Supplementary Information

Engineering bidirectional CMC-foam-supported HKUST-1@graphdiyne with enhanced heat/mass transfer for the highly efficient adsorption and regeneration of acetaldehyde

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Experimental

Thermal diffusion experiment

The original HKUST-1 and HK@GDY/CMC-B were pressed into thin sheets and heated at 35 °C for heat preservation for 20 min. Then, they were quickly placed in 10 °C cold source to measure and photograph the thermal diffusion using infrared camera. The cooling rate coefficient (k) was obtained according to Eq. S(1).

$$ln\frac{T_t - T_m}{T_0 - T_m} = kt + c \quad (1)$$

Acetaldehyde adsorption experiments and kinetics

The equilibrium adsorption of acetaldehyde was performed gravimetrically in TGA/DSC+ system (METTLER TOLEDO). In this system, an ultrasensitive microbalance of 0.1 μg resolution was mounted in the thermostat heatsink with high precision temperature control. Each sample was degassed at 353 K for 12 h. The measurements were carried out at 298 K for the determination of adsorption of vapor. Each sample was placed in a closed container. Each sample was placed in a closed container. Before this sample was put in, the closed container was swept with nitrogen for 20 minutes. Then, a quantitative concentration of acetaldehyde gas was injected into this container. After the adsorption equilibrium was reached, it was quickly transferred to the TGA/DSC+ instrument for the determination of mass. The equilibrium adsorption amount (Q_e, mmol/g) of acetaldehyde was calculated using Eq. S(2).

$$Q_e = \frac{W_e - W_a}{W_a M_a} \times 1000 \quad (2)$$

Where M_a (g/mol) is the molecular weight; W_a (g) is the initial weight of adsorbent and Q_e (mmol/g) is the adsorbed amount per gram at equilibrium.

The adsorption kinetics of acetaldehyde was tested by photoacoustic multi-gas analyser (GASERA ONE). 0.05 g of adsorbent was pre-placed in a sealed quartz tank reactor (400 mL) at 298 K, and the gaseous acetaldehyde (7.8 mg/m^3, 99% purity) was added to the reactor. Acetaldehyde concentrations in the reactor were detected at an interval of three minutes. Instantaneous adsorption was calculated using Eq. S(3).

$$Q_t = \frac{(C_0 - C_t)\ V_0}{W_a} \times 1000 \quad (3)$$

Where W_a (g) is the initial weight of adsorbent and Q_t (mmol/g) is the transient adsorption uptake per gram of adsorbent at time t (min).

The adsorption kinetics of acetaldehyde was fitted by general diffusion model and the diffusion coefficient (k_d) was calculated using Eq. S(4).

$$\frac{Q_t}{Q_e} = k_d\sqrt{t} + c \quad (4)$$

Where Q_e (mmol/g) and Q_t (mmol/g) represent the adsorbed amount per gram of the adsorbent at equilibrium and the transient adsorption uptakes per gram at time t (min), respectively.

Temperature programmed desorption (TPD) experiments

TPD experiment was performed on a TGA/DSC$^+$ (METTLER TOLEDO). Various HKUST-1 samples were pre-activated at 353 K under vacuum overnight, and then quickly transferred into a desiccator containing a given dehydrated acetaldehyde (C_0=7.8 mg/m^3). Adsorption experiments were conducted at 298 K and ambient pressure for 60 min. HKUST-1 samples adsorbed acetaldehyde were immediately placed in a small crucible. The heating program started from 313 to 443 K under high purity N_2 atmosphere at a flow rate of 40 mL/min and heating rate of

10 K/min while the acetaldehyde desorption were detected using TGA. Desorption kinetics of acetaldehyde was fitted by Pseudo-first-order kinetic model and desorption diffusion coefficient (k_{ds}) was obtained according to Eq. S(5).

$$ln\frac{Q_{ds}}{Q_e} = k_{ds}t + c \quad (5)$$

Where Q_e (mmol/g) shows the adsorbed amount per gram of the adsorbent at equilibrium and Q_{ds} (mmol/g) is the transient desorption amount per gram at time t (min).

