Copper Species-Loaded Hydrophobic Bi₂WO₆ for Photocatalytic Reduction of Carbon Dioxide with Water to Methane

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1. Photocatalytic CO₂ reduction activities test

The photocatalytic CO₂ reduction activity of the catalysts was investigated in a 160 mL homemade quartz reactor. A 300 W xenon lamp was employed as the light source, and the light intensity was adjusted to 150 mW/cm². In a typical measurement, the photocatalyst was dispersed on a glass holder in the reactor with an area of 20 cm². To obtain a gas mixture of CO₂ and water vapor, a CO₂ mixture (5% CO₂, 95% N₂) was bubbled through H₂O. The gas mixture was then introduced into the reactor at a flow rate of 50 mL/min for 30 minutes to purge the reaction system. Subsequently, the flow rate of the reactant gas was reduced to 4 mL/min. The photocatalytic activity of the sample was continuously measured after 1 hour of irradiation. The product gas was analyzed using a gas chromatography (Agilent 7820A GC) equipped with a thermal conductivity detector (TCD).

The photocatalytic reactor for photocatalytic CO₂ reduction was displayed in Fig.



Fig.S1. Schematic diagram of the set-up of photocatalytic CO₂ reduction experiment.

The yields of CH₄ and CO were calculated using Equation 1, while the yield of O_2 was determined using Equation 2. In these equations, Y represents the yield of the target gas, μ mol·g⁻¹·h⁻¹, V_{gas} refers to the volumetric flow rate of the product gas, L·h⁻¹, A_{used} denotes the amount of photocatalyst employed, g, and C is the concentration of CH₄, CO or O₂ measured by gas chromatography, μ mol·L⁻¹. The selectivity for CH₄ or CO selectivity was calculated using Eq.3, where S indicates the selectivity of the target product and Y is the yield of CH₄ or CO, μ mol·g⁻¹·h⁻¹.

$$Y_{CH_4 \text{ or } CO} = \frac{V_{gas} \times C_{CH_4 \text{ or } CO}}{A_{used}}$$
(S1)

$$Y_{O_2} = \frac{V_{gas} \times (C_{outlet, O_2} - C_{inlet, O_2})}{A_{used}}$$
(S2)

$$S = \frac{Y_{CH_4 \text{ or } CO}}{Y_{CH_4} + Y_{CO}}$$
(S3)

The apparent quantum yield (AQY) was calculated using Equation S4-8. In this equation, Ne represents the total number of electrons transferred in the reaction, and Np represents the number of incident photons. The reaction rate, v, is expressed in units of moles per second, mol·s⁻¹. N_A denotes the Avogadro constant, 6.02×10^{23} mol⁻¹, and K represents the number of electrons transferred in the reaction, the number of electrons transferred in the reaction the reaction. Specifically, the number of electrons transferred in the formation of CO is 2, while for CH₄ formation, it is 8. The Planck constant, h, is, 6.62×10^{-34} J·s, and c represents the speed of light, 3.0×10^8 m·s⁻¹. The light power

density, W, is 1500 W·m⁻², and S denotes the area of incident light exposure, 0.002 m². E_T , $P_{E\lambda}$, and E_{λ} represent the light power, the proportion of photon energy at wavelength λ in the total energy, and photon energy at wavelength λ , respectively. The wavelength of the incident light is denoted by λ . Additionally, λ_0 and λ_g represent the minimum and maximum wavelengths, respectively, that the catalyst can absorb, while λ_i and λ_e represent the minimum and maximum wavelengths, respectively, emitted by the xenon lamp. Finally, I_{λ} represents the light intensity of the xenon lamp at wavelength λ .

$$AQY = \frac{Ne}{Np} \times 100\% = \frac{(v_{CO} \times N_A \times K_{CO}) + (v_{CH4} \times N_A \times K_{CH4})}{Np} \times 100\%$$
(S4)

$$Np = \int_{\lambda_0}^{\lambda_g} \frac{P_{E\lambda} \times E_T}{E_\lambda} d\lambda$$
 (S5)

$$P_{E\lambda} = \frac{I_{\lambda}}{\int_{\lambda_i}^{\lambda_e} I_{\lambda} d\lambda}$$
(S6)

$$E_{\lambda} = \frac{hc}{\lambda} \tag{S7}$$

$$E_T = \frac{W \times S}{1.602} \times 10^{19} \ (eV. \ s^{-1}) \tag{S8}$$

The internal quantum efficiency (IQE) was calculated as Equation S9-11. In these equations, Npi represents the number of photons absorbed by catalyst. $P_{A\lambda}$ denotes the proportion of photon energy absorbed at wavelength λ relative to the total energy absorbed by the catalyst. Finally, $I_{\lambda a}$ represents the light intensity of the xenon lamp at wavelength λ that is absorbed by catalyst. Fig S2 illustrates the light intensities absorbed by different catalysts.

