

ORIGINAL ARTICLE

Electrodeposition of Zn-doped Cu₂O in Acidic and Alkaline Solution and Its Catalytic Activity for Ethanol Electrooxidation

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ABSTRACT – In this study, Zn-doped Cu₂O films were synthesized by electrodeposition technique in acidic (pH 4) and alkaline (pH 10) solution. Catalytic activity of the film was evaluated toward ethanol electrooxidation which was carried out using cyclic voltammetry technique. X-ray diffraction (XRD) analysis showed the formation of cubic structure of Cu₂O from both conditions. Morphological characterization conducted under a field-emission scanning electron microscope exhibited that Cu₂O particles electrodeposited in the acidic condition were smaller compared to those obtained in the alkaline condition. The photoelectrochemical responses, which were recorded using a linear sweep voltammetry technique, showed that the highest photocurrent density was 31.5 mA.cm⁻² that obtained at 0.76 V vs. Ag/AgCl using Zn-doped Cu₂O film prepared in the acidic condition. The film also possesses a low resistance charge transfer as measured by the electrochemical impedance spectroscopy (EIS) technique. These electrochemical characteristics resulted in a high catalytic performance of the Zn-doped Cu₂O film on the ethanol electrooxidation as shown by the high anodic current of 22 mA.cm⁻² at 0.968 V. These results indicated that the Zn-doped Cu₂O film electrodeposited in the acidic condition has a good catalytic activity towards ethanol electrooxidation process.

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INTRODUCTION

Global energy requirements are continuously expanding and current societies remain highly dependent on fossil fuels (i.e., petroleum) although oil reserves continue to decrease [1]. These conditions have prompted the development of science and technology in the energy field with alternative sources developed through fuel cell technology. The direct ethanol fuel cell (DEFC) is one of these intriguing technologies. In recent decades, DEFCs have attracted much attention as promising chemical resources due to their characteristics of high energy conversion efficiency, low operating temperature, easy fuel handling, low processing costs, and convenient usage [2]. However, the main challenges faced by direct DEFCs are poor electrooxidation reaction kinetics, the tendency of some intermediates, such as adsorbed CO, to poison the anode catalyst, and considerable potential for oxygen reduction reactions [2]–[4]. Pt/C electrocatalysts are commonly used as anodes in low-temperature fuel cells. However, they are costly and tend to be poisoned during operation.

Another material that has the potential as an electrocatalyst in DEFC systems is copper oxide (Cu₂O), a *p*-type semiconductor with a narrow bandgap of 1.9–2.2 eV and a high absorption coefficient of visible light (i.e., a wavelength of up to 650 nm) [5]–[7]. This narrow bandgap plays a vital role in determining the catalytic properties that can increase the electron transfer process in electrooxidation reactions [8]. Copper oxide is an abundant metal oxide that is stable and non-toxic and has high conductivity, good catalytic properties, and fairly low cost [9],[10]. The potential of Zn as a dopant to increase the photoconductivity of Cu₂O has also been predicted using density function theory [11]. According to previously reported experimental and theoretical investigations, Zn cation doping in Cu₂O can modulate the energy band structure by forming impurities that can affect the electrical characteristics of the whole system, resulting in improved performance for photocatalysis and photoelectrochemistry [12].

Hu et al. have synthesized Cu₂O by including Zn doping to suppress the oxidation of Cu₂O to CuO and to reduce photocorrosion of Cu₂O [13]. Zn cation dopant can substitute interstitial Cu atoms in Cu₂O crystals, thereby changing the carrier concentration. In principle, higher carrier concentration can increase the conductivity and the binding force to the substrate thus allow charge transfer to occur [13]. In addition, Zn doping in Cu₂O generates important properties, suitable for enhancing photocatalysis, such as lattice shrinkage, bandgap tuning, defects, and enhancement of optical and electrical properties [14]. However, despite these promising advantages, the doping of Zn cation in the electrodeposited Cu₂O thin film, which has low bandgap energy and good photocatalytic activity, has not been experimentally proven, particularly regarding its electrocatalyst activity for ethanol electrooxidation applications. The aim of the present study was to synthesize Zn-doped Cu₂O thin films by an electrodeposition, which is known as versatile method to fabricate metal [15]–[17] and metal oxide film, on indium tin oxide (ITO) substrate. The structure,

morphology, and electrochemical properties of the material were analyzed to determine the effect on photocatalytic performance and the feasibility of their application to the electrooxidation of ethanol.