Characterization and instrumentation

The prepared HKUST-1 composites were characterized using scanning electron microscope (SEM, SU8020). Prior to analysis, each sample was gold coated under high vacuum. Powder X-ray diffraction (PXRD) data were recorded from 5° to 50° at a scanning rate of 0.03 °/min (SMARTLAB3KW, Japan). Fourier transform infrared (FT-IR) spectrometry was performed on a Bruker Vector instrument, and data were collected in wavenumber range of 400-4000 cm^{-1}. Thermogravimetric analysis (TGA) were performed on a METTLER TOLEDO (TGA/DSC3+) instrument in a temperature range of 363-843 K under 10 K/min under dry N_2 atmosphere. X-ray photoelectron spectroscopy (XPS) tests were monitored by Escalab 250Xi X-ray photoelectron spectrometer (Thermo Fisher, USA). The pore textural properties of the prepared composites were analyzed through N_2 adsorption-desorption isotherms using a surface area analyzer (ASAP-2460, Micromeritics). Before each adsorption experiment, the samples were dried under vacuum at 353 K for 10 h and a vacuum of < 0.05 Pa. Thermal conductivity was measured by Hot Disk TPS 2500S instrument (Hot Disk AB, Sweden).

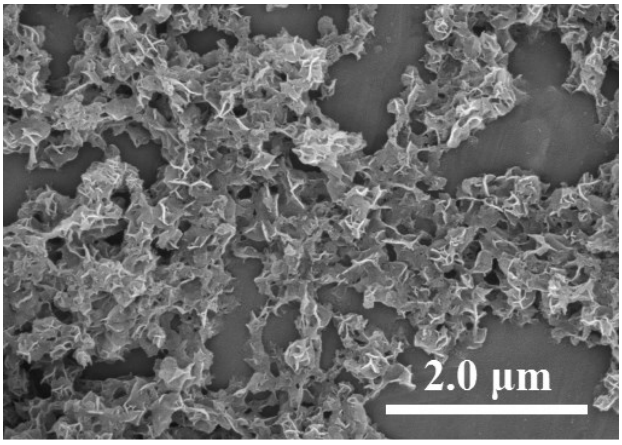

Fig. S1 SEM image of GDY

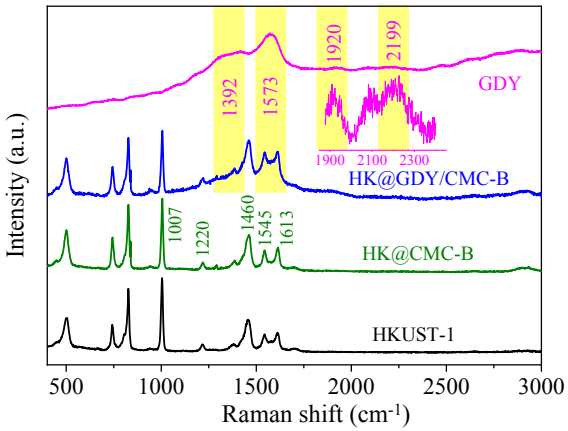

Fig. S2 Raman spectrum of GDY,HKUST-1,HK@CMC-B and HK@GDY/CMC-B

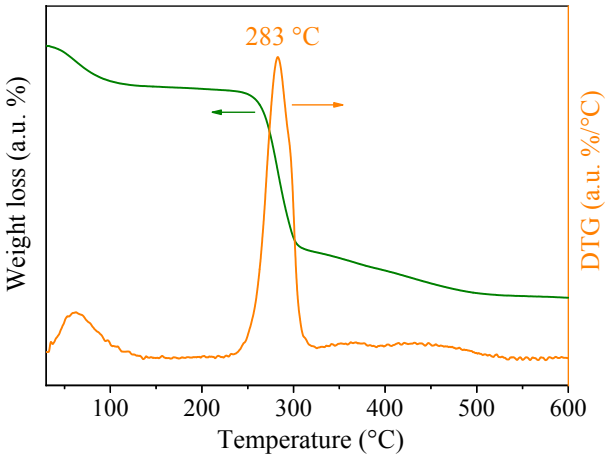

Fig. S3 TG and DTG curves of CMC

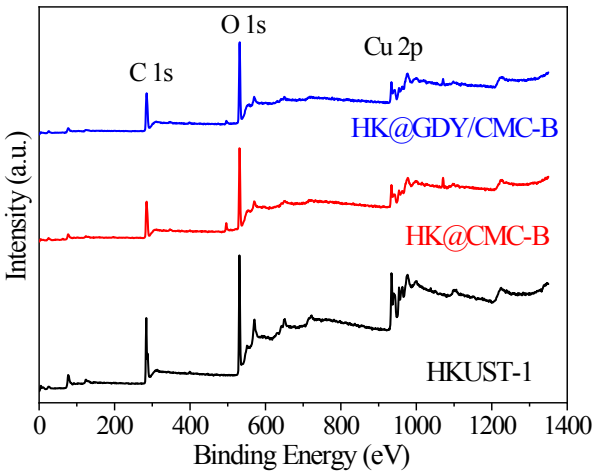

Fig. S4 XPS survey spectra of HKUST-1, HK@CMC-B foam, and HK@GDY/CMC-B foam

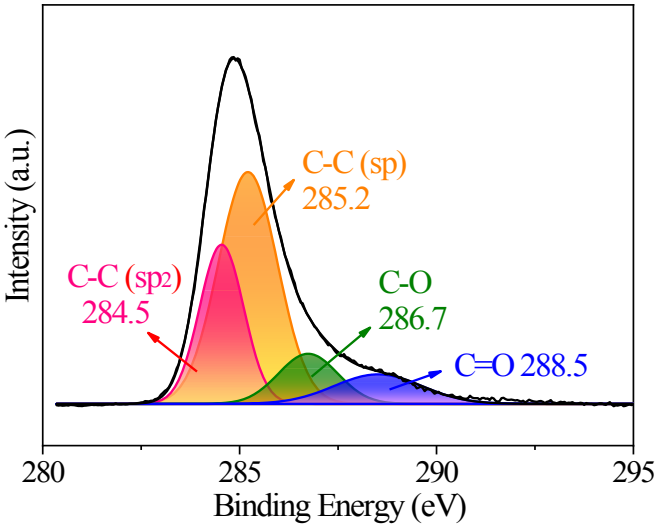

Fig. S5 High resolution XPS spectrum of C 1s in GDY

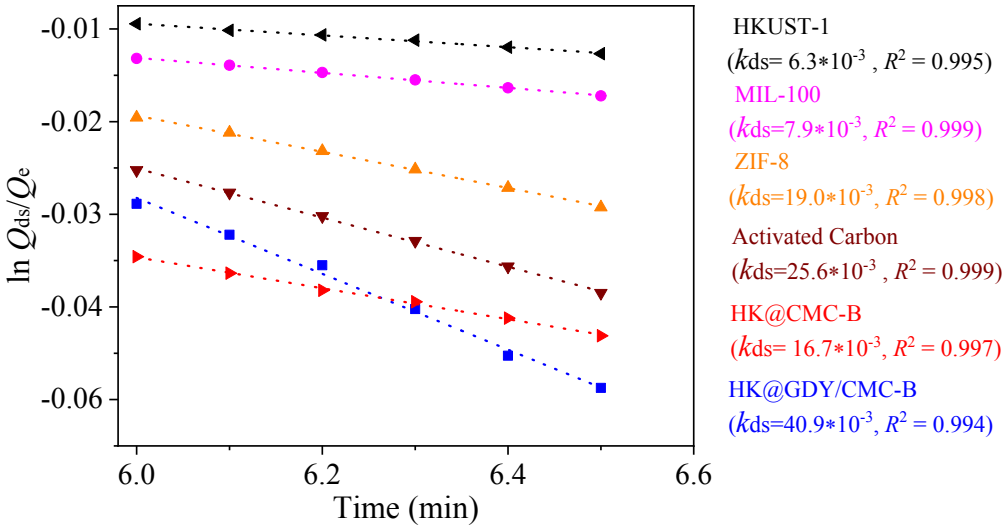

Fig. S6 Pseudo-first-order kinetic simulated desorption results on HKUST-1, HK@CMC-B foam, HK@GDY/CMC-B foam and other common adsorbents

