordination of additional water molecules during the acquisitions of the spectra. The sample was exposed to the 532-nm laser light at 10% of its nominal power (25 mW). Regeneration took place after 32 scans, where one scan requires 5 s.

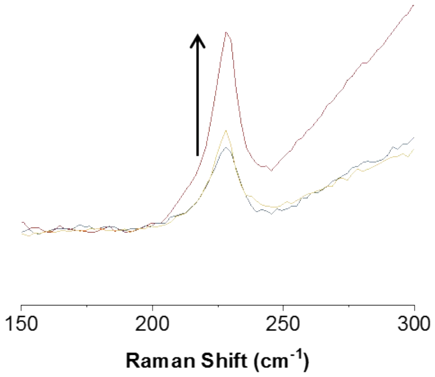

Figure S19. Raman spectra of O_2-0-HKUST-1 (moisture exposure for 5 h). The peak intensity at 229 cm^{-1} was restored after exposure of laser light (532 nm). Raman spectroscopy was performed under inert conditions to prevent the coordination of additional water molecules during the acquisitions of the spectra. The sample was exposed to the 532-nm laser light at 10% of its nominal power (25 mW). Regeneration took place after 32 scans, where one scan requires 5 s.

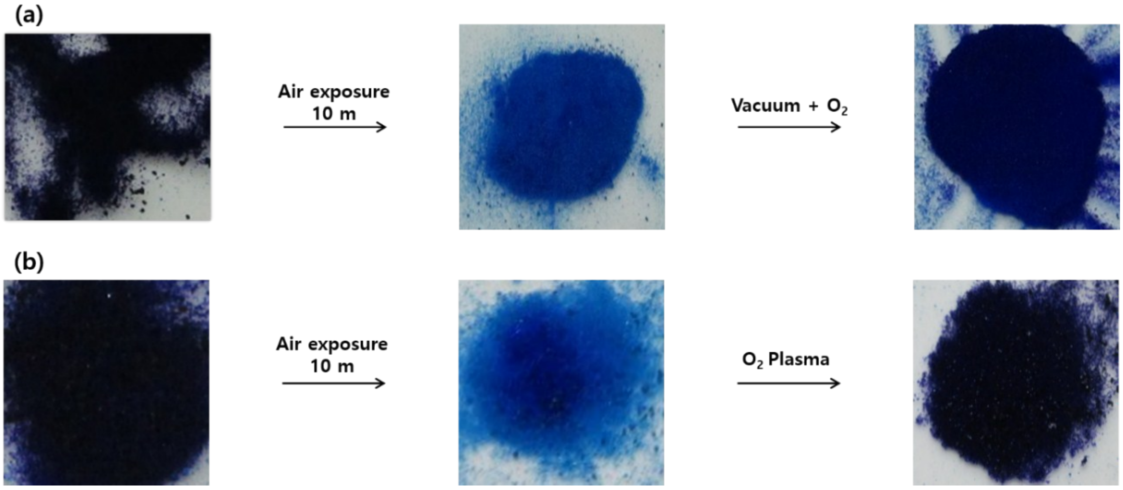

Figure S20. (a) Color change of activated HKUST-1 (left) upon air exposure (middle) and then O_2 blowing under 0.701 torr (right). (b) Color change of activated HKUST-1 (left) upon air exposure for 10 min (middle) and then O_2 Plasma treatment for 40 min (right).

