

Supporting Information

Combustion synthesis of Cr_2O_3 octahedrons with a chromium-containing metal-organic framework as a sacrificial template

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References

S1 - Experimental details: MIL-101 synthesis, Cr(NO₃)₃-glycine confinement, combustion and Cr₂O₃ characterization.

MIL-101 was prepared according to a previously reported method.¹ Briefly, 18g Cr(NO₃)₃·9H₂O, 7.38 g 1,4-benzene dicarboxylic acid and 1 ml HF were dissolved in 216 ml H₂O, and then the mixture was heated in a hydrothermal bomb at 220°C for 8h. The as-prepared MIL-101 was washed several times by hot ethanol and was then immersed in 30 mM NH₄F solution overnight at 60 °C to remove terephthalic acid, which is generally present within the pores of MIL-101.²

To confine the Cr(NO₃)₃-glycine mixture, 2 g of outgassed MIL-101 was suspended in 5 ml H₂O containing 2 g of dissolved Cr(NO₃)₃·9H₂O and 0.62 g of glycine overnight. In all experiments, the Cr(NO₃)₃/glycine (1:1.67 molar ratio) stoichiometric ratio was used. Then, the mixture was heated at 80 °C under static vacuum for 4 hours to complete impregnation. The obtained dark green gel was transferred onto a hot plate and was heated at 150 °C in air to initiate combustion reaction. After the reaction, the final powder was collected for further characterization.

For comparison, a pyrolysis of MIL-101 was conducted at 600 and 400 °C with a heating rate of 2 °C min⁻¹ for 6 and 1 h in air, respectively.

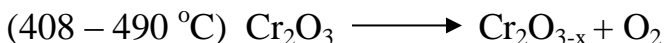
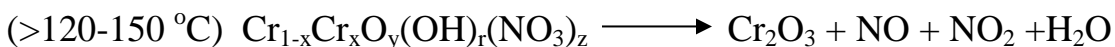
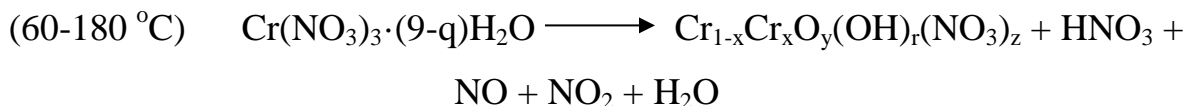
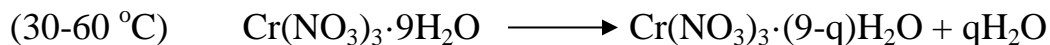
Characterization

K-type thermocouples with 0.1 mm diameter were used to monitor the temperature-time history of the combustion process. The outlet signals of the thermocouples were passed to a computer using a multichannel data acquisition line (Data Translation Inc.) with a monitoring frequency of 1 kHz using Quick

DAC software. At least three measurements were performed to obtain the combustion data. Thermal gravimetric analysis (TGA) was performed under 20ml/min gas flow with a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was performed under 20ml/min air flow at a heating rate of 10 °C/min. The compositions of as-synthesized powders were determined using powder X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation at 40 kV and 40 mA (D8 Advance, Bruker). The powder microstructures were imaged using scanning electron microscopy (SEM) (Hitachi S-4800 with an accelerating voltage of 7kV) equipped with an energy dispersive X-ray spectrometer (EDS). Transmission electron microscopy (TEM) and selected area diffraction (SAED) studies were conducted to characterize the structure and composition of the reaction products (Phillips THECNAI 20 with an accelerating voltage of 200kV). A Micromeritics ASAP 2020 analyzer was used to carry out the Brunauer-Emmet-Teller (BET) surface areas and Barrett-Joyner-Halenda (BJH) pore size distributions of oxides using nitrogen as the adsorbent gas at 77K. Oxide powders were degassed at 473K overnight under the vacuum before the analysis.

S2 – Decomposition reaction mechanism of chromium nitrate

The steps in the decomposition reaction mechanism of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ have been proposed in the literature as follows.³



After initial loss of water of crystallization at low temperature, further water release from $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ salt is accompanied with nitrate decomposition at different steps at higher temperature. At temperature above 400°C , further removal of oxygen from Cr_2O_3 lattice can take place.

