Int. J. Electrochem. Sci., 12 **(2017)** 8288 – 8294, doi: 10.20964/2017.09.36

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Photoelectrochemical Reduction of Carbon Dioxide to Ethanol at Cu_2O Foam Cathode

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Received: 8 May 2017 / *Accepted:* 3 July 2017 / *Published:* 13 August 2017

Direct reduction of CO_2 to ethanol with a high rate at a low overpotential is quite difficult. In this study, the Cu_2O foam electrode with three-dimensional coaxial network structure is fabricated by electrodeposition of Cu_2O coatings on copper foam substrate. It shows unprecedented photoelectrocatalytic performance on the reduction of CO_2 to ethanol. The formation rate of ethanol as high as 71.67 μmol cm^{-2} h^{-1} is obtained at the overpotential as low as 131 mV within 1.5 h.

Keywords: Carbon dioxide, Ethanol, Photoelectrochemical reduction, Cuprous oxide, Foam electrode.

1. INTRODUCTION

The rapid increase of CO_2 gas in the atmosphere causes serious global warming. Some technologies of CO_2 capture, sequestration and conversion have been developed, among which the technology of converting CO_2 into useful chemicals is the most promising [1,2]. Converting CO_2 to ethanol will promote closed cycle of CO_2, and ethanol can be used as fuels and chemicals.

CO_2 can be reduced to ethanol by electrochemical method, and the catalysts such as metallic Cu, Cu oxides have been developed [3-7]. At metallic Cu electrode, CO_2 is reduced to ethanol at extremely high overpotential (>0.9 V), and the faradaic efficiency of ethanol formation is less than 10% [4,5]. At Cu_2O electrode, CO_2 is reduced to ethanol, formic acid and methanol, among which ethanol is the major product [6]. However, Cu_2O electrode is unstable, and can be reduced to metallic

Cu within 30 min; the faradaic efficiency of ethanol formation decreases from 96.2% at 5 min to 38.5% at 25 min [6]. CuO/carbon paper electrodes have been fabricated for CO_2 reduction, and the product ethanol is obtained [7]. Nevertheless, CuO electrode is also unstable [7]. At Cu_2O and CuO electrodes, the overpotential of the reduction of CO_2 to ethanol is extremely high (>1.0 V), and the high overpotential promotes the reduction of Cu_2O and CuO to metallic Cu, which causes the poor stability of Cu_2O and CuO electrodes [7]. In our previous study, pyridine cocatalyst can decrease the overpotential of CO_2 reduction via the formation of the intermediate, $C_5H_5N\text{-}H^+\ldots O{=}C{=}O$ [8].

Due to large surface area, well-defined pore size, good hydrodynamic characteristics and high conductivity, copper foam substrates are better supports for catalysts than conventional planar supports. It is expected to improve the catalytic performance of Cu_2O for CO_2 reduction by loading Cu_2O catalysts on copper foam support. In this study, using the Cu_2O foam electrode as the photocathode and pyridine as the cocatalyst, CO_2 is reduced photoelectrochemically to ethanol with a high rate at a low overpotential.

2. EXPERIMENTAL

2.1 Fabrication of Cu_2O foam electrodes

Cu_2O foam electrodes were fabricated by electrodeposition of Cu_2O coatings on copper foam substrates. A copper foam substrate (the working area is 2 cm^2 and the thickness is 0.5 mm), platinum foil and saturated calomel electrode (SCE) were used as the working electrode, the counter electrode and the reference electrode, respectively. The electrolytic solution (50 mL) containing 0.4 mM $CuSO_4$ and 3 M lactic acid was adjusted to pH 10 by adding concentrated NaOH aqueous solution [9,10]. The electrodeposition was employed for 20 min at -0.60 V (vs. SCE) and 60 ^oC.

The morphology of Cu_2O foam electrode was determined by a field emission scanning electron microscopy (FESEM, S-4700, Hitachi, Japan). The crystal structure of Cu_2O coatings was determined by X-ray diffractometry (XRD, Bruker D8 Advance, Germany), and the crystal grain size was then calculated from X-ray line broadening using the Scherrer's equation. The UV-Vis spectrum of Cu_2O foam electrode was measured with UV-vis-NIR spectrophotometer (UV-3600, Shimadzu, Japan).

