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Thermal and Surface Evaluation on The Process of Forming a Cu₂O/CuO Semiconductor Photocatalyst on a Thin Copper Plate

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Abstract. This research aims to investigate the process of forming a multi-scale copper oxide semiconductor (CuO/Cu₂O) through a process of calcining a copper plate. The changes that occur during the formation of the oxide are thermally and surface evaluated. Evaluation using Differential Thermal Analysis (DTA) obtained by surface change of copper plate happened at temperature 380°C. Calcination of oxide formation was carried out at temperature 380°C for 1 hour. Surface evaluation process by using Scanning Electron Microscope (SEM) surface and cross-section, to determine diffusion of oxide formation on copper plate. The material composition is monitored by XRF and XRD to explain the process of structural and physical changes of the copper oxide plate formed during the heating process. The thickness of Cu plates used is 200-250 μm. SEM analysis results, the oxygen atom interruption region is in the range of 20-30 μm, and diffuses deeper during thermal oxidation process. The maximum diffusion depth of oxygen atoms reaches 129 μm.

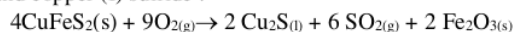
1. Introduction

Copper oxide is a semiconductor material that is widely used as a photocatalyst(1). In its role as a photocatalyst, the electrons in the valence band will be excited to the conduction band. Semiconductor resistivity is about $5 \times 10^7 \mu\Omega \text{ cm}^{-1}$ (2). The ability of electron excitation will be easier when the distance between PV and PK is getting smaller. The energy needed to excite the electron is called an energy gap.

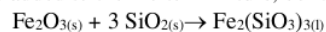
The yellow copper metal surface will be oxidized by air containing oxygen to form a thin, Cu₂O, reddish layer. This color is due to the electron being filling the d orbitals with energy of 220 kJ/mol, lower than the s and p orbitals. As a result, electrons can be excited to higher energy levels by photons, the red and blue spectrum. Meanwhile, the copper atoms will reflect the red and yellow spectrum(3).

The abundance of copper metal in nature is 0.005%(4). However, the copper oxide is not present in nature independently, but rather in the form of a copper (I) iron (III) sulfide, CuFeS₂, a metallic-looking solid that has the two mineralogical names of chalcopyrites and copper pyrites. A rarer mineral, CuAl₆(PO₄)₄(OH)₈.4H₂O is valued blue gemstone turquoise.

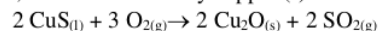
Cu₂O extraction process can be done with pyrometallurgy technique (thermal process) and an aqueous process (hydrometallurgy). For the pyrometallurgical process, the concentrated ore is heated (a process called roasting) in a limited supply of air. This reaction decomposes the mixed sulfide to give iron (III) oxide and copper (I) sulfide :



Sand is added to the molten mixture, converting the iron (III) oxide into a slag of the iron (III) silicate :



This liquid floats on the surface and can be poured off. Air is again added, causing sulfide to be oxidized, and simultaneously copper (I) sulfide is converted to copper (I) oxide :



In this study, the formation of copper oxide is carried out by thermal oxidation method with a direct copper thin plate calcination technique. The process of oxide formation is evaluated by optical and gravimetric methods. The internal surface and morphological evaluation of copper plate to copper oxide was analyzed with temperature thermodynamic variables using SEM, DTA, XRF and XRD. It aims to find out how the thermodynamic condition of copper oxide thin plate synthesis process is optimum, to obtain Cu₂O photocatalyst material which can be used as light room electrode panel.

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2. Experimental Section

2.1. Tools and Materials

In this study, molecular and spherical analysis of crystals using software Balls & Sticks ver. 1.81a (created by Sung J.Kang et al) using a computer brand hp pavilion processor intel core i5 with memory (ram) 12 GB. The others tools used in this research is a SEM (Hitachi S-3400N), XRD (PANalytical pw30/40), X-Ray Fluorescence, Differential Thermal Analysis (DTA), Furnace, Analytic Tools, and Scales tools glasses. The materials used in this research is the glass, Plate of Cu (PT Metalindo), NaOH (Merck), acetic acid (CH₃COOH) (Merck) and aquadest.

