Direct Synthesis of Amine-Functionalized MIL-101(Cr) Nanoparticles and Application to CO_2 Capture

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Supporting Information:

Experimental Details, Powder X-ray Diffraction patterns, scanning electron microscope images, transmission electron microscope, element analysis, N_2 adsorption-desorption isotherms, X-ray photoelectron spectroscopy analysis, CO_2 and CH_4 adsorption isotherms, Thermogravimetric and differential thermal analysis, and Isosteric heat calculation details.

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1. Experimental details

1.1 Synthesis of amine-functionalized metal-organic framework

Chromic nitrate hydrate (800 mg, 2 mmol), 2-aminoterephthalic acid (360 mg, 2 mmol) and sodium hydroxide (200 mg, 5 mmol) were dispersed in deionized water (15 ml) and stirred for 5 minutes, then the reaction solution was transferred to a 50 ml Teflon-lined stainless steel autoclave and kept at 150 ℃ for 6~16 h. The optimized sample was synthesized for 12 h. The autoclave was then left to cool down to room temperature. The green precipitate was collected by centrifugation, and washed with DMF at room temperature to remove the most unreacted 2-aminoterephthalic acid, and then the products were further washed with hot alcohol at 100 ℃ for 24 h in an autoclave to remove unreacted 2-aminoterephthalic acid in the pores of the products. Finally, the products were dried at 80 ℃ in air. To detect the effect of OH^- ions in the synthesis solution, sodium chloride and potassium hydroxide was use to replace the sodium hydroxide for amine-functionalized metal-organic framework synthesis. It was found that the unreacted starting materials were observed by adding sodium chloride. The product of the synthesis solution with additional KOH was also amine-functionalized MIL-101(Cr) with the similar morphology and BET surface area (Fig. S17 and S22).

1.2 Synthesis of bulk MIL-101

Chromic nitrate hydrate (800 mg, 2 mmol), terephthalic acid (280 mg, 2 mmol) and HF (164 uL, 2 mmol) were dispersed in deionized water (10 mL), which were heated for 16 h in 220 ºC under hydrothermal conditions. To eliminate the unreacted carboxylic acid, the product was filtered first using a large pore paper filter and was recovered by centrifugation. Finally the MIL-101 product was washed with hot ethanol solution for 12 h, and dried at 80 ºC in air.

1.3 Nitrogen adsorption-desorption isotherm

The nitrogen adsorption-desorption isotherm was measured on ASAP 2020M apparatus at 77.3 K. In a general procedure, the dry sample (~200 mg) was loaded into the glass analysis tube. Then fix the glass tube to the degas port to be heated and evacuated, including two stages, initially to 90 ℃ at 10 ℃·min^{-1} and hold the temperature for 30 min then to 150 ℃ for 8 h. After this, the outgas rate was less than 5 μmHg. The sample was then backfilled with N_2 before transfered to the analysis port. Before analysis, the sample was evacuated for 300 min. Finally, N_2 adsorption-desorption isotherm was measured at 77.3 K and the range of relative pressures between 0 and 1**.** The BET surface area was calculated over the range of relative pressures between 0.05 and 0.20.

1.4 Elemental analysis

The element analysis for the products was taken on a CHNS/O Elemental Analyzer, model PE2400 (II). Before the measurement, the samples were outgassed at 200 ºC for 12 h.

1.5 Fourier Transform Infrared Spectroscope

Infrared spectra were recorded on KBr/NMOF pellets in a Thermo model Nicolet 6700 spectrometer. Before collecting the spectra, the sample was pretreated under vacuum at a temperature of 150 ℃ for 12 h.

1.6 X-ray photoelectron spectroscopy

The chemical composition and bonding states were measured by XPS using a Kratos AXIS ULTRA^{DLD} instrument with a monochromic Al-Kα X-ray source (hν=1486.6 eV). The power was 120 W and the X-ray spot size was set to 700×300 μm. The pass energy of the XPS analyzer was set at 20 eV. The base pressure of the analysis chamber was better than 5×10^{-9} Torr. All spectra were calibrated using the binding energy (BE) of C 1s (284.8 eV) as a reference.

1.7 Powder X-ray Diffraction

XRD data of the products were collected on a Bruker AXS D8 Advance diffractometer using CuKα (λ= 1.5406 Å) radiation at a voltage of 40 kV and 40 mA. The powder diffraction pattern was scanned over the angular range of 1-25° (2θ) with a step size of 0.02°.

1.8 Adsorption measurement

The adsorption isotherms of the probe gas CO_2 (purity of 99.999), N_2 (purity of

99.999) and CH_4 (purity of 99.99) were measured using volumetric technique by an apparatus from SETARAM France (PCTpro-E&E). Before each measurement, the sample was evacuated at 150 ℃ for 12 h. The adsorbed amounts (Q_i) were calculated by the volumetric method. The ideal selectivity (α) of the sample was defined as: α (A/B)= Q_A/Q_B, where Q_A is the adsorption uptake for gas A, and Q_B is the adsorption uptake for gas B.

1.9 Morphology tests

The as-prepared particle morphology was examined using a field emission scanning electron microscope (Hitachi, S-4800) and a transmission electron microscope (Tecnai F20).