$$IQE = \frac{Ne}{Npi} \times 100\% = \frac{(v_{CO} \times N_A \times K_{CO}) + (v_{CH4} \times N_A \times K_{CH4})}{Npi} \times 100\%$$
(S9)

$$Npi = \int_{\lambda_0}^{\lambda_g} \frac{P_{A\lambda} \times E_T}{E_{\lambda}} d\lambda$$
(S10)

$$P_{A\lambda} = \frac{I_{\lambda a}}{\int_{\lambda_i}^{\lambda_e} I_{\lambda a} d\lambda}$$
(S11)



Fig. S2. Light intensity spectrum of the xenon lamp and the corresponding light intensities absorbed by different catalysts.

2. Supplementary results and discussions



Fig. S3. Zeta potentials of BWO-P and Cu NPs at the pH of 7.



Fig. S4. XPS spectra survey spectrum of BWO-P, BWO-Cu-1, BWO-Cuhy-1, BWO-Cu-2 and BWO-Cuhy-2.

In order to investigate the reduction process of BWO-Cu in hydrogen, a programmed temperature-raising reduction (TPR) was performed. The H₂-TPR spectrum of the BWO-Cu-2 sample showed three reduction peaks, with the main sharp peak at around 427 °C and the remaining two at around 659 °C and 749 °C, respectively. In addition, from the thermal conductivity detector (TCD) signals at 100 \sim 250 °C, another small reduction peak was found at 150 °C. While BWO-P did not show a reduction peak at 150 °C, therefore, it is presumed that BWO-Cu-2 reduces surface-loaded copper oxide at 150 °C. To confirm this idea, after hydrogen reduction of BWO-Cu-2 at 250°C for 5 h, the samples were examined by XRD and showed no phase change and no impurities. In contrast, after hydrogen reduction for 5 h at 465°C for 5 h, the Bi-O bond was also broken in its entirety, as well as part of the W-O bond, and Bi₂WO₆ was reduced to a mixture of Bi metal and WO_{2.625}.



Fig. S5. (a) H_2 -TPR profile of BWO-P and BWO-Cu-2. (b) The XRD spectra of H_2 reduction of BWO-Cu-2 at 250°C for 5 h and H_2 reduction of BWO-Cu-2 at 465°C for 5 h.

Table. S1. Determination of the percentage of different valence states of Cu in the surfacelayer of four BWO-Cu samples by XPS.

	Percent of Cu ⁰	Percent of Cu ²⁺	Percent of Cu ⁺	Percent of Cu ²⁺ and Cu ⁺
samples	(%)	(%)	(%)	(%)
BWO-Cu-1	55.55	23.90	20.55	44.45
BWO-Cuhy-1	52.21	25.51	22.28	47.79
BWO-Cu-2	27.02	42.03	30.95	72.98
BWO-Cuhy-2	24.81	51.52	23.67	75.19



Fig. S6. ATR-FTIR profiles (resolution 4 cm⁻¹, 32 scans) of BDC-NH₂, BWO-Cuhy-1, BWO-Cu-1 and BWO-P.

The contact angles were measured to be 25.5° for BWO-P, 23.3° for BWO-Cu-1, and 23.9° for BWO-Cu-2. The surface of Bi₂WO₆ was found to be hydrophilic and highly wettable without the use of a hydrophobic agent. However, when a hydrophobic agent was added, the hydrophilicity of the surface decreased. The contact angles of BWO-Cuhy-1, BWO-Cuhy-2, and BWO-hy were measured to be 43.8° , 46.1° and 44.6° , respectively. This suggests that the addition of BDC-NH₂ results in the formation of a hydrophobic surface in Bi₂WO₆.



Fig. S7. Contact angle tests of water on (a)BWO-P, (b)BWO-Cu-1, (c)BWO-Cu-2, (d)BWO-Cu-1, (e)BWO-Cu-1, (e)BWO-Cu-2 and (f)BWO-hy samples.

