

Supporting Information

Development of γ -Al₂O₃ with oxygen vacancies induced by amorphous structure for photocatalytic reduction of CO₂

Shao-Qiang Li^a, Ying Liu^{a*}, Yi-Lei Li^{a,b}, Ying-Juan Hao^a, Rui-Hong Liu^a, Lan-Ju Chen^a, Fa-Tang Li^{a*}

^a *Hebei Key Laboratory of Photoelectric Control on Surface and Interface, College of Science, Hebei University of Science and Technology, Shijiazhuang 050018, China.*

^b *Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education, College of Chemistry, Beijing Normal University, Beijing, 100875, China*

Experimental

Preparation of catalysts

Triton X-100 (analytical grade) was purchased from MACKLIN. All other chemicals (analytical grade) were bought from Aladdin. Reference P25 TiO₂ was obtained from Degussa. All the chemicals were not further purified and used as received.

3.3 g of Al₂(SO₄)₃·18H₂O, 7.2 g of CO (NH₂)₂ and 6.469 g of Triton X-100 were mixed with 70 mL deionized water to form a transparent solution. Then the mixture was stirred for 0.5 h under the condition of room temperature. The mixed solution was crystallized in a Teflon-lined autoclave. The reaction system was maintained 120 °C for 24 h. The crystallization product (Boehmite) was washed three times with deionized water, subsequently washed one time with anhydrous alcohol before in an oven at 80 °C overnight. Then, the dried sample was calcined at a heating rate of 4 °C min⁻¹ to 350, 400, 450, and 500 °C for 4 h. The samples were titled as Al-350, Al-400, Al-450, Al-500, respectively.

Catalyst characterization

The crystal phases and composition of catalysts were implemented on a X-ray diffractometer (Rigaku D/MAX 2500). The morphology of the catalysts was observed on JEOL JSM-7500 scanning electron microscope (SEM). ASPA-2020 was used for Brunauer-Emmett-Teller (BET) method. The optical absorption property can be analyzed by UV-Vis diffuse reflectance spectra (DRS) on Thermo Fisher Scientific Evolution 200 spectrophotometer. Photoluminescence spectra (PL) of the catalyst were measured by F-4600 fluorescence spectrophotometer from Hitachi, Japan. The CO₂ temperature-programmed desorption analysis (CO₂-TPD) was obtained using Beijing Biotech PCA-1000 chemical adsorption instrument. Electron spin resonance (ESR) test was detected on JES FA200 ESR spectrometer. The electrochemical properties were implemented on an electro-chemical analyzer CHI660E (Shanghai, China). To detect the intermediates in the reaction process and photocatalytic mechanism, the in-situ Fourier-transform infrared (FTIR) spectroscopies were

performed on an Bruker INVENIO spectrometer (Germany). The electrochemical tests were conducted by a standard system containing three electrodes. The counter electrode and reference electrode are platinum electrode, saturated Ag/AgCl electrode, respectively. The preparation of working electrode was as follows: 50 mg of catalyst and 10 mg of polyethylene glycol (PEG) were ground and dispersed in 0.3 mL of absolute ethanol, and the mixed solution was evenly coated on the conductive surface of clean indium tin oxide conductive glass (ITO) with the fixed area of about 1 cm².

Photocatalytic activity

Photocatalytic CO₂ reduction is employed to evaluate the activity. The photocatalytic performance were carried out in a offline stainless steel reactor. A 300 W xenon lamp for simulating sunlight is the light source. First of all, 5 mg photocatalyst was evenly added on a plate with a bottom area of 14.5 cm². Later, 2.5 mL H₂O was placed at the base of the stainless steel reactor. Subsequently, the quartz plate coated with the photocatalyst was put on the quartz container containing water. The above-mentioned reaction system was evacuated by a vacuum pump. After that, highly pure CO₂ gas was injected into the reactor to insure normal pressure. The light source illuminated the stainless steel reactor from the top. The system of constant temperature circulating water was adopted to ensure that the reaction temperature was 40 °C. The product was detected on a GC9560 gas chromatography. 1 mL gas mixture was injected to gas chromatography by a syringe for every 2 h to analyse qualitatively .

