Fabrication of Cu$_2$O nanostructured thin film by anodizing

C.H. Voon[1,*], B.Y. Lim[2], S.C.B. Gopinath[1,3], Y. Al-Douri[4,5], K.L. Foo[1],
M.K. Md Arshad[1], S.T. Ten[6], A.R. Ruslinda[1], U. Hashim[1], V.C.S. Tony[1]

[1]Institute of Nano Electronic Engineering (INEE), Universiti Malaysia Perlis, 01000, Kangar, Perlis, Malaysia

[2]School of Materials Engineering, Universiti Malaysia Perlis, Jejawi, 02600 Arau, Perlis, Malaysia

[3]School of Bioprocess Engineering, Universiti Malaysia Perlis, 02600 Arau, Perlis, Malaysia

[4]Nanotechnology and Catalysis Research Center (NANOCAT), University of Malaya, 50603 Kuala Lumpur, Malaysia

[5]Physics Department, Faculty of Science, University of Sidi-Bel-Abbes, 22000, Algeria

[6]Malaysian Agricultural Research And Development Institute, Serdang 43400, Malaysia

Cuprous oxide, a narrow bandgap p-type semiconductor, has been known as a potential material for applications in supercapacitors, hydrogen production, sensors, and energy conversion due to its properties such as non-toxicity, easy availability, cost effectiveness, high absorption coefficient in the visible region and large minority carriers diffusion length. In this study, Cu$_2$O nanostructured thin film was fabricated by anodizing of Cu plates in ethylene glycol containing 0.15 M KOH, 0.1 M NH$_4$F and 3 wt.% deionized water. The effects of anodizing voltage and temperature of electrolyte were investigated and reported. It was found that nanoporous Cu$_2$O thin film was formed when anodizing voltages of 50 V and 70 V were used while a dense Cu$_2$O thin film was formed due to the aggregation of smaller nanoparticles when 30 V anodizing voltage was used. Nanoplatelets thin film was formed when the temperature of electrolyte was reduced to 15 °C and 5 °C. X-ray diffraction confirmed the presence of Cu$_2$O phase in thin film formed during anodizing of Cu plates, regardless of the anodizing voltage and temperature of electrolyte. Photoluminescence spectroscopy showed the presence of Cu$_2$O peak at 630 nm corresponding to band gap of 1.97 eV. A mechanism of the formation of Cu$_2$O thin film was proposed. This study reported the ease of tailoring Cu$_2$O nanostructures of different morphologies using anodizing that may help widen the applications of this material.

Keywords: *anodizing; cuprous oxide; nanopores; nanoplatelets; thin film*

1. Introduction

Cuprous oxide (Cu$_2$O), a narrow bandgap (Eg = 1.9 eV to 2.2 eV) p-type semiconductor, has received increasing attention among scientific community due to its non-toxicity, environmental friendliness, abundance of resources and low cost. For this reason, Cu$_2$O has tremendous potential for applications in supercapacitors [1], hydrogen production [2], sensors [3], and energy conversion [4]. Consequently, various morphologies of Cu$_2$O nanostructures have been synthesized, including nanowires [5], nanotubes [6], nanocages [7] and nanoparticles [8]. Many methods have been attempted for the synthesis of Cu$_2$O nanostructures, such as hydrothermal process [9],

sonochemical method [10], sol-gel process [11], reactive sputtering [12], anodizing [13] and electrodeposition [14]. However, these methods have their own drawbacks, such as expensive equipment, costly reagents, stringent reaction conditions, uncontrollable structures and complicated experimental setup.

Among these methods, anodizing is a well-established surface oxidation method for the fabrication of protective coatings on metal surfaces. Anodizing involves electrochemical reactions between a working electrode where the coating is formed and an inert counter electrode in an electrolyte. Anodizing is a low temperature, versatile, economical and reproducible technique for the preparation of metal oxide coatings on metal surfaces. Besides, anodizing enables the tailoring of morphology and size of metal oxide nanostructure