EXPERIMENTAL METHOD

Electrodeposition of Zn-doped Cu₂O was conducted in an electrolyte solution, containing of CuSO₄·5H₂O, 0.025 M; C₃H₆O₃, 2 M; ZnSO₄·7H₂O, 0.025 M; and Na₂SO₄, 0.2 M. The electrolyte solution was prepared using demineralized water. The pH of the solution was adjusted by adding sufficient NaOH pellets to achieve pH values of 4 and 10. The platinum wire was used as counter electrode, Ag/AgCl as reference electrode, and indium tin oxide (ITO) coated polyethylene terephthalate (PET) with the dimension of 3 × 1 cm as working electrodes. The electrodeposition was carried out at a temperature of 60°C with the applied current density of -1 mA/cm².

To determine the characteristics of the deposit, samples analysis was carried out using several techniques. X-ray diffraction technique (XRD, Rigaku SmartLab 3 kV) was used to examine the structure and phase of the deposit. Field-emission scanning electron microscopy (FESEM; JEOL JIB-4610F Multi Beam System), equipped with an energy-dispersive X-ray analyzer (EDX) (Oxford Instruments), was used to examine the surface morphology and elemental composition.

Photoelectrochemical (PEC) evaluation was conducted in a three-electrode system with a Pt wire as a counter electrode, an Ag/AgCl as a reference electrode, and Zn-doped Cu₂O samples as the working electrode. The measurement was carried out in the potential range 0.5 V to 1.5 V and was controlled using EChem software connected to an ER466 potentiostat. The experimental test solution was 0.5 M Na₂SO₄. Electrochemical impedance spectroscopy (EIS) measurement was conducted using the Corrtest CS50 in an electrolyte containing 0.5 M KCl as the experimental test solution. The frequency was scanned from 1 kHz to 0.01 Hz. The electrocatalytic performance test was evaluated from the electrooxidation reaction of ethanol conducted using cyclic voltammetry (CV). The test was carried out in a three-electrode system that controlled by the EChem software connected to an ER466 potentiostat containing. The CV measurement was carried out in 25 mL of 1 M NaOH containing 1 M ethanol at potential of 0.3 V to 1 V with a sweep rate of 25 mV/s.

RESULT AND DISCUSSION

Figure 1 shows the XRD pattern of Zn-doped Cu₂O electrodeposited from acidic (pH 4) and alkaline (pH 10) solution. From the pattern of the Zn-doped Cu₂O electrodeposited at pH 4, the diffraction peaks appeared at $2\theta = 36.39^\circ$, 42.28° , and 61.34° , representing the Bragg reflections from (111), (200), and (220) planes of the Cu₂O phase, respectively (PDF card number 01-073-6237). Other peaks from Cu phase were observed at $2\theta = 43.29^\circ$, 50.42° , and 74.12° that could be assigned to the the (111), (200), and (220) planes, respectively (PDF card number 00-004-0836). No significant shift was noted in the Zn-doped Cu₂O diffraction pattern at pH 10 that appeared at $2\theta = 36.41^\circ$, 42.27° , and 61.34° , which corresponded to (111), (200), and (220) planes, respectively. While peaks of the Cu phase at $2\theta = 43.29^\circ$, 50.43° , and 74.12° . The remaining peaks that observed on the pattern came from the indium tin oxide (ITO) substrate. A slightly different intensity of the pattern could be associated to the crystallinity degree of the sample. There is no peak corresponds to Zn or ZnO phases observed from the patterns. This result indicates that Zn cation enter the Cu₂O lattice [12]. The presence of Zn in the Cu₂O structure does not change the relative orientation or peak width compared to the XRD pattern of the pure Cu₂O film, indicating that Zn doping caused no significant change in the Cu₂O lattice and no structural distortion. Doping Cu₂O by Zn was possible because Cu⁺ and Zn²⁺ have adjacent ionic radius values of 0.46 and 0.40, respectively [18].

