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SURFACE OXIDATION OF COPPER FOR CuO NANOWIRES FORMATION AND THEIR CATALYTIC PROPERTIES

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled **"Surface oxidation of copper for CuO nanowires formation and their catalytic properties"**. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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LIST OF ABBREVIATIONS

0-D   Zero Dimensional

1-D   One Dimensional

2-D   Two Dimensional

3-D   Three Dimensional

ppm   Part per Million

NWs   Nanowires

DPC   Diphenyl-carbazide

FESEM   Field Emission Scanning Electron Microscope

XRD   X-Ray Diffraction

UV-Vis   Ultraviolet-Visible

PENGOKSIDAAN PERMUKAAN KUPRUM UNTUK PEMBENTUKAN KUPRUM OKSIDA DAWAI NANO DAN SIFAT PEMANGKINNYA

ABSTRAK

Cr (VI) adalah logam berat toksik yang diklasifikasikan sebagai karsinogen kepada manusia. Cr (VI) memasuki ke dalam alam sekitar daripada sumber-sumber seperti sisa air industri tekstil yang mengandungi lilin, pewarna dan logam berat pepejal terampai. Kajian ini mengkaji keupayaan CuO dawai nano untuk penyingkiran Cr(VI) dalam larutan akueus. CuO dawai nano dibentuk melalui pengoksidaan gegelung tembaga melalui haba terus pada suhu antara 300 °C dan 600 °C. CuO dawai nano telah disifatkan oleh Mikroskop Elektron Pengimbas Pancaran Medan (FESEM) dan Pembelauan Sinaran-X (XRD). Parameter pengoksidaan yang dikaji ialah kesan suhu pengoksidaan, masa dan kehadiran kalium hidroksida sebagai pemangkin. Dalam julat suhu 400-600 °C, dawai nano terbentuk dengan dua morfologi yang berbeza iaitu lurus dan melengkung, dengan panjang antara 4 dan 12 µm dan diameter antara 50 dan 240 nm. Masa pengoksidaan yang berbeza pada 500 °C telah dijalankan untuk mengkaji pertumbuhan dawai nano pada gegelung tembaga. Beberapa dawai nano pendek dalam lingkungan 1-2 µm dan diameter 20-40 nm terbentuk pada 20 minit masa pengoksidaan. Manakala dengan pemanjangan masa pengoksidaan kepada 135 minit, pertumbuhan dawai nano menjadi lebih padat dengan panjang 5-7 µm dan diameter 130-180 nm. Pengoksidaan tembaga dengan kehadiran kalium hidroksida menyebabkan bahawa hanya beberapa dawai nano yang lebih pendek dibentuk pada suhu 500 °C pengoksidaan untuk masa 45-135 minit. Sampel dioksidakan pada 300 °C dan 500 °C diuji keupayaannya untuk pengurangan Cr(VI) di bawah cahaya matahari. 75%

penuranan dicapai di atas gegelung kuprum yang diosidakan pada 500 °C dengan kepanjangan dawai nano antara 3-5 µm.

SURFACE OXIDATION OF COPPER FOR CuO NANOWIRES FORMATION AND THEIR CATALYTIC PROPERTIES

ABSTRACT

Cr(VI) is toxic heavy metal which has been classified as human carcinogen. Cr(VI) enters into environment from sources such as textile industries wastewater that contains wax, dyes in colouring and heavy metal suspended solids. This study investigated the applicability of CuO nanowires for removal of Cr(VI) form that aqueous solution. The CuO nanowires were synthesized by direct thermal oxidation of copper coils at temperature between 300 and 600 °C. The CuO nanowires were characterized by Field Emission Scanning Electron Microscope (FESEM) and X-Ray Diffraction (XRD). Oxidation parameters investigated were the effect of oxidation temperature, time and presence of potassium hydroxide as catalyst. Within the temperature range of 400-600 °C, the nanowires formed have two different morphologies, straight and curved, with lengths between 4 and 12 µm and diameters between 50 and 240 nm. Different oxidation time at 500 °C was conducted to investigate the growth of nanowires on copper coil. A few nanowires with short length in range of 1-2 µm and diameter of 20-40 nm was formed at 20 minutes of oxidation time. While prolonging of the oxidation time to 135 minutes, the development of nanowires become denser with length 5-7 µm with diameter 130-180 nm. Oxidation of copper in the presence of potassium hydroxide resulted that only a few nanowires with short length can be formed at temperature of 500 °C annealed for 45-135 minute. Then, the sample oxidised at 300 °C and 500 °C were tested to reduce Cr(VI) under sunlight. 75% reduction of Cr(VI) was achieved on oxidised copper coil at 500 °C with nanowires length in range of 3-5 µm.

