Electronic Supplementary Material (ESI) for RSC Advances

Supplementary Information

Hierarchically structured metal-organic framework/vertically-aligned carbon nanotubes hybrids for CO_2 capture

Lei Ge; Li Wang; Victor Rudolph; Zhonghua Zhu*

The University of Queensland, School of Chemical Engineering, St Lucia, Brisbane 4072 Australia

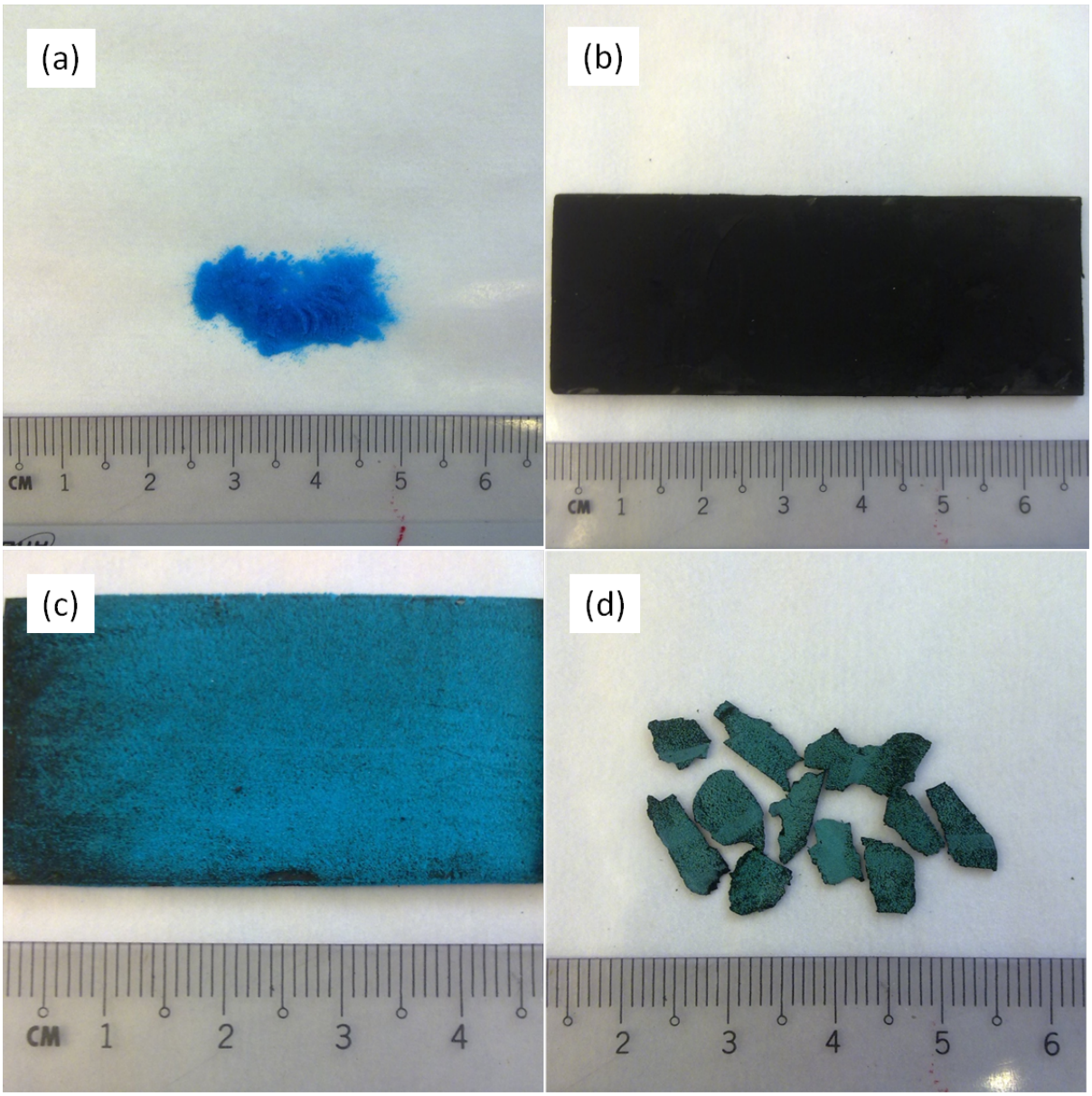

Fig.S1 Digital images of (a) HKUST-1, (b) VACNT forest with quartz substrate, (c) HKUST-1/VACNT composite with quartz substrate and (d) scratched HKUST-1/VACNT composite without quartz substrate

