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SYNTHESIS AND CHARACTERIZATION OPTICAL PROPERTIES OF Cu_2O NANOPARTICLES WITH COPRECIPITATION METHOD BASED CONCENTRATION VARIATIONS PRECIPITATOR

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ABSTRACT

Cuprous oxide (Cu_2O) nanoparticles were synthesized using co-precipitation method with varying concentrations precipitates ammonium hydroxide (NH_4OH) i.e. 0,5 M , 0,75 M and 1 M. This research was carried out in order to synthesis nanoparticle with simple chemical co-precipitation and determine the influence of various concentrate precipitates NH_4OH on the optical properties of Cu_2O nanoparticles. Cu_2O nanoparticles were prepared by the reaction of $CuSO_4.5H_2O$ (5 gr), isopropanol (15 ml), and Polivinyl Alkohol (4 gr) as the reagen solution with the various of NH_4OH aqueous solution (0,5 M, 0,75 M, and 1 M). The samples were characterized by FTIR, XRD, SEM and UV-vis Spectroscopy. The results of XRD show that the products are nanocrystals of Cu_2O with cubic shaped and followed by another phase. FTIR analyzes indicates that the nanoparticles followed by O-H group on the surface of Cu_2O and showed Cu-O vibrations. Optical Charaterization showed that nanoparticles Cu_2O has direct band gap 3,081 eV, 4, 491 eV , dan 4,391 eV, slightly higher than the theoretical direct band gap of 2.2 eV. The influence of concentrate precipitates NH_4OH show that the cuprous oxide particles have smaller particle size at orde 69 nm , 61 nm, and 58 nm, whereas the optical properties showed that the absorbance, transmittance, and the band gap was increased.

Keywords: *nanoparticle, cuprous oxide (Cu_2O), coprecipitation, characterization*

INTRODUCTION

The development of science and technology, especially in the field of material being led to the revolution of nanoparticles which in this period occurred remarkable acceleration in the application of nanoscience and nanotechnology in the industry field. This matter is shown by the increasing development and nanotechnology application in variety of products that are used throughout the world.

Nanotechnology is science engineering to create materials, functional structures, and devices on nanometer-scale (≤ 100 nm). At the nanoscale, the chemical and physical properties of materials differ in fundamental and valuable ways from the properties of molecules or bulk matter. Above properties could be altered by controlling the size of the material, setting the chemical composition, surface modification, and control of the interactions between the particles.

The development of nano technology inseparable of research on nanoscale materials, especially in the development of methods of synthesis. The focus of interest many researchers are how development methods to synthesis nanoparticles [1]. Among the above methods for the preparation of nanoparticles, coprecipitation method was simple and efficient used. Coprecipitation method is a simple chemical process that brings a solution down forming a desired precipitate. The advantages of this method is that the process using low temperatures and easier to control the particle size and needed a relatively short time [16]. In chemical synthesis techniques, the growth and assembly of nanoparticles is controlled by optimizing reaction parameters (e.g., temperature, varying the reaction cuhemistry, reagent concentration, etc) [18]. Some of the most common substance used as precipitator agent in coprecipitation method is hydroxide, carbonate, sulfate and oxalate [1].

Cuprous Oxide (Cu_2O) is one of the materials that could be synthesized into nano-sized. Cuprous oxide has been the subject of much current research interest, since Cu_2O is an important metal-oxide p-type semiconductor and has a direct small band gap of 2.2 eV, which makes it a promising material for the conversion of solar energy into electrical or chemical energy [6, 8, 14]. Recently, a variety of interesting Cu_2O micro- and nanostructures such as nanocubes [9, 19], octahedra [17], nanocages [4], hollow spheres [19], nanowires [13], and other highly symmetrical structures have been synthesized.

H.Sekhar et al, [14] reported Cu_2O nanopowders synthesized by a simple chemical co-precipitation method at room temperature by varying the concentration of NaOH. XRD, FTIR, and SAED data confirms the formation of single-phase Cu_2O. Optical UV-VIS analysis showed that nanoparticles Cu_2O has direct band gap 2.6 eV, 2.3 eV, dan 2.1 eV. The average grain size of Cu_2O calculated using Scherrer's formula. The average grain size was found to be around 20 nm.

Kuo C.H et al., [9] reported Cu_2O nanocubes synthesized by seed-mediated approach in aqueous solution. The resulting nanocubes in samples have approximate diameters of 65, 100, 230, and 420 nm. Optical characterization showed that nanocubes smaller than 100 nm absorb at ~490 nm, while nanocubes larger than 200 nm display an absorption band at 515–525 nm. The calculated band gaps for these nanocubes of different size vary in the range 2.36 eV – 2.53 eV.