1.10 Thermogravimetric and differential thermal analysis

Thermal stability was measured using a system provided by Mettler Toledo (model Pyris Diamond TG/DTA) in air at a heat rate of 5 ℃ / min up to 800 ℃.

2. Additional Figures

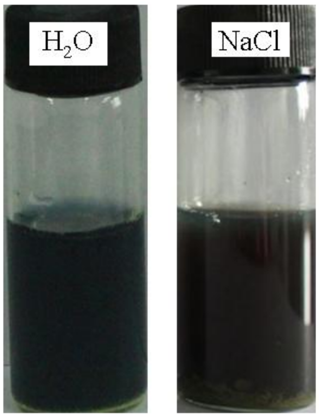

Fig. S1 The products of reactions of chromic nitrate and 2-aminoterephthalic acid in aqueous solution and NaCl-assisted aqueous solution at 150 ℃ for 12 h.

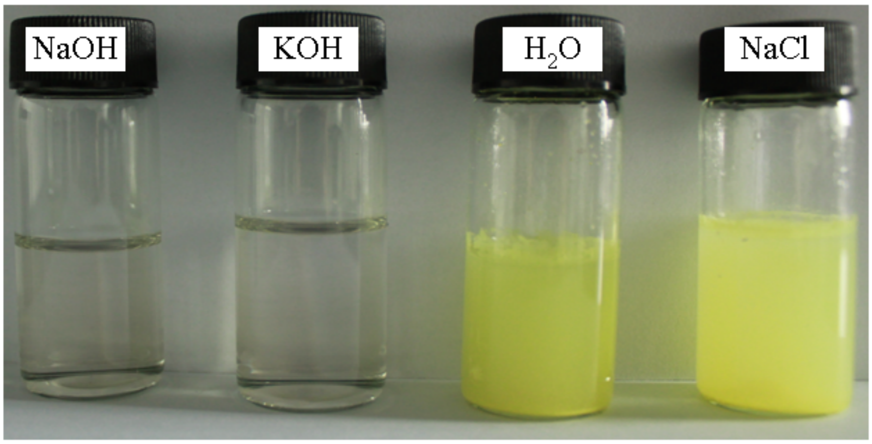

Fig. S2 The dissolution of 2-aminoterephthalic acid in NaOH, KOH, H_2O and NaCl aqueous solution.

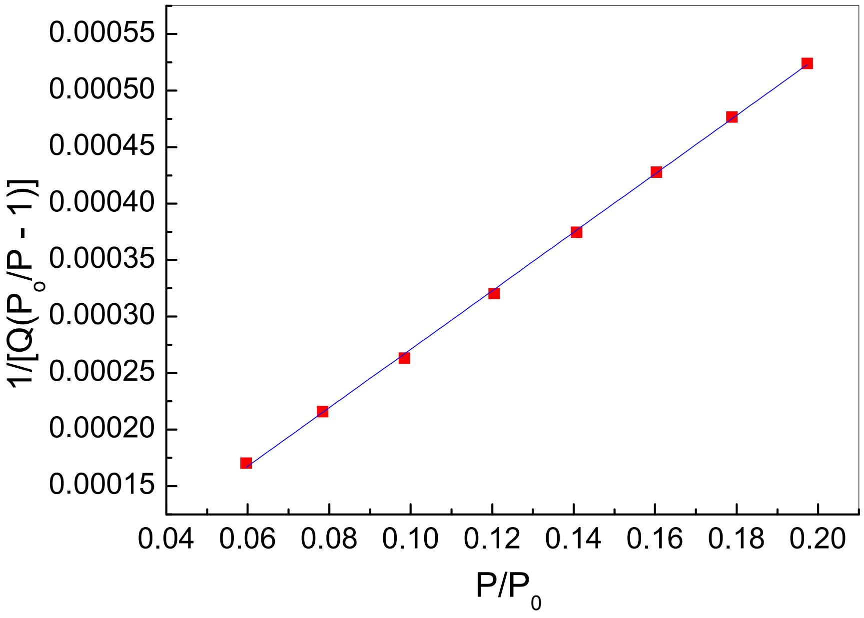

Fig. S3 The BET plot for the product synthesized for 12 h.