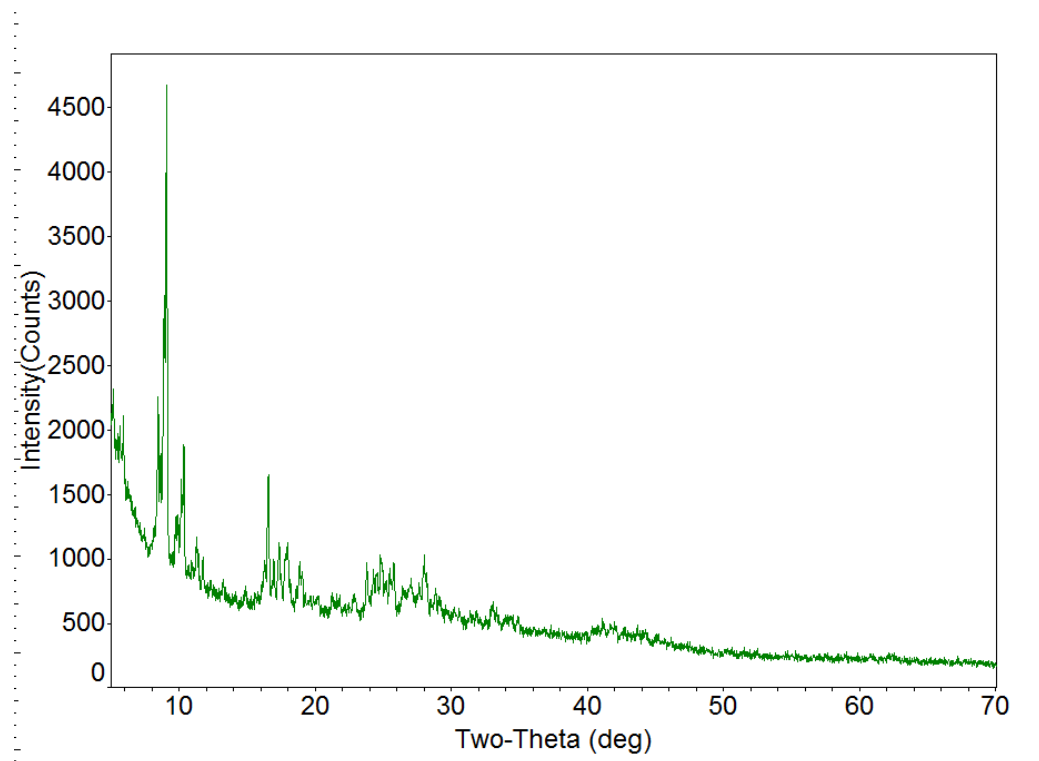


Figure S1. XRD pattern of MIL-101.

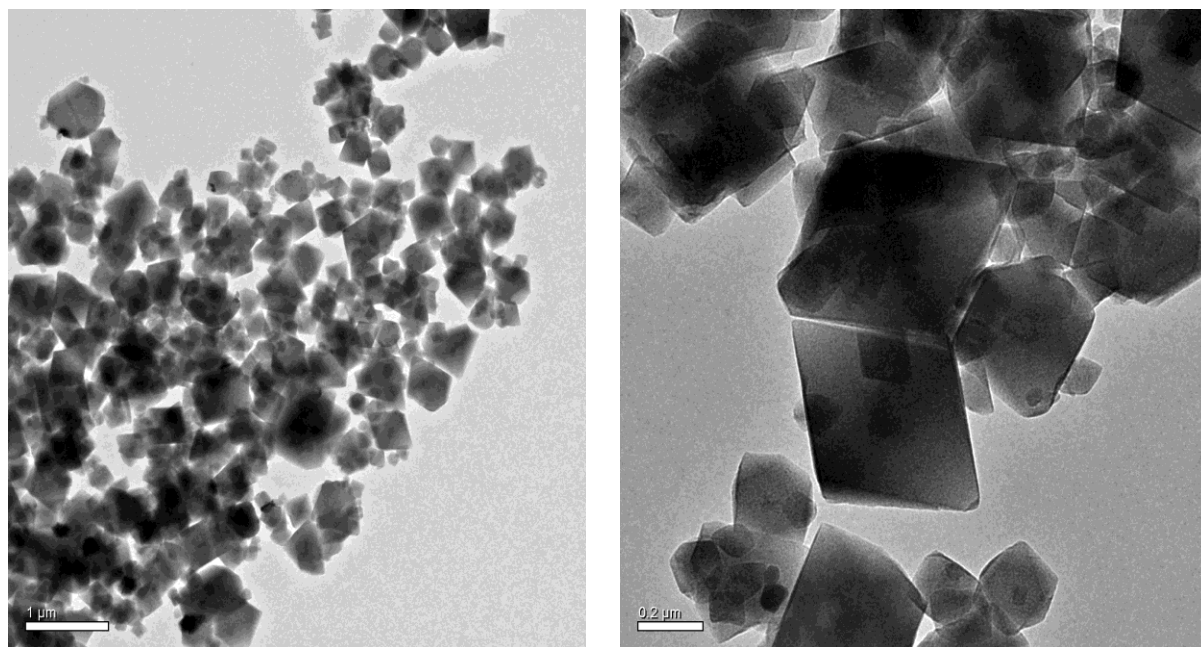


Figure S2. TEM images of MIL-101.

