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PHOTOELECTROCATALYTIC CONVERSION OF CO_2 INTO VALUE-ADDED ORGANIC COMPOUNDS USING CU_2O PHOTOCATHODE

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ABSTRACT: The global warming from CO_2 emission effect and finding renewable energy are two major issues in today's environmental and energy problems. The conversion of CO_2 into value-added chemicals to achieve an energy-saving and low-carbon economy is needed to be developed. Photoelectrocatalytic technology is one of the most alternative ways to reduce CO_2 under the advantage of high efficiency and inexpensive resembles the artificial photosynthesis process. This research focuses on photoeletrocatalytic reducing CO_2 solution into organic compounds at a Cu_2O photocathode. The Cu_2O electrode fabrication was developed by electrochemical deposition method to enhance the catalytic activity of reduction reaction under visible light irradiation. The effects of light intensity, apply potential, pH and catalytic mechanism parameters were studied to enhance the CO_2 conversion to organic compounds efficiency. Carbonyl and methanol compounds were produced at the applied potential of 0.2 V and -0.4 V (vs. Ag/AgCl), respectively with the suitable pH in a solution of carbonate under visible light irradiation. These results illustrate that an applying potential and pH adjustment are the key factors of organic compounds production. This developed photoelectrocatalytic cell shows that the interesting method for reducing CO_2 from air pollutant and also producing value-added chemicals for alternative energy supplies.

Keywords: Photoelectrocatalytic cell, CO_2 reduction, Organic compounds, Cu_2O, Electrodeposition

1. INTRODUCTION

The global warming is main problems of the world by the effect of CO_2 emission to an environment from the combustion of industrial plants or fossil fuel [1]. The methods to convert CO_2 into value-added production has attractive been developed to solve the air pollutant and value creation of waste. There are many methods to convert a CO_2 compound into fuel or a valuable chemical especially photocatalytic, electrocatalytic and photoelectrocatalytic methods [2-4]. The photoelectrocatalytic method has been attracted to many advantages of reducing the recombination effect of the photocatalyst and using low bias potential than the electrocatalytic method [5]. The performance of the photoelectrocatalytic method is depended on the semiconductor selection and the efficiency of semiconductor deposition on the substrate. Cu_2O has been selected to develop for several reduction reaction applications with the narrow band gap energy and high negative potential of conduction band [6]. Recently Cu_2O photocathodes were also applied in photoelectrocatalytic CO_2 reduction with good properties for hydrocarbon formation [4]. The photocatalytic activity of Cu_2O photoelectrode is also related to the efficiency of semiconductor deposition on the substrate. The electrodeposition is one of the most attractive methods to deposit Cu_2O on the substrate which the advantage of simple, rapid methods, and suitable to scaling up for the large scale applications. This research is developed the electrodeposition method of the Cu_2O semiconductor on fluorine-doped tin oxide (FTO) conductive glass by using cyclic voltammetry deposition method (CVD). The developed FTO/Cu_2O photoelectrode was used to reduce CO_2 solution into organic carbonyl and methanol compounds.

2. EXPERIMENTAL

2.1 Preparation of FTO/Cu_2O electrode

FTO/Cu_2O electrode fabrication was developed with the cyclic voltammetry deposition method (FTO/Cu_2O (CVD)) which is a new method for Cu_2O deposited on FTO substrate. The electrochemical cell containing three electrodes system consists of FTO substrate as a working electrode, Ag/AgCl as a reference electrode and Pt

as a counter electrode that immersed in the electrolyte solution of 0.01 M $Cu(NO_3)_2$ and 0.1 M KNO_3. The potential range in cyclic voltammetry mode at -0.5 V to 0.5 V for 20 cycles, scanning rate 50 mV/s and keep the temperature of an electrolyte at 55 ^oC were performed with the optimum condition for FTO/Cu_2O preparation. The FTO/Cu_2O (CVD) was compared with the previous research of fix potential deposition method (FTO/Cu_2O (FPD)) by considering the photoelectrocatalytic reduction properties [6].