2.2. Methods

2.2.1. *Preparation of Cu Plate.* The copper thin plate is manufactured by PT Metalindo. The plate used has a thickness of 200 μm-250 μm. Plates prior to use should be cleaned using sodium hydroxide (alkaline) and acetic acid (acidic). After rinsing at acidic and alkaline conditions, followed by washing with water and drying for 15 minutes at 45°C. After drying, the next process is characterized by a thin copper plate with SEM, XRF and DTA(5-7).

2.2.2. *Synthesis Cu₂O Thin-Plate.* The preparation of Cu₂O plates is carried out by oxidation techniques at high temperatures under oxygen conditions. The cleansed Cu plates are then calcined with the temperature of the optimization time of evaluation with DTA during optimum calcination time. The length of calcination in accordance with work procedures in previous studies reported Rahadian et al (2015), the duration of Cu calcination plate is 1 hour (6). Result of a plate of Cu₂O characterized using XRD, XRF and SEM.

2.2.3. *Measurement of Mass Addition of Copper Oxide Plate.* After the calcination process is done, the thin copper oxide plate is weighed using an analytic scale. The used plate is 4 cm wide and 38.5 cm high.

3. Results and Discussion

In thermodynamic conditions 25°C and 1 atm, the distribution of atoms of Cu at the surface area of 1nm² reaches 20 atoms. In volumetric 1 nm³ there are 84 Cu atoms with radius size 1.278 Å (127.8 pm). In this thermodynamic condition, there is no gap between atoms of Cu (Cu-Cu) as shown in Figure 1. According to Lange, the size of Cu atoms in thermodynamic conditions 1 atm and 25°C are 1.278 Å (atomic radius), 1.17 Å (covalent radius) and when ionized in the crystallized system will be reduced to 0.96 Å (Cu⁺¹) and 0.72 Å (Cu⁺²). Analysis with Ball & Sticks ver. 1.81a, there is a spherical potential that causes oxygen interruption on the surface of the copper thin plate as shown in Figure 1b.

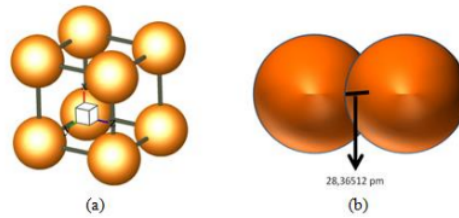


Figure 1. Atomic Cu illustration by using software Balls & Sticks ver. 1.81a (created by Sung J.Kang et al). (a) Simple Cubic for Cu Crystalline and (b) No gap between Cu atoms, but overlap of 28.36512 pm

The crystallographic analysis to Cu crystal found that Cu crystal lattice has side (a) of 3.6147 Å (at 20°C), and cubic crystal (face-centered cubic, fcc) the oxygen atom and Cu bonds reach 1.86 Å (Cu⁺¹) and 1.97 - 2.66 Å in Cu(II) and the 1083°C liquid point as shown in Figure 2. From the Lange data, Cu metal has a density of 8920 kg/m³ and a thermal expansion coefficient of 16.5 x 10⁻⁶ K⁻¹. However, if the calculation is done with Lange data, it is known that there are 4.38 Cu atoms at 25°C, in 1000 nm side length. Based on this analysis, the position of Cu atoms on the plates will be united or attached at 28.36512 pm because of the compressibility factor of the preparation of metal atoms.