DFT calculation details

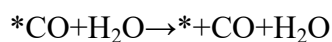
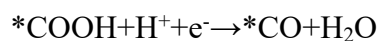
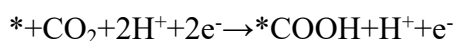
All the calculations are implemented by the VASP code.¹ The GGA-PBE functional is selected for the exchange and correlation potential.² Weak van der Waals interaction is considered by the DFT-D3 functional.³ The cut off energy for the plane-wave is 400 eV. The Gamma point in the Brillouin-zone is chosen for integration. Total energies of the systems converge to 10⁻⁵ eV in the iteration solution of Kohn-Sham equation. The force on each atoms reduce to 0.05 eV/Å after geometry optimization. The amorphous component is built using ab-initio molecule dynamics

simulations with 3 ps at 5000 K for melting of the crystal in the 4x4x1 supercell and 10 ps for quenching from 5000 K to 300 K. The time step is set to 3 fs. A vacuum layer of more than 15 Å is added vertical to the surface Al₂O₃ for adsorption calculations.

The Gibbs free energy is defined as:

$$G=E+E_{ZPE}-TS$$

E, E_{ZPE}, and TS represents the total energy, zero-point energy, and entropy of the system. The CO₂ reaction pathway follows:



The asterisk represents the clean catalyst.

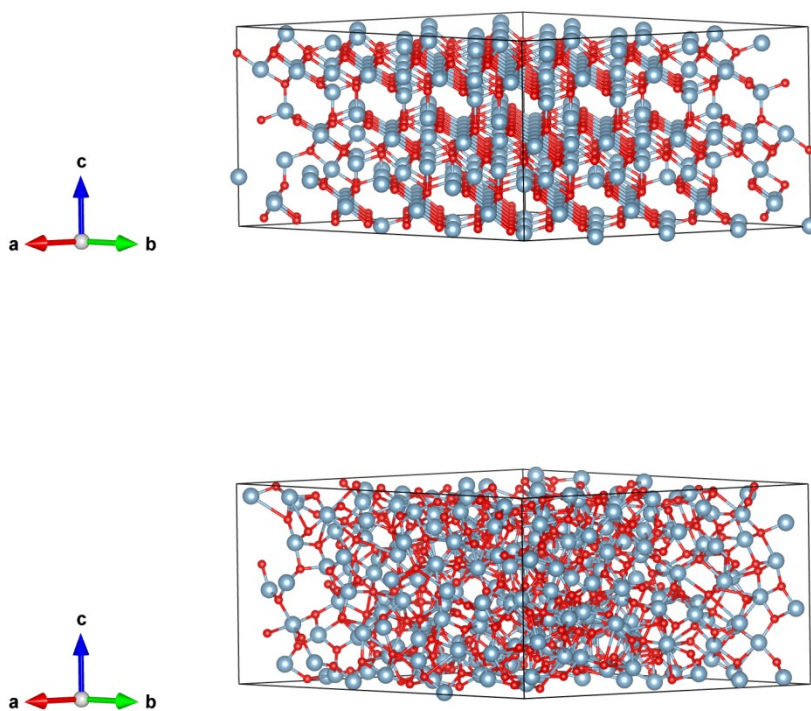


Figure S1. Side view of the crystalline and amorphous γ -Al₂O₃. The Al and O atoms are shown by the blue and red balls.