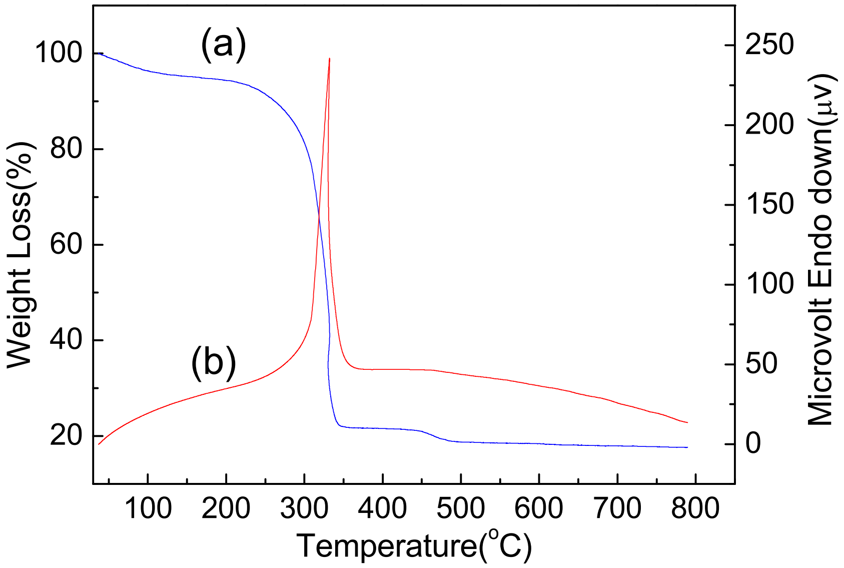

Fig. S4 The thermogravimetric (a) and differential thermal analysis (b) spectra of the resulting powders. The sharp endothermic peak 320 ℃ was due to the rapid decomposition of the resulting powders. Thermogravimetric curve showed the start decomposition temperature was about 270 ℃.

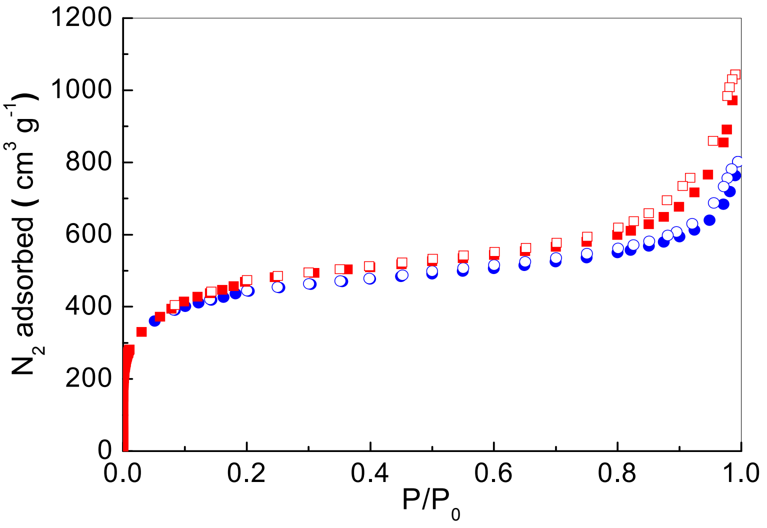

Fig. S5 N_2 adsorption-desorption isotherms at 77.3 K after exposing the samples for 1 days (square) and 15 days (circle) in air. Filled shapes: adsorption; open shapes: desorption. The calculated Brunauer-Emmett-Teller (BET) surface areas are 1675 $m^2 \cdot g^{-1}$ and 1569 $m^2 \cdot g^{-1}$ respectively. The slightly decreased BET surface area indicated the moisture-resistant stability of the sample is well.

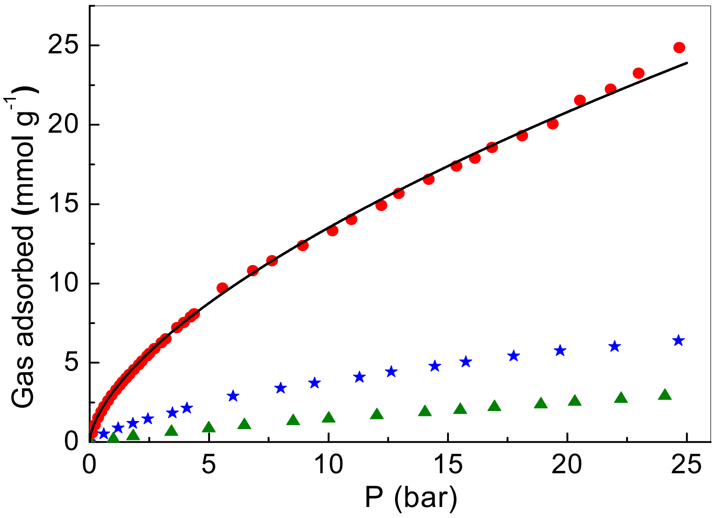

Fig. S6 Adsorption isotherms for the product prepared at 150 □ for 12 h. Key: ● CO_2 at 0.4 □, ★ CH_4 at 0.4 □, ▲ N_2 at 0.4 □. Line: fitted isotherm for CO_2 using Langmuir-Freundlich model.

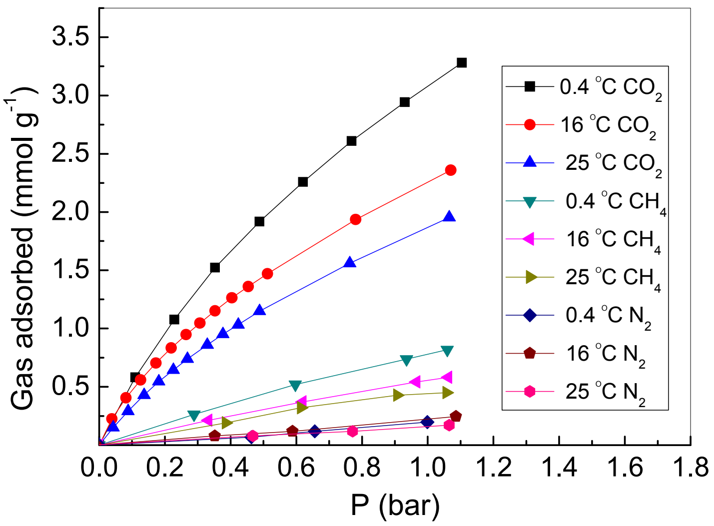

Fig. S7 CO_2, N_2 and CH_4 capture ability of the amine-functionalized MIL-101 at low pressure.