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to some extent by varying the anodizing parameters. Furthermore, metal oxide nanostructures can be prepared directly on a metal substrate that allows efficient metal back contact for device integration [15]. Recently, nanostructures of various metal oxides have been successfully synthesized by using anodizing, including Al_2O_3 [16–19], ZnO [20, 21], CuO [22], Cu_2O [15] and TiO_2 [23]. For the fabrication of nanostructures by anodizing of copper, only few studies have been reported, involved in the fabrication of CuO [22], $Cu(OH)_2$ [22] and Cu_2O [15] nanostructures. Fabrication of Cu_2O nanostructures by anodizing was performed by Allam et al. [15] and they successfully fabricated Cu_2O nanostructures on Cu foil by anodizing of Cu followed by vacuum annealing at 280 °C for 15 min. The detailed study of the influence of anodizing parameters such as anodizing voltage and temperature of electrolyte has not been reported yet. Herein, we report a facile fabrication of Cu_2O nanostructures of different morphologies on Cu substrate by anodizing of Cu substrate. The effect of electrolyte temperature and anodizing voltage on the morphologies of Cu_2O nanostructures has also been described. The Cu_2O nanostructures of different morphologies reported in this study may help widen the applications of this material.

2.   Experimental

Commercially available copper plates (99.9 %, 1 mm thick) were used in this study. Each sample was cut into dimension of 5 cm × 1 cm. Prior to anodizing process, copper plates were grinded with SiC paper of subsequently finer grit (down to 2400 grit) to remove the damage caused by the cutting process. The samples were then polished with alumina paste with the grain size of 5 μm and 1 μm to obtain a smooth mirror-like finish on the sample surface. The polished samples were ultrasonically cleaned with ethanol and rinsed thoroughly with deionized water. Anodizing was conducted using a two-electrode cell as described previously. Copper plate was used as a working electrode and lead plate with similar size was used as a counter electrode. Area of 1 cm × 1 cm of both the electrodes was immersed in the electrolyte during

the anodizing process. Ethylene glycol containing 0.15 M KOH, 0.1 M NH_4F and 3 wt.% deionized water was used as electrolyte. 500 mL of fresh electrolyte was used for the anodizing of each sample. The distance between Pb plate and Cu plate was fixed at 40 mm. The anodizing duration was fixed at 300 s. Anodizing process was conducted under potentiostatic conditions. Temperatures of electrolyte were maintained at pre-set value throughout the anodizing process by using ice-water bath and handy cooler (JEIO Tech HC-20). The current density versus time was recorded. The anodizing voltage and temperature of electrolyte were varied from 30 V to 70 V and 5 °C to 25 °C, respectively, to study their effect on the morphology and composition of as-anodized product. As-anodized Cu plates were rinsed with deionized water and dried in air for characterization. The morphology of the anodized samples was examined by using field emission scanning electron microscopy (FE-SEM) Nova NanoSEM 450. Phase identification was done at a scanning rate of 2.0 °/min by using X-ray diffractometer (XRD-6000, Shimadzu Scientific Instruments) with CuKα radiation (λ = 1.5406 Å) in the 2θ range between 20° and 80°. The photoluminescence (PL) spectra of the as-anodized Cu plates were measured using Hg–Xe lamp from spectrofluorometer Horiba Jobin-Yvon FluoroLog-3 with an excitation wavelength of 325 nm at a power of 400 W at room temperature.

3.   Results and discussion

3.1.   Study of the effect of anodizing voltage

Fig. 1a to Fig. 1c show the FE-SEM images of Cu plates anodized at a voltage ranging from 30 V to 70 V. It can be seen that the morphology and porosity of the nanostructured thin film is voltage-dependent. Nanostructured thin film formed at 30 V (Fig. 1a) is a dense aggregation of smaller nanoparticles that are distributed uniformly on the surface of Cu plate. As the anodizing voltage was increased to 50 V, a nanoporous thin film was formed over the Cu plate as shown

in Fig. 1b. Highly porous thin film in Fig. 1c was formed when the anodizing voltage was further increased to 70 V while keeping all other process parameters the same. In general, the porosity of the nanostructured thin film increases with increasing anodizing voltage. The current density versus time in Fig. 1d supports the observation from FE-SEM images in Fig. 1a to c. Similar to the anodizing of aluminum, the current density versus time for Cu in Fig. 1d can be divided into three stages [24]. At the first stage, the current density drops sharply to a minimum value which is attributed to the formation of oxide layer on the initially clean surface. The formation of oxide layer leads to the decrease of ionic transport across the electrolyte/metal interface. This is followed by the gradual increase of current density at the stage two, which is due to the localized dissolution of the nanostructured thin film and the emergence of nanopores. At the final stage, the steady state growth of nanostructured thin film is achieved when the rate of oxide dissolution at the oxide/electrolyte interface equals the rate of oxide formation at the oxide/metal interface. The current density versus time for the anodizing of Cu plate at higher anodizing voltage (70 V in this study) shows a larger increase of current density at stage 2, denoting higher oxide dissolution rate that led to the formation of highly porous nanostructured thin film.