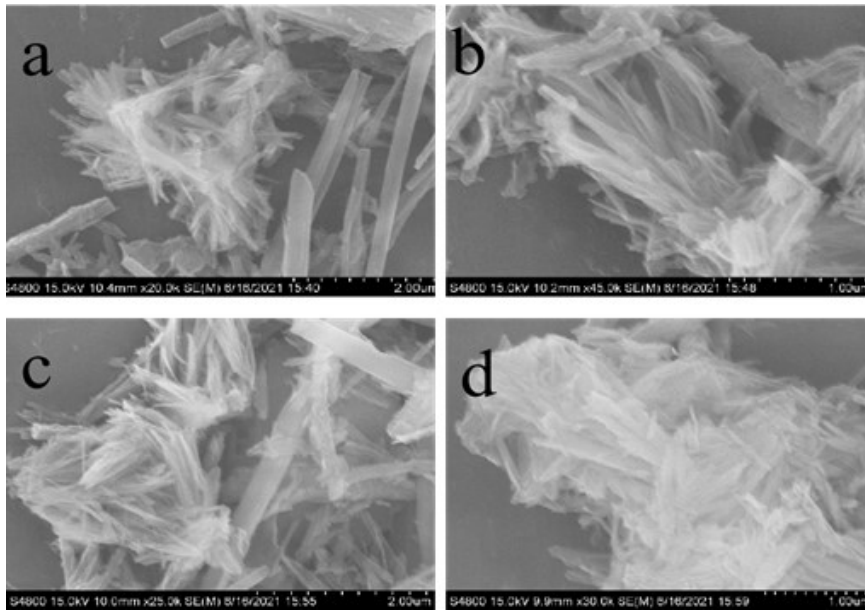


Figure S2. The SEM images of (a) Al-350 (b) Al-400 (c) Al-450 (d) Al-500

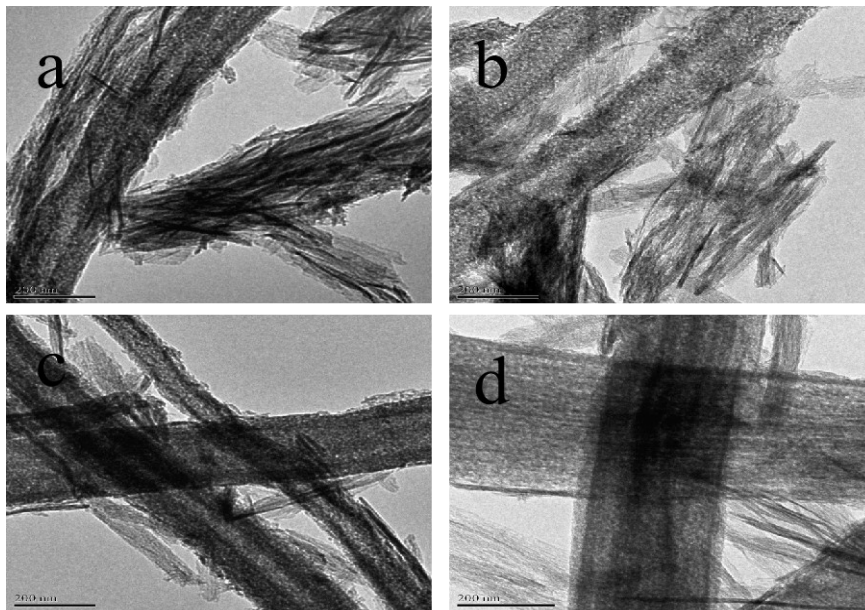


Figure S3. The TEM images of (a) Al-350 (b) Al-400 (c) Al-450 (d) Al-500

Table S1. The crystallinity of samples. The calculation method can be described as the ratio of the crystal peak area to the total peak area referring to Ref : 4. & Ref : 5.

Sample	Crystallinity (%)	Margin of error	Degree of amorphous (%)
Al-350	23.48	1.28	76.52
Al-400	24.54	3.31	75.46
Al-450	28.41	1.95	71.59
Al-500	51.47	2.68	48.53

Table S2. The specific surface area , pore size and average pore diameter of samples.

