Supporting Information for

3D porous flower-like $CoAl_2O_4$ to boost photocatalytic CO_2 reduction reaction

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	(inset) of (a) CoAl-LDH; (b) CoAl-650; (c) CoAl-750; (d) CoAl-850.
Fig.S5	(a) TEM image of CoAl-750.
Fig.S6	Valence band XPS spectra of the CoAl-750.
Fig.S7	Comparison of gas chromatograms of photocatalyzed CO_2 reduction gas products over CoAl-750 catalyst after reaction under different conditions for 1 h.
Fig.S8	SEM image of the CoAl-750 catalyst after five photocatalytic CO_2 reduction cycles (35h).
Fig.S9	Model for (a) $CoAl_2O_4$ (111) and (b) $CoAl_2O_4$ (111) adsorbs CO_2 molecules.

S1 Materials and chemicals

All of the chemical reagents were analytical grade and used without further purification. Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), Aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$), urea(CH_4N_2O) and ammonium fluoride (NH_4F) were purchased from Aladdin Reagent Co., Ltd. and carbon dioxide gas (CO_2 99.99 %), carbon monoxide gas (CO 99.90 %), methane gas (CH_4 99.999 %) were purchased from Wuhan Wu Gang Gas Co. Ltd. Deionized (DI) water was used in all experiments.

S2 Synthesis of 3D flower-like CoAl-LDHs

A urea hydrolysis reaction was used to synthesize CoAl-LDHs without surfactant. 0.8 mmol $Co(NO_3)_2 \cdot 6H_2O$, 0.4 mmol $Al(NO_3)_3 \cdot 9H_2O$, 4 mmol NH_4F and 28 mmol urea were mixed in 40 mL DI water and the mixed solution was continuously stirred for 1 h.

The solution was transferred into a 100 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 90°C for 8 h in an electric blower drying box. After cooling to room temperature, the obtained pink CoAl-LDHs were thoroughly cleaned with DI water and ethanol. The prepared powder was dried in air at 60℃ for 12 h and named as CoAl-LDHs.

S3 Materials characterizations

In order to identify the crystal phase of the samples, the powder X-ray diffraction (XRD) patterns of the sample were obtained using Cu Kα radiation source (λ=1.54056 Å) at a scan rate of 5° min^{-1} on a D/MAX-2500 diffractometer (Riga, Japan). Scanning electron microscope (SEM) images were obtained on the MIRA3 field emission SEM. Transmission electron microscope (TEM) images, high-resolution transmission electron microscope (HRTEM) images and selected electron diffraction (STEM) patterns were converged on the JEM-2100 TEM. X-ray photoelectron spectroscopy (XPS) data was obtained by ESCALAB 250Xi. The solid-state UV diffuse reflectance absorption spectrum in the region of 200 ~800 nm was recorded on a Shimadzu 2450 spectrophotometer using $BaSO_4$ as the reflectance standard. Brunauer- Emmett-Teller (BET) surface areas were measured using a JW-BK100B with N_2 adsorption-desorption after drying under vacuum at 150 ℃ for 5 h. Fourier transform infrared spectra (FT-IR) were recorded on a PerkinElmer Spectrum FT-IR spectrometer. The AutoChem TP5080 chemisorption analyzer performs temperature program desorption (TPD) investigations of CO_2, using mass spectra (QIC-20, Hidden) to record CO_2 signals. Thermogravimetry combined with Fourier transform infrared spectroscopy (TG–FTIR)

and thermogravimetry coupled with mass spectrometry (TG–MS) were used to analyze the thermal degradation products from the synthesis of $CoAl_2O_4$.

S4 CO_2-TPD measurement

The measurement method of CO_2-TPD is as follows. (1) Take 50 mg catalyst and put it into TP-5080-D instrument special quartz tube. (2) Purge the system with He at room temperature at a flow rate of 30 mL/min for 10 minutes to remove contaminants on the surface of the catalyst, and then TPD is characterized. (3) Purge system with CO_2 at room temperature for 30 minutes at a flow rate of 30 mL/min. (4) Stop CO_2 feeding when the CO_2 baseline is stable. Clean the system with He for 10 minutes at a flow rate of 30 mL/min to remove any gaseous CO_2 residue. (5) The temperature is heated to 800℃ and the heating rate is 10℃/min. Mass spectrometry (QIC-20, Hidden) is used to measure CO_2 desorption.

S5 Photoelectrochemistry measurement

The electrochemical measurements are carried out on an electrochemical workstation (CHI760C, Chinstruments, China) utilizing a three-electrode setup. The counter electrode is a Pt foil, the reference electrode is an Ag/AgCl electrode, and the working electrode is an FTO conductive glass (11cm) with the conducting side covered with thin sample film. The electrolyte is 0.5 M Na_2SO_4 solution.