CHAPTER 1

INTRODUCTION

1.1 Background

Recently, semiconducting metal oxides have attracted considerable attention due to their unique physical and chemical properties rendering their use in emerging and potential engineering applications. Semiconducting metal oxide like copper oxide (CuO) can be fabricated as nanostructured material. Various one-dimensional (1-D) copper oxide nanostructures such as nanowhiskers, nanowires and nanorods can be fabricated by several well-known processes. A simple and cost effective process is however desired as to reduce on the complexity of nanostructured CuO formation. 1-D CuO nanostructures in a form of nanowires can be grown by thermal oxidation process at wide temperature range on various copper substrates such as plates, foils, grid sand.

In this work, CuO nanowires were produced on copper wire by direct oxidation in a furnace. The CuO nanowires produced were then used as photocatalysts to reduce hexavalent chromium, Cr(VI) to trivalent chromium, Cr(III) under solar irradiation. Cr(VI) compounds are of concerned because they posses harmful effect to human and environment yet they have been used significantly in various industries. Among them, textile industry is known to be one of the main contributors to Cr(VI) pollutant to water body.

The textile industry is one of the fastest growing industries and has contributes extensively to the economic growth of Malaysia. Nevertheless, the development of textile industries resulted in water pollution. In textile industry a high possibility to cause health-risk issues and serious environmental pollution exists due to extensive application of

organic dyes in dyeing, large scale production. The untreated textile wastewater is high in color, biochemical oxygen demand (BOD), suspended solids (SS), chemical oxygen demand (COD), total organic carbon (TOC), temperature, pH, toxicity and turbidity (Verma et al., 2012). The characteristics of wastewater at various stages involved during cotton-based textile production are shown in figure 1.1.

Process		Wastewater characteristics
Fiber manufacturing	⟹	High BOD & COD, medium SS
Spinning and weaving	⟹	High BOD, COD & SS
Pretreatment		
(a) Desizing	⟹	High COD, BOD (34-50 % of total), 70-80 °C
(a) Scouring	⟹	BOD (30 % of total), high pH, 70-80 °C, dark color
(a) Bleaching	⟹	High pH
(a) Mercerisation	⟹	High BOD, pH & SS
Dyeing	⟹	High toxicity, pH & SS, BOD (6 % of total)
Printing	⟹	High toxicity, pH, SS, COD, BOD, strong color
Finishing	⟹	High toxicity, low alkalinity & BOD

Figure 1.1: Wastewater characteristics of different streams involved in a typical cotton-based textile industry (Verma et al., 2012).

Each textile industry factory in Malaysia treated its own effluents and wastewater are normally discharged to a drain but not consolidated treatment system. In order to decrease the seriousness of water pollution meet the legislative requirement, they are compulsory to remove colored wastewater and highly polluted but still failed to meet the discharge limits (Idris et al., 2007).

As the demand of textile is ever increasing due to an increase of population of the world, the textile industry will continuously produce high discharge rate of wastewater with a high load of contaminants including wax, grease, pigment and dyes in colouring processes, and heavy metal ions or in a form of suspended solids. The release of pigments and dyes into the environment during textile fibre dyeing and finishing processes is the main source of water pollution. Nevertheless, these pollutants can be treated from the waste water before the water can be safely discharged. Among most used wastewater treatment processes can be done to remove pollutants.

Majority of small scaled textile factories in Malaysia treated their own effluents and wastewater is normally discharged to a drain but not consolidated treatment system. In order to decrease the seriousness of water pollution that meet with the legislative requirement, it is compulsory for the textile factories to remove coloured wastewater which may contains pigments and dyes made out of environmentally dangerous compounds. If untreated properly these compounds may enter the water bodies.