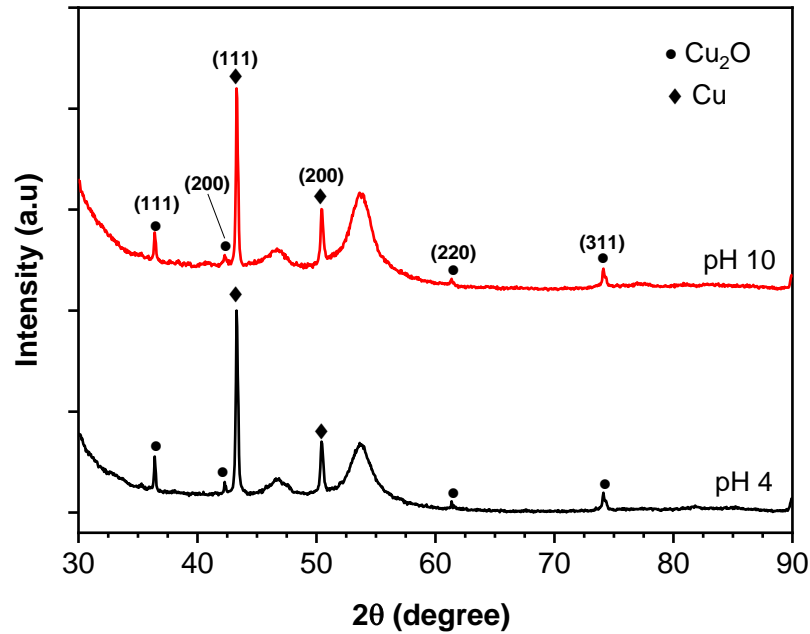


Figure 1. XRD patterns of Zn-doped Cu_2O electrodeposited in different pH solution: (a) pH 4 and (b) pH 10

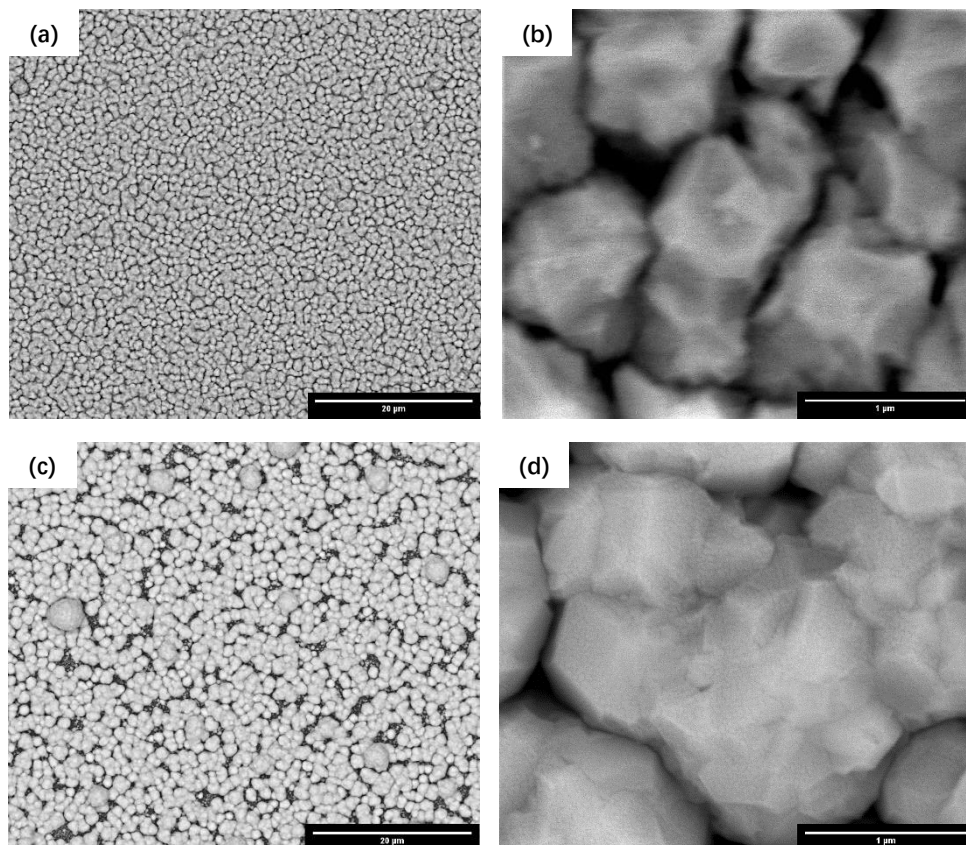
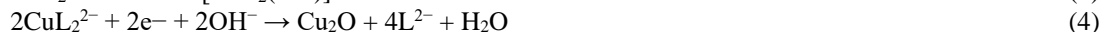


