Electronic Supporting Information

Selective photocatalytic CO₂ reduction on copper-titanium dioxide-a study of the relationship between CO production and H₂ suppression

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1. Chemicals

Ti-isopropoxide, 2-phenyl ethanol, octylamine, cyclohexane, ethanol, (Cu(NO₃)₂·3H₂O), KHCO₃ and phosphate buffered saline were obtained from Alfa Aesar. The 0.05wt% Nafion was obtain from Hispec Fuel Cell Co. Ltd.

2. Characterizations

X-ray powder diffraction (XRD) patterns were recorded by using a Rigaku Smartlab Xray diffractometer (XRD) with Cu K α radiation. The field emission scanning electron microscopy (FE-SEM) images were obtained by using a ZEISS Gemini-300 SEM. The transmission electron microscopy (TEM) images and high resolution TEM images were obtained by using JEM-2100 TEM with an acceleration voltage of 200 kV and a tungsten filament. The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of the samples were measured by a Perkin Elmer Lambda 750 UV/Vis/ NIR spectrometer. Barium sulphate (BaSO₄) was used as a reference material. X-ray photoelectron spectral (XPS) data was collected from ES-CALAB 250Xi (ThermoFischer) with Al K α (hu=1253.6 eV) as the excitation source. The binding energies obtained in the XPS spectral analysis were corrected for sample charging by referencing C1s to 284.8 eV. Nitrogen adsorption isotherms of all the synthetic samples were measured by using an automatic microporous physical and chemical gas adsorption analyzer (ASAP 2020).

3. Experimental detail

3.1 Synthesis of pure TiO₂. In the experiment, 4 mL of Ti-isopropoxide was doped into 36 mL of 2-phenyl ethanol solution in a beaker and then the mixture was stirred for 10 min. Then 4 mL of octylamine solution was dropped slowly to the solution.^[1] After stirring, the mixture was transferred to a Teflon-lined stainless steel autoclave, heated for 40 h in an electric oven at 200 °C, and cooled to room temperature. Finally, a white powder was obtained by centrifugation, washed with the mixture of cyclohexane and ethanol (1:4) for three times and then dried overnight in vacuum at 90 °C for further characterization and use.

3.2 Synthesis of TiO₂ with Cu loaded. According to the similar procedure in the above experiment, after the mixture solution was prepared, a certain concentration (0.5 wt%, 1.0 wt% and 2.0 wt%) of metal precursor (Cu(NO₃)₂·3H₂O) was added. After stirring, this mixture was transferred to a Teflon-lined stainless steel autoclave, heated for 40 h in an electric oven at 200 °C, and cooled to room temperature. After the reaction, a brown powder was obtained by centrifugation, washed with the mixture of cyclohexane and ethanol (1:4) three times and then dried overnight in vacuum at 90 °C for further use and characterization.

3.3 Photocatalytic experiments. The photocatalytic reduction experiment of CO_2 was carried out on our online gaseous photocatalytic system (Labsolar-IIIAG, Beijing Perfectlight Technology Co., Ltd). Firstly, 0.03 g of catalysis powder was suspended in 100 mL of DI water under magnetic stirring conditions. A 300-W Xe lamp (PLS-SXE300, Beijing Perfectlight Technology Co., Ltd.) was used as the light source. The photocatalytic CO₂ reduction experiments were irradiated through the quartz window. Prior to irradiation, highpurity CO₂ gas was bubbled into the solution for ejecting the dissolved oxygen in the vessel. The reaction system was vacuum-treated for three times and then CO₂ was pumped into the system to reach an atmospheric pressure. The temperature of vessel was kept at about 5 °C by recirculating cooling water in order to increase the solubility of CO₂ and dissipate the heat generated during the process of photocatalytic reduction of CO₂. The gas sample was analyzed with a gas chromatograph (Shiweipx GC-7806) equipped with the thermal conductivity detector (molecular sieve 5A column) and flame ionization detector (TM-PLOT U column) as well as argon (99.999%) as carrier gas. The column temperature was held at 120 °C. The gaseous products were compared with the authentic gas standards. The liquid products were quantified by nuclear magnetic resonance (NMR, Bruker Avance III 400M) spectroscopy.

