**Electronic Supporting Informations (ESI):**

Dry-gel conversion synthesis of Cr-MIL-101 aided by grinding:
High surface area high yield synthesis with minimum purification

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1. Materials Syntheses

Dry-gel conversion synthesis of MIL-101: Initially, a chromium(III) nitrate nonahydrate granular precursor was ball milled (Retsch MM200) at 20 Hz for 30 min to obtain a fine powder. Subsequently, the ground Cr source was mixed with 1,4-benzenedicarboxylic acid (H₂BDC) at a molar ratio of 1:1, and ground again for 15 min. The finely ground mixture of substrates (140 mg) was placed on a holed Teflon-plate inside a 30 mL Teflon-lined stainless steel autoclave (see Scheme S1). H₂O (6.25 mL) and HF (1.0 mg, 47% aq.) were then added to the bottom of the autoclave and the entire assembly was heated at 220 °C for 12 h. After the reaction, the autoclave was quenched in cold water, and the dark green-colored and weakly agglomerated product was recovered by filtration. Finally, the product was washed 2~3 times with de-ionized water and dried at 80 °C for 12 h.

Hydrothermal synthesis of MIL-101: Chromium(III) nitrate nonahydrate (1.6 g), H₂BDC (0.64 g), HF (0.02 g, 47% aq.) and H₂O (19.2 mL) were mixed with stirring. The substrate mixture was transferred to a Teflon-lined steel autoclave and heated at 220 °C for 8 h in a convection oven. After the hydrothermal reaction, the mixture was maintained at 150 °C for 1 h, and cooled naturally to room temperature. The solid green product was filtered through 100 μm sieves to remove the crystalline BDC and then through 25 μm filter paper to separate the MIL-101 product. The separated MIL-101 product was (1) washed 2-3 times with H₂O, and purified further using the following steps: (2) soaked in H₂O at 70 °C for 12 h, (3) hot ethanol at 80 °C for 24 h, (4) an aqueous 0.03 M NH₄F solution at 60 °C for 12 h, (5) hot H₂O at 60 °C for 12 h, and dried in a vacuum at 150 °C for 12 h after filtration.

Dry-gel conversion synthesis of MIL-101-NO₂: Ball-mill ground chromium(III) chloride (67 mg) and 2-nitrobenzene-1,4-dicarboxylic acid (H₂BDC-NO₂, 53 mg) were well mixed and placed over a Teflon-plate located at the inside top position of a Teflon-lined stainless steel autoclave via a vertical Teflon column. H₂O (6.25 mL) was introduced at the bottom of the autoclave and the whole unit was heated at 180 °C for 96 h. The product was washed with de-ionized water for 2~3 times, and dried at 60 °C for 12 h in air after filtration.
Dry-gel conversion synthesis of MIL-101/PTA: H$_2$BDC (40 mg), chromium(III) nitrate nonahydrate (100 mg), and phosphotungstic acid (PTA, 100 mg) were ground and placed over a Teflon-plate located at the inside top position of a Teflon-lined stainless steel autoclave via a vertical Teflon column. H$_2$O (6.25 mL) was added to the bottom of the autoclave and heated at 220 °C for 18 h. The product was washed with de-ionized water for 2~3 times, and dried at 60 °C for 12 h in air after filtration.

2. Characterizations

X-ray powder diffraction (XRD) of the MIL-101 samples was performed on a Rigaku diffractometer using CuK$\alpha$ ($\lambda$= 1.54 Å) radiation at 0.5 °/min. N$_2$ adsorption and desorption isotherms were measured in a BELsorp-Max (BEL, JAPAN) at liquid nitrogen temperature. Before the adsorption measurements, the samples were activated at 150 °C for 12 h in a vacuum. The BET surface areas of the samples were calculated over the range of 0.05<P/P$_0$<0.15 (the corresponding correlation coefficients were typically >0.997) [1,2]. The thermal stability of the samples was examined by thermogravimetric analysis (TGA, SCINCO thermal gravimeter S-1000) For TGA, 10 mg of each sample was heated from room temperature to 600 °C at 5 °C/min under a N$_2$ flow. The FTIR spectra were obtained on a VERTEX 80V FT-IR spectrometer (Bruker) at ambient temperature. The morphological features were examined by scanning electron microscopy (SEM, Hitachi S-4300).