Figure 2. Micrograph of SEM of Zn-doped Cu_2O electrodeposited in different pH solution: (a) pH 4 and (b) pH 10

The morphological characteristics of the Zn-doped Cu_2O thin films were evaluated by a scanning electron microscope (SEM). Figure 2a shows that the electrodeposited particles are truncated cubic crystals. The morphological feature obtained because the grow of particles occurred in different directions and rates. This typical reaction process took place could be associated to the polyhedral particles that exposed different facets with different surface energy. Lactate ions (Lac^-), as capping or stabilizing agents, can adsorb onto the surface of Zn-doped Cu_2O particles by physical and chemical bond through the following reactions [19]: intentional



This result indicates that the Cu(II)Lac_2 species was formed in the electrolyte and precipitation of insoluble species at alkaline solution can be diminished. In the presence of lactate, Cu(II) ion was reduced to form the lactate complex to Cu(I) and then produced Cu_2O . This is a two-step process given following reaction mechanism as shown in equation (1) and (2). In alkaline solution, Cu(II) ions prefer to form copper hydroxide $[\text{Cu(OH)}_n]^{2-n}$ and copper lactate $[\text{Cu(L)}_n]^{2-n}$ which are known as complex compounds. The lower pH value, more $[\text{Cu(L)}_n]^{2-n}$ was formed, while higher pH led to domination of $[\text{Cu(OH)}_n]^{2-n}$. The $[\text{Cu(OH)}_n]^{2-n}$ encourages the growth along (111) axis, whereas $[\text{Cu(L)}_n]^{2-n}$ promotes the growth along the (100) axis of the Cu_2O crystal [20].



Thus, in the alkaline condition with the presence of lactic acid, Cu(II) is found in the form of CuL_2^{2-} and $[\text{CuL}_2(\text{OH})]^{3-}$. The Cu(II) complex in the diffusion layer is reduced to Cu_2O as shown by equation (4) and (5). When the L_2^{2-} ion is liberated, Cu_2O is adsorbed onto the cathode surface and a nucleus formed. As a face-selective adsorption additive, lactate ion is adsorbed onto the (111) plane and limit growth along the (111) direction. Consequently, compared to the (111) plane, the (100) plane grows faster. Simultaneously, the ions can be protonated and the OH^- ion released as shown by equation (6). This process is useful in balancing the local pH surrounding the working electrode.

Figure 2a shows that micrograph of the film obtained at pH 4 is denser and more uniform with relatively smaller size compared to one electrodeposited at pH 10 (Figure 2b). In this case, at pH 10 (Figure 2b), the electrodeposited particles are relatively large and the agglomerated particles were clearly observed. The fine particles growth at pH 4 (Figure 2a) provide more active sites on the surface. By contrast, at pH 10, the agglomeration among the particles makes some of the active sites is covered by other particles and not exposed on the surface. Previous study reported that the increase of pH solution resulted a more effective precursor ion complexation. Consequently, the particle clusters grow together to produce larger particles [21]. This morphological change could be attributed to the increase of OH^- ions at alkaline condition which change the attractive and repulsive forces controlling particle growth. A higher concentration of OH^- ions lead to a faster reaction rate that reduce the repulsion and increasing the attractiveness and allowing the growth of oriented attachment [22]. Consequently, particles agglomeration occurred at pH 10. In this case, agglomeration takes place when the particles are parallel to each other with a perfect match and the general boundary is removed to form larger particles. The EDX spectra of the Zn-doped Cu_2O (Figure 3) show the presence of copper (Cu), oxygen (O), and Zn, confirming the Zn content in the Zn-doped Cu_2O synthesis.