3.4 Electrochemical evaluation. 4 mg of the as-prepared pure TiO_2 and Cu/TiO_2 photocatalysts were dispersed in 200 μ L of ethanol with 0.05 wt% Nafion, respectively. The

catalyst ink was prepared according to the method described in those reports.^[2-4] 15 μ L of the solution was drop-coated on to a glassy carbon electrode. The electrode was obtained after the solution was dried. All the electrochemical measurements were performed in a standard three-electrode cell. The saturated calomel electrode reference electrode (SCE) and the platinum wire was the counter electrode. The electrolyte was CO₂ saturated 0.1 M KHCO₃. Linear sweeps and transient photocurrent were measured by an Autolab potentiostate, PGSTAT-302N.

Electrochemical Impedance Spectroscopy (EIS) were collected in a 0.1 M KHCO₃ solution at open circuit voltage over a frequency range from 10^5 to 1 Hz with an AC voltage at 5 mV.The Mott-Schottky plots were gained at a fixed frequency of 5 kHz to determine the flat band potential and carrier density.^[5] Linear sweep voltammetry with a scan rate of 50 mV·s⁻¹ was carried out in CO₂-saturated 0.1 M KHCO₃ solution (The KHCO₃ electrolyte was purged with CO₂ for 30 min prior to the measurement). All the experiments were performed at room temperature under atmospheric pressure.

According to the Mott-Schottky equation:^[5-7]

Equation
$$\frac{1}{C^2} = \frac{2}{N_D e \varepsilon_0 \varepsilon} (E - E_{FB} - \frac{kT}{e})$$
(1)

Where C is the space charge capacitance in the semiconductor, N_D is the electron carrier density, e is the elemental charge, ε_0 is the permittivity of a vacuum, ε is the relative permittivity of the semiconductor, E is the applied potential, E_{FB} is the flat band potential, T is the temperature, and k is the Boltzmann constant. The Mott-Schottky plots of $1/C^2$ as a function of the applied potential was shown in **Fig. 2** b. The flat band position of as-prepared samples was estimated at $1/C^2 = 0$ ($E_{NHE} = E_{SCE} + 0.24$ V).^[8] It was usually accepted that the conduction band (CB) in many n-type semiconductors is more negative by about 0.1 V than E_{FB} . Carrier density N_D was calculated from Fig.2 b by using the following equation:^[6, 7]

$$N_D = \frac{2}{e\varepsilon_0 \varepsilon} \left(\frac{dE}{d(\frac{1}{C^2})}\right)$$
(2)

Equation

Where $e = 1.6 \times 10^{-19} \text{ C}$, $\mathcal{E}_0 = 8.86 \times 10^{-12} \text{ F} \cdot \text{m}^{-1}$, and $\mathcal{E} = 48$.

3.5 Theoretical calculations. VASP computational package was used for all the calculations. The Cu slab is established by cleaving the 001 surface as be 001 surface of Cu is usually considered to be the active surface. We applied projector-augmented-wave method with Perdew–Burke–Ernzerh of GGA functional.^[9] Electronic convergence limit was set to be 1×10^{-5} eV.^[10] Optimization of atomic coordinates was considered to be converged if Hellmann–Feynman force was smaller than 1×10^{-2} eV·Å⁻¹. The Cu slab was constructed. The vacuum region was about 15 Å in height

The adsorbed energy of hydrogen could be defined using the following formula Equation (3):

$$E_{ab} = E_{tot} - E_{sub} - E_{H_2}/2$$
(3)

Where E_{ab} was the adsorption energy; E_{tot} was the total energy of the copper substrate with hydrogen, while E_{sub} was the energy of clear copper substrate. Therefore, the E_{tot} , E_{sub} and $E_{H_2/2}$ was calculated to be -53.70, -50.20 and -3.39 eV, respectively, and the E_{ab} was calculated to be -0.11 eV.

Similarly, the adsorption energy of carbon monoxide was obtained according to the Equation (4):

$$E_{ab} = E_{tot} - E_{sub} - E_{CO} \tag{4}$$

the E_{tot} , E_{sub} and E_{CO} was calculated to be -65.55, -50.12 and -14.77 eV, respectively, and the E_{ab} was calculated to be -0.77 eV. Overall, the adsorption energy of CO was much higher than that of hydrogen.



Fig. S1. SEM images of investigated as-prepared pure TiO_2 (a), 0.5 wt% Cu/TiO₂ (b), 1.0 wt% Cu/TiO₂ (c) and 2.0 wt% Cu/TiO₂ (d) photocatalysts, respectively.