This research mainly focused on the size-controlled preparation of Cu_2O nanocrystals less than 100 nm via co-precipitation method with varying concentrations precipitates NH_4OH i.e. 0.5 M , 0.75 M and 1 M. Furthermore, the influence of various concentrate precipitates on the optical properties of Cu_2O nanoparticles control was discussed.

METHODOLOGY

All of the chemical reagents used were of analytical grade purity and were used without further purification.

Prior to the experiment, all of instruments used in preparation process were cleaned successively using detergent, deionized water and alcohol. The Cu_2O nanoparticles were prepared by the following procedure. A 100-mL aqueous solution containing $CuSO_4.5H_2O$ (5 g), polyvinyl alcohol (4 g), and isopropanol (15 mL) as a reagent solution was stirred for 2 h. During the mixing, precipitator solution (NH_4OH) prepared in different places with various concentration of 0.5 M, 0.75 M, and 1 M, then precipitator was added drop wise to the reagent solution with vigorous stirring at room temperature. After 1 h of stirring, the precipitate particles were isolated from the solution by centrifugation at 6,000 rpm for 30 min and the solution changed into green-yellowish precipitates. The product was filtered using whatman paper, then washed by aquabidest and absolute ethanol, respectively for three times, to reduce impurities and decrease pH value of the filtrate. The final product was dried in oven at 80°C for 4 h.

RESULT AND DISCUSSION

FTIR Characterization

The IR spectra were measured from 500 to 4,000 cm-1 with PerkinElmer Spectrum 100 model operating. FTIR Spectra were recorded to confirm the structure of the particle. Metal oxide generally gives absorption bands below 1,000 cm-1 that arise from interatomic vibrations[25]. In the FT-IR spectrum of the various sample (Fig.1), the absorption peak at 628 cm-1 (sample A), 627 cm-1 (sample B), and 624 cm-1(sample C) is assigned to the Cu-O vibration. In the high energy region, the broad peak at 3,588 cm-1 (sample A), 3,387 cm-1 (sample B, C) is assigned to O-H stretching of absorbed water on the surface of Cu_2O. The presence of water is confirmed by its bending vibration at 1,123 cm-1.

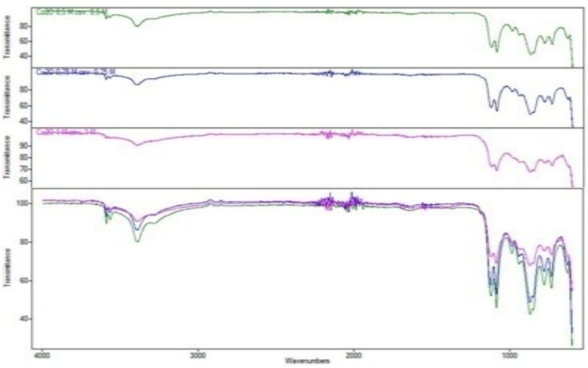

Figure 1. FTIR spectrum of Cu_2O nanoparticles by various concentration precipitator.

Overview in phase, another group of molecules detected in the spectra imply that there is a possibility of defective process of decomposition occurs. Another possibility that affect the quality of the air phase molecules are bound factor physically with Cu_2O sample during the preparation process FTIR characterization.

XRD Characterization

The powder XRD analysis was performed using a Phillips X-ray diffractometer with graphite monochromatized Cu Kα radiation (λ= 1.54178 Å) and the operation voltage and current were maintained at 40 kV and 70 mA, respectively.

X-ray diffraction pattern of Cu_2O samples were tested by XRD and yield peaks of X-ray scattering intensity for particular angle and shows the crystal size Cu_2O sample. The results of X-ray diffraction pattern with variations in the concentration of sediment contained in the image below (Figure 2).

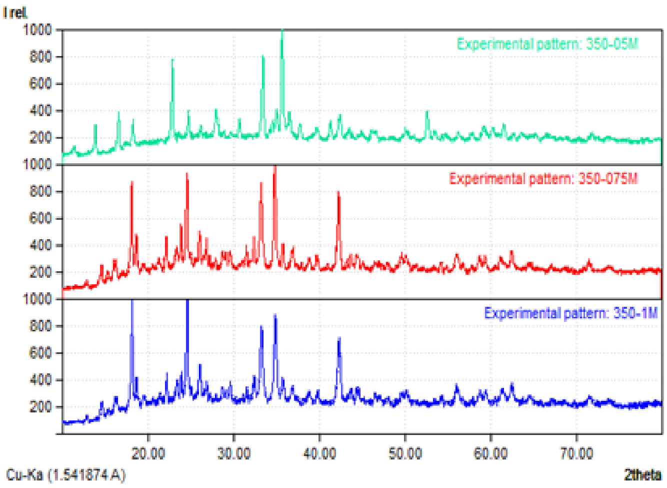

Figure 2. Powder XRD patterns of Cu2O nanoparticles by various concentration precipitator.