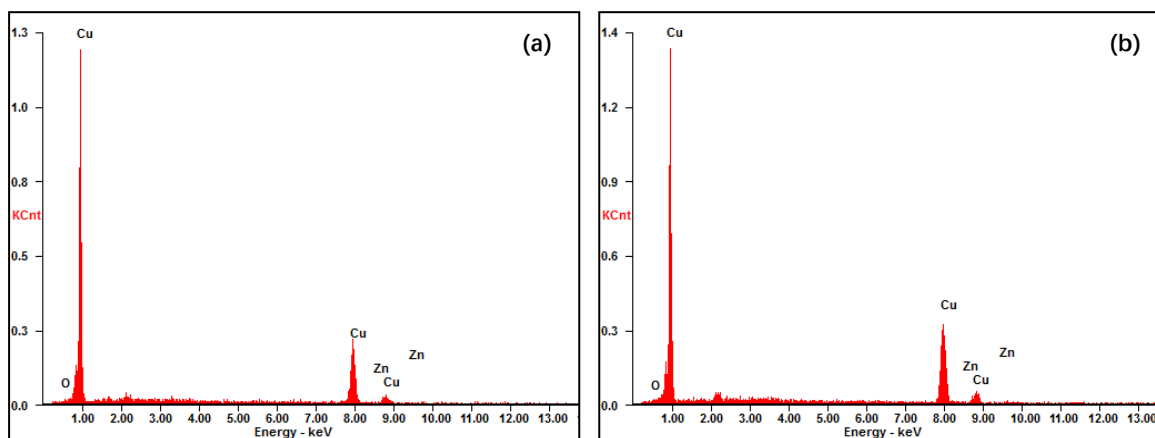


Figure 3. EDX spectra of the Zn-doped Cu_2O electrodeposited in different pH solution: (a) pH 4 and (b) pH 10.

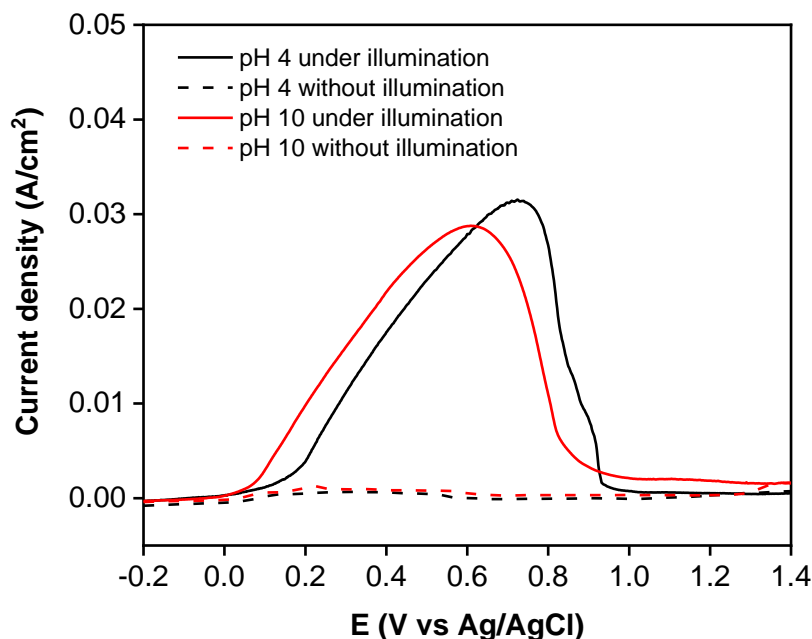


Figure 4. Linear sweep voltammetry curves recorded under visible light irradiation and dark condition from Zn-doped Cu₂O electrodeposited in different pH solution.

Figure 4 shows the photocurrent measured using linear sweep voltammetry under illumination and dark condition. Under visible light condition, electron-hole pairs were generated by an electric field in the space-charge region between the Zn-doped Cu₂O semiconductor and the electrolyte. This affects the bending of the conduction and valence band edges on the semiconductor surface and increases the supply of free carriers to the electrodes [23]. In the dark condition, almost flat responses were observed from the Zn-doped Cu₂O films. This is due to no driving force which cause the thermally generated electron and hole separation [24]. The current density for the Zn-doped Cu₂O prepared at pH 4 is higher than one prepared at pH 10. This result indicates that at alkaline condition, the photocurrent performance of Zn-doped Cu₂O does not increase the efficiency of charge transport and photocurrent activity. This phenomenon can be noted from the morphology of the sample obtained at pH 4 (Figure 2b) which showed smaller crystal size compared to one obtained at pH 10. Previous study [25] showed that small particles can produce high photocurrent due to better carrier transfer since more significant surface contact with the electrolyte.

