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Methanol yield depends on mass transfer resistance resulting from pyridine adsorption layer on $CuInS_2$ photocathode in photoelectrochemical reduction of CO_2 .

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CO₂ to methanol at CuInS₂ Thin Film Electrode

Role of Pyridine in Photoelectrochemical Reduction of

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The crystal size and composition of CuInS₂, coverage of pyridine at CuInS₂ thin film photocathode and the applied bias have significant effects on methanol yield in photoelectrochemical reduction of CO₂. The mass transfer resistance resulting from pyridine adsorption layer is proposed to be the determining step.

In order to suppress global warming, the conversion of CO₂ into value-added products is a promising approach. Electrochemical and photoelectrochemical routes of the reduction of CO₂ to methanol, a bulk chemical, have been developed;¹ however, due to high redox potential of CO₂ to CO₂⁻⁻ (-1.90V vs standard hydrogen electrode, SHE), extremely high overpotential is required, leading to high energy consumption.¹ Moreover, owing to inevitable hydrogen evolution reaction (HER) in an aqueous electrolyte, methanol yield and selectivity are usually very low.¹ Pyridine, as a cocatalyst, has been proven to be successful in decreasing the overpotential of CO₂ reduction and inhibit the HER.²⁻⁸ However, the relatively low rate in photoelectrochemical and electrochemical reduction of CO₂ with the cocatalysis of pyridine limits its application. There has been serious disagreement on how pyridine affects photoelectrochemical and electrochemical reduction of CO2. A carbamate radical adduct (Py-CO₂H[•]) mechanism was proposed by Bocarsly group;⁵⁻⁷ nevertheless it was proven that the reduction of pyridinum (PyH⁺) to pyridinyl radical (PyH') was unfavourable in an aqueous solution.⁹⁻¹¹ A proton-coupled hydride transfer mechanism activated by PyH⁺ was suggested,¹² whereas it could not explain the relatively low rate and the formation of methanol.^{2,3}

In our previous study, the p type $CuInS_2$ photocathode, an ideal photovoltaic material in visible light range, has been proposed for highly selective reduction of CO₂ to methanol at a lower overpotential under visible light illumination, and the average rate of CO₂ reduction, about 2.6 g/m²/h has been obtained.³ Herein we suggest that the low rate of CO₂ reduction with pyridine is resulted from the pyridine adsorption layer at p-CuInS₂ photocathode.

CuInS₂ thin films were fabricated by electrochemical codeposition of Cu-In alloy layers followed by sulfurization. ^{3,13} Chalcopyrite CuInS₂ thin films can be obtained at electrodeposition potential from -970 to -1030 mV (vs saturated calomel electrode, SCE), and the best crystalline structure occurs at -1000 mV (Figure S1). The molar ratio of Cu to In (Cu/In) at $CuInS_2$ thin film surface and crystal size of $CuInS_2$ can be regulated by deposition potential as shown in Table 1.

Table 1. Effect of deposition potential on crystal size of $CuInS_2$, Cu/In at thin film surface, and methanol concentration in photoelectrochemical reduction of CO_2^{a}

F				
Deposition	Crystal	Cu/In (mol/	CH ₃ OH	
potential (mV)	size (nm)	mol)	(mM)	
-970	61.4	1.12	0.25	
-985	46.9	1.45	0.99	
-1000	38.4	1.46	1.67	
-1015	53.7	1.08	0.53	
-1030	28.4	0.85	0	

^a Photoelectrochemical reduction experiments are conducted at CuInS₂ thin film photocathode ($1 \times 2 \text{ cm}^2$) at -590 mV (vs SCE) in 0.1 M acetate buffer solution containing 10 mM pyridine at pH 5.2 for 7 h, with visible light irradiation of 100 mW/cm².