Powder diffraction analysis indicated that the product was nanoparticles Cu_2O. Fig 2. shows the typical powder X-ray diffraction (XRD) patterns of the as-prepared Cu_2O samples, Interplanar distances calculated for (110), (111), (200), (220), and (311) from XRD patterns match well with standard data confirming the formation of a single cubic phase Cu_2O with a cuprite structure. In addition, the results of XRD show that the products are nanocrystals of Cu_2O, though still followed by another phase.

The particle size was predicted by using Debye Scherrer formulae, Average Crystalline Size :

$$D = 0.9\,\lambda / \beta \cos\theta \qquad (1)$$

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Tabel 1. The value 2θ and crystal field orientation in highest peak

Peak	0.5M		0.75M		1M	
	2θ	hkl	2θ	hkl	2θ	hkl
1	29,25	(221)	28,03	(021)	16,16	(110)
2	33,31	(212)	24,73	(130)	24,73	(111)
3	22,79	(310)	18,74	(011)	39,90	(200)
4	24,73	(130)	33,20	(022)	33,20	(220)
5	27,96	(400)	33,45	(420)	45,76	(311)

Where λ is wave length of X-Ray(1.5406 x 10-10 m) and β = Full width at half maximum (radian). The influence of concentrate precipitates NH_4OH show that the cuprous oxide particles have smaller particle size at orde 69 nm (sample A), 61 nm (sample B), and 58 nm (sample C).

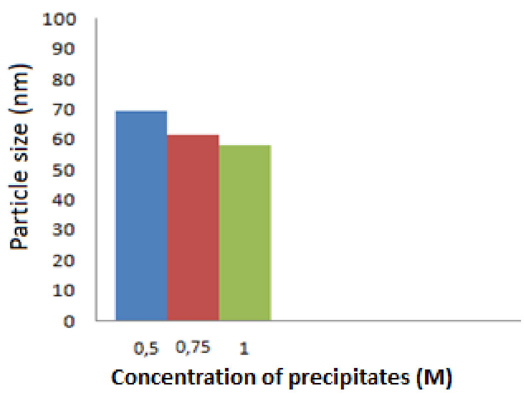

Figure 3. Relationship between pre cipitant concentration and particle size (based on Scherrer equation) of the Cu_2O nanocrystal.

SEM Characterization

The morphology and particle size of Cu_2O particles were investigated by field-emission scanning electron microscopy (JSEM-360LV) operated at 5 kV. Fig. 5a , 5b and 5c depicts the SEM images of nanoparticles. It shows that the Cu_2O nanoparticles are cubic shaped. The size of particle observed in SEM image is in the range of 500 nm.

Morphological structure produced in sample C showed that the presence of a homogeneous granular pile and the product had better quality of grain compared with samples A and B. This indicates that additional variation of precipitator has significant role as indicated by the evolution of particle morphology. Thus Forms morphology and structure of particle could be a factor in influencing the characteristics of optical properties.

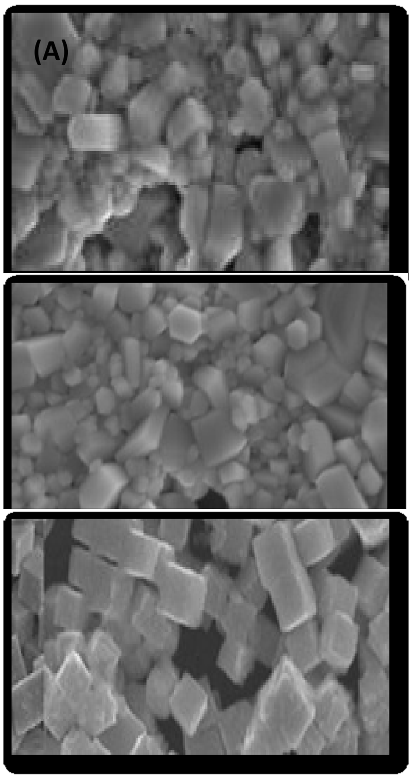

Figure 4. Typical SEM image of the Cu_2O nanoparticle by various concentration precipitator (a) 0.5 M, (b) 0.75 M, (c)1 M