The formation of crystalline Cu_2O on the as-anodized Cu plates was confirmed by XRD analysis. The XRD patterns of the nanostructured thin films anodized at 30 V and 50 V were similar to the XRD pattern of thin film anodized at 70 V. Fig. 2 shows the XRD pattern of nanostructured thin film anodized in ethylene glycol containing 0.15 M KOH, 0.1 M NH₄F with 3 wt.% deionized water at 25 °C and 70 V. The peaks marked with red triangles at 2θ of 43.4°, 50.82° and 74.4° are attributed to the (1 1 1), (2 0 0) and (2 2 0) planes of Cu substrate (JCPDS 04-0836). The diffraction peaks marked with black circles at 2θ of 29.6°, 35.4° and 61.1° are attributed to the (1 1 0), (1 1 1) and (2 2 0) planes of Cu_2O (JCPDS 05-0667). Similar XRD pattern was reported by Allam et al. [15] in their study of synthesis of Cu_2O nanostructured

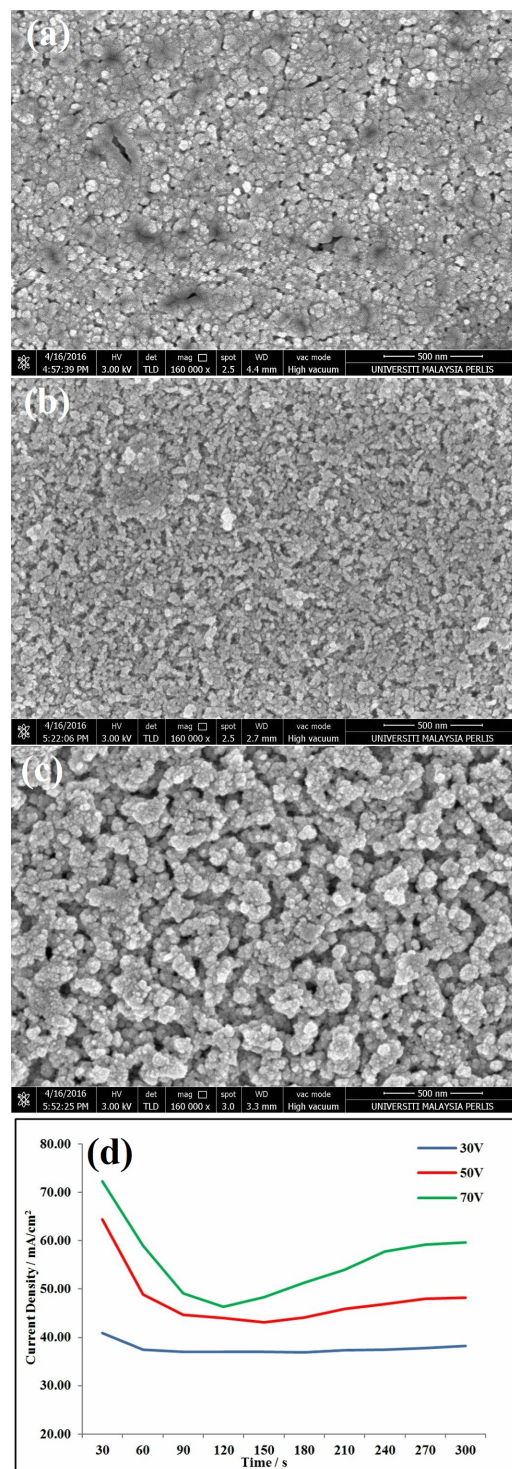Fig. 1. FE-SEM images of Cu_2O nanostructured thin film anodized in ethylene glycol containing 0.15 M KOH, 0.1 M NH₄F with 3 wt.% deionized water at 25 °C, at (a) 30 V, (b) 50 V, (c) 70 V; and (d) the corresponding current density curves versus time.