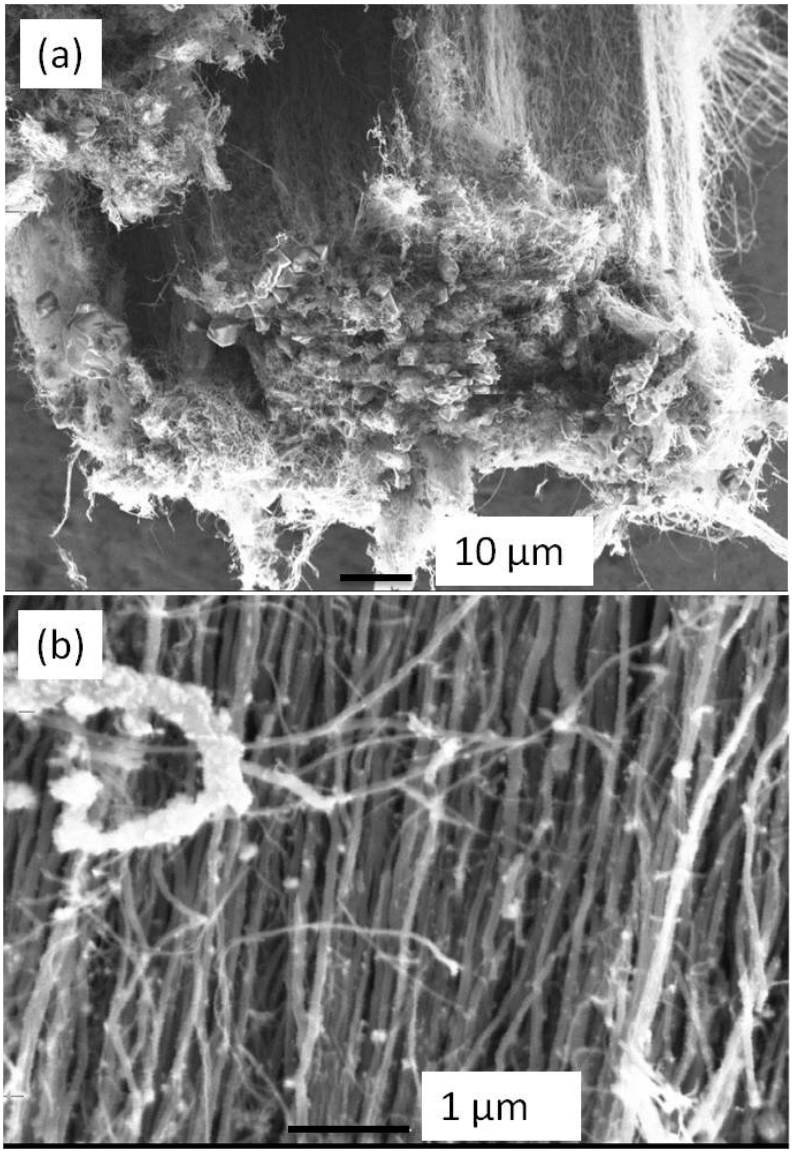

Fig. S2 SEM images of HKUST-1 growth on untreated VACNT arrays (a: cross-section tip region; b: cross-section central region)