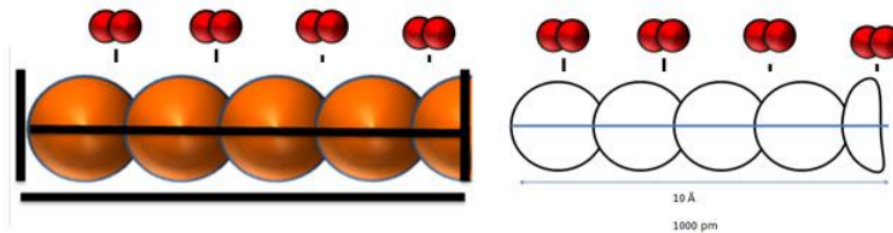


Figure 2. Position of Cu atoms according Lange

Based on spherical analysis and atomic size, there is no gap between Cu atoms at 25°C and 1 atm pressure. In this condition, the oxygen atom can only be located on the surface layer (external interface) as shown in Figure 2. This is because the oxygen molecule (O₂) has a larger size that is 60.3 pm in a straight position and 140 pm (position transverse O⁻²) and 176 pm (O⁻¹ cross-sectional position)(8). Another factor that prevents O₂ interruption from entering or migrating into Cu crystals is the Van der Wall bonding force which has 140 pm grating. DTA evaluation of the thin plate of Cu, known at 370.44°C becomes an unstable state in the surface structure of copper.

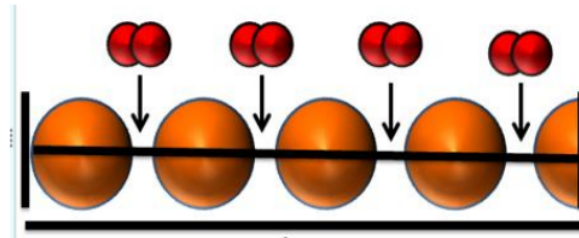


Figure 3. The gap between atoms is formed when heating at 370.44oC for 1 hour.

The DTA results inform the unstable instability of the atomic atoms of Cu due to the increase in the distance between the atoms and the electron velocity distribution in the conduction band increases so that the Cu atoms becomes smaller by the temperature increase. The decrease of the digit finger Cu with electron movement to the conduction band reaches 31.8 - 55.8 pm. Expansion of the distance between Cu atoms reaches 0.1650 pm. Although thermal expansion is insignificant, electron velocity distribution under thermodynamic conditions 370.44°C has caused a significant decrease in Cu radius radius. With this decrease, as shown in Figure 3, the gap between the Cu-Cu atoms grew to the range of 73.63 pm. In this condition, the invasion (O_2 molecular oxygen spatial migration) into the internal Cu thin plate causes the opening of the copper atomic gap deeper and lasts for a calcination process for 1 hour.

The result of SEM analysis as shown in Figure 4, the surface of Cu covered by oxygen molecule reaches 20-30 μm thickness. In this area, the molecular oxygen density reaches 1,0002713 g/cm^3 . In thermodynamic conditions 25°C and 1 atm pressure, there are 25 oxygen molecules in 1000 nm^3 . According to J. O. M. Bockris et al (in Gordon M. Barrow, 1988: 771), the thickness of the first metal layer and its environment ranges from 10-100 μm (9). If this assumption is used in the atomic interaction analysis between the atoms of Cu and the oxygen gas molecule, then in volumetric from the area of 1 A^2 with the thickness there are about 8,400,000 to 84,000,000 O_2 molecules. The potential of this invention will increase with the opening of a slit of copper atoms on the surface of the thin plate and the momentum of oxygen atoms increasing as a result of kinetic energy by the increase of heat during the calcination process.