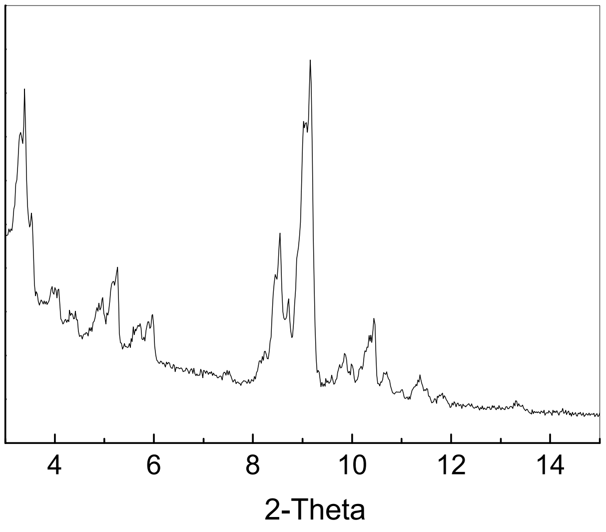

Fig. S8 The Powder XRD pattern of the synthesized MIL-101.

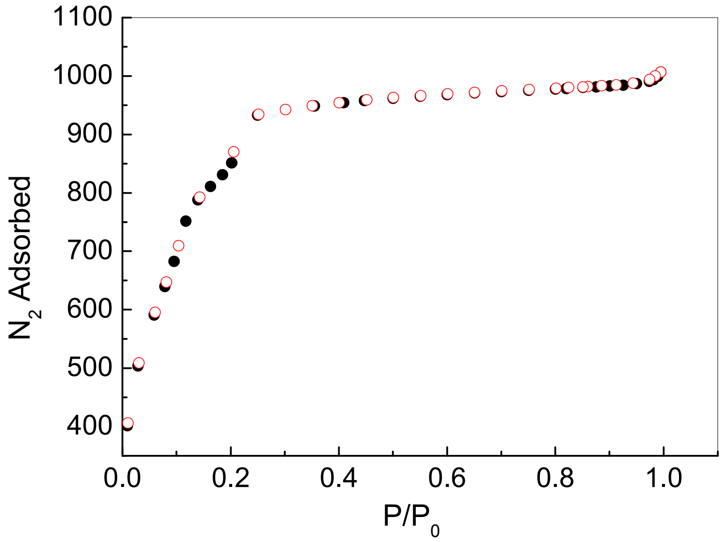

Fig. S9 N_2 adsorption-desorption isotherm at 77.3 K for the original MIL-101. The calculated BET surface is 3200 m^2 g^{-1}, which is similar to that most often reported[1].

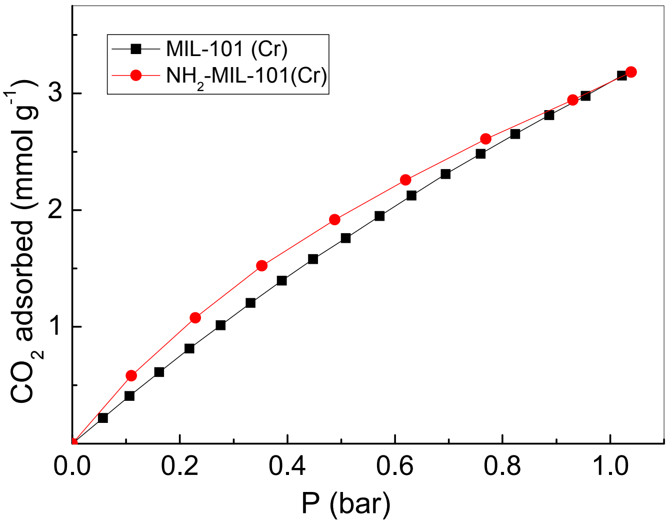

Fig. S10 CO_2 adsorption isotherms for MIL-101 and amine-functionalized MIL-101 at 0.4 □.

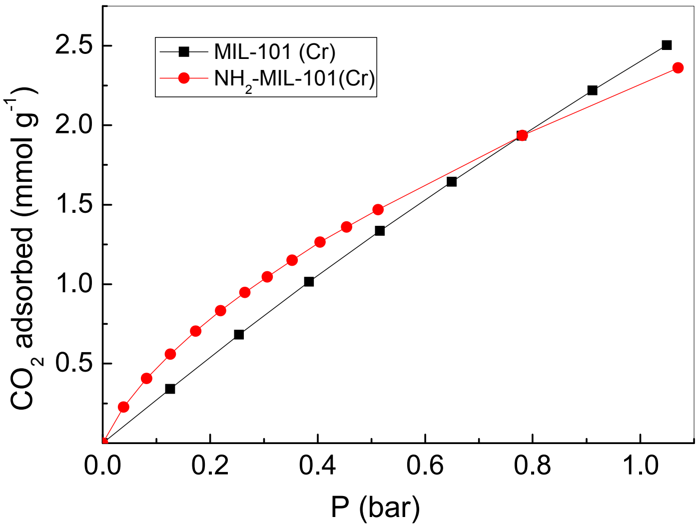

Fig. S11 CO$_2$ adsorption isotherms for MIL-101 and amine-functionalized MIL-101 at 16 □.