2.2 Characterization and photoelectrocatalytic properties of FTO/Cu_2O electrodes study

Optical absorption of the FTO/Cu_2O electrodes were studied by UV-Vis spectrophotometer (Shimadzu, UV-1601) in the wavelength range of 200 – 1,000 nm. The photoelectrocatalytic performance of FTO/Cu_2O photocathodes were performed by measure the photocurrent response from water reduction at the applied potential of -0.2 V (vs. Ag/AgCl) in 0.1 M Na_2SO_4 solution under visible light irradiation. Electrochemical impedance spectroscopy (EIS) with VersaSTAT3 (Princeton Applied Research, Inc.) was introduced to study the charge transfer resistant of electrode surface which carried out under the frequency range from 100 kHz to 0.1 Hz with -0.2 V (vs. Ag/AgCl).

2.3 Photoelectrocatalytic conversion of CO_2 to carbonyl compound study

The photoelectrocatalytic cell for CO_2 compound conversion to carbonyl compound study was performed by using the FTO/Cu_2O electrode as working electrode, Ag/AgCl as a reference electrode and Pt wire as a counter by using an amperometry mode with VersaSTAT3 (Princeton Applied Research, Inc.). The effect of bias potential, pH of electrolyte and the intensity of light were studied with the optimum condition for the highest photoreduction current of the fabricated FTO/Cu_2O electrode. The three electrodes were immersed in the Na_2CO_3/$NaHCO_3$ buffer solution which used as the CO_2 saturated solution to study the CO_2 conversion to carbonyl compounds. UV-Vis spectrophotometer was used to confirm carbonyl compound production at the wavelength (λ) of 280 nm [4, 7].

2.4 Photoelectrocatalytic conversion of CO_2 to methanol (MeOH) compound study

The experimental was set up similar to the carbonyl compound production process except for the bias potential and electrolyte solution. 0.1 M Na_2CO_3 solution was performed as the saturated CO_2 solution which used to study the CO_2 conversion to methanol compound. The cyclic voltammetry technique was used to determine the methanol production at the potential range of -0.5 V to 0.5 V (vs. Ag/AgCl) using Pt wires as working and counter electrode [8].

3. RESULTS AND DISCUSSION

3.1 Characterization and photoelectrocatalytic properties of the fabricated FTO/Cu_2O electrodes

3.1.1 Absorption properties

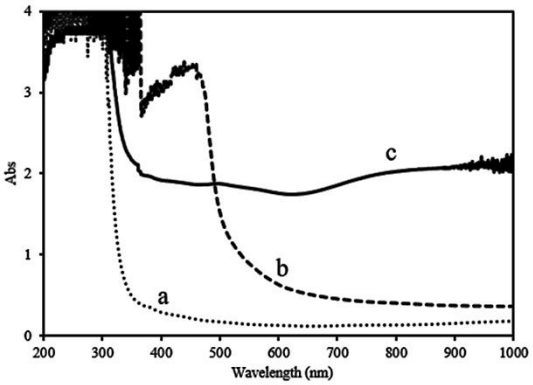

Fig. 1. UV-Vis spectra of (a) FTO and the FTO/Cu_2O films electrodes prepared by the different method of (b) FPD (c) CVD.

Fig. 1 shows that the UV-Vis spectra comparison of FTO/Cu_2O prepared by CVD and FPD method. The absorption edge of FTO/Cu_2O (FPD) electrode was set at 650 nm corresponding to the band gap of 2.2 eV. While the absorption of FTO/Cu_2O (CVD) electrode was red-shifted to 700 nm indicates that the narrower band gap corresponding to the higher visible light absorption properties.

3.1.2 Photoelectrocatalytic activity

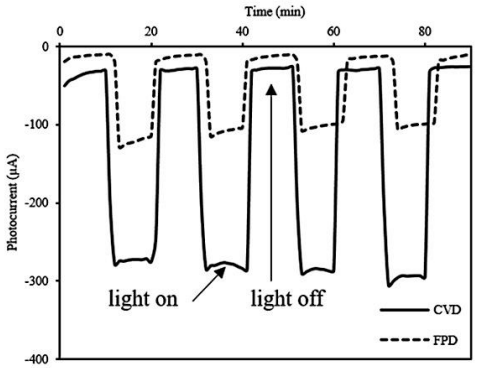

Fig. 2. Photocurrent responses of FTO/Cu_2O electrodes under the chopped visible light illumination.

The photocurrent response of FTO/Cu_2O electrodes from water reduction at the applied potential of -0.2V vs. Ag/AgCl and under the chopped visible light illumination were operated to study the photoelectrocatalytic activity of photoelectrode. Fig. 2 shows that the photocurrent of the FTO/Cu_2O electrode prepared by CVD method is higher than that the FPD method about two times. The enhancing photoelectrocatalytic activity of FTO/Cu_2O (CVD) is related to a narrower band gap energy properties caused by the increasing of the photoelectron generated efficiently to enhance water reduction efficiency.