S6 Photocatalytic CO_2 reduction

The photocatalytic CO_2 reduction experiment was conducted in a 200 mL customized Pyrex reactor; the two openings of the reactor were sealed with silicone rubber. A 300W Xenon lamp is placed 10 cm above the reactor, serving as the light

source that induced the photocatalytic process. In a typical photocatalysis experiment, 5 mL of DI water was added and swirled by ultrasonic for three minutes to make a suspension out of 50 mg of prepared $CoAl_2O_4$ photocatalyst in a glass petri dish with a diameter of 6 cm. The petri dish was dried in the oven at 60 °C. In order to provide a hydrogen source for photocatalytic reduction of CO_2, 500 μL of DI water was uniformly covered on the surface of the dried photocatalyst. After purging the system with CO_2 at a rate of 30 mL/min for 20 min, turned on the xenon lamp, and the system was kept at 0.8 KPa pressure (all-glass automatic online trace gas analysis system, Labsolar 6A, Beijing Perfectlight Technology Co., Ltd., China). Gas chromatography and flame ionization detection (GC-9790II) were employed to measure products every 30 minutes. The catalytic temperature was maintained at about 25 ° C under light irradiation with cooling water, and the temperature was measured every hour with an IR608A thermometer **(Table S1)**.

Table S1 Temperature change of photocatalytic CO_2 reduction under visible light irradiation

Test times (h)	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Temperature (℃)	25.2	25.1	25.0	25.2	25.0	25.1	25.0	25.3

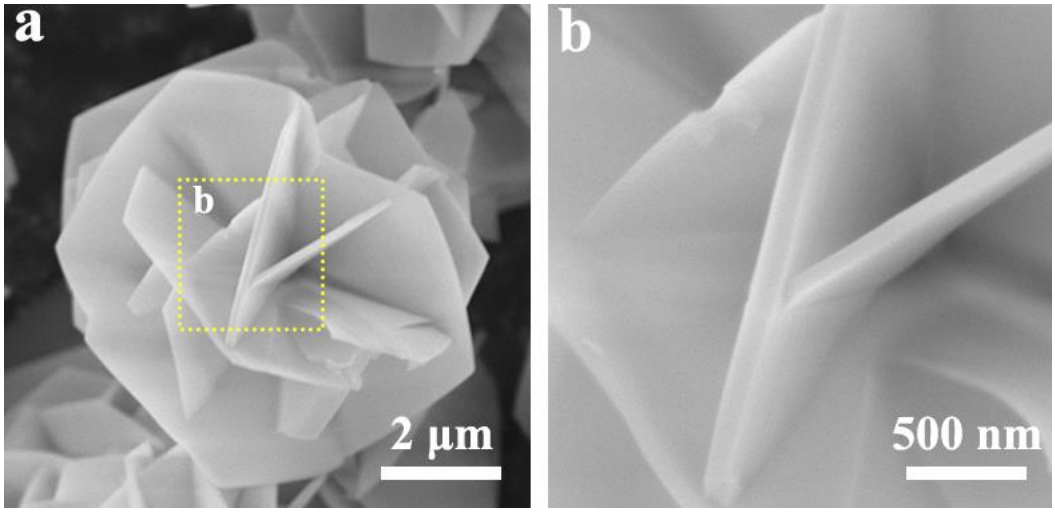

Fig.S1. The SEM images of CoAl-LDH.