thin films by anodizing of Cu foil in ethylene glycol containing 0.15 M KOH, 0.1 M NH_4F and 3 wt.% deionized water followed by vacuum annealing at 280 °C for 15 min. This XRD pattern suggests that the crystalline Cu_2O nanostructured thin film can be fabricated by anodizing of Cu plates in ethylene glycol electrolyte containing 0.15 M KOH, 0.1 M NH_4F with 3 wt.% deionized water at 25 °C, at anodizing voltage of 30 V to 70 V. The morphologies of the Cu_2O thin film can be controlled by varying the anodizing voltage.
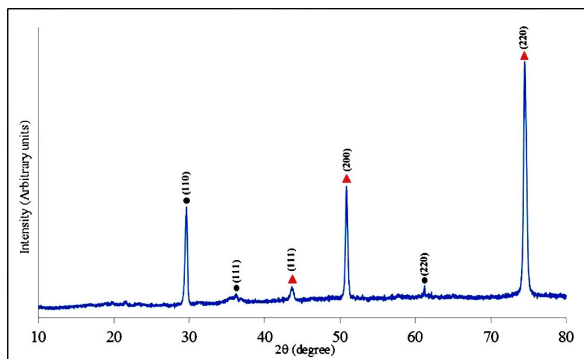

Fig. 2. XRD pattern of of Cu_2O nanostructured thin film anodized in ethylene glycol containing 0.15 M KOH, 0.1 M NH_4F with 3 wt.% deionized water, at 25 °C and 70 V.

3.2. Study of the effect of electrolyte temperature

Fig. 3a and Fig. 3b show the FE-SEM images of Cu plates anodized at 50 V in ethylene glycol containing 0.15 M KOH, 0.1 M NH_4F with 3 wt.% deionized water at 15 °C and 5 °C, respectively. Compared with the nanostructured thin film fabricated at 25 °C as in Fig. 1b, the morphology of the nanostructured thin film changed significantly when the temperature of electrolyte was decreased to 5 °C (Fig. 3c). As the temperature decreased to 15 °C (Fig. 3b), the as-anodized Cu plate has covered with nanoplatelets over the Cu surface. Further decreasing in the temperature of electrolyte to 5 °C has not changed the surface morphology of the as-anodized Cu, but the size of nanoplatelets increased. Higher magnification of Fig. 3b in Fig. 3c shows that the nanoplatelets have irregular shapes

and thickness around 30 nm to 60 nm. The difference in morphology of the nanostructured thin film on Cu plates as a function of temperature can be analyzed by considering the current density versus time in Fig. 3d. As can be observed, the current density versus time for anodizing of Cu plates in electrolyte at 15 °C and 5 °C, is significantly different from the anodizing curve recorded when 25 °C was used. The current density curves versus time recorded at 15 °C and 5 °C, decreased as the anodizing was continued instead of increasing after achieving the minimum value, like in the case of 25 °C curve. This indicated the formation of densely packed nanoplatelets on Cu plates that reduced the access of electrolyte to metal surface, and thus caused the current density to decrease with the anodizing duration. Lower current density was recorded for anodizing conducted at lower temperature and this was probably due to the dissolution of Cu_2O that was retarded at lower temperature. XRD was also used to investigate the effect of temperature on the composition of nanostructured thin film. Fig. 4 shows the XRD pattern of of Cu_2O nanostructured thin film anodized in electrolyte containing 0.15 M KOH, 0.1 M NH_4F with 3 wt.% deionized water at 5 °C and 50 V. The XRD pattern is similar to the pattern obtained for the process carried out at 25 °C when Cu_2O was formed, denoting temperature of electrolyte affects the morphology but not the composition of the nanostructured thin film.