2.2 Photoelectrochemical reduction of CO_2

The solar-driven photoelectrochemical reduction of CO_2 was performed in 0.1 M acetate buffer solution (50 mL) containing 30 mM pyridine. A conventional three-electrode cell was used with Cu_2O foam electrode (working area is 2 cm^2) as the working electrode, the graphite sheet as the counter electrode and SCE as the reference electrode. The irradiation intensity on the working electrode was calibrated to be 100 mW cm^{-2}. Before the reduction experiment, the electrolyte solution was bubbled with CO_2 gas (99.99%) for 30 min. CO_2 gas was constantly introduced into the electrolyte solution at a flow rate of 60 mL min^{-1} during the whole experiment. Liquid product analysis was accomplished using gas chromatography-mass spectroscopy (GC-MS, Trace 1300-ISQ, ThermoFisher Scientific,

USA), and ethanol concentration was measured by a gas chromatography (GC 2014C, Shimadzu, Japan) with a DB-Wax (30 m×0.53 mm×3.00 μm, Agilent Technologies). The injector temperature was held at 200 ^{o}C, the oven temperature rose from 50 to 200 ^{o}C at a rate of 5 ^{o}C min^{-1}, and the detector temperature was kept at 230 ^{o}C. Five runs were done for one experiment.

The linear scanning voltammetric measurement of the Cu_2O foam electrode was conducted in the above setup, and the scanning potential was set from 0 to -1.000 V (vs. SCE) at 5 mV s^{-1}. The current density was determined on the geometric area of the foam electrode (2 cm^2).

3. RESULTS AND DISCUSSION

3.1 Fabrication and characterization of Cu_2O foam electrodes

The FESEM images of Cu_2O foam electrode are shown in Fig. 1. The Cu_2O foam electrode has well-developed porous structure, and the pore size is about 400 μm, and it exhibits three-dimensional coaxial network structure of outer Cu_2O tube and inner Cu wire, which facilitates the light-driven charges in Cu_2O semiconductor to transfer rapidly along Cu wire to the external circuit, thus promoting the separation of light-driven charges. It is observed that Cu_2O coatings on copper foam substrate have the thickness of about 2 μm, and the surface of Cu_2O coatings exhibits truncated pyramid geometry, similar to Cu_2O thin films electrodeposited on stainless steel substrates [9].

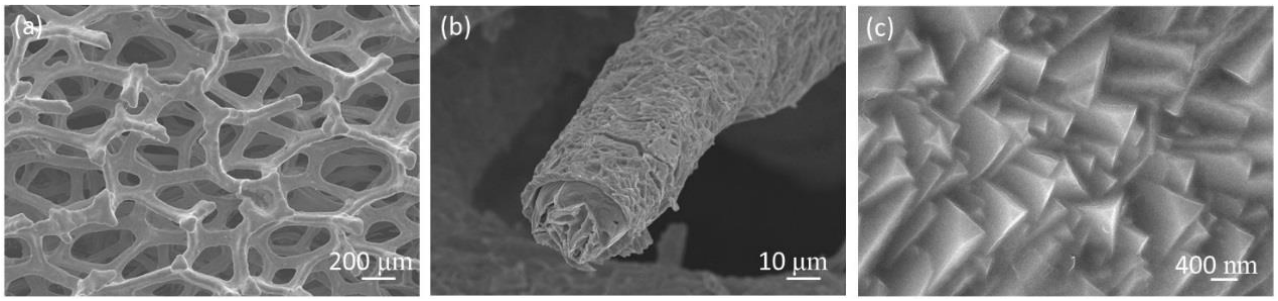

Figure 1. FESEM images of the Cu_2O foam electrode. (a) full view, (b) cross section view, (c) enlarged surface.

The XRD pattern of the Cu_2O foam electrode is presented in Fig. 2. The peaks at 43.4, 50.5 and 74.1^{o} can be indexed to Cu (111), (200) and (222) facets. The peaks at 29.8, 37.4 42.6 and 61.8^{o} can be indexed to cuprite Cu_2O (110), (111), (200) and (220) facets, and a very strong peak at 37.4^{o} indicates that Cu_2O crystal grows preferentially along (111) facet. It has been reported that the preferential growth facet of Cu_2O is dependent on pH of electrodeposition solution, and it is (111) facet at pH>9 [11]. The grain size of Cu_2O, estimated from XRD pattern, is about 26.5 nm.