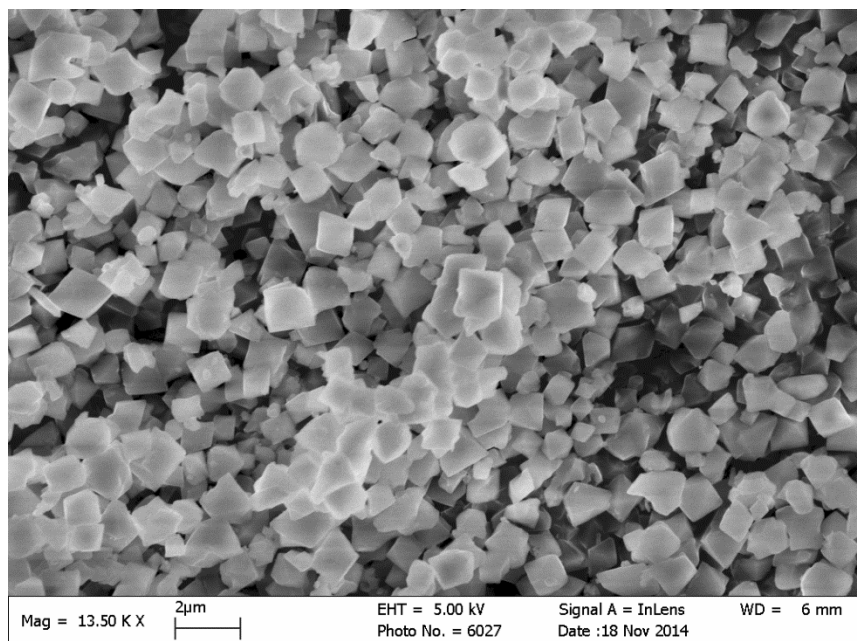


Figure S3. SEM image of MIL-101.

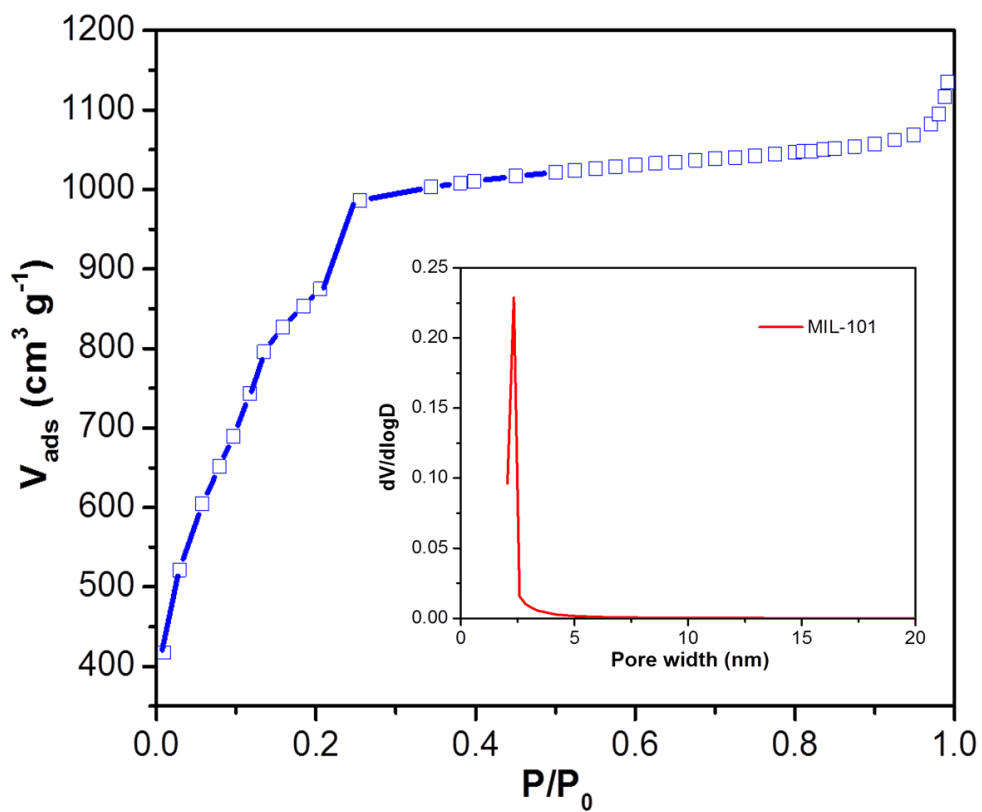


Figure S4. N_2 sorption isotherm at 77K for MIL-101(inset: pore size distribution).

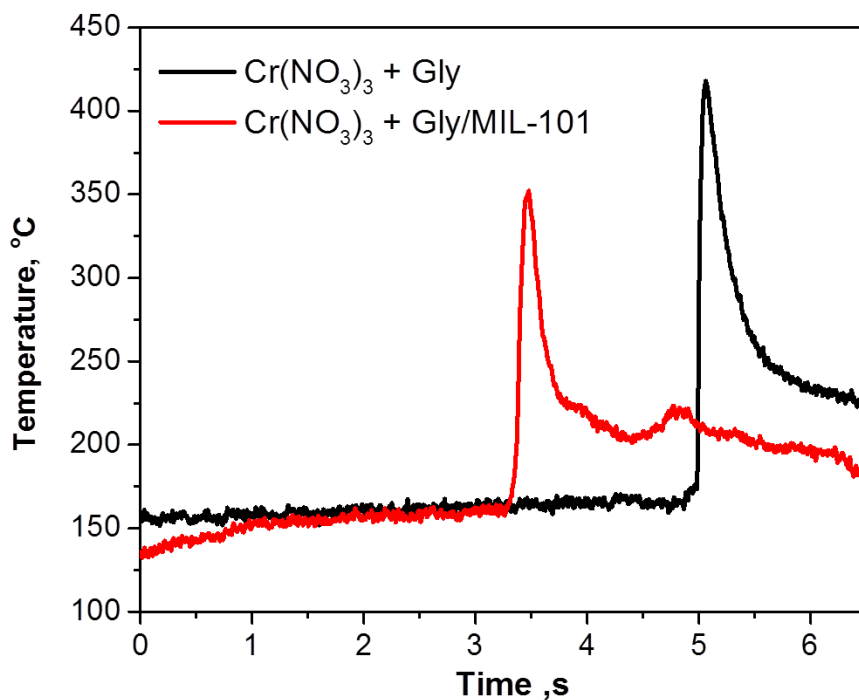


Figure S5. Temperature-time profiles for $\text{Cr}(\text{NO}_3)_3$ -glycine and $\text{Cr}(\text{NO}_3)_3$ -glycine/MIL-101.