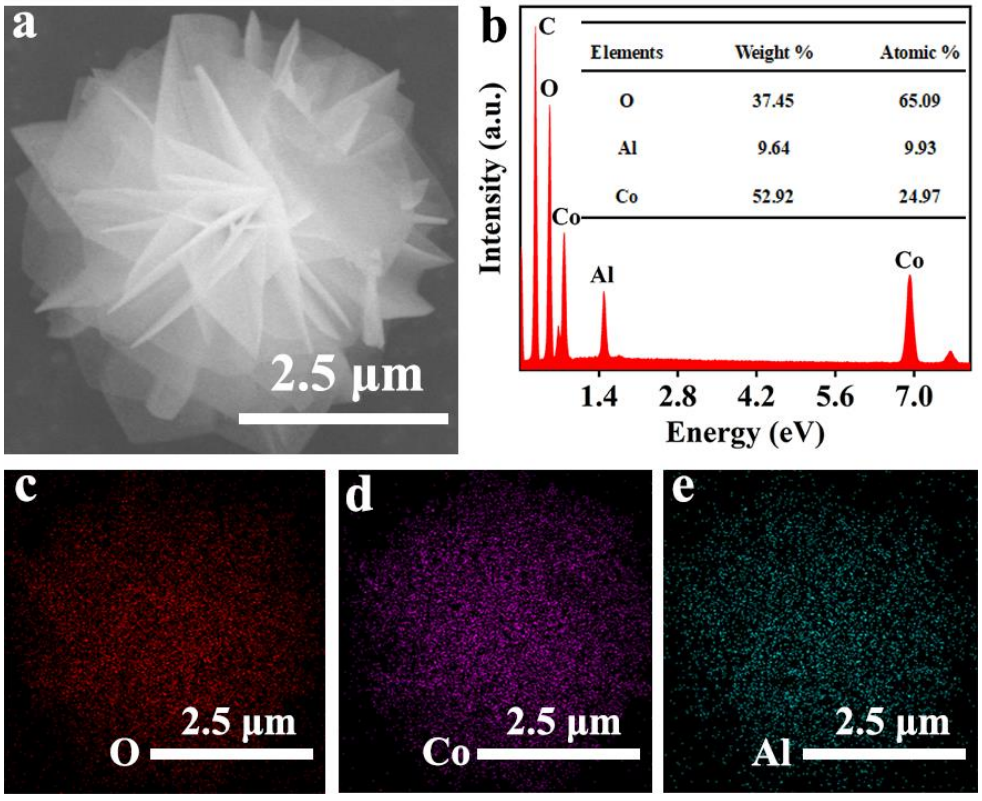

Fig.S2. (a) SEM image of CoAl-650; (b)EDS of CoAl-650; (c-e) elemental mapping of (a).

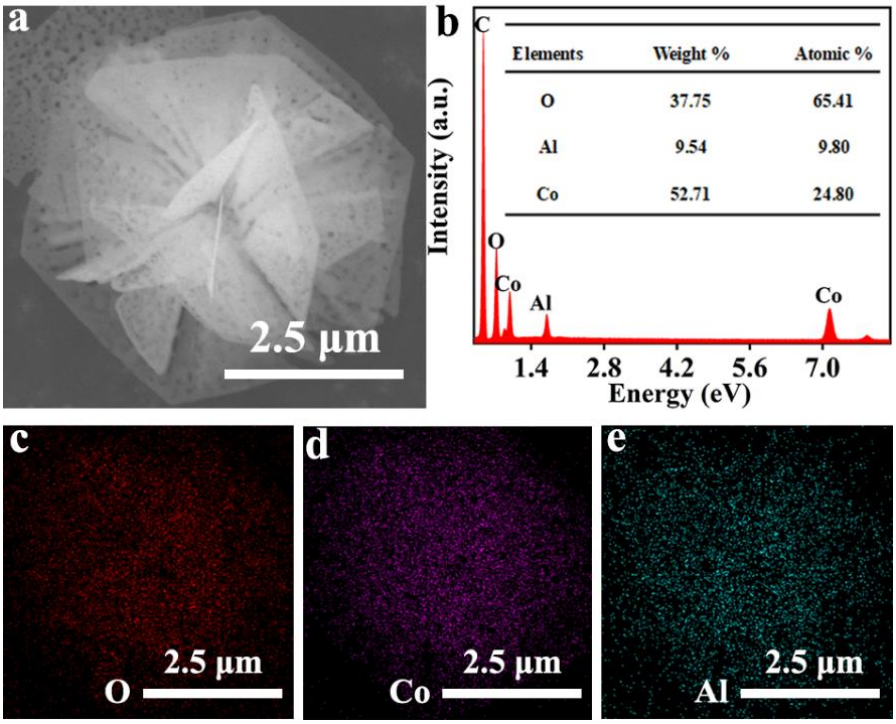

Fig.S3. (a) SEM image of CoAl-850; (b)EDS of CoAl-850; (c-e) elemental mapping of (a).