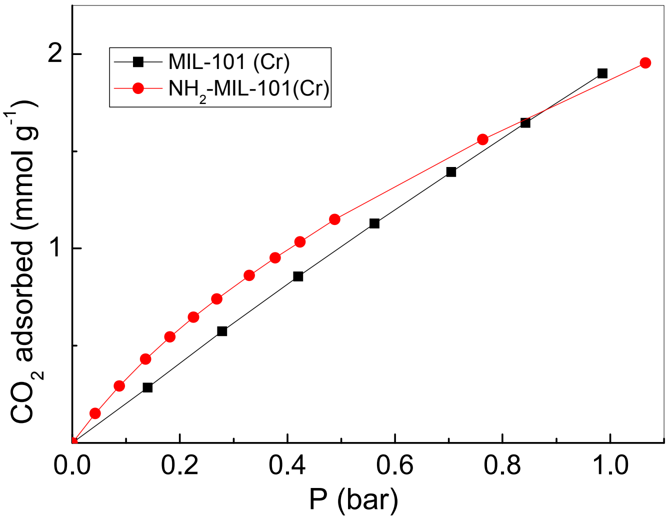

Fig. S12 CO$_2$ adsorption isotherms for MIL-101 and amine-functionalized MIL-101 at 25 □.

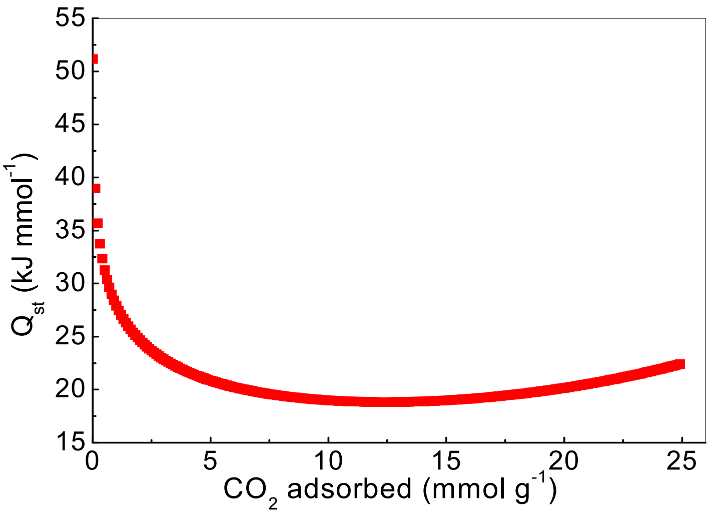

Fig. S13 The isosteric heat of the CO_2 adsorption calculated from the adsorption isothermals measured at 16 ℃ and 25 ℃.

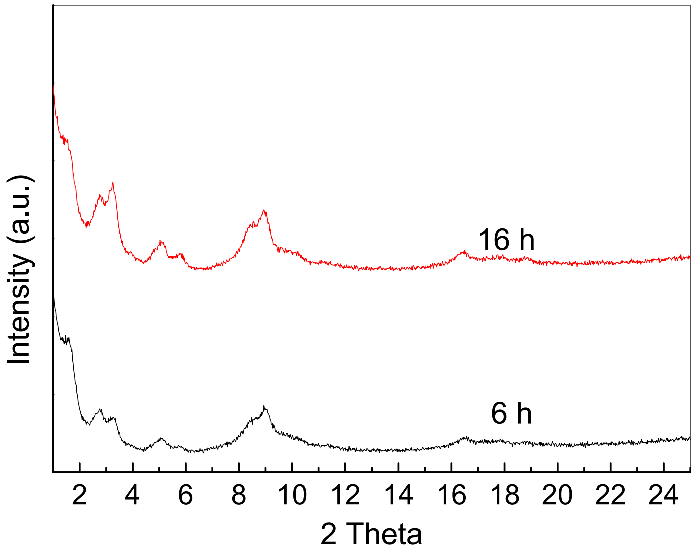

Fig. S14 Powder X-ray diffraction patterns of the products synthesized at 150□ for 6 h and 16 h. They are similar to the pattern for the product synthesized at 150□ for 12 h.