The valence band (VB) potential, which has been tested by VB-XPS, can be calculated by the formula $E(NHE) = \varphi + E(VB-XPS) - 4.44$, where E(NHE) represents the standard hydrogen potential of the valence band, E(VB-XPS) is the value of the VB measured by VB-XPS, and φ is the instrumental work function (4.53 eV)^[S1]. The VB values of BWO-P, BWO-Cu-1, BWO-Cu-2, BWO-Cuhy-1 and BWO-Cuhy-2 are 1.62, 1.17, 0.93, 1.51 and 1.29 V (vs NHE), respectively (Fig.S7). The equation E(VB) = Eg + E(CB) was employed to calculate the conducting band (CB) potentials, which yielded values of -1.31, -1.40, -1.49, -0.90, and -0.86 V (vs NHE) ^[S2]



Fig. S8. VB-XPS spectra of BWO-P, BWO-Cu-1, BWO-Cu-2, BWO-Cuhy-1 and BWO-

Cuhy-2.



Fig. S9. CO, CH₄ and O₂ products formation rate over BWO-P, BWO-Cu-1, BWO-Cu-2, BWO-hy, BWO-Cuhy-1, and BWO-Cuhy-2 (means \pm S.E.M., n = 3).

Samples	СО	CH ₄	O ₂
BWO-P	0.11	0	0.12
BWO-Cu-1	0.25	0.04	0.13
BWO-Cu-2	0.18	0.06	0.11
BWO-hy	0.11	0.02	0.08
BWO-Cuhy-1	0.08	0.11	0.12
BWO-Cuhy-2	0.11	0.08	0.16

Table. S2. The standard error of the mean of catalyst yield (n = 3).



Fig. S10. CO, CH₄ and O₂ products formation rate over BWO-Cuhy-1 and BWO-Cuhy-2 after photocatalysis for 3 h, 6 h, 9 h and 12 h.



Fig. S11. In situ FT-IR spectra on catalysts (a)BWO-P and (b) BWO-Cu-2. The curves from bottom to top correspond to the time intervals of 0, 3, 6, 9, 12, 15, 18, 21, 24, 27 and 30 min.

samples	Light source	Types of photocatalytic reactions	AQY	Ref.
Bi ₂ WO ₆	Xenon lamp	Hydrogen evolution	0.9	[\$3]
IOBi ₂ WO ₆ /15Bi ₂ O ₃	Xenon lamp	Hydrogen evolution	8.9	[\$3]
Bi ₂ WO ₆	Xenon lamp	Toluene oxidation	1.34	[S4]
1.8 Ni/BWO	Xenon lamp	Toluene oxidation	6.01	[S4]
15-ZnCo ₂ S ₄ /Bi ₂ WO ₆	Xenon lamp $\lambda > 420 \text{ nm}$	Hydrogen evolution	13.2	[85]

Table. S3. Bi_2WO_6 performance comparison for photocatalytic reactions.

samples	Light source	Photosensitizer and sacrificial agents	AQY	Ref.
BWO-Cu-	Xenon lamp	None	2.60	This work
BDC-NH ₂	$\lambda > 400 \text{ nm}$			
Ni-Co ₃ O ₄	Xenon lamp	Ru(bpy) ₃ and TEOA	3.70	[S6]
NSDHN	$\lambda > 420 \ nm$			
Co/NiO	Xenon lamp	Ru(bpy) ₃ and TEOA	1.96	[S7]
	$\lambda > 420 \text{ nm}$			
Ni(OH) ₂ -GR	Xenon lamp	Ru(bpy) ₃ and TEOA	1.03	[S8]
	$\lambda > 420 \ nm$			
g-C ₃ N ₄	Xe lamp	TEOA	1.96	[S9]
/[Co(dmbpy) ₃] ²⁺	$\lambda = 400 \text{ nm}$			
g-C3N4 (NH3)	Xe lamp	TEOA	0.43	[S10]
	$\lambda = 400 \text{ nm}$			
CdS Quantum	Xenon lamp	TEOA	1.40	[S11]
Dot Aerogels	$\lambda > 420 \text{ nm}$			
Ce-MOF	Xe lamp	none	0.93	[S12]
	λ>400 nm			
g-C ₃ N ₄ /Ni ₂ P	Xe lamp	TEOA	3.20	[S13]
	$\lambda = 435 \text{ nm}$			
PCdS/NiCoLDH	Xe lamp	DMF and TEA	3.80	[S14]
BiO _{2-x} /g-C ₃ N ₄	Xe lamp	none	1.50	[S15]

Table. S4.	. Comparison of the	e performances of	photocatalytic	CO ₂ conversion systems.	

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