Cu/In for CuInS₂ thin films fabricated at deposition potential from -970 to -1015 mV is above 1.00, while that at -1030 mV is below 1.00. The maximum Cu/In occurs at -1000 mV. Photoelectrocatalytic reduction results show that methanol can only be obtained at Cu/In over 1.00 (Table 1), indicating that Cu(I) species at CuInS₂ surface might be active site. Cu/In has little relationship to methanol yield for Cu-rich thin films; however, crystal size of CuInS₂ has a significant effect on methanol yield (Table 1). With decreasing crystal size, methanol concentration increases dramatically.

Due to π bond in pyridine ring and lone pair electrons at N atom, pyridine molecules can specifically adsorb on CuInS₂ cathode surface.⁴ Carter group suggested that electron-donating molecules such as pyridine might adsorb at electron-deficient GaP surface.¹⁴ The coverage of pyridine is measured by voltammetric study, and the results show that pyridine coverage increases with increasing pyridine concentration (Figure 1). Methanol concentration increases as the increase of pyridine concentration up to 10 mM, while it decreases with the increase from 10 to 25 mM, indicating that excessive pyridine molecules adsorbed on CuInS₂ surface might cover active centers, causing the decrease of methanol yield.

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Figure 1. Effect of pyridine concentration on its coverage and methanol concentration. Photoelectrochemical reduction experiments are conducted at $CuInS_2$ thin film photocathode (1×2 cm²) at -590 mV (vs SCE) in 0.1 M acetate buffer solution containing pyridine at pH 5.2 for 7 h, with visible light irradiation of 100 mW/cm².

The linear scanning voltammetric curve at p-CuInS₂ electrode in the electrolyte containing 10 mM pyridine at pH 5.2 is studied (Figure 2). The cathodic peak potential locates at -590 mV, and HER dominates when applied bias is negative to -660 mV. The maximum methanol concentration also occurs at -590 mV, and methanol concentration at various applied bias shows strong relationship to cathodic current in voltammetric curve (Figure 2).



Figure 2. Linear scanning voltammetric curve at $p-CuInS_2$ electrode and effect of applied bias on methanol concentration. Photoelectrochemical reduction experiments are conducted at CuInS₂ thin film photocathode (1×2 cm²) in 0.1 M acetate buffer solution containing 10 mM pyridine at pH 5.2 for 7 h, with visible light irradiation of 100 mW/cm².

There are two distinctive semicircles in electrochemical impedance spectroscopy in the frequency range from 0.01 Hz to 100 kHz for photoelectrochemical reduction of CO_2 (Figure 3a, 3b). The size of the first semicircle in high frequency region remains almost unchanged with the polarization, indicating that this portion of the impedance is attributed to the ohmic process within the electrode structure. The size of the second semicircle decreases with polarization, which is expected for kinetic impedance of electrochemical reactions. In addition, the distortion in the kinetic semicircle indicates an additional mass-transport resistance.

An equivalent circuit model is proposed based on the above discussion (Figure 3c). This model includes electrolyte resistance between the working and the reference electrodes (R_e) , electronic resistance of the electrode material (R_i) and faradic impedance (Z_f) . The double layer capacitance is distributed between the ohmic and faradaic processes and represented by C_{dI} and C_{d2} , respectively. The faradaic impedance can be further divided into a kinetic resistance



Figure 3. Electrochemical impedance spectroscopy for CO_2 reduction at p-CuInS₂ electrode (1×2 cm²) in the electrolyte containing 10 mM pyridine at pH 5.2. (a) Nyquist diagram, (dash line) experimental data, (solid line) fitted data; (b) Enlarged Nyquist diagram, (red) -640 mV, (green) -590 mV, (blue) -550 mV, (black) -450 mV; (c) Equivalent circuit model.

 (R_k) and a mass transfer impedance (Z_m) . The mass transfer impedance consists of mass transfer resistance (R_m) and capacitance (C_m) . The values of the equivalent circuit components are shown in Table S1. The mass transfer resistance is an order of magnitude higher than the kinetic resistance; namely, it is the determining step.