1.2 Heavy Metal in Environment

Water pollution affects all the major water bodies of the world such as rivers, groundwater and marine water. Pollution creates further problems: contamination of marine life and soil which then polluting fish and crops respectively. Upon consumption,

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human will also be affected by the pollutants. There are many different types of pollutants in water, but heavy metal ions is can be considered as one of the most severe. Metallic elements that have a relatively high density compared to water are defined as heavy metals. Their multiple industrial, domestic, agricultural, medical and technological applications have led to their wide distribution in the environment; raising concerns over their potential effects on human health and the environment. It has been reported that heavy metal pollution is very prominent in point source areas such as mining, foundries and smelters, and other metal-based industrial operation (Fergusson, 1990).

Heavy metals are commonly defined as metal having a specific density of more than 35 g/cm such as lead, cadmium, mercury, selenium, chromium, arsenic and nickel. Many heavy metals such as lead, cadmium and mercury are toxic materials even presence in minute of concentration. Although heavy metals are naturally occurring elements that are found throughout the earth's crust, most environmental contamination and human exposure result from anthropogenic activities such as mining and smelting operations, usages in industrial productions, domestic and agricultural use of metals, and metal-containing compounds (Verma & Gupta, 2015).

1.3   Toxicity of Heavy Metal Ions

Wastewater from many industries cointans heavy metal ions (Chen et al., 2006). These wastewater with heavy metal ions are discharged into natural water directly, not only threat the aquatic organisms, but may be enriched by precipitation, adsorption, and harmed human health through the food chain. Thus, the removal of such toxic metal ions from wastewater is becoming a crucial issue.

In biological systems, heavy metals have been reported to affect cellular organelles and components such as cell membrane, mitochondrial, lysosome, endoplasmic reticulum, nuclei, and some enzymes involved in metabolism, detoxification, and damage repair. Cell components such as DNA and nuclear proteins have been found to interact with metal ions, while causing DNA damage and conformational changes that may lead to cell cycle modulation, apoptosis or carcinogenesis (Wang et al., 2001).

The key role in the carcinogenicity and toxicity of metals such as cadmium (Tchounwou et al., 2001), chromium (Patlolla et al., 2009), and arsenic (Yedjou et al., 2007) are the reactive oxygen species (ROS) production and oxidative stress. These elements rank are great public health significance because of their high degree of toxicity. Even at lower levels of exposure, they are all systemic toxicants that are known to induce multiple organ damage.

1.4   Cr(VI) Treatment Technologies

The conventional processes for removing heavy metals from wastewater include many processes (Barakat 2011). Various methods have been employed to remove Cr(VI) from wastewater like membrane filtration, electrochemical treatment, chemical precipitation, ion exchange and adsorption (Budiman et al. 2016). In chapter 2, the Cr(VI) treatment technologies will be explained briefly including the summarization of advantages and disadvantages of these technologies.

1.5   Photocatalytic Material

The photocatalytic technology has been widely explored and studied since 1970s. In the presence of a solid catalysts which can only be activated under light irradiation, it

is especially beneficial for the transformation of toxic material to less dangerous product. On the surface of photocatalyst, a reaction happens whereby the reactions are initiated by the absorption of illumination with energy equal to or greater than the band gap of the photocatalytic material which should be a semiconductor. There are many semiconductor material that can be selected.

Metal oxide photocatalytic materials which are n-type semiconductors such as TiO_2 and ZnO commonly used. They are ultraviolet light-triggered and have wide band gaps: 3.0 eV for rutile TiO_2, 3.2 eV for anatase TiO_2 and 3.2-3.7 eV for ZnO. Thus, to enhance the photocatalytic response of metal oxide materials under visible light illumination, many efforts have been made. Some of these methods include doping and coupling. On one hand, energy levels within the band gap of the material have been produces by doping but demands complicated procedures for the process of doping. To generate electron-hole pairs, smaller energy gap material is needed (Gorospe & Herrera, 2017).

CuO is a narrow band gapped semiconductor (1.7 eV) and hence the oxide can be activated under sunlight for photocatalytic effect to occur. Band gap is one of the factors that affect absorbed of photocatalytic properties. Smaller band gap semiconductors tend to have better photocatalytic activities as they just need small amount of energy to be absorbed in order to perform its photocatalyst properties. The position of the conduction band and valance band of a semiconductor is also important. For CuO, the position of the conduction band is 0.95 vs SHE. The reduction pontential of Cr(VI) to Cr(III) is +1.33V. Therefore, reduction of Cr(VI) can occur on CuO by photogenerated electrons transfer from CuO conduction band.