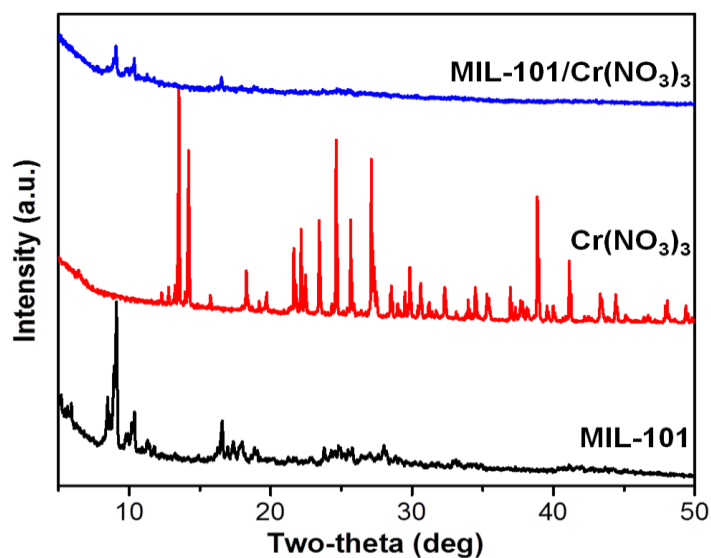


Figure S6. XRD patterns of MIL-101, $\text{Cr}(\text{NO}_3)_3$ and MIL-101 impregnated with $\text{Cr}(\text{NO}_3)_3$ and dried in air, MIL-101/ $\text{Cr}(\text{NO}_3)_3$.

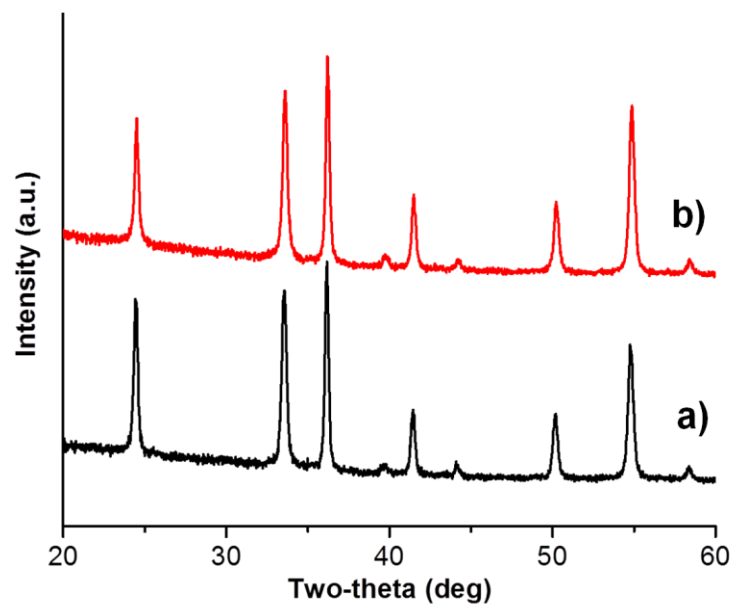


Figure S7. XRD pattern of prepared Cr₂O₃ by combustion synthesis a) without MOF template b) with MOF template.