3.1.3 Charge transfer resistant properties

The electrochemical impedance spectroscopy (EIS) was carried to verify the FTO/Cu_2O electrodes performance of interfacial charge transfer properties at the bias potential of -0.2 V vs. Ag/AgCl under visible light illumination. Fig. 3 shows the Nyquist plots of FTO/Cu_2O (CVD) electrode has a smaller semicircle than that of FTO/Cu_2O (FPD) electrode related with charge transfer resistant (R_{ct}) values of FTO/Cu_2O electrodes prepared by CVD, and FPD methods were 364.8 and 1,754 ohm, respectively. It could indicate that the FTO/Cu_2O electrode prepared by CVD method obtained the high efficiency for charge separation at the interfacial electrode electrolyte caused to improve the photoelectrocatalytic activities for water reduction.

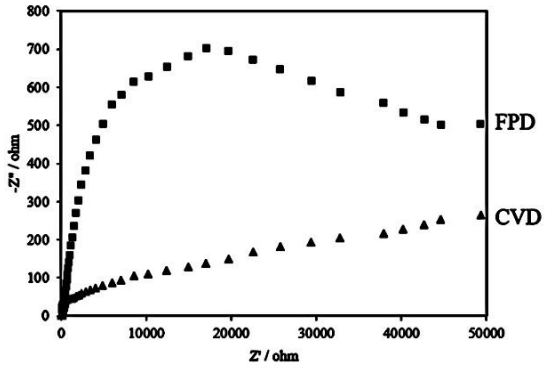

Fig. 3. Nyquist plots of FTO/Cu_2O electrodes prepared by different methods of CVD and FPD in 0.1 M Na_2SO_4 under bias potential of -0.2 V vs. Ag/AgCl and visible light illumination condition.

The results show that the FTO/Cu_2O electrode fabricated by CVD method has many good characteristics and photoelectrocataytic activities for water reduction suitable to further apply to the CO_2 reduction to carbonyl and methanol compounds.

3.2 The CO_2 conversion to carbonyl compound performance using the developed FTO/Cu_2O photocathode

Based on the comparison of the electrodes properties, FTO/Cu_2O (CVD) electrode was selected to study the optimum condition for CO_2 compound conversion to carbonyl compound by using photoelectrocatalytic process. The photoelectrocatalytic cell was contained with FTO/Cu_2O as a working electrode, Ag/AgCl as a reference electrode and Pt wire as a counter electrode in the Na_2CO_3/$NaHCO_3$ buffer solution. The effects of bias potential, pH of electrolyte, the power of light intensity were studied for the optimum condition of carbonyl compound production. The absorbance band at 280 nm which related with the formation of carbonyl compounds [4] was monitored for considering the optimum condition (Fig.4).

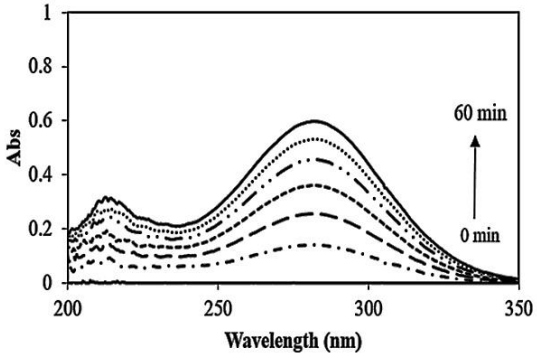

Fig. 4. UV spectra of carbonyl compound functional with the time of photoelectrocatlytic CO_2 reduction process.

The effect of the applied potential is studied at -0.1, 0.0, 0.1, 0.2 and 0.3 V vs. Ag/AgCl and observed the absorbance value at the wavelength of 280 nm. Fig. 5 shows that the applied potential significantly affects with the CO_2 conversion to a carbonyl compound. The specific bias potential of 0.2 V presented the highest performance for carbonyl compound production.