CuO is however intrinsically a *p*-type semiconductor. Therefore, the process of extracting electrons form this oxide may be a bit more difficult. Nevertheless, in recent

year, CuO had been used as adsorbent and photocatalytic to reduce Cr(VI) (Gorospe & Herrera, 2017).

1.6   Nanostructure Materials

Nanotechnology is a subdivision under technology that involves the use of nanostructured materials. Nanostructured materials also known as nanomaterials are low-dimensional materials made up of building units in a submicron or nanoscale size at least in one direction plane and showcase size effects. Great control of nanometer scale structure properties can lead to development of new field to be evolved in new devices and technologies. The synthesis of nanomaterials must be closely guarded to control the results in nanomaterials sizes, shape and structure (Tiwari et al., 2012). Nanomaterials can be classified into four categories according to the number of dimensions which are not restricted to the nanoscale range: zero-dimensional (0-D), one-dimensional (1-D), two-dimensional (2-D) and three-dimensional (3-D).

Nanowires are one of one-dimensional nanomaterials example with the diameter of nanometer range (10nm). The nanowires made up of highly ordered wires in nanoscale grown on a suitable substrate. Several methods have been developed to form nanowires with controlled growth parameters to synthesize desired results on size, composition and growth distribution.

1.7   Problem Statement

Heavy metal elements, such as chromium always cause environmental problems during industrial procedures. Chromium enters various environmental matrices (air, water, and soil) from a wide variety of natural and anthropogenic sources with the largest

release coming from industrial establishments. Industries with the largest contribution to chromium release include metal processing, colour production, tannery facilities, chromate production, stainless steel welding, ferrochrome and chrome pigment production. The increase in the environmental concentrations of chromium has been linked to air and wastewater release of chromium, mainly from metallurgical, refractory, and chemical industries. Chromium released into the environment from anthropogenic activity occurs mainly in the hexavalent form Cr(VI). Hexavalent chromium, Cr(VI) is a toxic industrial pollutant that is classified as human carcinogen by several regulatory and non-regulatory agencies. Cr(VI) must therefore be removed from wastewater. Among various methods of removal, a sensitive technique is required.

In this project, photocatalysis process was done in an attempt to reduce Cr(VI) to Cr(III) under sunlight. To date TiO_2 is the most used photocatalysts, but it has wide band gaps thus cannot be activated under sunlight to trigger its photocatalytic activity (Lee and Park, 2013). In this work, CuO nanowires were used as the photocatalysts for photoreduction process of Cr(VI). CuO is a narrow band gap semiconductor and hence can be activated under sunlight and nanowires have high surface to volume ratio can enhance photocatalytic process.

There are many electronic waste with Cu coil being one of them. Copper coils were collected from electronic waste and washed before being subjected to thermal oxidation process. Oxidation process despite appears to be rather straight forward can result in a formation of compact oxide as oppose to nanowires. In here, the conditions to produce only CuO nanowires were identified. Even though CuO nanowires can be produced rather easily, not a lot has been published on the applications on CuO. For this, the use of nanostructured copper oxide is beneficial for wastewater treatment due to their availability, ease of separation, low cost, low toxicity and enhanced stability.

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1.8   Research Objectives

This project focused on fabrication of copper oxides nanowires by thermal oxidation method by control a few parameters such as oxidation time and oxidation temperature. The following are specific objectives of this project:

i.   To synthesize copper oxide with nanowires structures by thermal oxidation of copper coil from electronic waste.

ii.   To investigate thermal oxidation conditions for CuO nanowires formation.

iii.   To assess on the capability of CuO nanowires as photocatalysts under sunlight to reduce Cr(VI) to Cr(III).