Fig. 5 shows the PL spectrum of of Cu_2O nanostructured thin film anodized in electrolyte of 0.15 M KOH, 0.1 M NH_4F with 3 wt.% deionized water at 25 °C and 70 V. As it is shown in Fig. 5, PL spectrum of of Cu_2O nanostructured thin film shows one emmision peak centered at 630 nm and corresponding to band gap of 1.97 eV. This confirms the formation of Cu_2O with band gap of 1.9 to 2.2 eV. The presence of this peak is attributed to defects in the Cu_2O films. Similar observation was made by Wang et al. [25] in which they reported a red emmision band located at 630 nm. They suggested that the presence of this peak was due to the presence of oxygen vacancies in the Cu_2O thin film. It was also found that the shape as
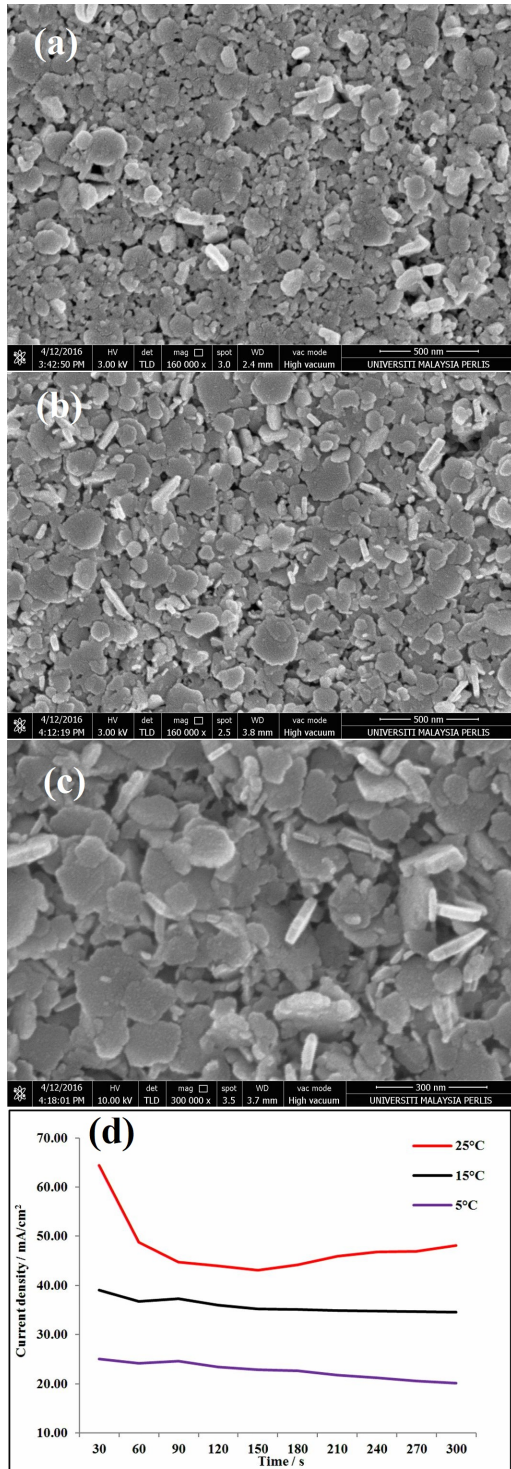
Fig. 3. FE-SEM images of Cu$_2$O nanostructured thin films anodized at 50 V in ethylene glycol containing 0.15 M KOH, 0.1 M NH$_4$F with 3 wt.% deionized water at (a) 15 °C; (b) 5 °C; (c) higher magnification of image (b); and (d) the corresponding current density versus time.
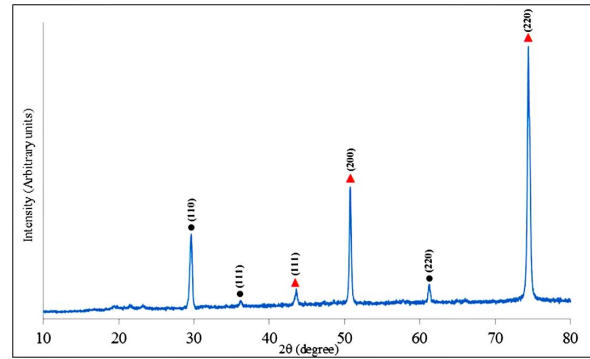

Fig. 4. XRD pattern of of Cu$_2$O nanostructured thin film anodized in ethylene glycol containing 0.15 M KOH, 0.1 M NH$_4$F with 3 wt.% deionized water at 5 °C and 50 V.