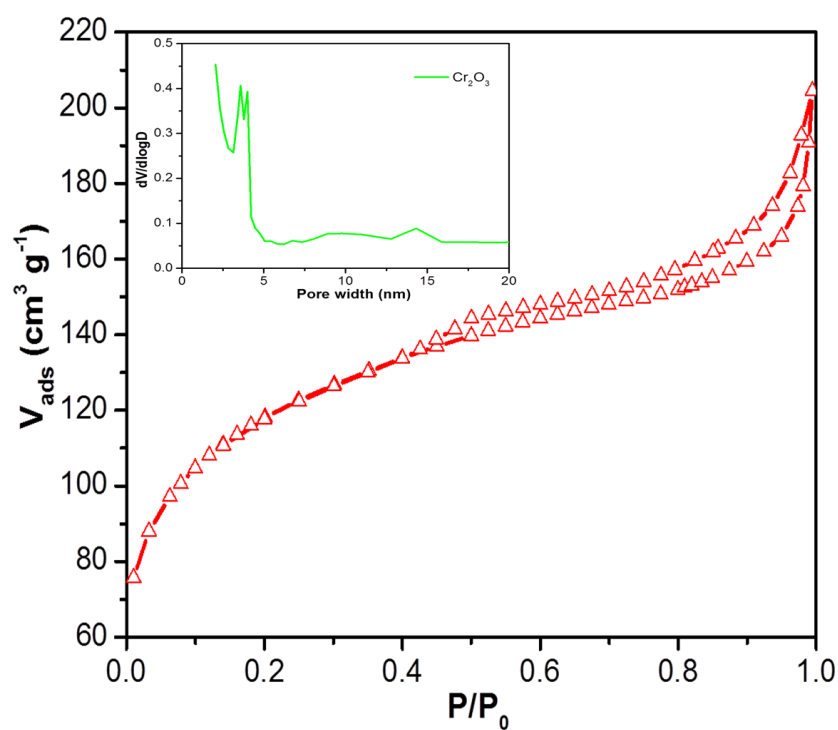


Figure S8. N₂ sorption isotherm at 77K for Cr₂O₃ octahedrons (inset: pore size distribution).

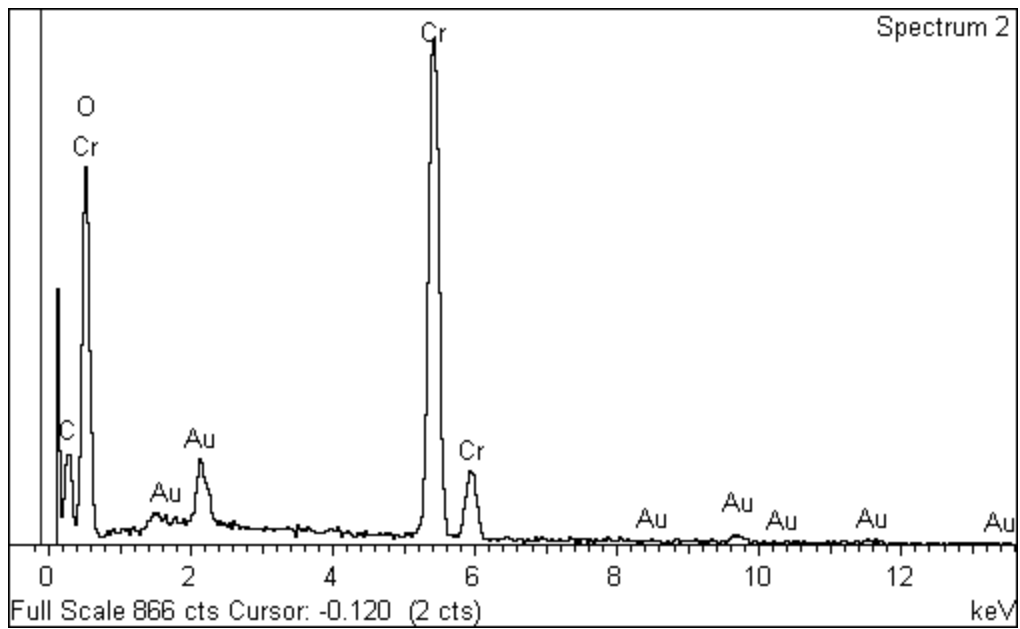
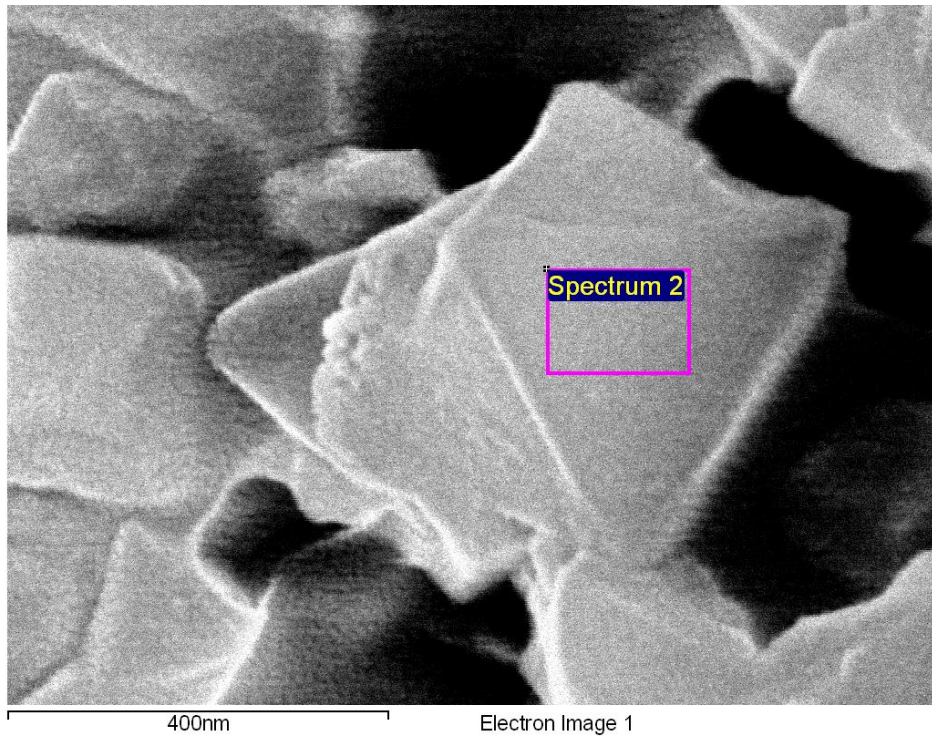


Figure S9. SEM images and EDX of the gold coated Cr₂O₃ octahedrons.

