Methanol yield depends on mass transfer resistance resulting from pyridine adsorption layer on CuInS$_2$ photocathode in photoelectrochemical reduction of CO$_2$. 
Role of Pyridine in Photoelectrochemical Reduction of CO$_2$ to methanol at CuInS$_2$ Thin Film Electrode

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Received 00th January 2012,
Accepted 00th January 2012,
DOI: 10.1039/xxxxxxx

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 is proposed to be the determining step.

In order to suppress global warming, the conversion of CO$_2$ into value-added products is a promising approach. Electrochemical and photoelectrochemical routes of the reduction of CO$_2$ to methanol, a bulk chemical, have been developed; however, due to high redox potential of CO$_2$ to CO$_2$- (1.90V vs standard hydrogen electrode, SHE), extremely high overpotential is required, leading to high energy consumption. Pyridine, as a cocatalyst, has proven to be successful in decreasing the overpotential of CO$_2$ reduction and inhibit the HER. However, there is low rate in photoelectrochemical and chemical reduction of CO$_2$ with the cocatalysis of pyridine limits its application. There has been serious disagreement on how pyridine affects photoelectrochemical and electrochemical reduction of CO$_2$. A carbamate radical adduct (Py-CO$_2$H) mechanism was proposed by Bocarsly group; nevertheless it was proven that the reduction of pyridinium (PyH$^+$) to pyridinyl radical (PyH$^-$) was unfavourable in an aqueous solution. A proton-coupled hydride transfer mechanism activated by PyH$^+$ was suggested, whereas it could not explain the relatively low rate and the formation of methanol.

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 CO$_2$ to methanol at a lower overpotential under visible light illumination, and the average rate of CO$_2$ reduction, about 2.6 g/m$^2$/h has been obtained. Herein we suggest that the low rate of CO$_2$ reduction with pyridine is resulted from the pyridine adsorption layer at p-CuInS$_2$ photocathode.

CuInS$_2$ thin films were fabricated by electrochemical co-deposition of Cu-In alloy layers followed by sulfurization. Chalcopyrite CuInS$_2$ 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>
<thead>
<tr>
<th>Deposition potential (mV)</th>
<th>Crystal size (nm)</th>
<th>Cu/In (mol/CH$_3$OH (mM))</th>
</tr>
</thead>
<tbody>
<tr>
<td>-970</td>
<td>61.4</td>
<td>1.12</td>
</tr>
<tr>
<td>-985</td>
<td>46.9</td>
<td>1.45</td>
</tr>
<tr>
<td>-1000</td>
<td>38.4</td>
<td>1.46</td>
</tr>
<tr>
<td>-1015</td>
<td>53.7</td>
<td>1.08</td>
</tr>
<tr>
<td>-1030</td>
<td>28.4</td>
<td>0.85</td>
</tr>
</tbody>
</table>

CuInS$_2$ 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 CuIn over 1.00 (Table 1), indicating that Cu(I) species at CuInS$_2$ surface might be active site. Cu/In has little relationship to methanol yield for Cu-rich thin films; however, crystal size of CuInS$_2$ 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 CuInS$_2$ cathode surface. Carter group suggested that electron-donating molecules such as pyridine might adsorb at electron-deficient GaP surface. 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 CuInS$_2$ surface might cover active centers, causing the decrease of methanol yield.
The double layer capacitance is distributed between the ohmic and semicircle decreases with increase in frequency. The size of the second semicircle decreases with increase in frequency.

There are two distinctive semicircles in electrochemical impedance spectroscopy in the frequency range from 0.01 Hz to 100 kHz for photoelectrochemical reduction of CO2 (Figure 3a, 3b). The size of the first semicircle in high frequency region remains almost unaltered 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 (Rw), electronic resistance of the electrode material (Rs) and faradic impedance (Zf).