1.9   Scope of Work

The research was focused on the synthesizing CuO nanowires by thermal oxidation method. In this study, different parameters for nanowires formation on CuO were investigated, which are the effect of temperature, time growth of nanowires and the present of additive on copper wire surface. Recycle copper wires in electronic device was used in this research to reduce the cost. Microstructure and morphology characterization of nanostructure of copper oxide was analysed using the Field Emission Scanning Electron Microscopy (FESEM) and High Resolution Transmission Electron Microscopy (HRTEM). X-Ray Diffraction (XRD) was used for composition and phase of CuO analysis. The photocatalyst test done by using CuO nanowires undergo photoreduction under sunlight for certain period of time while Ultraviolet-Visible (UV-Vis) Spectrometer was used for Cr(VI) reduction purposes.

CHAPTER 2

LITERATURE REVIEW

2.1   Introduction

This chapter provides overview of water pollution effected by textile industry in Malaysia and focuses on the problems of chromium as heavy metal ion pollutant. Its impact to environment and the recent developments of wastewater treatment techniques available in the market. Next, this chapter also discussed the formation of copper oxide by thermal oxidation and its photocatalytic activities for the removal of hexavalent chromium.

2.2   Textile Industry in Malaysia

In Malaysia, man-made textile fibre is a very popular textile industry. Textile are among the basic need of human being. Textile industries therefore have great economic significance by virtue of their contribution to human and employment generation but they leave on of the largest water footprints on the earth. Textile industries are using large amount of water daily and using more than 8000 chemicals in order to complete the processing involved in textiles manufacturing (Bhatt & Rani, 2013).

Average sized textiles mills having a production about 8000 kg per day consume at least 1.6 million litters of water. Mills discharge millions of gallons of waste which contain hazardous toxic, colours, organic chemical form finishing process. This waste water flowed through drains and pipe line will be corroded and may lead to leakage due to the presence of hazardous chemical substance in water (Bhatt & Rani, 2013).

Point and non-point sources are mainly caused by water pollution in Malaysia. Other than textile industries waste, major point source includes sewage treatment plants, manufacturing, agro based industries and animal farm. Next, the non-point sources are diffused sources such as agricultural and surface runoff (Pang & Abdullah, 2013).

2.3   Nanomaterial

Nanoscience and nanotechnology involves of synthesis, characterization, exploration, and exploitation of small-sized structures or nanomaterials. Nanomaterials can be classified as (a) individual nanostructures e.g. quantum dots, clusters, nanowires, nanocrystals, and nanotubes, and (b) collections of nanostructures such as arrays, assemblies, and super-lattices of the individual nanostructures. The physical and chemical properties of nanomaterials can vary significantly from those of bulk materials of the same composition. In fact, by suitable control of the size, one can alter the properties of nanomaterials remarkably and make possible new devices and technologies (Gogotsi, 2006).

Nanomaterials can be classified into four categories according to the number of dimensions which are not restricted to the nanoscale range: zero-dimensional (0-D), one-dimensional (1-D), two-dimensional (2-D) and three-dimensional (3-D). Typically, the dimension of nanomaterials ranges from subnanometer to several hundred nanometers. These types of materials have different properties compared to conventional materials whereby their thermal, mechanical, electronic, and biological properties differ and not found in conventional materials (Tielas et al, 2014).
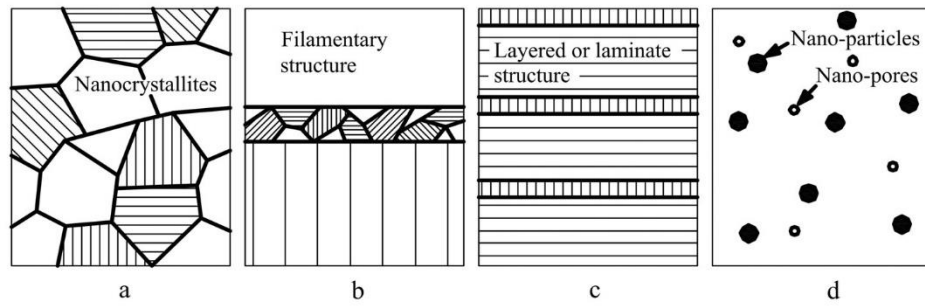
Figure 2.1: Classification of nanomaterials: (a) three-dimensional (3D) structures, (b) two-dimensional (2D) structure, (c) one-dimensional (1D) structure and (d) zero-dimensional structures (Pokropivny et al., 2007).