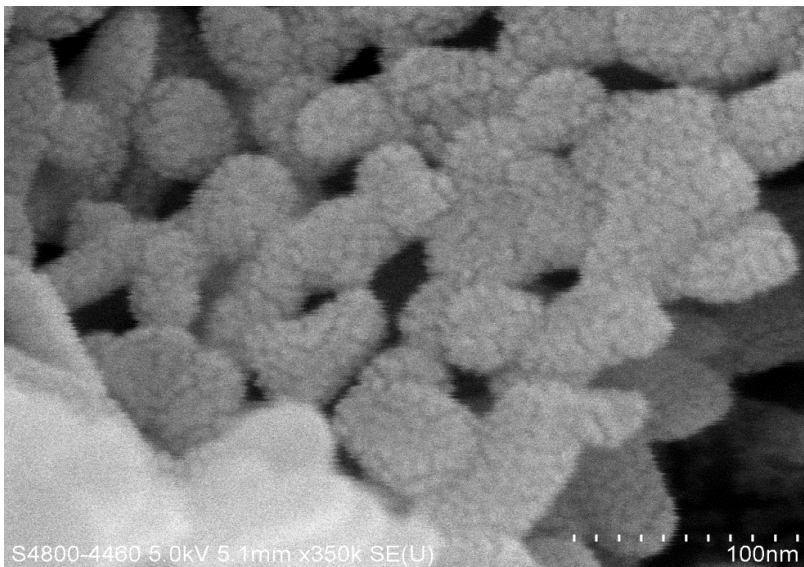
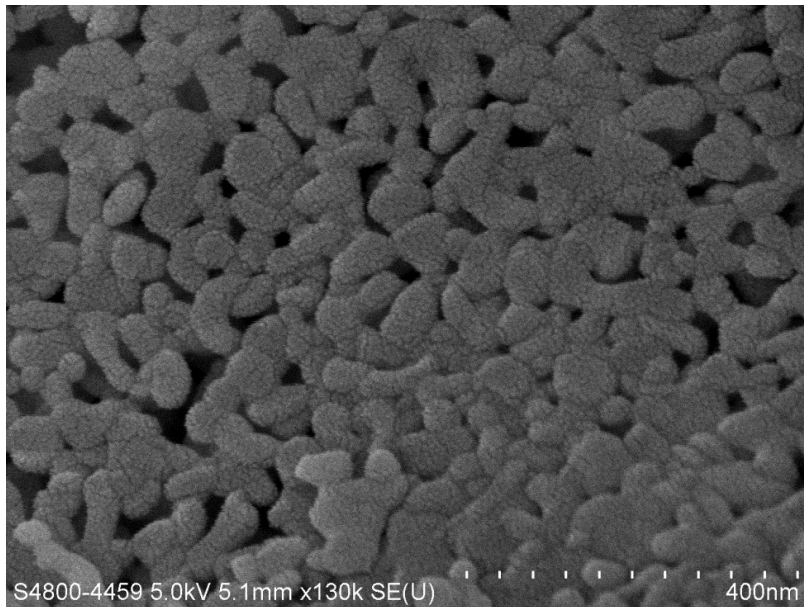


Figure S10. SEM images of Cr_2O_3 synthesized without MIL-101 template.