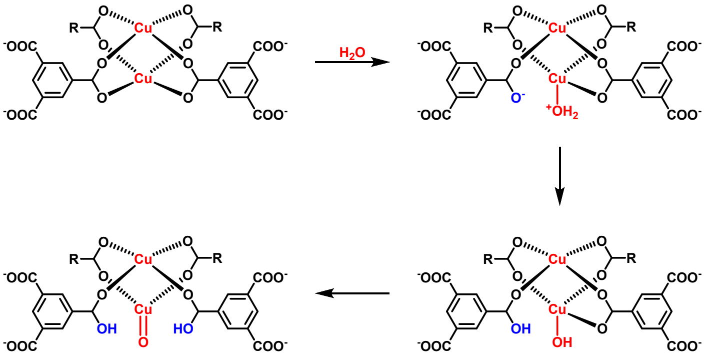

Figure S21. Proposed mechanism of the hydrolysis of Cu_2-unit in HKUST-1. (US 8633331 B2, nanocomposite materials comprising metal-organic-framework units and methods of using same)

Part S7. Preparation process of MOF-5

Terephthalic acid (5.07 g, 30.5 mmol) and triethylamine(8.5 ml) in 400 ml of DMF were sonicated to make a clean solution. Zn(acetate)$_2$·2H$_2$O (16.99 g, 77.4 mmol) in 500 ml of DMF were sonicated to make a clean solution.* The Zn(acetate)$_2$ solution was added to the terephthalic acid solution with stirring. The mixture was further stirred for 3 h to form white precipitates. The white powder was washed with DMF every 15 minutes for 10 h and then with CHCl$_3$ every 15 minutes for 10 h. The white powder was activated at 100 °C for 5 hours under vacuum (10^{-2} KPa).

*David J. Tranchemontagne, Joseph R. Hunt, Omar M. Yaghi, *Tetrahedron*, 2008, 64, 8553-8557

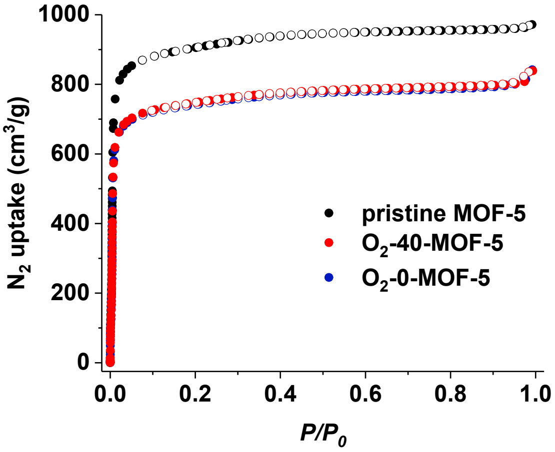

Figure S22. N$_2$ adsorption and desorption isotherms of pristine MOF-5 (black dots), and O$_2$-0-MOF-5 (blue dots) and O$_2$-40-MOF-5 (red dots) after air exposure 10 min.

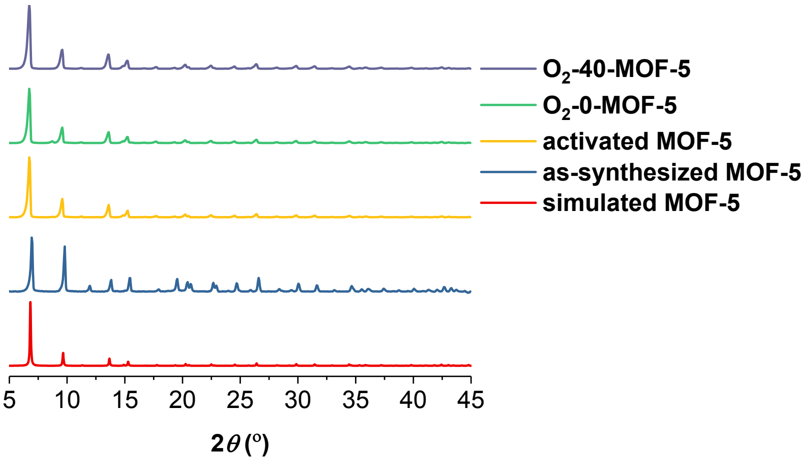

Figure S23. PXRD patterns of simulated MOF-5 (red), as-synthesized MOF-5 (blue), activated MOF-5 (yellow), and O$_2$-0-MOF-5 (green) and O$_2$-40-MOF-5 (purple) after air exposure 10 min.