Fig. S2. EDX mapping of 2.0 wt% Cu/TiO₂ photocatalysts. a) HAADF. b) the representation of titanium. c) the representation of oxygen. d) the representation of copper.



Fig. S3 XPS spectra of O 1s for as-prepared pure TiO_2 , 0.5 wt% Cu/TiO₂, 1.0 wt% Cu/TiO₂ and 2.0 wt% Cu/TiO₂ photocatalysts.

we do discover oxygen vacancies in the samples after carefully investigating oxygen spectra. The peak located at around 531.53 eV corresponds to oxygen vacancies.^[11, 12]



Fig. S4. XPS spectra of Ti 2p for as-prepared pure TiO₂ and 0.5 wt% Cu/TiO₂ photocatalysts.



Fig. S5 XPS spectra of Cu 2p for as-prepared pure TiO₂, 0.5 wt% Cu/TiO₂, 1.0 wt% Cu/TiO₂ and 2.0 wt% Cu/TiO₂ photocatalysts.



Fig. S6. TEM images of investigated as-prepared 1.0 wt% Cu/TiO₂ (a and c) and 2.0 wt% Cu/TiO₂ (b and d) photocatalysts, respectively.



Fig. S7. The N₂ adsorption-desorption of investigated as-prepared TiO₂, 0.5 wt% Cu/TiO₂, 1.0 wt% Cu/TiO₂ and 2.0 wt% Cu/TiO₂ photocatalysts, respectively.



Fig. S8 Investigated $(ahv)^{1/2}$ of as-prepared pure TiO₂ and 0.5 wt% Cu/TiO₂.



Fig. S9 a) Raman spectra of TiO₂ (P25), as-prepared TiO₂ and 0.5 wt% Cu/TiO₂ photocatalysts. b) EPR spectra of TiO₂ (P25), as-prepared TiO₂ and 0.5 wt% Cu/TiO₂ photocatalysts.

Raman spectra of as-prepared TiO_2 and 0.5 wt% Cu/TiO₂ exhibited five characteristic Raman-active modes, which was similar with P25. Raman spectra of as-prepared TiO₂ and 0.5 wt% Cu/TiO₂ have a slight shift compared to that of P25 in the insert Fig. R5. This should be due to the presence of oxygen vacancies in TiO₂ and 0.5 wt% Cu/TiO₂, as reported before.^[13, 14]

Furthermore, the presence of oxygen vacancies was confirmed by EPR spectra. The P25 does not show apparent oxygen vacancies, while TiO_2 and 0.5 wt% Cu/TiO₂ photocatalysts exhibit apparent peak of oxygen vacancies ^[15], and the peak of 0.5 wt% Cu/TiO₂ is stronger than that of TiO₂. This indicates the Cu/TiO₂ contains more oxygen vacancies than TiO₂.

Based on the results of Raman and EPR, the decrease of bandgap should be due to the presence of oxygen vacancies because oxygen vacancies will create donor levels in the bandgap. ^[13, 16]



Figure S10. a) and b) were ¹H NMR spectra of the 5 mM standard substance for CH_3OH and HCOOH, respectively. c) and d) were ¹H NMR spectra of the aqueous solution after photocatalytic reduction CO_2 by 0.5 wt%Cu/TiO₂ using water-suppression method. 1 mM DMSO was the internal standard.



Fig. S11 Photoreduction of CO_2 in water by all as-prepared photocatalysts.



Fig. S12 The XRD pattern of 0.5 wt% Cu/TiO₂ before and after photocatalytic reduction of CO_2 .



Fig. S13 Nyquist plots of investigated as-prepared pure TiO_2 , 0.5 wt% Cu/TiO₂, 1.0 wt% Cu/TiO₂ and 2.0 wt% Cu/TiO₂. The frequency is from 0.1 to 10⁶ Hz.



Fig. S14 Relationship between the band structures of as-prepared TiO_2 , 0.5 wt% Cu/TiO₂, 1.0 wt% Cu/TiO₂ and 2.0 wt% Cu/TiO₂ photocatalysts and the reduction potentials (vs NHE at pH=7) for the processes of oxidation and reduction.