Sample	BET Area (m ² /g)	Surface Pore Size (nm)	Pore Volume (cm ³ /g)
Al-350	212.03	11.68	0.62
Al-400	190.71	20.96	0.99
Al-450	176.03	12.09	0.53
Al-500	161.88	29.14	1.18

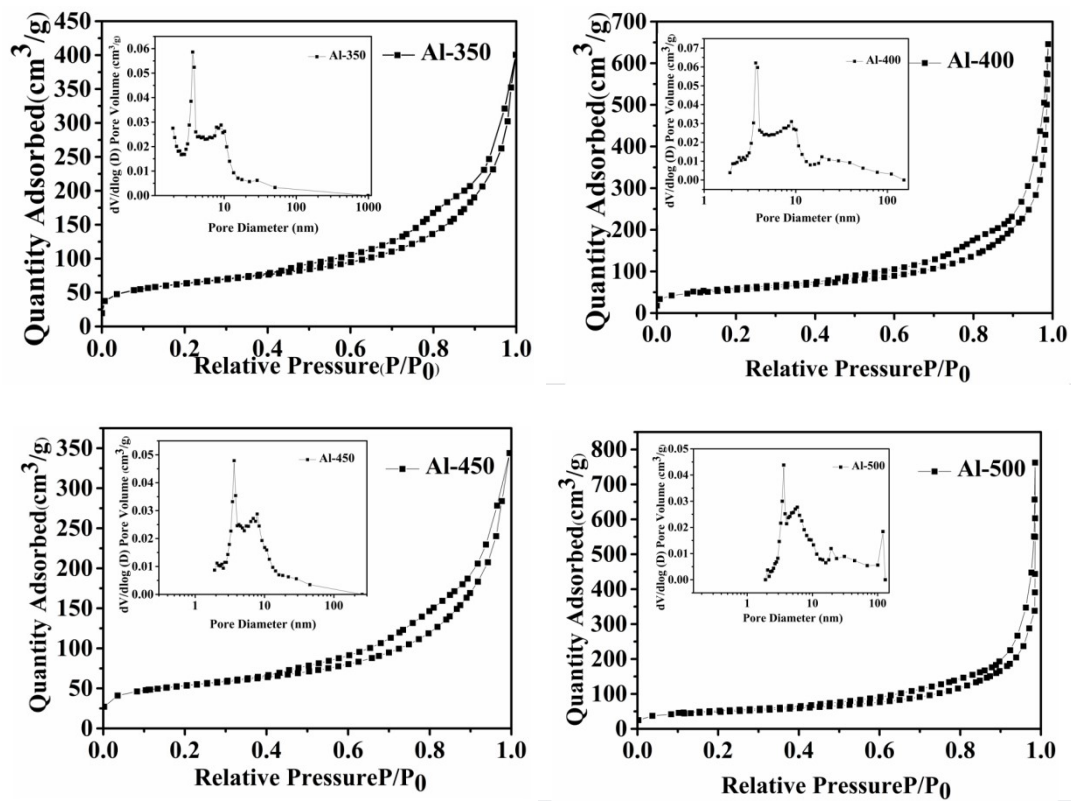
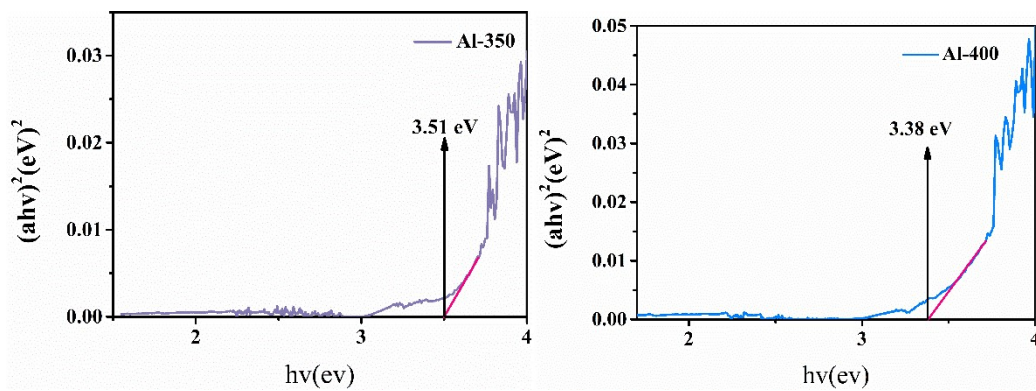