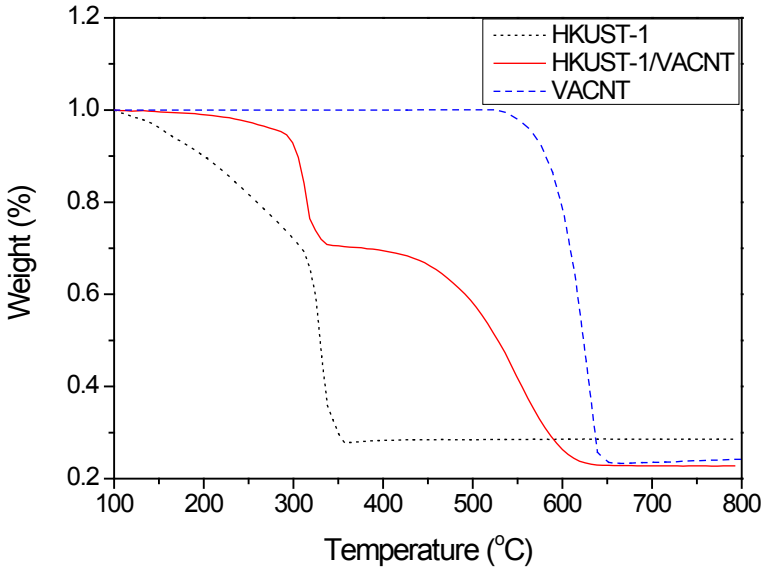

Fig.S3 Thermogravimetric analysis of HKUST-1, as-synthesized VACNTs and HKUST-1/VACNT hybrids