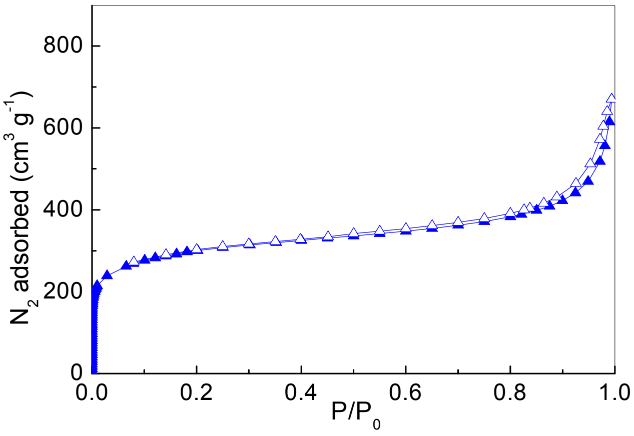

Fig. S15 (a) N_2 adsorption-desorption isotherm at 77.3 K for the product prepared at 150 ℃ for 6 h, The calculated BET surface area is 1040 m^2 g^{-1}.

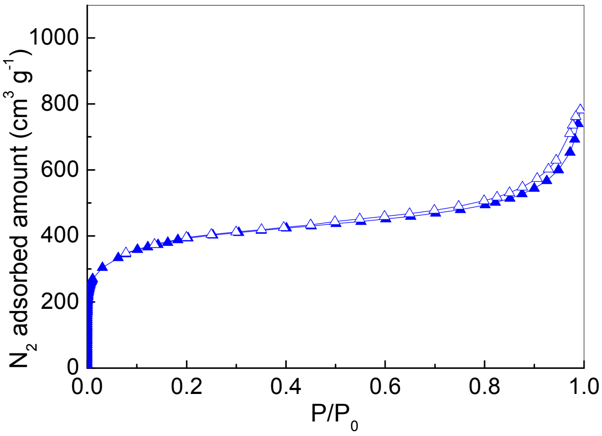

Fig. S16 (a) N_2 adsorption-desorption isotherm at 77.3 K for the product prepared at 150 ℃ for 16 h, The calculated BET surface area is 1371 m^2 g^{-1}.

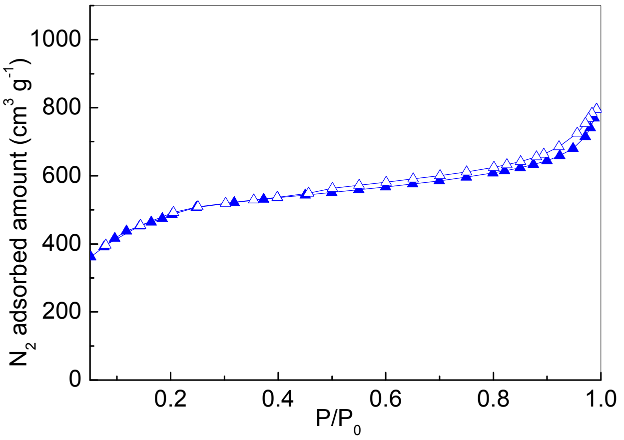

Fig. S17 N_2 adsorption-desorption isotherm at 77.3 K for the product prepared by KOH at 150 ℃ for 12 h. The calculated BET surface area is 1755 m^2 g^{-1}, which is similar to that of the product prepared by NaOH.

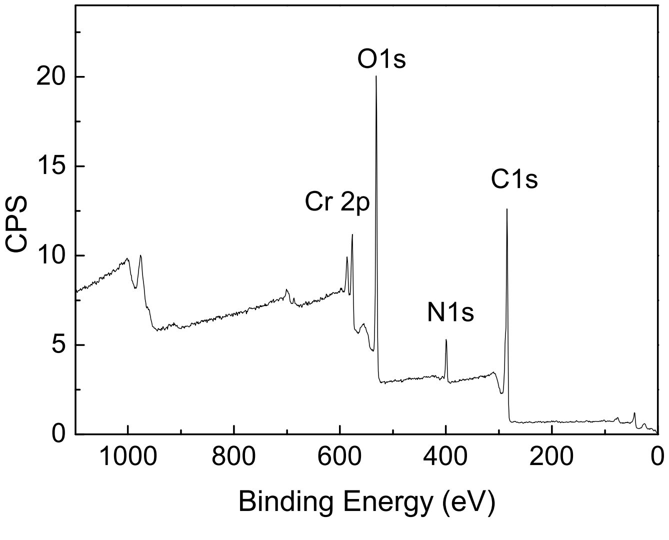

Fig. S18 X-ray photoelectron spectroscopy for the product prepared at 150 ℃ for 12 h.

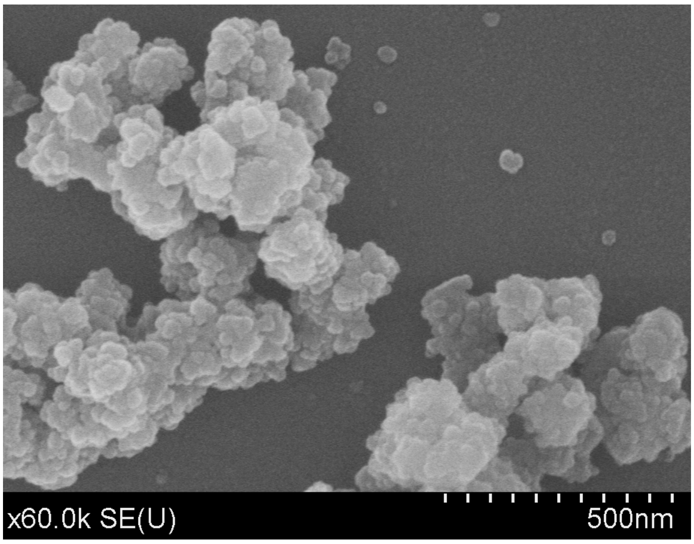

Fig. S19 SEM image for the product prepared at 150 ℃ for 6 h.