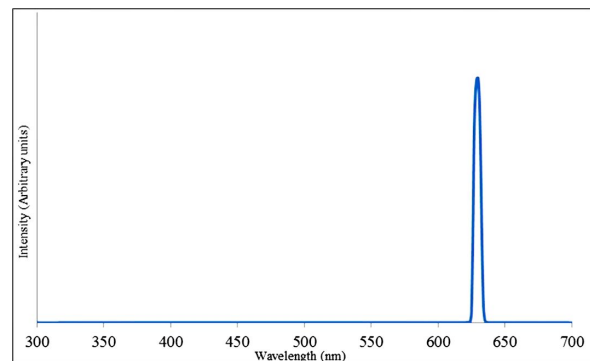Fig. 5. PL spectrum of of Cu$_2$O nanostructured thin film anodized in ethylene glycol containing 0.15 M KOH, 0.1 M NH$_4$F with 3 wt.% deionized water at 25 °C and 70 V.

well as the wavelength of the peak in the PL spectra (not shown here) remains unchanged as the anodizing voltage was increased from 30 V to 70 V and the temperature decreased from 25 °C to 5 °C, respectively.
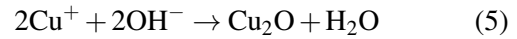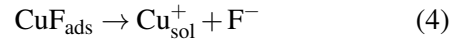
3.3. Mechanism of formation of Cu$_2$O thin film
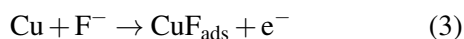
In this study, water was added to ethylene glycol as a source of oxygen. Compared to aqueous electrolyte that leads to disordered structure due to the high rate of chemical dissolution and oxidation of metal during the anodizing process, anodizing in organic electrolytes, such as ethylene glycol and glycerol, forms a relatively regular structure [26]. Previous studies have shown that

water addition into ethylene glycol based electrolytes can induce localized dielectric breakdown of the anodic thin film by increasing the dielectric constant of the electrolytes, causing enhanced local field strength and Joule heating in thin film during anodizing [27]. This can form anodic thin films with a morphology different from the anodic thin film fabircated by anodizing in aqueous based electrolyte, as reported by Allam et al. [15] in their study of synthesis of Cu_2O nanostructured thin film in aqueous solution based on ethylene glycol electrolytes with addition of water. Addition of KOH into electrolyte can increase the conductivity of the ethylene glycol based electrolytes due to the high number of OH^-, which facilitate the ionic transport across the metal/electrolyte interface [28]. Anodizing conducted in fluoride (NH_4F) containing electrolyte can enhance the localized dissolution and continuous pits formation which transform subsequently into pores [29].

The exact mechanism for the growth of Cu_2O thin film by anodizing process is still unknown. The most widely accepted mechanism for the growth of anodic film on a metal such as aluminium, zinc, titanum and copper is the field-assisted dissolution mechanism. A mechanism can be proposed for the growth of Cu_2O thin film by anodizing. The formation of the Cu_2O nanostructured thin film can be represented by equation 1 below [15]:

$$2Cu + 2OH^- \rightarrow Cu_2O + 2e^- + H_2O \quad (1)$$
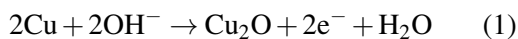
Under the influence of electric field, Cu plate which acts as the anode, releases one electron and forms Cu^+ in the electrolyte according to equation 2. Besides, in the presence of F^- ion, initial electrodissolution of copper may also occur according to equation 3 and equation 4 [30]. The electrons flow from anode to cathode through an external circuit and oxygen reduction occurs at the cathode. OH^- ions in the electrolyte are attracted to anode and combine with Cu^+ to form Cu_2O thin film, according to equation 5.

$$Cu \rightarrow Cu^+ + e^- \quad (2)$$

$$Cu + F^- \rightarrow CuF_{ads} + e^- \quad (3)$$

$$CuF_{ads} \rightarrow Cu^+_{sol} + F^- \quad (4)$$

$$2Cu^+ + 2OH^- \rightarrow Cu_2O + H_2O \quad (5)$$

Defects such as impurities, scratches, protrusions, or grain boundaries are present on the intial Cu surface. In this paper, these defects are illustrated as disordered protrusions in Fig. 6a. The intially formed Cu_2O thin film is flat over the entire Cu plate, as in Fig. 6b. Two interfaces are formed on the Cu surface, which are electrolyte/oxide interface and oxide/metal interface. The current density versus time decreases to the minimum value at this stage. The Cu_2O thin film growth at the Cu surface continues by the migration of OH^- through the intially formed oxide layer under the influence of electric field. The surface defects are associated with high energy and thus electric field concentration (illustrated with red arrows in Fig. 6b) at these defects occurrs and leads to the localized oxide formation as shown in Fig. 6c. This leads to the formation of a relatively flat oxide/metal interface. In the second stage, which is the pore formation, localized dissolution of Cu_2O thin film occurs due to the presence of uneven thickness of the oxide thin film. This subsequently leads to the electric field concentration at the spots with thin oxide film due to the relatively low resistances of these spots. Electric field concentration occurs at the spots on the oxide film with relatively low resistance, which are the spots with thin oxide film, as illustrated in Fig. 6d. Field assited oxide dissolution results in the metallic Cu surface exposed to electrolyte at these locations and leads to localized formation of Cu_2O, shown in Fig. 6e. The Cu_2O thin film is again subjected to localized dissolution at the spots with electric field concentration and the cycle is repeated until the anodizing stops.