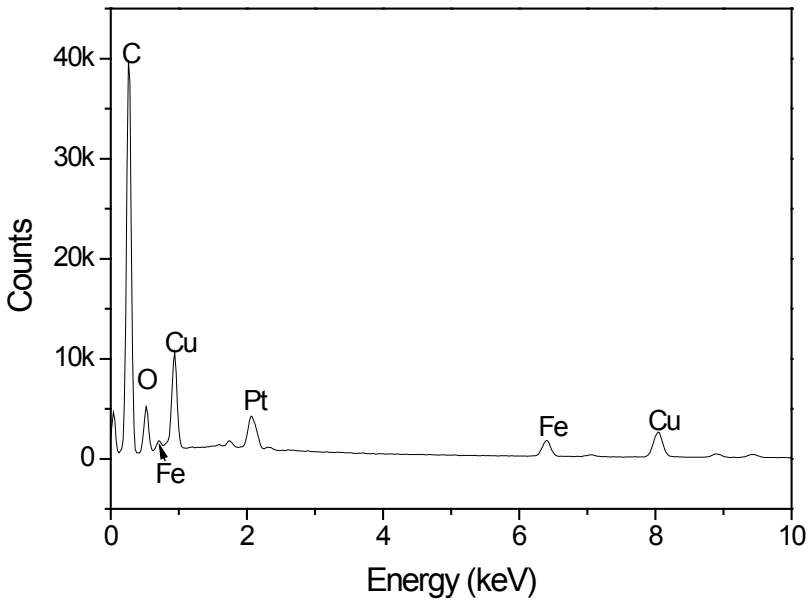

Fig.S4 EDS spectra of HKUST-1/VACNT composite

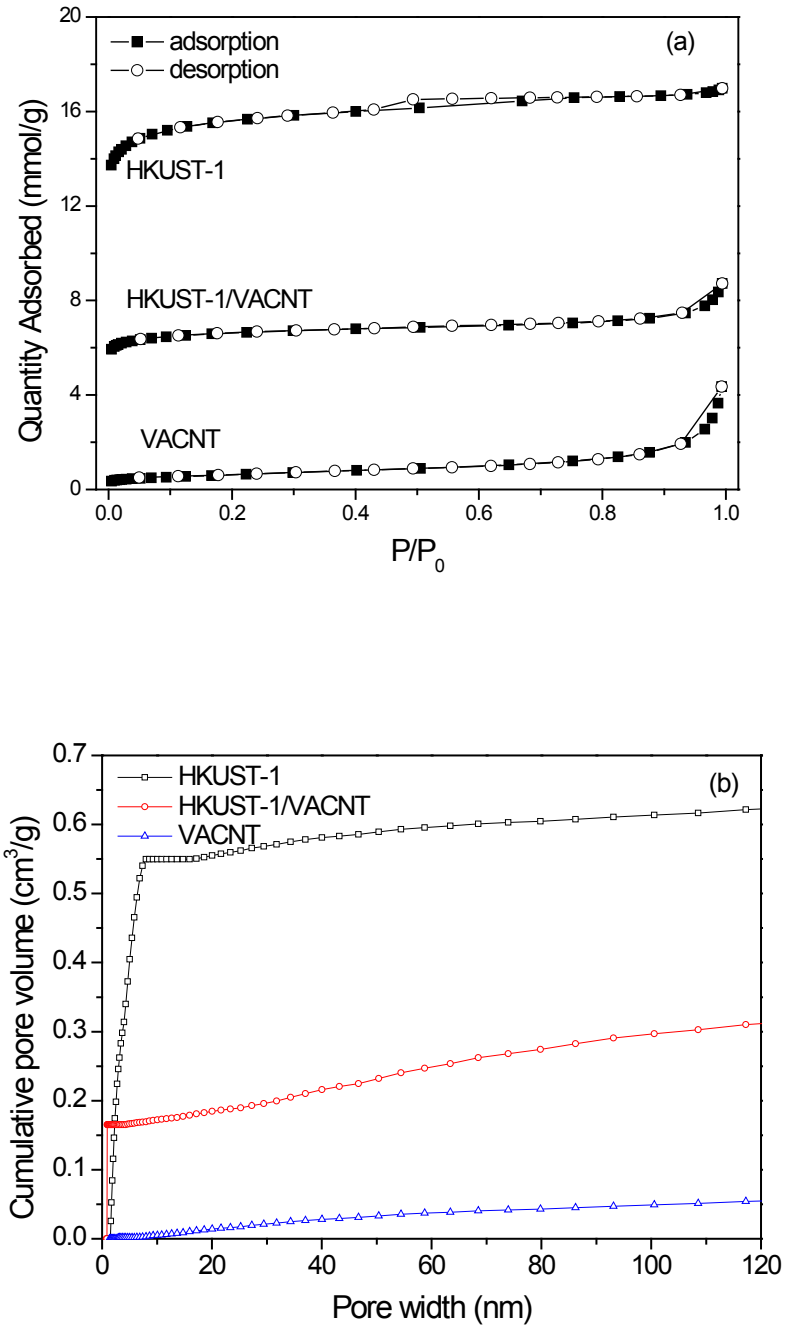

Fig.S5 (a) Nitrogen sorption isotherms and (b) cumulative pore volume of HKUST-1, VACNTs and HKUST-1/VACNT composite