UV-VIS Characterization

The visible absorption spectra of as-obtained samples were performed on Shimadzu UV-2100S from 400 to 800 nm. UV-Vis Spectrophotometer Characteri-zation is used to determine the value of absorbance, transmittance, and the band gap energy of Cu_2O nanoparticles.Item number 7 discusses the legal concept of Kirchoff. The aim is to uncover misconceptions about students of the factors that affect the value of resistance. With this matter is expected that students are able to explain the variables that affect a large drag on a conductor Answer obtained 52.17 % students had misconceptions on this matter.

Absorbance

Generally, the absorbance values for all samples decreased with larger wavelength, which it was characteristic absorption in semiconductor Cu_2O.Item number 15 deals with the legal concept ohms . The purpose of this question is to reveal miskonsespsi ohms law students to the application of the series and parallel circuits. With this matter is expected that students are able to analyze the differences lights if lamput arranged in series . Answer obtained 50.00 % of students who have misconceptions .

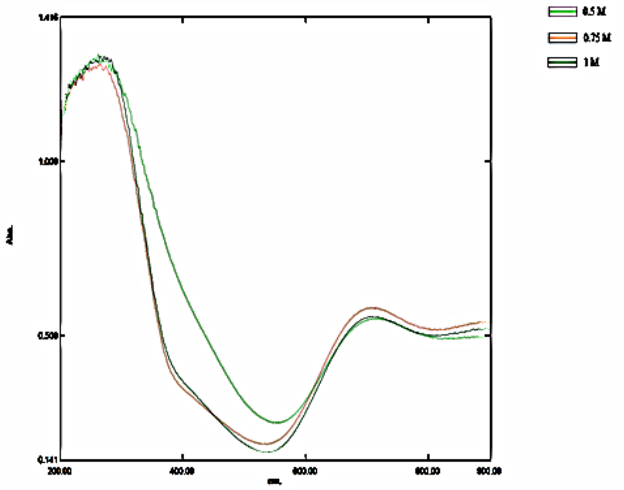

Figure 5. UV-Vis absorption spectra of Cu_2O nanoparticles.

Figure 5 shows that in concentration of 0.5 M were the highest absorbance with value 1,31 au at 259 and 1 M is the second highest absorbance with value 1,31 at 265 nm, and the absorbance decreases at a concentration of 0.75 M with value 1,28 au at 265 nm. The influence of NH_4OH concentration variation, showed absorbance values were varied and the increasing concentration of NH_4OH given provide a minimum increase.

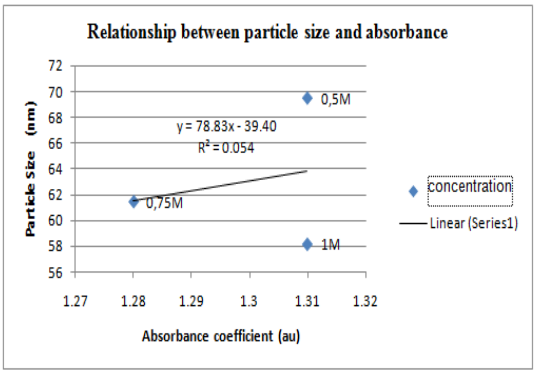

Figure 6. Relationship between particle size and absorbance

Based on data obtained the influence of precipitators concentration given greater caused absorbance values have decrased at 0.75 M concentration, and the concentration of 1 M increased.

Transmittance

Transmittance is the ratio between the intensity of light passed sample, compared with reference intensity. In general, the larger the particle size causes more molecules involved in the absorption of light energy were supplied, then less of energy fraction that can be passed.

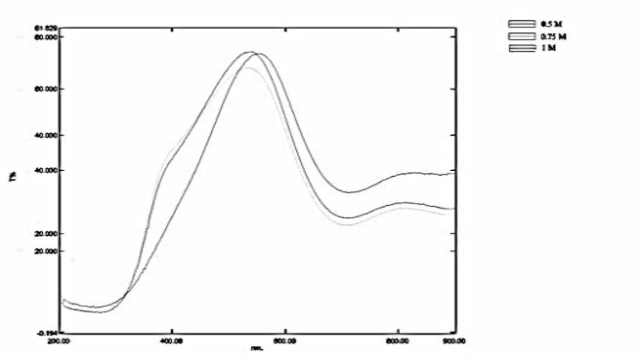

Figure 7. UV-Vis transmittance spectra of Cu2O nanoparticles.