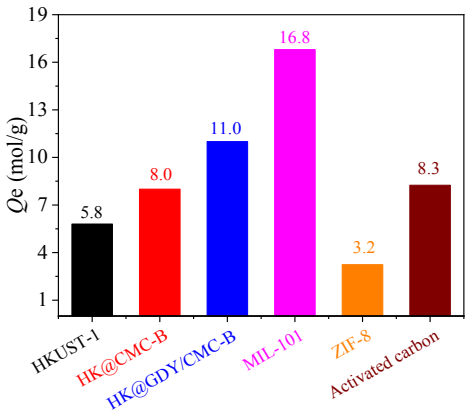

Fig. S7 Equilibrium adsorption (Q_e) on HKUST-1, HK@CMC-B foam, HK@GDY/CMC-B foam and other common adsorbents

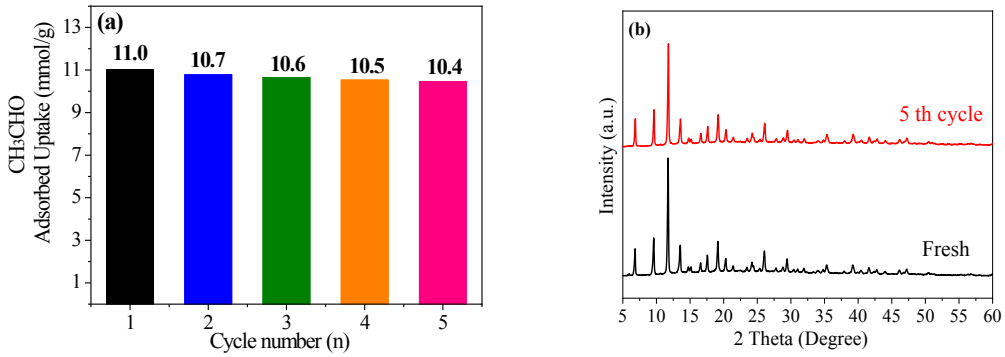

Fig. S8 HK@GDY/CMC-B continuous cyclic adsorption (a) of acetaldehyde at 303 K; XRD (b) after 5^{th} cycle.

Table S1 BET parameters of reported MOF foams.

Sample	S_{BET} (m^2/g)	Reference
UiO-66/cellulose	826	S1
COF-IL@chitosan	103	S2
GA-UiO-66-NH2	707	S3
3D rGO / ZIF-67	491	S4
CNFS-ZIF-8	273	S5
HK@GDY/CMC-B	945	This work

Table S2 Pore structure parameters of HKUST-1, HK@CMC-R foam, HK@CMC-B foam, and HK@GDY/CMC-B foam.

Sample	$S_{Langmuir}$ (m^2/g)	S_{BET} (m^2/g)	S_{micro}^* (m^2/g)	S_{meso} (m^2/g)	V_t^* (cm^3/g)	V_{micro}^* (cm^3/g)
HKUST-1	953.0	823.9	736.5	87.4	0.43	0.28
HK@CMC-R	1035.5	930.7	825.3	105.4	0.43	0.31
HK@CMC-B	1136.5	960.2	854.1	106.1	0.45	0.32
HK@GDY/CMC-B	1113.8	945.1	807.9	137.2	0.42	0.30

S_{micro}: surface area supplied from micropores (<2.0 nm);

V_t and V_{micro}: total pore volume and pore volume supplied from micropores (< 2.0 nm).

Table S3 Distribution of surface element (C, O and Cu) of HKUST-1, HK@CMC-B and HK@GDY/CMC-B determined from XPS.

Sample	Atomic content (%)		
	C	O	Cu
HKUST-1	57.97	33.91	8.13
HK@CMC-B	57.36	38.45	4.19
HK@GDY/CMC-B	58.60	37.34	4.06

Table S4 Binding energy of peaks separated from C 1s XPS spectra of HKUST-1, HK@CMC-B, HK@GDY/CMC-B, and GDY.

Sample	Binding Energy (eV)			
	C-C(sp2)	C-O-C/C-O	-O-C=O/C=O	C-C(sp)
HKUST-1	284.8	-	288.6	-
HK@CMC-B	284.8	286.4	288.2	-
HK@GDY/CMC-B	284.8	286.4	288.0	285.5
GDY	284.5	286.7	288.5	285.2

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