Catalyst	Crystallite	S _{BET} ^b	wt% of Cu ^c	E _{FB}	N _D ^d
	size ^a (nm)	$(m^2 \cdot g^{-1})$		(V vs.NHE)	$(\times 10^{21} \text{ cm}^{-3})$
TiO ₂	11.2	29.6	0	-0.50	8.41
0.5 wt% Cu/TiO ₂	11.6	36.9	0.76	-0.88	13.64
1.0 wt% Cu/TiO ₂	11.8	30.6	0.96	-0.85	10.14
2.0 wt% Cu/TiO ₂	12.2	32.9	1.63	-0.68	9.64

^a Evaluated from XRD data using the Scherrer equation: $D_{(hkl)} = k \lambda / (\beta \cos \theta)$, where λ is the X-ray wavelength ($\lambda = 1.5418$ Å), β is the half-width of the (101) planes, θ is the bragg diffraction angle, and k is a correction factor (k = 0.89).

^b Surface areas determined by N₂ adsorption-desorption.

° Voltage of EDX was 15 kV.

Entry	Catalyst	Light	System	Major product	R _{max} ^a (μmol·g ⁻¹ ·h ⁻¹)	Ref.
1	TiO ₂ (0.5 g)	Hg (300 W)	$CO_2+H_2O(1)$	НСООН	1.9	1
2	1.0% Cu/TiO ₂ (0.1 g)	UV lamp (12 mW/cm^2)	$CO_2+H_2O(g)$	CO CH4	0.5 3.6	17
3	$1\% Cu/Ti(H_2)$	Infrared lamp	$CO_2+H_2O(g)$	CO CH	25 4 4	18
4	$5\% \text{ Cu/Ti(H_2)}$	Infrared lamp	$CO_2+H_2O(g)$	CO CH	20	18
5	(0.05 g) 3.0 Cu-TiO ₂ (0.025 g)	Hg lamp	0.013 M Na ₂ S	CO HCOOH	2.8 25.7	19
6	(0.025 g) 3.0 Cu-TiO ₂	Hg lamp	$CO_2+H_2O(l)$	CO	0.3	19
7	(0.023 g) 0.5 wt.% Cu/TiO ₂	(123 W) Hg (8 W)	0.2 M NaOH	CH ₄ CO	0.3 2.0	20
8	(0.1 g) 1.0 wt.% Cu/TiO ₂	Hg (8 W)	0.2 M NaOH	CH ₄ CO	1.3 0.2	20
9	(0.1 g) 2.0 wt.% Cu/TiO ₂	Hg (8 W)	0.2 M NaOH	CH ₄ CO	0.4	20
10	(0.1 g) TiO ₂	Xe (300 W)	$CO_2+H_2O(l)$	$ \begin{array}{c} \mathrm{CH}_4\\ \mathrm{CO} \end{array} $	2.2 6.2	This work
11	(0.03 g) 0.5 wt% Cu/TiO ₂ (0.03 g)	Xe (300 W)	$CO_2+H_2O(l)$	СО	32.5	This work
12	(0.03 g) 1.0 wt% Cu/TiO ₂ (0.03 g)	Xe (300 W)	$CO_2+H_2O(l)$	СО	8.7	This work
13	$2.0 \text{ wt\% Cu/TiO}_2$ (0.03 g)	Xe (300 W)	$CO_2+H_2O(l)$	СО	7.9	This work
14 ^b	$0.5 \text{ wt\% Cu/TiO}_2$ (0.03 g)	Xe (300 W)	$CO_2+H_2O(l)$	-	-	This work

Table S2 Comparison of photocatalytic CO₂ with copper decorated TiO₂ catalysts

^a R_{max} Maximum formation rate reported for the major product, in μ mol·g⁻¹·h⁻¹.

^b Performed under Ar atmosphere, without CO₂.

It has been reported that oxygen vacancies can severs an important adsorption and active sites for heterogeneous catalysis, which will strongly influence the activity of metal oxides. ^[21] The selectivity toward CO should be attributed to the oxygen vacancy. According to literatures, the conversion of CO₂ to CO energetically prefers to take place on the surface of defective TiO₂ with oxygen vacancies. ^[22-24] In principle, the formation of oxygen vacancies on TiO₂ leads to the creation of unpaired electrons or Ti³⁺ centers, ^[25] which could provide electronic charge, making oxygen vacancies the active sites. Also, the oxygen vacancies can sever as sites for adsorption of CO₂. An oxygen atom from CO₂ could be adsorbed on the oxygen vacancy of TiO_2 , which facilitates dissociative adsorption of CO_2 and lead to the formation of CO. ^[22-25] This should be the reason for the high selectivity.

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