2.3.1 Nanostructure Oxide Material

Zero-dimensional (0D) nanostructures are materials whose sizes are confined to the nanoscale in all three dimensions (Li & Wu, 2013). There are several terms which are used for zero-dimensional (0D) nanostructures such as nanoparticles, nanospheres and nanocrystals for nanoparticles which are single crystals. Recently, zero-dimensional (0D) nanostructures such as quantum dots (Landry et al., 2014), core–shell quantum dots (Gyorgy et al., 2012) and hollow spheres (Abdollahi et al., 2013) have been synthesized by several research groups.
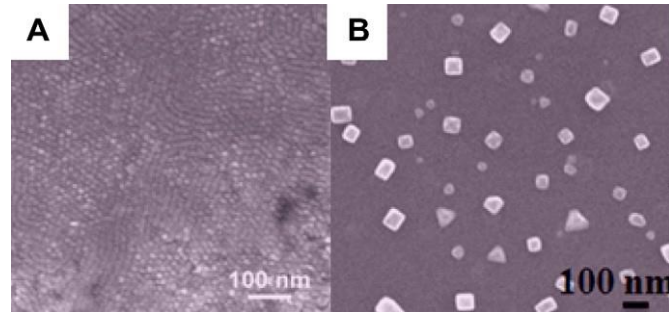
Figure 2.2: Typical scanning electron microscope (SEM) images of zero-dimensional (0D) nanostructures: (A) quantum dots and (B) nanoparticles arrays (Tiwari et al., 2012).

One-dimensional (1D) nanostructures have demonstrated many novel properties due to their high aspect ratios, large specific surface areas and structural confinement on the circumference. Nanowires, nanotubes and nanorods are among the terms used for one-dimensional (1D) nanostructures. Since its discovery, one-dimensional (1D) nanostructures have made profound in the field of nanoelectronic and devices as well as nanocomposites.
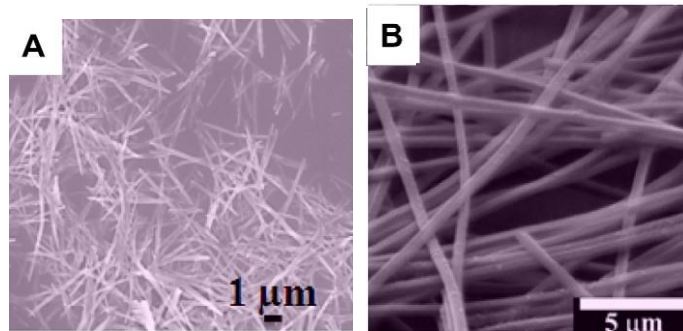
Figure 2.3: Typical SEM image of different types of one-dimensional (1D) nanostructures: (A) nanowires and (B) nanoribbons (Tiwari et al., 2012).

Two-dimensional (2D) with certain geometries exhibit unique shape-dependent characteristic and subsequent utilizationas building blocks for the key components of nanodevices. In addition, a two-dimensional (2D) are particularly interesting not only for basic understanding of the mechanism of nanostructure growth, but also for investigation and developing novel applications in sensors nanoreactors, photocatalysts, nanocontainers, and templates for 2D structures of other materials. There are a lot of terms that are used for two-dimensional (2D) nanostructures such as nanofilm, nanosheets, nanodisks and nanolayers.
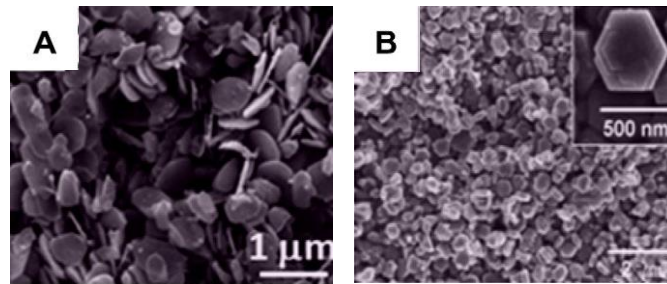
Figure 2.4: SEM image of different kinds of two-dimensional (2D) nanostructures: (A) nanoplates and (B) nanodisks (Tiwari et al., 2012).