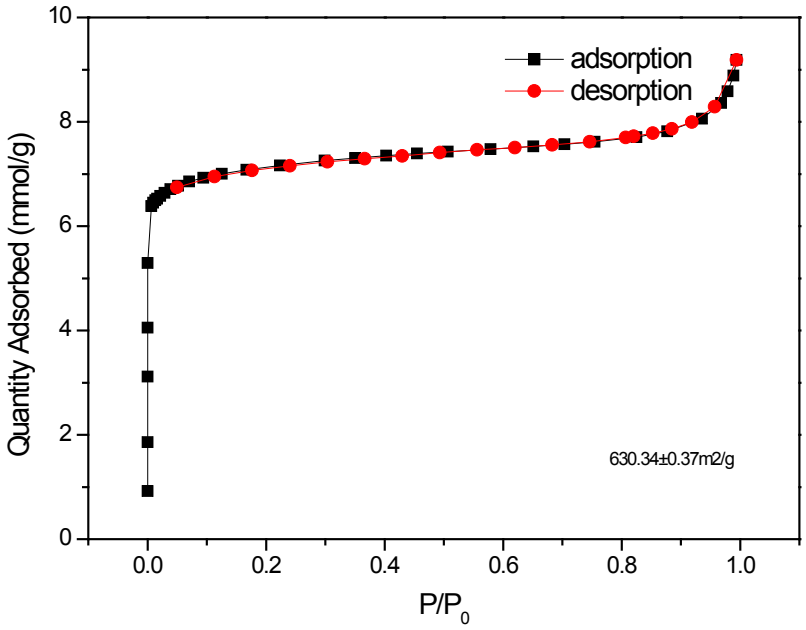

Fig.S6 Nitrogen sorption isotherms of HKUST-1 and VACNTs mixture (HKUST-1 wt%=44.3%)

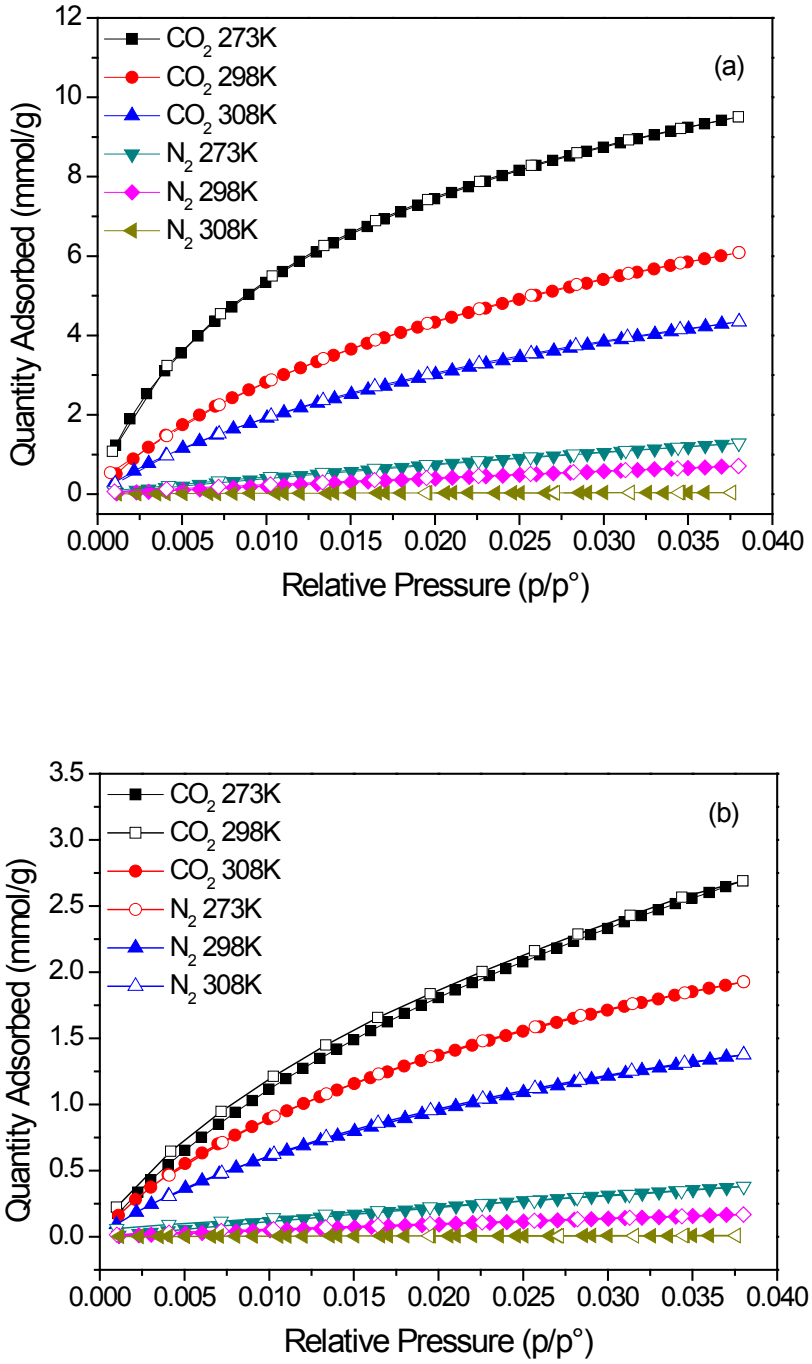

Fig. S7 CO_2 and N_2 adsorption isotherms of (a) HKUST-1 and (b) physical mixture of the VACNT and HKUST-1 at different temperatures