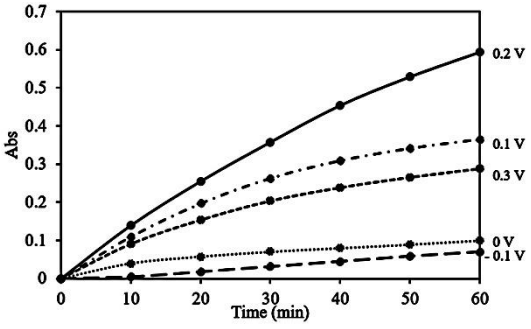

Fig. 5. The absorbance value of carbonyl compound production (λ=280nm) with the different bias potential in the range of -0.1 to 0.3 V vs. Ag/AgCl.

The pH of the electrolyte was varied from 9 to 11 at an applied potential of +0.2 V under visible light irradiation. Fig. 6 shows the proper pH value of 9 for CO_2 compound conversion to the carbonyl compound. The power of light intensity was directly related to the carbonyl compound production due to the high power of light intensity irradiate at the photosemiconductor cause high efficient to generate photoelectron for reducing CO_2 to carbonyl compound as well.

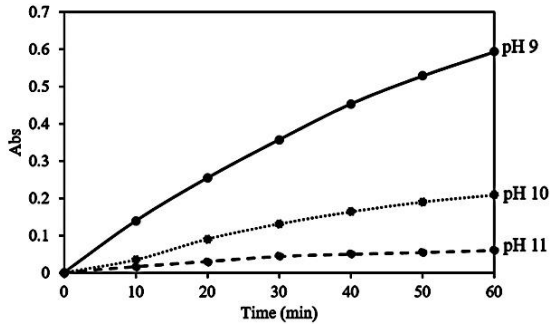

Fig. 6. The absorbance value of carbonyl compound production (λ=280nm) with the different pH value of 9, 10 and 11.

Moreover, the catalytic mechanisms to induce FTO/Cu_2O photoelectrode for carbon dioxide conversion to carbonyl compounds were studied under photoelectrocatalysis (PEC), photocatalysis (PC) and electrocatalysis (EC) process. The result shows that the photoelectrocatalytic process (PEC) presented the highest efficiency for the CO_2 compound conversion to carbonyl compound (Fig. 7). This result confirms that the highest efficiency of PEC process due to the catalytic action applied potential and light irradiation at photoelectrode cause decreased the recombination effect of the electron-hole pair at the Cu_2O semiconductor efficiently induce photoelectron to reduce CO_2 to carbonyl as well.

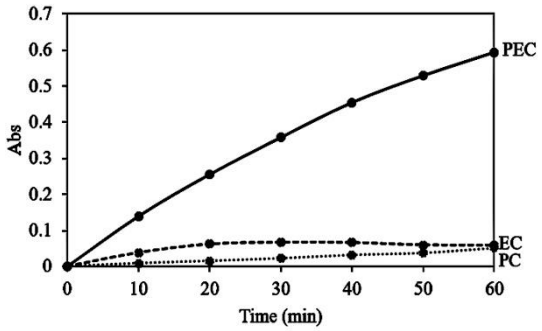

Fig. 7. The absorbance value of carbonyl compound production (λ=280nm) with the different catalytic mechanism of photoelectrocatalysis (PEC), photocatalysis (PC) and electrocatalysis (EC) process.

3.3 The CO_2 conversion to MeOH compound performance using the developed FTO/Cu_2O photocathode

The CO_2 conversion to MeOH was performed by using photoelectrocatalytic process with the working electrode of FTO/Cu_2O. The effects of applied potential, the power of light intensity and catalytic mechanism were studied with the optimum condition for MeOH production. A cyclic voltammetry method was introduced to analyze the methanol concentration from the process using Pt wire as working and counter electrode and Ag/AgCl as a reference electrode. The correlation of methanol oxidation current at 0 V as a function of methanol concentrations range of 0 (blank) - 5,000 ppm (MeOH) were performed to use as the standard calibration curve (Fig. 8).

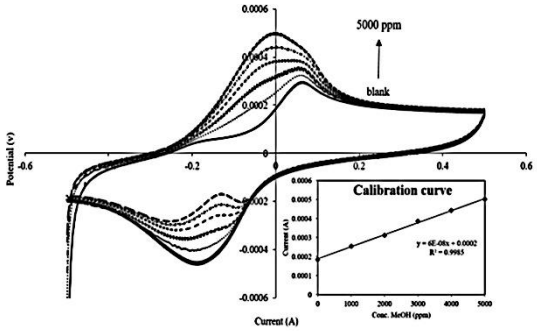

Fig. 8. Cyclic voltammograms of methanol oxidation reaction at Pt wire electrode in 0.1 M Na_2CO_3 and the inset shows the standard calibration curve as a relation of oxidation current versus methanol concentrations.