The double layer capacitance is distributed between the ohmic and faradaic processes and represented by Cdl and Cfe, respectively. The faradaic impedance can be further divided into a kinetic resistance and a mass transfer impedance. 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 CO2 to methanol, and isolated it at higher total concentration of pyridine and pyridinium. According to this statement, the maximum yield of methanol should be obtained at pH 5.2; it is true in our study.3

When CO2 gas is introduced into the electrolyte, pyridine dimer might react with CO2 into pyridine and the positively charged adduct of pyridinium and CO2 (Scheme 1). The energy of this reaction is

![Figure 1: Effect of pyridine concentration on its coverage and methanol concentration. Photoelectrochemical reduction experiments are conducted at CuInS2 thin film photocathode (1x2 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.](image)

![Figure 2: Linear scanning voltammetric curve at p-CuInS2 electrode and effect of applied bias on methanol concentration. Photoelectrochemical reduction experiments are conducted at CuInS2 thin film photocathode (1x2 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.](image)

![Figure 3: Electrochemical impedance spectroscopy for CO2 reduction at p-CuInS2 electrode (1x2 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.](image)

![Scheme 1: Activation of CO2.](image)
estimated to be ~47 kcal/mol, and the energy of barrier is only 2 kcal/mol.

The positively charged adduct moves to CuInS₂ photocathode surface; unfortunately, pyridine adsorption layer at CuInS₂ cathode prevents them from arriving at cathode surface, it is therefore difficult to go on with the subsequent reactions. With the increase of applied bias from ~450 to ~590 mV, pyridine coverage at CuInS₂ surface decreases, the diffusion resistance therefore becomes smaller (Figure 3a, Table S1), leading to the increase of methanol concentration.

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).²⁰ 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 4s 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, d⁰⁰⁰, 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 2).

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

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Active site</th>
<th>Electron configuration</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuInS₂</td>
<td>Cu(I)</td>
<td>3d⁰⁰⁰⁰⁰⁰⁰⁰</td>
<td>Methanol</td>
</tr>
<tr>
<td>GaP</td>
<td>Ga(III)</td>
<td>3d⁰⁰⁰⁰⁰⁰⁰⁰</td>
<td>Methanol</td>
</tr>
<tr>
<td>Pd</td>
<td>Pd(0)</td>
<td>4d⁰⁰⁰⁰⁰⁰⁰⁰</td>
<td>Methanol</td>
</tr>
<tr>
<td>Pt</td>
<td>Pt(0)</td>
<td>5d⁰⁰⁰⁰⁰⁰⁰⁰</td>
<td>Formic acid, formaldehyde, methanol, hydrogen</td>
</tr>
<tr>
<td>FeS₂</td>
<td>Fe(II)</td>
<td>3d⁰⁰⁰⁰⁰⁰⁰⁰</td>
<td>Formic acid</td>
</tr>
<tr>
<td>CdTe</td>
<td>Cd(II)</td>
<td>4d⁰⁰⁰⁰⁰⁰⁰⁰</td>
<td>Formic acid, hydrogen</td>
</tr>
</tbody>
</table>

Without pyridine involving, even if the active site has the electron configuration of d⁰⁰⁰, methanol cannot be obtained. At hydrogenated Pd electrode, products with carbonyl group, CO or formic acid, are obtained via a CO₂⁻ route.²⁷ At cuprous halide-confined Cu-mesh electrodes, ethylene is the main product in acidic solutions.²⁸

Although Cd(II) has the electron configuration of 4d⁰⁰⁰⁰⁰⁰⁰⁰, only formic acid is produced.³ 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 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 on CuInS₂ photocathode, slows down the reduction rate of CO₂. The selectivity to methanol might depend on the electron configuration and electronegativity of active sites. The electron configuration of d⁰⁰⁰ and higher electronegativity of active sites are beneficial to the formation of methanol.

Acknowledgements

We gratefully acknowledge National Natural Sciences Foundation of China (Grant No. 20776013), Beijing Natural Science Foundation (Grant No. 2102034) and the Special Fund of Basic Research in Central Universities (Grant No. JD1107) for financial support.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details and additional results. See DOI: 10.1039/c000000x/