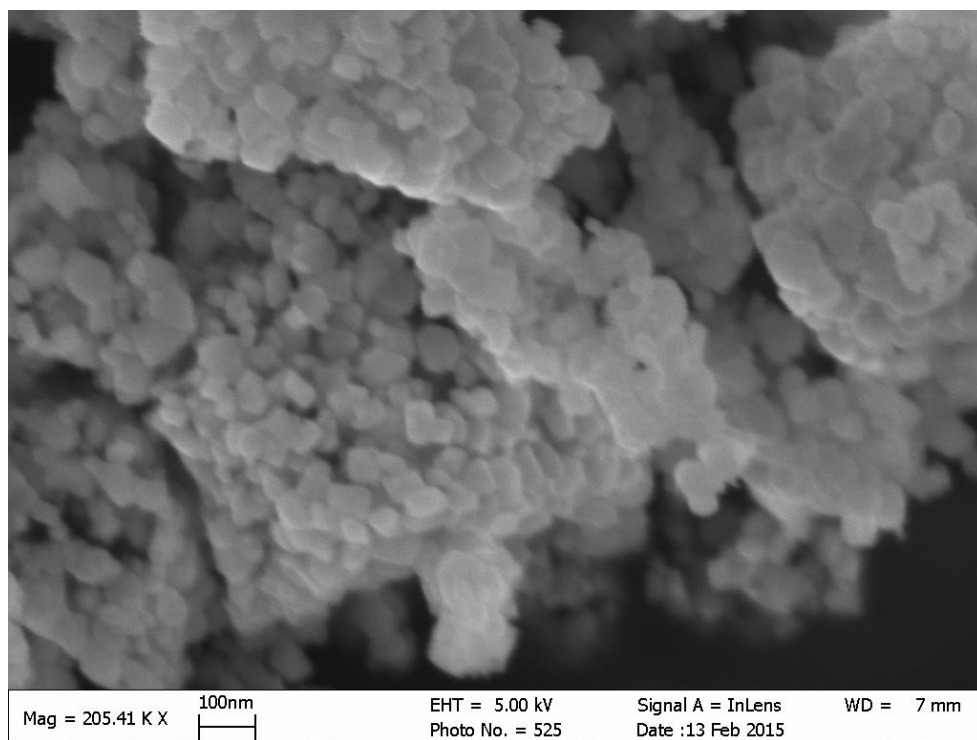
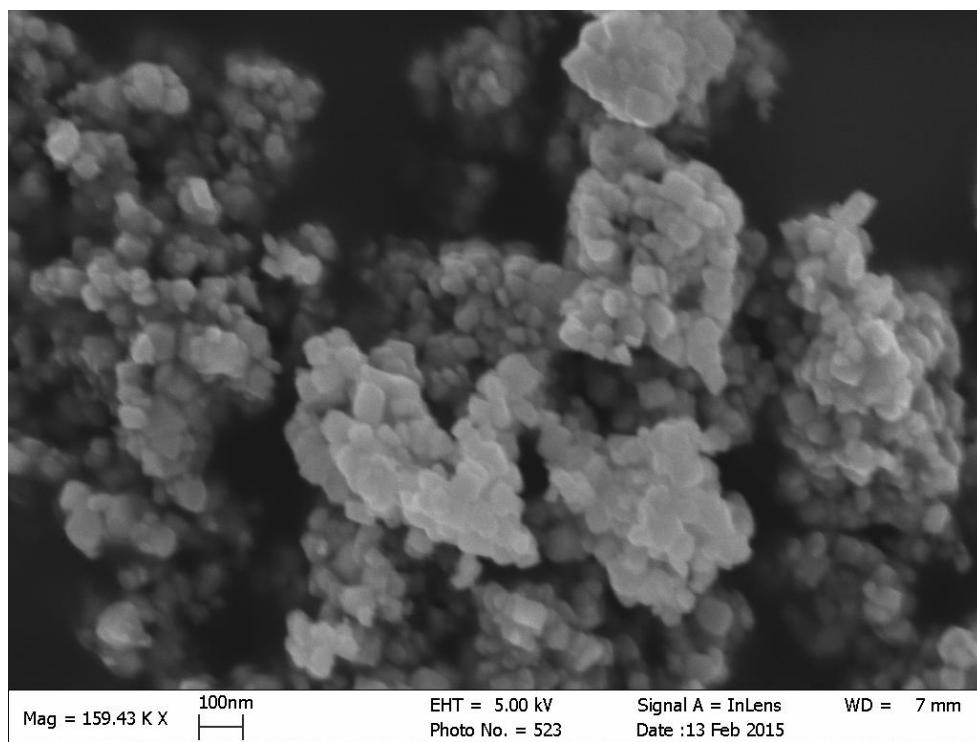


Figure S11. SEM image of Cr_2O_3 synthesized by pyrolysis of MIL-101 at 400 °C in air.

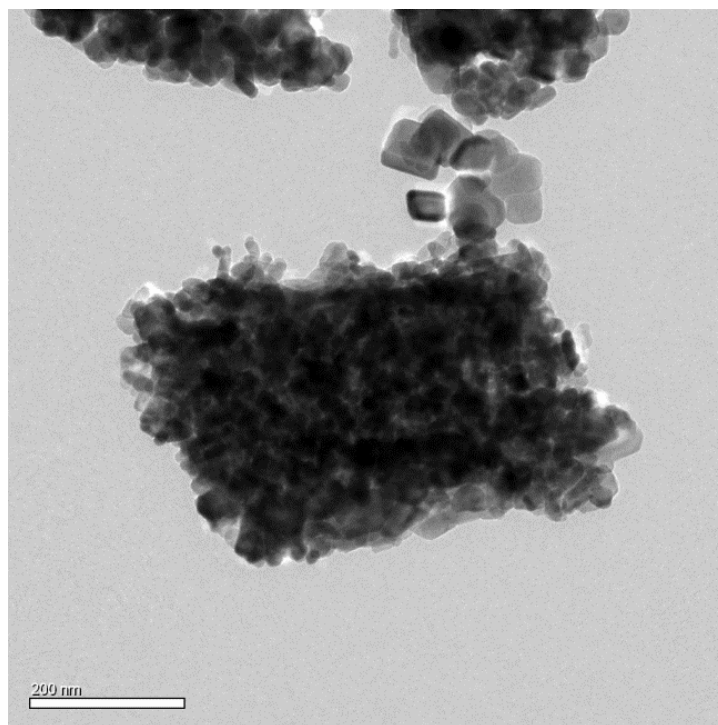
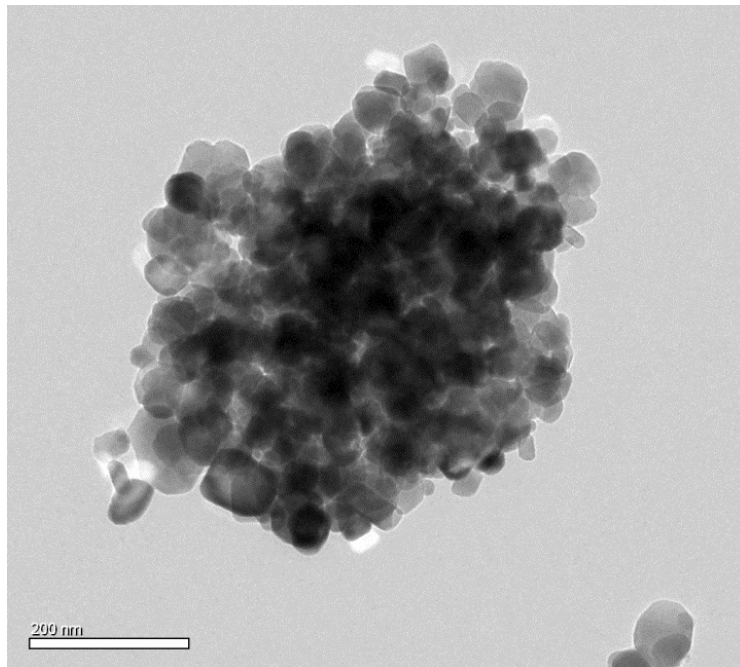