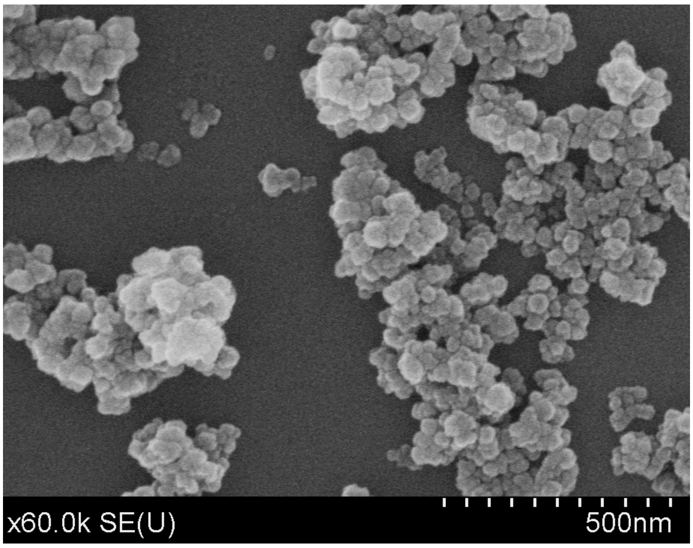

Fig. S20 SEM image for the product prepared at 150 ℃ for 12 h.

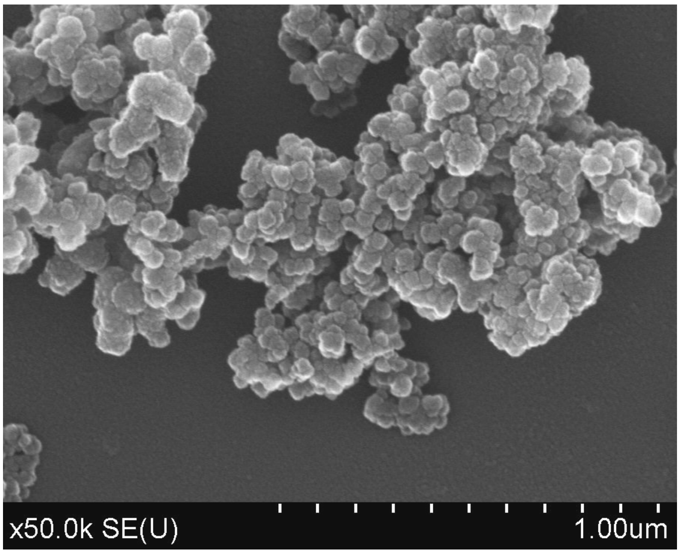

Fig. S21 SEM image for the product prepared at 150 ℃ for 16 h

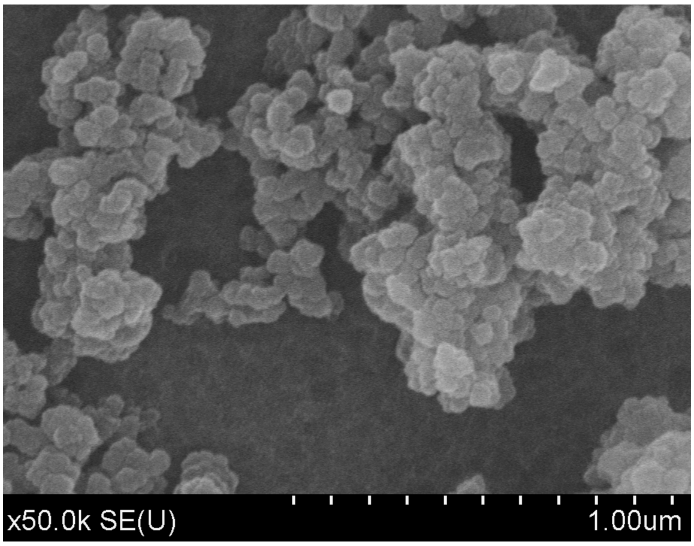

Fig. S22 SEM image for the product (using KOH) prepared at 150 ℃ for 12 h. The morphology is similar to that of the product prepared by NaOH.