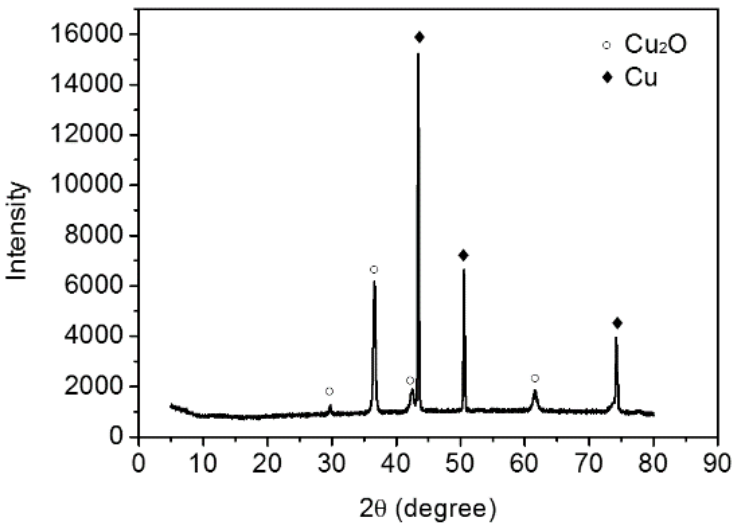

Figure 2. XRD of the Cu_2O foam electrode.

Fig. 3 shows the UV-vis spectrum of the Cu_2O foam electrode. The Cu_2O foam electrode exhibits strong absorbance in the visible light range, especially in 400-550 nm range. The bandgap is estimated to be 1.95 eV by Tauc equation.

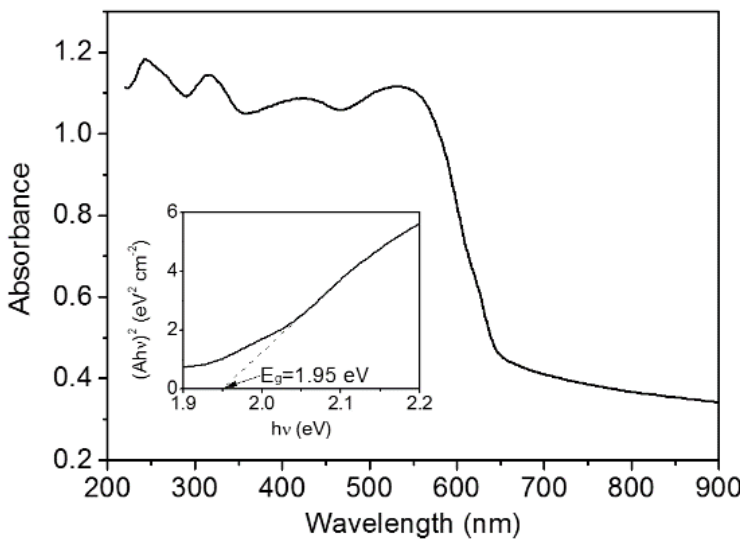

Figure 3. UV-vis spectrum of the Cu_2O foam electrode and the bandgap value (inset).

3.2 Photoelectrochemical reduction of CO_2 at Cu_2O foam cathodes

Linear scanning voltammetric curves of the Cu_2O foam electrode in dark and under illumination in 0.1 M acetate buffer solution containing saturated CO_2 and 30 mM pyridine are compared in Fig. 4. In contrast to the voltammetric behavior in dark, a dramatic increase in peak current density at -0.60 V (vs. SCE) is observed under illumination, indicating that the reduction of CO_2 becomes significant.

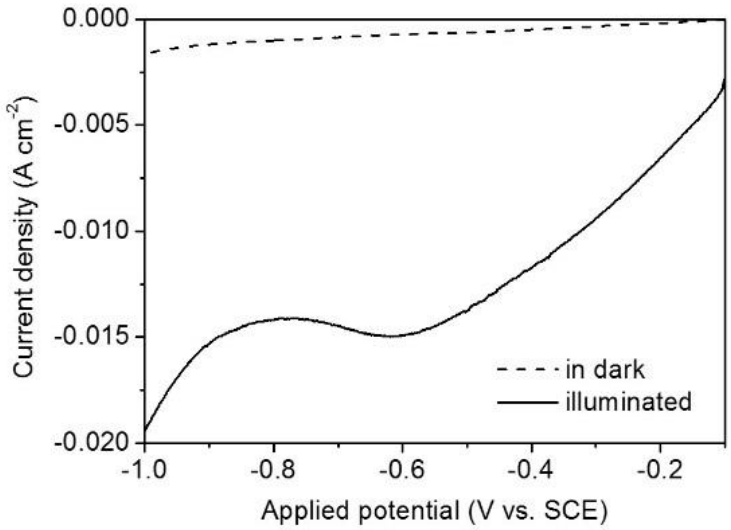

Figure 4. Linear scanning voltammetric curve of the Cu_2O foam electrode.