Figure 5 shows Nyquist plots recorded from the films prepared at pH 4 and 10. The plots exhibit that the pH solution considerably influenced the charge transfer characteristics of the system. The arc diameter of the Nyquist plot from Zn-doped Cu₂O prepared at pH 10 is larger than that of pH 4. This indicates an increase of the interfacial charge-transfer resistance that caused a decrease in the photocurrent as shown in Figure 4. Previous study showed that the charge-transfer resistance can be attributed to the film morphology and particle size [25]. In this case, the relatively small particles obtained at pH 4 produced the low charge-transfer resistance of the film. In case of pH 10, a larger arc diameter of the plot can also be due to several other factors, such as the presence of ohmic resistance, electrochemical reaction charge-transfer resistance, the adsorbed layer formed by complex electrochemical reaction intermediates, either by the layer or the presence of diffusion (transport phenomena) in solution as an inhibitory effect [26]. CuOH species at pH 10 can be assumed to be intermediate formed through the reduction of Cu₂O, as follows:



This intermediate phase is reported to inhibit the charge-transfer process in the system, thereby increasing the R_{ct} value (charge-transfer resistance), as indicated by the larger diameter of the formed plot [26]. The ethanol electrooxidation performance was investigated using cyclic voltammetry technique. Figure 6 presents the cyclic voltammograms which exhibit anodic peaks at potential range of 0.7 to 0.9 V vs. Ag/AgCl. These peaks are in accordance with the previous reported study which showed the ethanol electrooxidation process in the C1 pathway occurs according to the following reaction, where acetyl species are converted to CO₂ [27]:



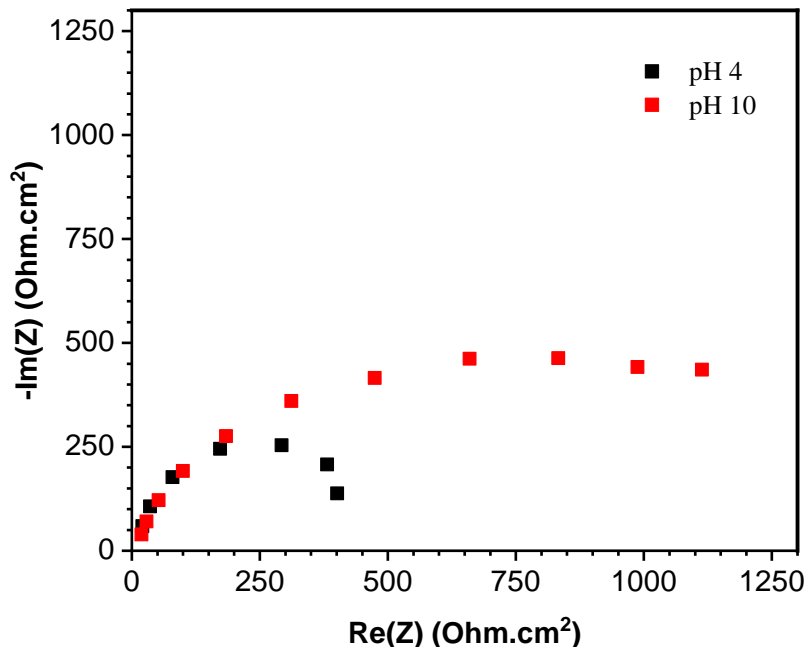
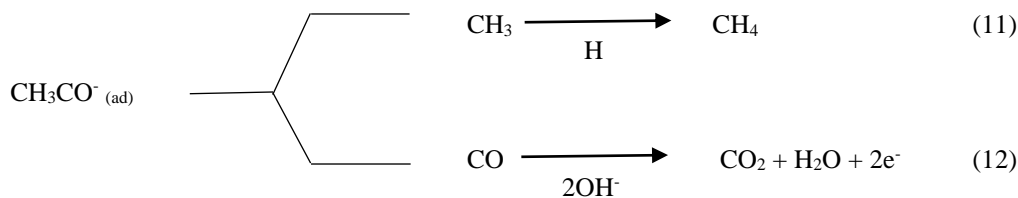


Figure 5. Electrochemical impedance spectra (EIS) Nyquist plot of Zn-doped Cu₂O electrodeposited in different pH solution.