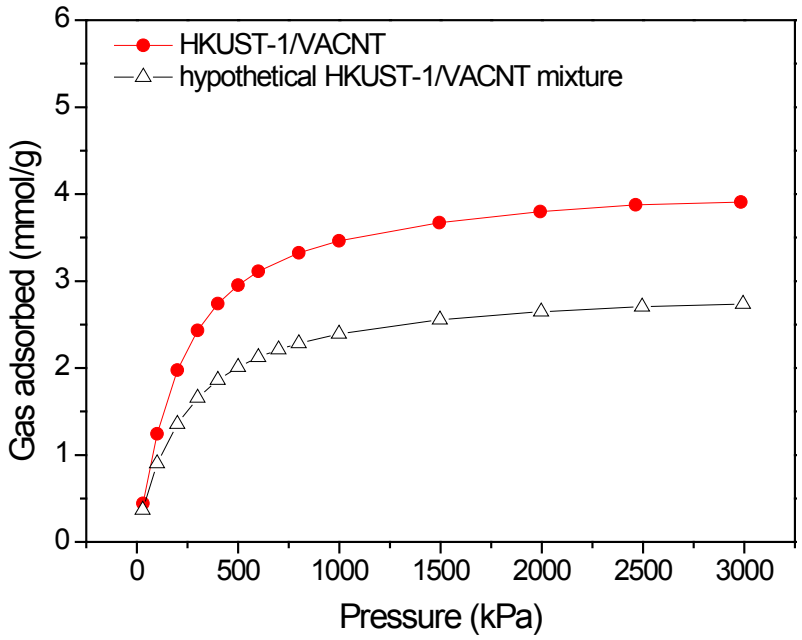

Fig. S8 High-pressure CO_2 adsorption on HKUST-1/VACNT composite and calculated CO_2 adsorption on physical mixture of HKUST-1 and VACNTs at 308K