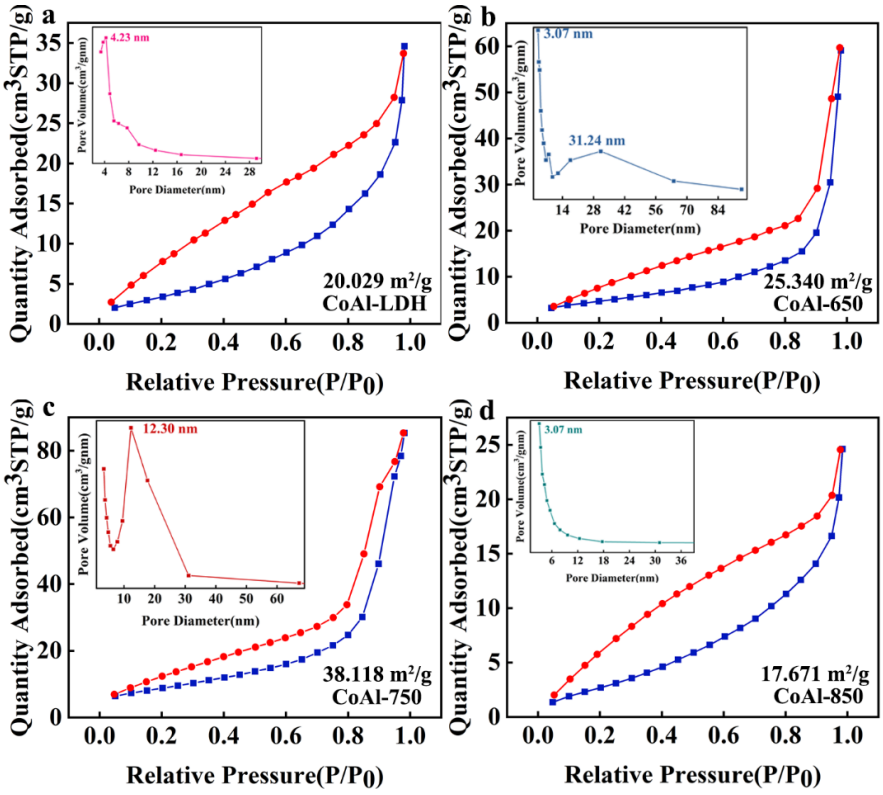

Fig.S4. The N_2 adsorption-desorption isotherms and pore size distribution (inset) of (a) CoAl-LDH; (b) CoAl-650; (c) CoAl-750; (d) CoAl-850.

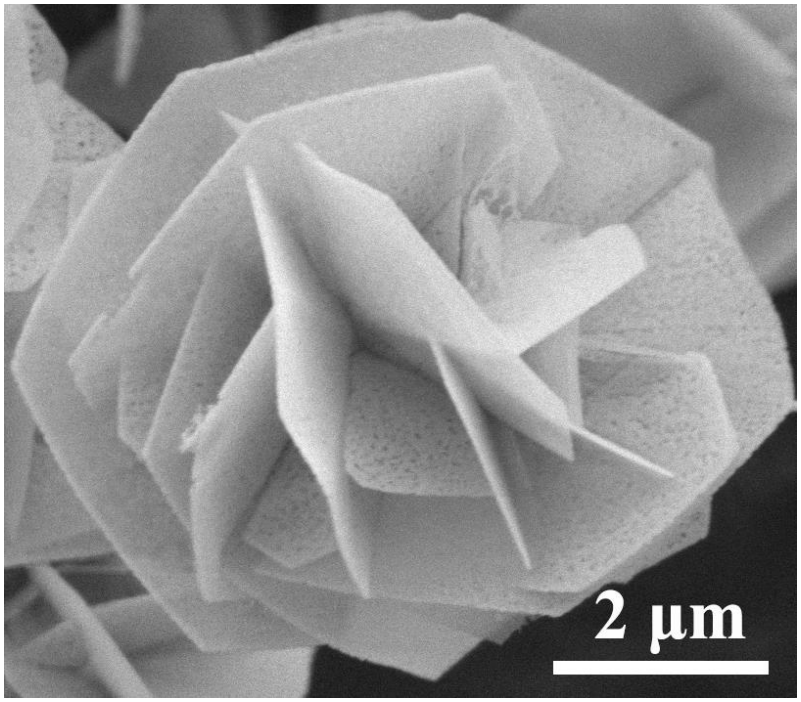

Fig.S5. (a) TEM image of CoAl-750.