Figure 7. shows the concentration of 1 M were the highest transmittance with value 69.30 at 538 nm, concentration of 0.75 M were second with transmittance value 65.50% at 532 nm and concentration 0.5 M were third highest transmittance with the transmittance value 56.70% at 552 nm. Effect of increasing concentration of NH_4OH given shows the resulting increase in transmittance value 5). Some students are still confused when doing experiments . They do not understand about what they need to do because they are unfamiliar with experimental activities

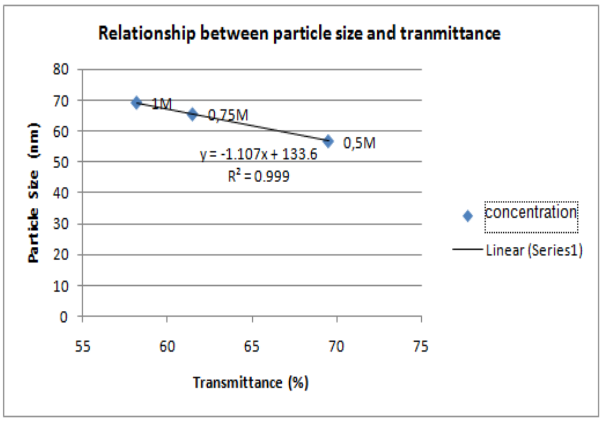

Figure 8. Relationship between particle size and transmittance

Band Gape

Band gap is an energy area that separates the conduction and valence energy level of a semiconductor material. if an intrinsic semiconductor material given greater energy than the band gap value is then the electrons contained in the valence level will be able to pass the forbidden band towards the conduction band.

The width of the energy band gap Cu_2O layer, can be calculated using the equation :

$$E_g = \frac{hc}{\lambda} \qquad (2)$$

Where Eg is direct band gap energy, h (planck constant) = 6.62 x 10-34 J.s, c (speed of light) = 3 x 108 m/s and λ (wavelength) obtained from using UV-Vis characterization. The width of the band gap energy produced in sample A equal to 3.081 eV, energy band gap of the sample B equal to 4.491 eV and sample C is equal to 4.391 eV . The difference in bandgap energy produced in sample A , B, and C is caused by differences in the size of the particles formed and with the addition of various precipitators. The value of the band gap energy produced as desired and can be further applied in the manufacture of solar cell devices. Determination of band gap value was important step become one of the main parameters in determining the appropriate application for a semiconductor material.

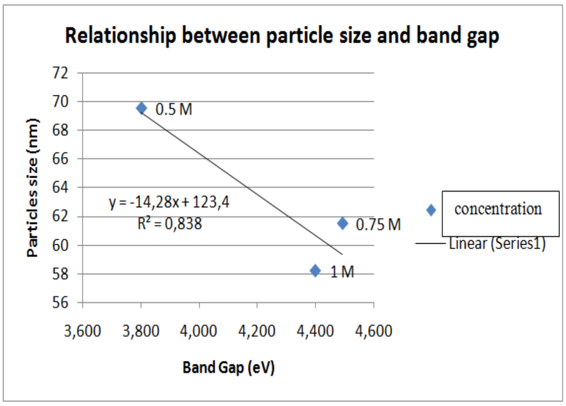

Figure 9.Relationship between particle size and band gap

CONCLUSION

Cuprous oxide (Cu_2O) nanoparticles were synthesized successfully using co-precipitation method by varying concentrations of ammonium hydroxide (NH_4OH). Results of XRD and SEM showed the products were nanocrystals of Cu_2O with cubic shaped and still followed by another phase. The influence of concentrate precipitates NH_4OH show that the cuprous oxide particles have small particle size at orde 69 nm (0,5 M), 61 nm (0.75 M), and 58 nm (1 M). The result showed that NH_4OH used as the reducing agent decreased the particle size of the Cu_2O nanoparticles. FTIR analyzes indicates that the nanoparticles followed by O-H group on the surface of Cu_2O. Optical Charaterization showed that nanoparticles Cu_2O has direct band gap 3,081 eV, 4, 491 eV , dan 4,391 eV, slightly higher than the theoretical direct band gap of 2.2 eV. The highest absorbance value 1.31 au at a concentration of 0.5 M and 0.75 M. Transmittance value greater when the particle size gets smaller and has the highest transmittance value of 69.30% at 538 nm on concentration 1 M. The succsessful synthesis of Cu_2O nanoparticles in co-precipitation method should allow future investigation of their potential applications in photovoltaic devices.

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