Figure S4. N_2 adsorption/desorption isotherms and the corresponding pore size distribution curves of all γ - Al_2O_3 catalysts



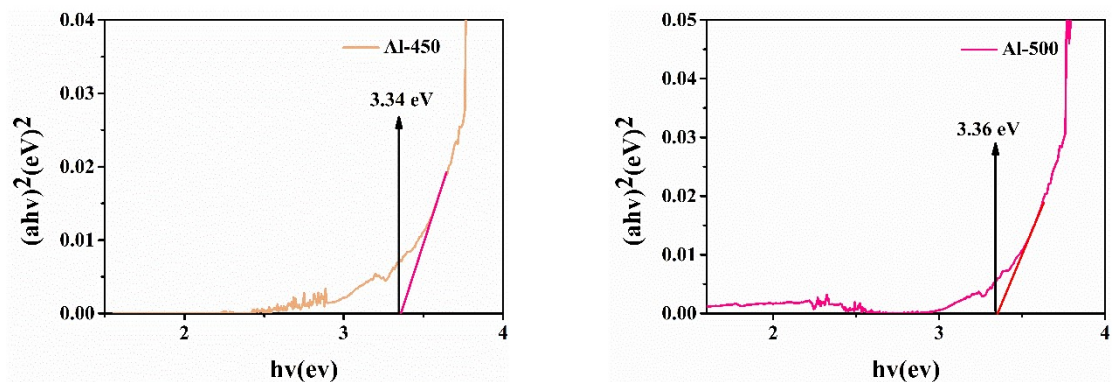


Figure S5. The band gaps of Al-350 (a), Al-400 (b), Al-450 (c), Al-500 (d).

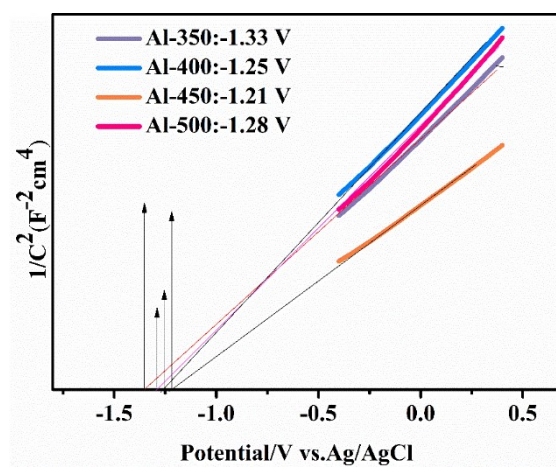


Figure S6. The Mott-Schottky plots of Al-350, Al-400, Al-450, Al-500.