Figure S12. TEM images of Cr_2O_3 synthesized by pyrolysis of MIL-101 at 600°C in air.

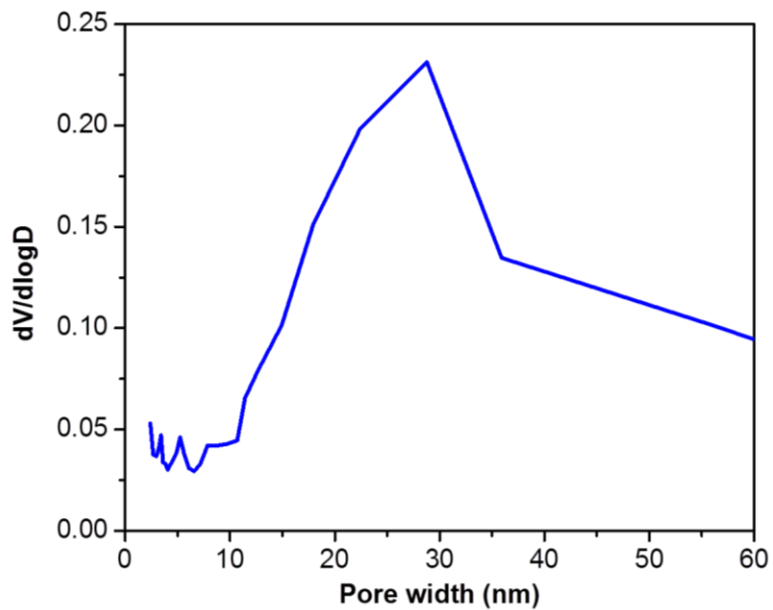
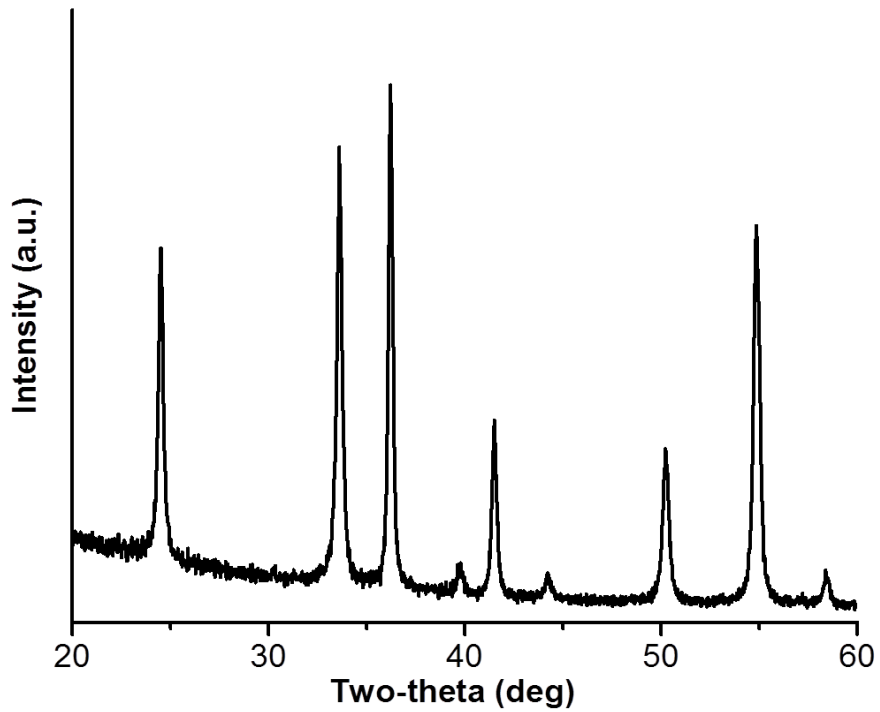


Figure S13. XRD pattern and BJH pore size distribution of Cr_2O_3 synthesized by pyrolysis of MIL-101 at 600°C in air.

References

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3. L. Li, Z.F. Yan, G.Q. Lu, Z.H. Zhu, *J. Phys. Chem. B* **2006**, 110, 178-183.