3. CO$_2$ adsorption measurement

High-pressure CO$_2$ adsorption measurements were carried out using a magnetic suspension balance (Rubotherm, Germany) with in-situ density measurements in a closed system. The samples were initially activated at 150 °C overnight. Before measuring the CO$_2$ adsorption capacity, the buoyancy effect was corrected in ultra-high-purity He (99.999%). High-pressure adsorption was carried out using ultra-high-purity CO$_2$ (99.999%) in a pressure range of 0-40 bar at 25 °C.

Table S1 BET surface areas of the MIL-101 samples after various purification steps

<table>
<thead>
<tr>
<th>Purification step</th>
<th>BET surface area (m²/g)</th>
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<tbody>
<tr>
<td></td>
<td>HTS-MIL-101</td>
</tr>
<tr>
<td>1. DF + H₂O washing</td>
<td>1924</td>
</tr>
<tr>
<td>2. hot H₂O (70 °C, 12 h)</td>
<td>2168</td>
</tr>
<tr>
<td>3. hot EtOH (80 °C, 24 h)</td>
<td>2534</td>
</tr>
<tr>
<td>4. 0.03 M NH₄F (60 °C, 12 h)</td>
<td>3268</td>
</tr>
<tr>
<td>5. hot H₂O (60 °C, 12 h)</td>
<td>3482</td>
</tr>
</tbody>
</table>

* DF=double filtration using 100 µm sieves and 25 µm filter paper.
Scheme S1 Schematic diagram of the reactor (left) and the holed-Teflon plate (left-bottom) for the dry-gel conversion synthesis of MIL-101, and water P-V phase diagram (right).
Fig. S1 Photographs of dry-gel conversion synthesis reactor and substrate mixture (a) before and (b) after reaction at 220 °C for 12 h.
Fig. S2 XRD patterns of the substrates for MIL-101 synthesis; (a) unground H$_2$BDC, (b) unground Cr salt (Cr(NO$_3$)$_3$•9H$_2$O), (c) Cr salt and H$_2$BDC ground together in a single step, (d) large grain Cr salt ground initially by ball milling, followed by repeated grinding after mixing the ground Cr salt with H$_2$BDC, (e) rehydrated sample (d) using excess amount of H$_2$O for 10 min, and (f) sample (d) kept in moist air for 24 h. The XRD intensities in (a) and (e) were reduced by 70%.
Fig. S3 (A) SEM images and (B) IR spectra of the H$_2$BDC before/after ball-mill grinding.
Fig. S4 (a) MIL-101 prepared using the hydrothermal synthesis method and the expanded images of the circled section in (a), and by dry-gel conversion synthesis method using a different substrate ratio: (b) Cr:H$_2$BDC=1:1 and (c) Cr:H$_2$BDC=1:1.2.
**Fig. S5** (A) XRD patterns and (B) IR spectra of the HTS-MIL-101 samples before/after purifications and DGC-MIL-101.
Fig. S6 (A) XRD patterns and (B) SEM images of DGC-MIL-101 samples synthesized with different amount of HF.
Fig. S7 (A) XRD patterns and (B) N\textsubscript{2}-adsorption-desorption isotherms of DGC-MIL-101 obtained at different synthesis time.
**Fig. S8** CO$_2$ adsorption isotherms of (a) DGC-MIL-101(4164), (b) HTS-MIL-101(3482), and (c) DGC-MIL-101(2690). Numbers inside the bracket designate the BET surface areas.
Fig. S9 XRD patterns of functionalized MIL-101 samples prepared by DGC method.
**Fig. S10** FT-IR spectrum of MIL-101-NO$_2$ synthesized by DGC method.
Fig. S11 SEM-EDX analysis of MIL-101/PTA synthesized by DGC method.