It is generally believed that anodizing involves three simultaneously occurring processes, namely the field-assisted oxidation (oxide formation), the field-assisted oxide and/or metal dissolution, and the chemical dissolution of metal and/or oxide by the reaction with anions such as fluoride ions. The balance of these competing reactions determines the morphology and composition of the anodic thin
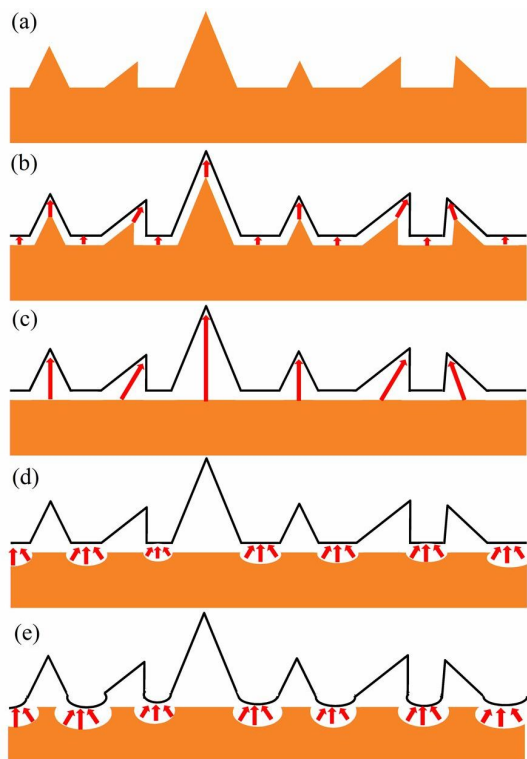
Fig. 6. Schematic illustration of the mechanism of formation of Cu$_2$O layer by anodizing.

film. Manipulation of the anodizing parameters, such as anodizing voltage, electrolyte temperature, concentration of electrolyte and composition of electrolyte would therefore result in changes of the morphology and composition of anodic thin film. In this study, increasing of anodizing voltage and reduction of temperature of electrolyte resulted in changes of morphologies of Cu$_2$O nanostructured thin films. Increasing of anodizing voltage to 50 V and 70 V resulted in the enhanced field assisted oxide dissolution that led to the formation of highly porous nanostructured thin film. However, decreasing temperature of electrolyte to 15 °C and 5 °C caused the reduction of the oxide dissolution process and as a result, Cu$_2$O nanoplatelets thin film was formed.

4. Conclusions

In conclusion, Cu$_2$O nanostructured thin films with different morphologies can be fabricated by anodizing in ethylene glycol electrolyte containing 0.15 M KOH, 0.1 M NH$_4$F with 3 wt.% deionized water. Highly porous Cu$_2$O nanostructured thin films were formed when 50 V and 70 V were used as the anodizing voltages at room temperature. Cu$_2$O nanoplatelets thin films were formed when Cu plate was anodized at 50 V in electrolyte of 15 °C and 5 °C. XRD analysis confirmed the formation of Cu$_2$O after the anodizing process, although the anodizing voltage and temperature of electrolye were varied. PL spectra of Cu$_2$O nanostructured thin films showed one emission peak centered at 630 nm, regardless of the temperature of the electrolyte and anodizing temperature. Current method can produce Cu$_2$O nanostructured thin film at low cost and low temperature, and the thickness and morphology of the thin film can be tailored easily by varying the anodizing parameters such as voltage, temperature and concentration of electrolyte. However, when current method is to be integrated into the fabrication of sensors and for hydrogen production and energy conversion, it is necessary to ensure the anodizing is only conducted on the desired copper surface.

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