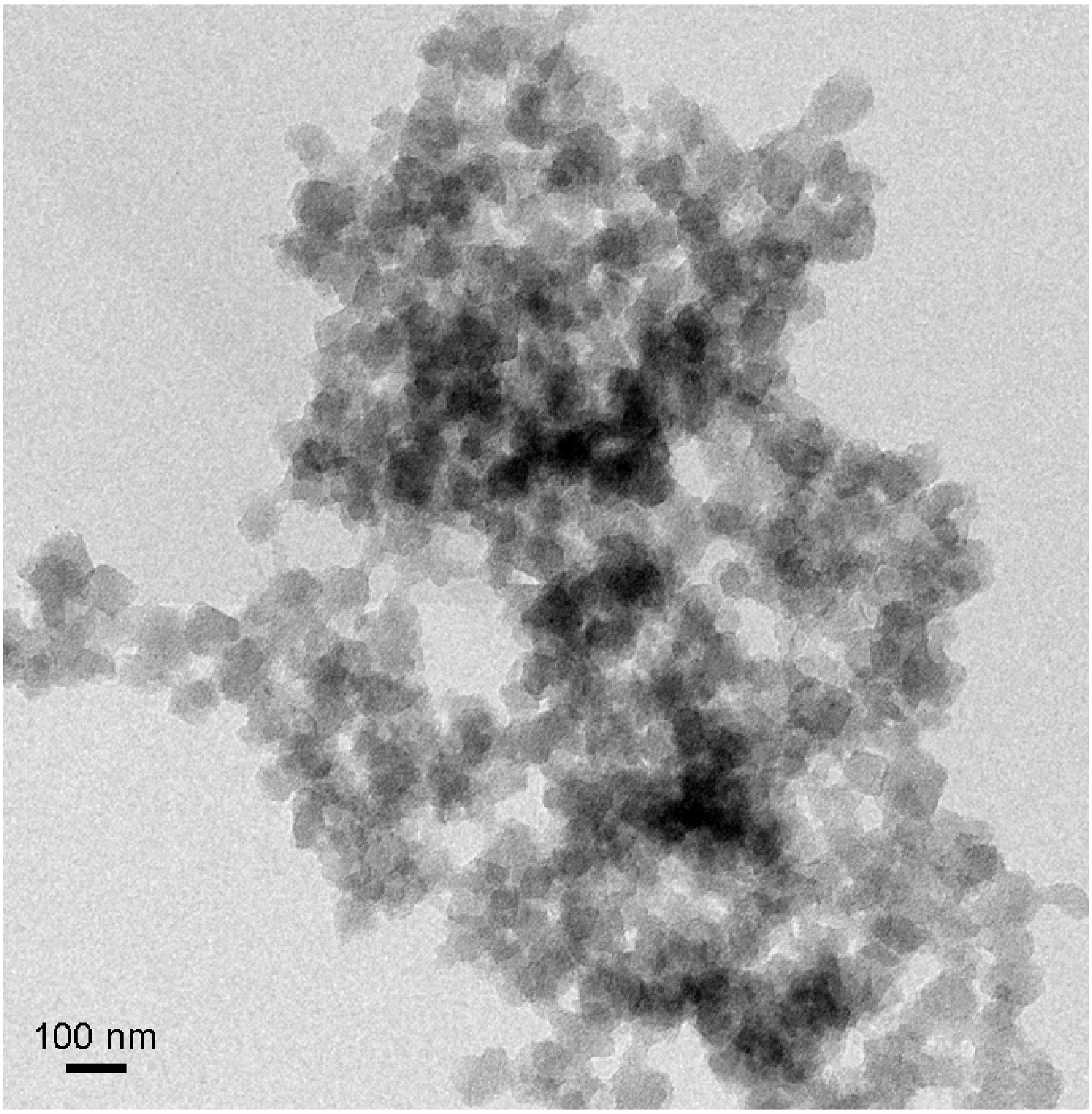

Fig. S23 TEM image of the as-prepared particles (using NaOH, 12h)

3. Additional Table

Table S1. The pH values of the solution.

Solution	APTA/NaOH/water	APTA/NaOH/ $Cr(NO_3)_3$/water	APTA/ $Cr(NO_3)_3$/water
Molar ratio	2:5:833:	2:5:2:833	2:2:833
pH	12.6	4.5	2.1

4. Isosteric heat calculation

The isosteric heat of CO_2 adsorption values were calculated using the Clausius-Clapeyron[2] equation: $\frac{d\ln P}{d(1/T)} = -\frac{Q_{st}}{R}$

The integral of the equation from T_1 to T_2: $\ln P_2 - \ln P_1 = -\frac{Q_{st}}{R}(\frac{1}{T_2} - \frac{1}{T_1})$

Pressure as a function of the amount of CO_2 adsorbed was determined using the Langmuir-Freundlich[3] fit for the isotherms:

$$\frac{N}{N_m} = \frac{B \times P^{(1/t)}}{1 + B \times P^{(1/t)}}$$

N is moles adsorbed. N_m *is moles adsorbed at saturation. P = Pressure. B and t = constants.* It can be rearranged to

$$P = \left(\frac{N/N_m}{B - B \times N/N_m} \right)^t$$

Reference

(1) (a) Y.-Y Liu, J.-L Zeng, J. Zhang, F. Xu, L.-X. Sun, *Int. J. Hydrogen Energy* 2007, **32**, 4005; (b) Y. Li, R. T.Yang, *AIChE J.* 2008, **54**, 269; (c) P. Chowdhury, C. Bikkina, S. Gumma, *J Phys Chem C* 2009, **113**, 6616.

(2) L. Czepirski and J. Jagiello, *Chem. Eng. Sci.*, 1989, **44**, 797.

(3) (a) R. Sips, *J. Chem. Phys.*, 1948, **16**, 490; (b) R. Sips, *J. Chem. Phys.*, 1950, **18**, 1024.