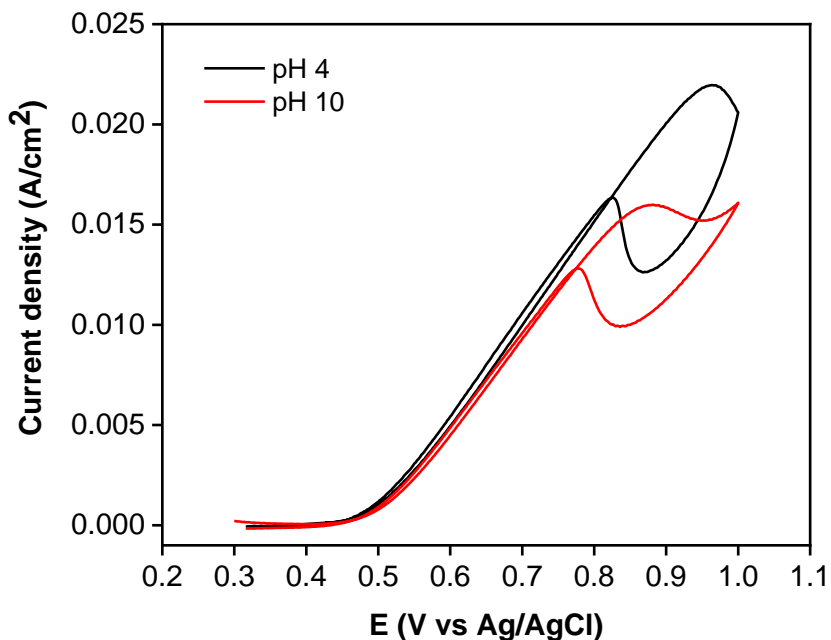


Figure 6. Cyclic voltammograms for electrooxidation of 1 M ethanol + 1 M Zn-doped Cu₂O NaOH pH 4 and 10 with the scan rate of 25 mV/s

A relatively high anodic peak from the film obtained at pH 4 appeared at 0.968 V vs Ag/AgCl with a current density of 22 mA.cm⁻², while at pH 10 the peak was found to decrease with a current density of 16 mA.cm⁻². This shows that Zn-doped Cu₂O at pH 4 can increase the electrooxidation activity in ethanol compared to pH 10. This result is in accordance with the results of the EIS measurement (Figure 5) that shows a small resistance charge transfer of the system with the film prepared at pH 4. In addition, the linear sweep voltammetry curves show higher photocurrent from

the film prepared at pH 4 compared to that of pH 10. These results could be assigned to the morphological features and particles size as indicated by the SEM measurement results (Figure 2). In this case, the relatively small particle exhibits high catalytic activity due to the increase of electron transfer as a contribution of small particles as reported in the previous work [25]. A high intensity of the current density can also be attributed to a more dominant OH adsorption, which played a role in the formation of CO₂ in the electrode-electrolyte interface, compared to CO species that caused poisoning of the photocatalyst. In this case, poisoning of the photocatalyst surface is known reducing the intensity of the anodic peak in the electrooxidation activity of ethanol [2],[28].



CONCLUSION

The Zn-doped Cu₂O films were fabricated from acidic (pH 4) and alkaline (pH 10) electrolytes using electrodeposition technique. Catalytic performance of the Zn-doped Cu₂O toward ethanol electrooxidation showed that the film prepared in the acidic condition is higher compared to the film obtained in the alkaline condition. This high catalytic activity is attributed to the morphological feature of the film that constructed by the smaller and denser particles showing compared to those obtained at pH 10. This characteristic is believed to contribute reducing charge transfer resistance in the system and increase electron transfer that involved in the ethanol electrooxidation process.

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