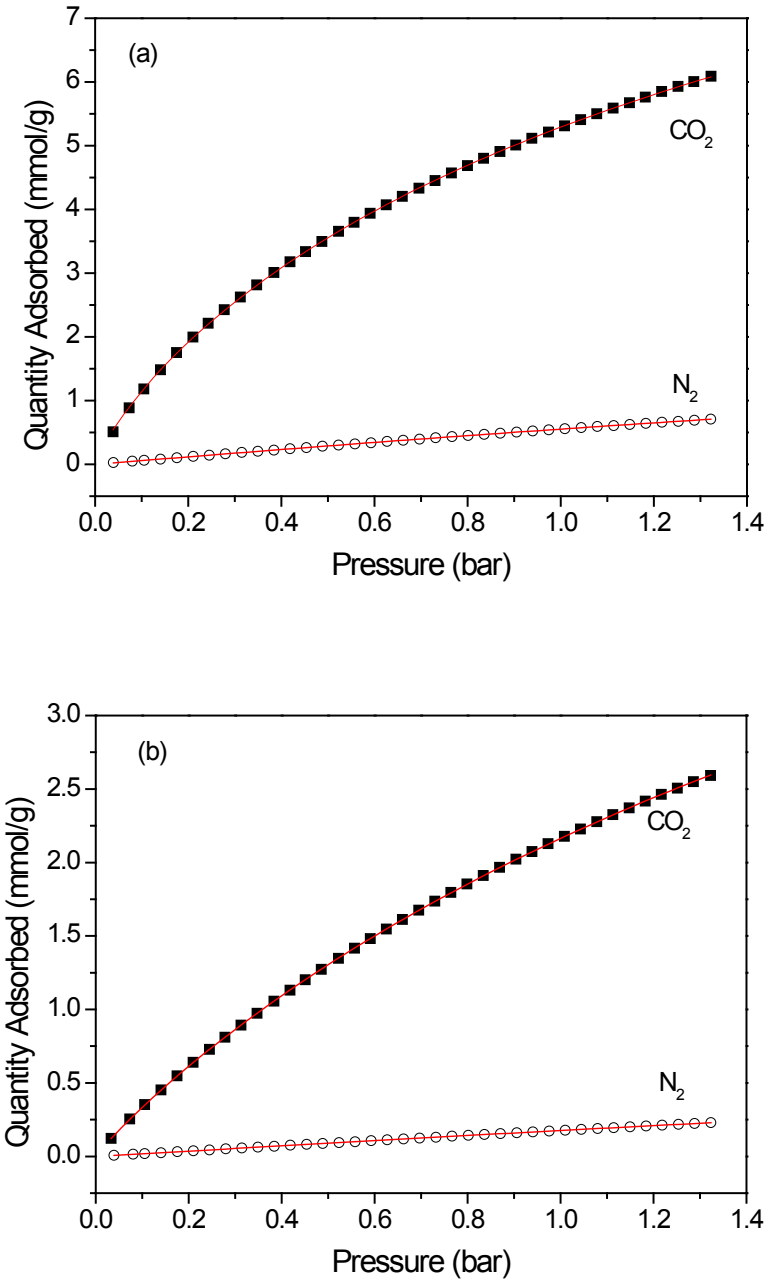

Fig.S9 Experimental data and corresponding Langmuir-Freundlich isotherm fit (red line) for adsorption in (a) HKUST-1 and (b) HKUST-1/VACNT composite at 298K

Table S1 Structure parameters of HKUST-1 based on Rietveld refinements

Samples	Space Group	Lattice Parameters (Å)	*R* factors (%)			
			R_{exp}	R_{wp}	R_p	χ^2
HKUST-1	Fm-3m	26.2980(20)	2.25	4.16	3.09	1.85

Table S2 Elemental analysis of HKUST-1/VACNT composite by EDS

Element	Weight%	Atomic%
C K	67.49	82.89
O K	13.68	12.61
Fe K	4.05	1.07
Cu K	14.77	3.43

The weight ratio of the HKUST-1 in the HKUST-1/VACNT composite (θ) was calculated as:

$$\theta = \frac{\theta_{composite}}{\theta_{HKUST-1}} \times 100\%$$

$\theta_{HKUST-1}$ is the copper weight percentage in HKUST-1 and $\theta_{Composite}$ is the copper weight percentage in the HKUST-1/VACNT composite.

Table S3 Langmuir-Freundlich fitting results of gas adsorption isotherms on HKUST-1 and HKUST-1/VACNT composite at 298K

	Adsorption component	Saturation capacity (mmol/g)	Langmuir-Freundlich parameter (bar^{-1})	Langmuir-Freundlich exponent
HKUST-1	CO_2	14.12	0.60	0.83
HKUST-1	N_2	4.62	0.14	1.03
HKUST-1/VACNT	CO_2	7.83	0.38	0.93
HKUST-1/VACNT	N_2	2.04	0.094	1.04

The Langmuir-Freundlich equation was applied as the gas adsorption model to predict the saturation sorption volume:

$$q = \frac{q_{sat} b p^{\alpha}}{1 + b p^{\alpha}}$$

Here, q is the amount of adsorbed gas (mmol/g), p is the exact gas pressure (bar), q_{sat} is the saturation capacity (mmol/g), b is the Langmuir-Freundlich parameter (bar^{-1}), and α is the Langmuir-Freundlich exponent. The adsorption selectivity of CO_2 to N_2 (S) is also calculated according equation:

$$S = \frac{q_{CO2} / q_{N2}}{p_{CO2} / p_{N2}}$$