Bocarsly group suggested a possible intermediate, hydrogen bond pyridine dimer, might be the pre-electrocatalyst in the electrocatalytic reduction of CO_2 to methanol, and isolated it at higher total concentration of pyridine and pyridinium. ¹⁵ Pyridine dimer concentration reaches the maximum at pH 5.2 since a near equimolar mixture of pyridine and pyridinium. ¹⁵ According to this statement, the maximum yield of methanol should be obtained at pH 5.2; it is true in our study.³

When CO_2 gas is introduced into the electrolyte, pyridine dimer might react with CO_2 into pyridine and the positively charged adduct of pyridinium and CO_2 (Scheme 1). The energy of this reaction is



Scheme 1. Activation of CO₂.

kcal/mol.

concentration.

2).

Due to its π bond in pyridine ring, the adduct can adsorb at cathode surface with pyridine ring paralleling to electrode surface, and the electrons at cathode surface can therefore transfer to the adduct (Scheme 2).¹⁶ With the increase of electron cloud density of carbonyl group in the adduct, the lone pair electrons of carbonyl O atom can enter the vacant 4*s* orbit of Cu(I), carbonyl group can therefore be activated (Scheme 2), and finally be reduced into hydroxyl group. The electron configuration of active sites, $d^{10}s^{0}$, just as that of Cu(I), is the most striking feature for all of reported electrode materials leading to highly selectivity to methanol with the cocatalysis of pyridine; otherwise, other products are formed (Table

estimated to be -47 kcal/mol, and the energy of barrier is only 2

prevents them from arriving at cathode surface, it is therefore difficult to go on with the subsequent reactions. With the increase of

(Figure 3a, Table S1), leading to the increase of methanol

applied bias from -450 to -590 mV, pyridine coverage at CuInS₂

surface decreases, the diffusion resistance therefore becomes smaller

The positively charged adduct moves to $CuInS_2$ photocathode surface; unfortunately, pyridine adsorption layer at $CuInS_2$ cathode

e N-H⁺⁻⁻O=C---O

Scheme 2. Electron transfer at CuInS₂ cathode surface.

Table 2. Effect of electron configuration of active sites on reduction products with the cocatalysis of pyridine

Electrode	Active	Electron	Product	
material	site	configuration		
CuInS ₂	Cu(I)	$3d^{10}4s^0$	Methanol ³	
GaP	Ga(III)	$3d^{10}4s^0$	Methanol ²	
Pd	Pd(0)	$4d^{10}5s^0$	Methanol ⁴	
Pt	Pt(0)	$5d^96s^1$	Formic acid,	
			formaldehyde, methanol,	
			hydrogen ^{5, 6}	
FeS ₂	Fe(II)	$3d^{6}4s^{0}$	Formic acid, hydrogen ⁷	
CdTe	Cd(II)	$4d^{10}5s^0$	Formic acid ⁸	

Without pyridine involving, even if the active site has the electron configuration of $d^{10}s^0$, methanol cannot be obtained. At hydrogenated Pd electrode, products with carbonyl group, CO or formic acid, are obtained via a CO₂⁻⁻ route.¹⁷ At cuprous halide-confined Cu-mesh electrodes, ethylene is the main product in acidic solutions.¹⁸

Although Cd(II) has the electron configuration of $4d^{10}5s^0$, only formic acid is produced.⁸ The reason might lie in its smaller electronegativity (1.69). In contrast, the electronegativity of Cu (1.90) and Ga (1.81) is higher. The elements of higher electronegativity allow the lone pair electrons of carbonyl O atom to enter their vacant *s* orbit, leading to the formation of hydroxyl group; while those of smaller electronegativity do not.

Conclusions

The crystal size and composition of CuInS_2 , coverage of pyridine at CuInS_2 thin film photocathode and the applied bias have significant effects on methanol yield in photoelectrochemical reduction of CO_2 . The mass transfer resistance, resulting from pyridine adsorption layer on CuInS_2 photocathode, slows down the reduction rate of CO_2 . The

selectivity to methanol might depend on the electron configuration and electronegativity of active sites. The electron configuration of $d^{10}s^0$ and higher electronegativity of active sites are beneficial to the formation of methanol.

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Notes and references

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