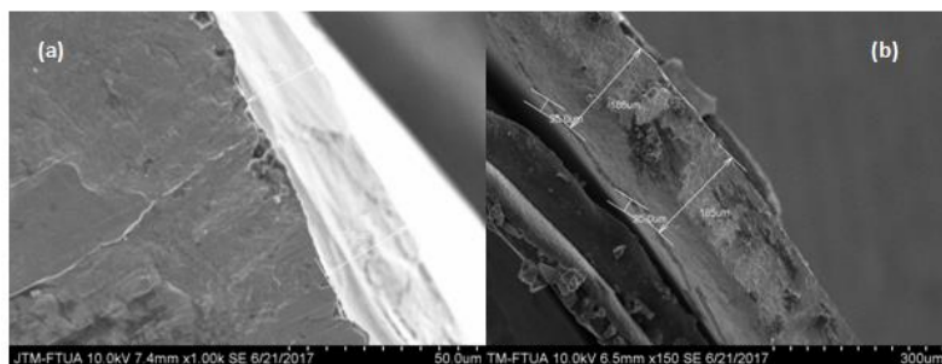


Figure 4. SEM Images of the diffusion layer of the oxygen molecule (a) and the mobility area of the oxygen atom into the thin copper plate during the formation of the copper oxide.

The calcination process lasts for 1 hour and the cooling process is reached after 12 hours. The copper oxide analysis was performed using XRD, which yielded 92.6% Cu_2O and the remaining CuO . This result is confirmed because after the oxygen migration into the copper plate internals, there is a high frequency collision resulting in the formation of ionic bonds between Cu(I) and O^{2-} atoms. In this condition, the oxide crystal structure is faced center cubic (fcc). The population of oxygen atoms that migrate during the calcination time ($t=1$ hour) causes an internal attack at a maximum depth of 129 μm . As the temperature begins to drop, after an hour, the internal migration of O_2 molecules begins to subside and reverse.

In this condition, molecules of Oxygen which are not experiencing ineffective momentum when collided with Cu atoms, will exit and leave space which increases the pressure on the gap and the intercellular space in the copper oxide crystals. This is what causes the transformation of Cu crystal from FCC into Monoclinic. However, the chance of transformation is still small (4%) because the energy that effects Cu atoms (Cu) becomes Cu atoms (II) is not capable of causing changes in larger quantities. The increase in temperature has led to an increase in the pressure in the intercellular space in the copper plate

and causes a decrease in the size of Cu ions from a radius of 96 μm to 72 μm . This results in a decrease in the density of the oxide and increase the band gap return.

Increased Band Gap occurs, because the size of Cu(II) ions is smaller than Cu(I) ions, and the interacting Oxygen ions are 1.40 Å (O^{2-} radius) and 1.76 Å (O^{-1} radius). In Cu crystal (cuprite) Cu_2O (cuprite) with red density 6.0 g/cm^3 , has a refractive index of 2,705 and a melting point of 1235°C(8). Meanwhile, CuO (tenorite) crystals are monoclinic with density 6.3-6.5 g/cm^3 , black, refractive index 2.63 and melting point 1325°C. Although the density of CuO is greater than Cu_2O , but because the crystallographic system is different so that the distance between Cu-O atoms is more separated (greater than Cu_2O), causing greater energy bandwidth. In Cu_2O the density is lower, but the lattice distance between the atoms is smaller so the energy band width is also smaller. This may lead to a change in the copper oxide photocatalytic capability, as the temperature rise causes the widening of the energy band, and the greater the gap energy to excite the electron from the valence band to the conduction band(10; 11).

The oxygen changes that migrate and bind to the surface of the copper thin plate are evaluated by XRF. The increase of the oxide compound is evaluated on the surface by calculating the mass gain. The copper oxide formed signifies the oxygen and Cu interactions on the thin plate surface has taken place at an optimum temperature of 370.44°C. The presence of a 4% shift could be due to the calcination experiment carried out at a constant temperature of 380°C.

4. Conclusion

Synthetic copper thin oxide plate successfully carried out at optimum temperature of 380°C. XRD analysis results confirmed that 92% Cu_2O and 4% CuO were formed during 1 hour of calcining and 5 hours of cooling. The thermal evaluation process through SEM and computational calculations with Ball & Sticks successfully reveals that Cu changes and the formation of Cu_2O and CuO occur as a function of the energy distribution and position of electrons and atomic atoms. Population and migration of atomic atoms can be described so that the synthesis process can be done effectively and efficiently. The level of efficiency of thin plate formation of Cu_2O reached 92%.

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