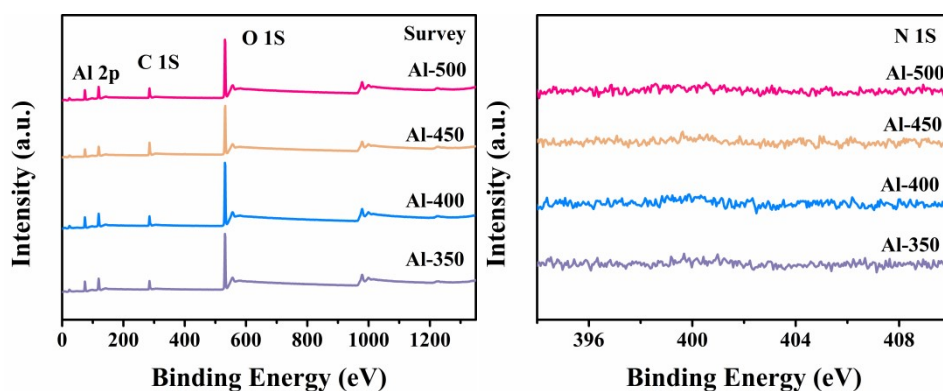
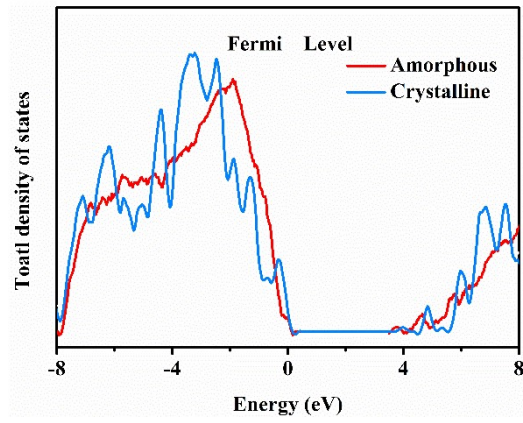
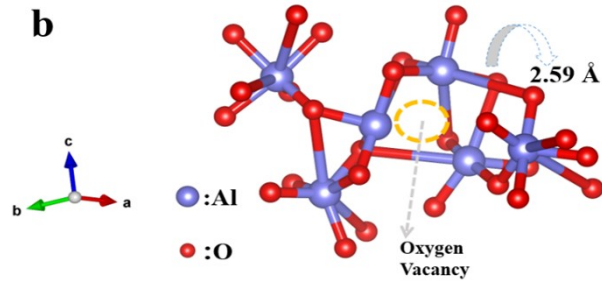
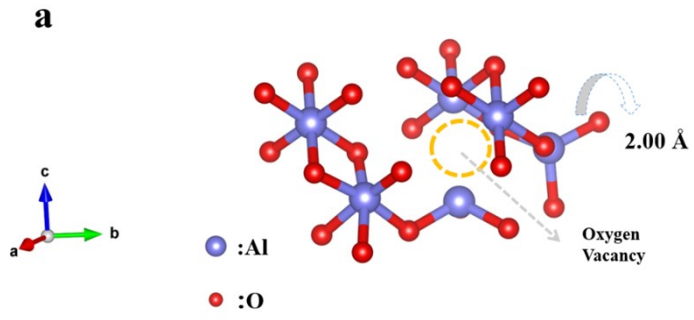


Figure S7. XPS survey spectra and N 1s spectra of all photocatalysts.



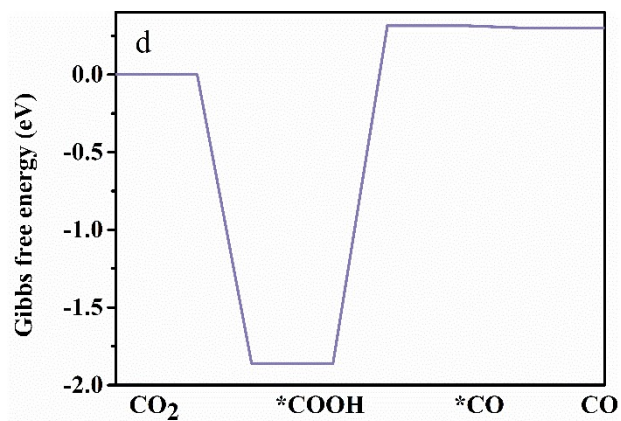


Figure S8. (a) The structural model of crystalline and (b) γ -Al₂O₃ containing amorphous components. (c) Total density of states of crystalline and amorphous Al₂O₃ (d) reaction profiles of CO₂ transition over Al-450

References

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