The effects of applied potential at -0.3, -0.4 and -0.5 V vs. Ag/AgCl in 0.1 M Na_2CO_3 (CO_2 saturated) under PEC process with 20 W tungsten lamp for 60 minutes were studied. Fig.9 shows that the applied potential of -0.4 V presented the highest methanol generation to 575 ppm for 1h.

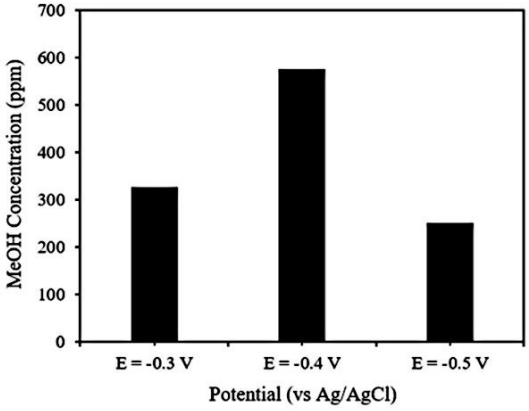

Fig. 9. Methanol production by PEC process with the difference of applied potentials for 1 h.

The result indicates that the applied potential is specific to the kind of product from CO_2 reduction process. The power of light intensity is one of the parameters affected by the CO_2 conversion to MeOH. The light intensity is directly related to the MeOH production efficiency. Therefore, the position and power of light source to irradiate at the photoelectrode have to consider the optimum condition. Furthermore, the catalytic mechanisms of FTO/Cu_2O photoelectrode for CO_2 compound reduced to methanol were studied with the process of PEC, EC, and PC. The result shows that the PEC process has the highest efficiency for the reduced CO_2 compound to methanol production of 726 ppm for 1 h.

3.4 Comparison of FTO/Cu_2O prepared by CVD and FPD methods for CO_2 compound conversion to carbonyl and methanol compounds

The carbonyl and MeOH compound production efficiency were compared to confirm the CO_2 reduction performance of FTO/Cu_2O(CVD) and FTO/Cu_2O(FPD) photoelectrodes. The results show that FTO/Cu_2O electrode prepared by CVD method presented the higher performance for converting CO_2 compound to both carbonyl (Fig.10a) and methanol (Fig.10b) compounds than that the FPD method.

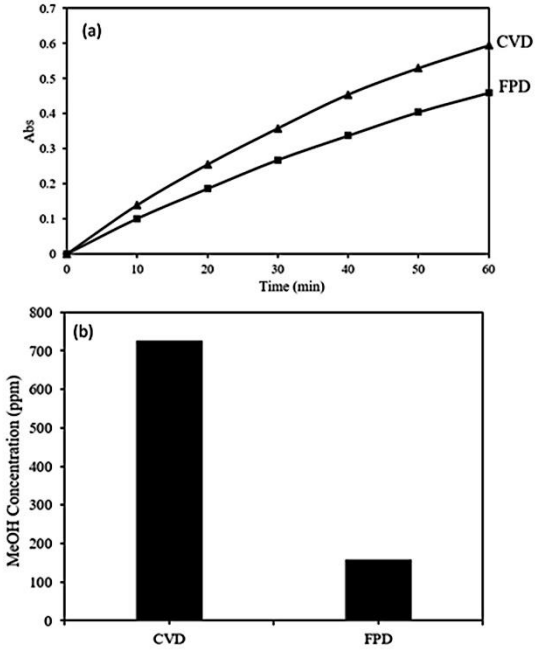

Fig. 10. Comparing the performance of FTO/Cu_2O electrodes prepared by CVD and FPD for CO_2 compound conversion to (a) carbonyl and (b) methanol compounds.

4. CONCLUSIONS

The developed cyclic voltammetry deposition method (CVD) electrodeposition method successfully for the Cu_2O semiconductor fabricated on fluorine-doped tin oxide (FTO) and presented the good characteristic of the photocathode and more photoelectrocatalytic activities than that the previous research. The developed FTO/Cu_2O photoelectrode was performed high efficiency to reduce CO_2 solution into organic carbonyl and methanol compounds as well. This developed photoelectrocatalytic cell indicates that the powerful method for reducing CO_2 from air pollutant and also producing value-added chemicals for alternative energy supplies.

5. ACKNOWLEDGEMENTS

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