In the liquid product of photoelectrocatalytic reduction of CO_2, only ethanol as the reaction product is detected by GC-MS. When the photoelectrochemical reaction is employed with the introduction of nitrogen gas rather than CO_2 gas, no ethanol is detected in the reaction product, indicating that ethanol is not derived from acetic acid, sodium acetate or pyridine, but from CO_2.

Ethanol concentration at various applied potential is shown in Table 1. It reveals that the applied potential has a significant influence on ethanol concentration. Ethanol concentration increases with increasing potential from -0.55 to -0.60 V (vs. SCE), and it achieves the optimum at -0.60 V; then it decreases with increasing potential from -0.60 to -0.70 V. The relationship between applied potential and ethanol concentration is similar to that between applied potential and current density as shown in Fig. 4. At -0.60 V, it adds up to 4.3 mM in 1.5 h; namely, the average formation rate of ethanol is 71.67 μmol cm^{-2} h^{-1} within 1.5 h, which is much higher than that in previous studies [6,7,12]. The high formation rate of ethanol can be attributed to high specific surface area which promotes the full contact of the catalytic active centers with the reactants in photoelectrochemical reduction of CO_2.

Table 1. Ethanol concentration at various applied potential.

Applied potential (V vs. SCE)	Ethanol concentration (mM)
-0.55	2.19
-0.60	4.28
-0.65	1.82
-0.70	1.26

Yadav et al. has proposed that, at above 1.5 V, Cu_2O cathode with the preferential (200) facet can reduce CO_2 to ethanol in $KHCO_3$ solution [6]. The extremely high overpotential is resulted from the high electrode potential of $CO_2/CO_2^{\cdot -}$ (-1.90 V vs. normal hydrogen electrode) [6]. In this study,

pyridine cocatalyst decreases the overpotential of CO_2 reduction, and the highest formation rate of ethanol is obtained at -0.60 V (vs. SCE), that is, at the overpotential of 131 mV.

Since the reduction potential of CO_2 decreases in this study, the reduction of Cu_2O becomes less significant, and the stability of Cu_2O foam electrodes is enhanced. However, the activity of Cu_2O foam electrodes in this study decreases after 1.5 h. Therefore, the stability of Cu_2O foam electrodes needs to improve further.

At the same Cu_2O foam electrode, methanol is obtained in $KHCO_3$ solution in our previous study [10]; in contrast, ethanol is produced in acetate buffer solution containing pyridine in the present study. It indicates that the electrolytic solution has a significant effect on the product species.

The possible reaction intermediates, methanol, acetaldehyde and formic acid are introduced in the electrolyte solution to replace CO_2 as the reactant, respectively. It is observed that ethanol occurs in the electrolyte solution containing methanol, and ethanol concentration increases with the reaction time, accompanied by the decrease of methanol concentration. However, no ethanol occurs in the electrolyte solution containing acetaldehyde or formic acid. It indicates that methanol might be the intermediate in the reduction of CO_2 to ethanol. The mechanism needs further investigation.

4. CONCLUSIONS

The Cu_2O foam electrode with three-dimensional network structure has been fabricated by electrodeposition of Cu_2O coatings on copper foam substrate, and it has the coaxial structure of Cu_2O tube and Cu wire. The Cu_2O foam electrode exhibits strong absorbance in visible light range, and its bandgap is estimated to be 1.95 eV. At the Cu_2O foam photocathode, solar driven photoelectrochemical reduction of CO_2 to ethanol occurs with a high rate at a low overpotential. The formation rate of ethanol as high as 71.67 μmol cm^{-2} h^{-1} is obtained at the overpotential as low as 131 mV within 1.5 h. Methanol might be the intermediate in the reduction reaction of CO_2 to ethanol.

ACKNOWLEDGEMENTS
The project is funded by Special Found for Beijing Common Construction Project (Grant No. jwgj201707) and National Natural Science Foundation of China (Grant No. 21676010).

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