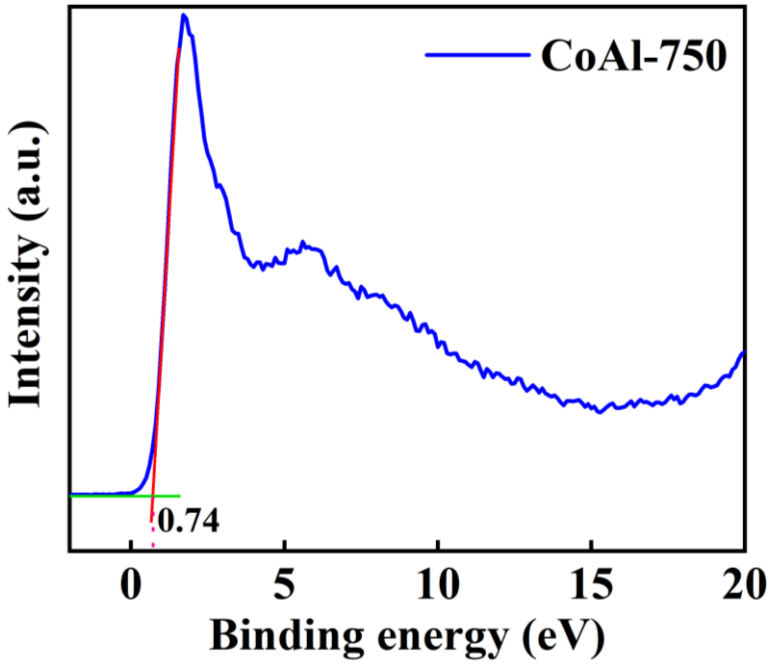

Fig.S6. Valence band XPS spectra of the CoAl-750.

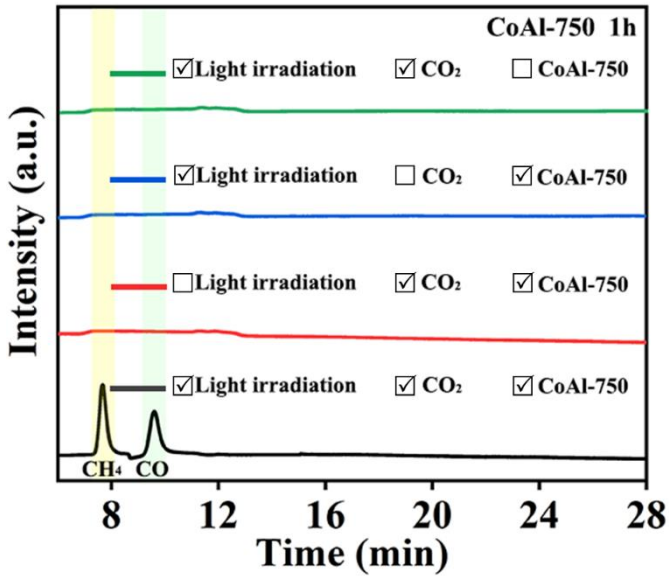

Fig.S7. Comparison of gas chromatograms of photocatalyzed CO_2 reduction gas products over CoAl-750 catalyst after reaction under different conditions for 1 h.

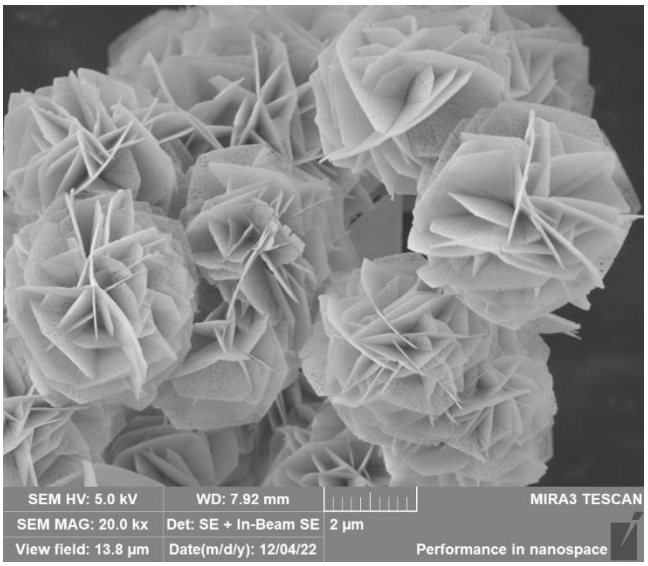

Fig.S8. SEM image of the CoAl-750 catalyst after five photocatalytic CO_2 reduction cycles (35h).

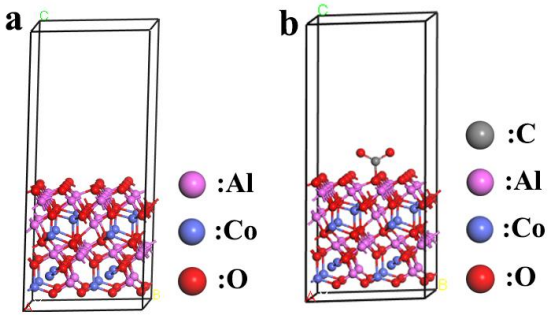

Fig.S9. Model for (a) $CoAl_2O_4$ (111) and (b) $CoAl_2O_4$ (111) adsorbs CO_2 molecules.