Three-dimensional (3D) nanostructures are other types of nanostructures which are attached to a bulk material. The nanostructures attached to the bulk material usually are the form of nanoparticles or nanospheres which are zero-dimensional (0D) nanostructures. Three-dimensional (3D) nanomaterials can also contain dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multinanolayers. Box-shaped graphene (BSG) nanostructure is an example of three-dimensional (3D) nanomaterial (Lapshin, 2016). This nanostructure is a multilayer system of parallel

hollow channels which the quadrangular cross-section extending along the surface. Moreover, the three-dimensional (3D) nanomaterial have recently attracted intensive research interests because the nanostructures have higher surface area and supply enough absorption sites for all involved molecules in a small space. On the other hand, such materials with porosity in three dimensions could lead to a better transport of the molecules (Shen et al., 2008).
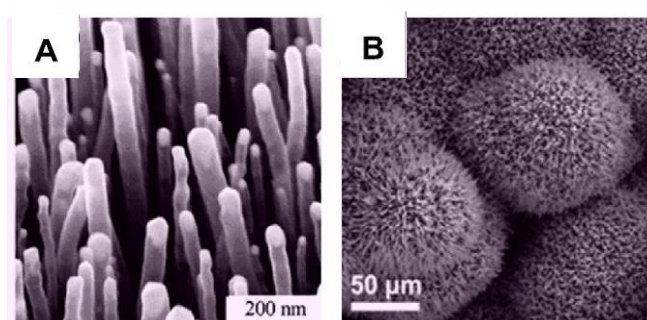
Figure 2.5: SEM image of different kinds of three-dimensional (3D) nanostructures:

(A) nanopillers and (B) nanoflowers (Tiwari et al., 2012).

2.3.2 One Dimensional (1D) Nanowires

Paving the way to deployment into high performance electronics, nanowires can be mass produced by either bottom-up or top-down technologies, while the constituting materials can be doped with impurities to modulate their conductivity. Doped nanowires have been demonstrated at devices with basic functionality or more complex circuits on both rigid and flexible substrates. The mechanical and unique optical properties of nanowires led to extensive use as sensing devices. Electrical currents can be used to promote electrons and stimulate nanowires into the conduction band of

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semiconducting nanowires followed by emission of photons, radiative decay, and multi color-emitting LEDs based on nanowires have been demonstrated (Ranzoni and Cooper, 2017). The investigated being further developed because of their shapes and possibilities to be used directly as they are. Therefore many methods and techniques have been investigate produced quickly, controllable and in large quantities of nanowires.

Compared to other forms of oxide nanostructures, 1D metal oxide nanostructures have several advantages such as superior stability owing to the high crystallinity, possibility of field-effect transistor configuration, very large surface-to-volume ration and possible surface functionalization.

2.4   Formation of Copper Oxide Nanostructure

Cupric oxide or copper oxide (CuO) has received extensive investigations for its prospective applications in many fields. CuO is an antiferromagnetic material with local magnetic moment per unit formula of 0.60 µB and also a monoclinic structure p-type semiconductor with a narrow band gap of 1.4 eV. CuO has been used as a basic material properties with high-T_c superconductors. It also has potential application in solar cells, electronic cathode materials, field emission emitters, gas sensors and catalysts (Liu et al., 2014). In recent years, the nanowires were synthesized by heating copper in various forms at 200-600 °C in air for long period of time. It was found that the growth temperature and time influence the diameter, length and density of nanowires. CuO is very important from the morphology affects the properties of a catalyst and the standpoint of the catalytic usage in general (Prathap et al., 2012). It is therefore significant to synthesize novel sizes and shaped of the CuO nanostructure and to further improve its application as a catalyst.

In 2017, Gorospe & Herrera used CuO for Cr(VI) reduction. Then results shows the visible light photocatalytic activity of CuO powder is lower compared to CuO coupled with ZnO, but higher than that of ZnO powder. It is known that CuO has low photocatalytic activity. However, this may be enhanced by coupling it with copper metal forming a Schottky-type junction/interface. Such interface/junction may work synonymously like that of the p-n heterojunction.

2.4.1 Synthesis Process of Copper Oxide Nanostructure

Copper oxide nanostructure can be grown using many different methods. Nanowires, nanowhisker, nanosheets and nanorods of CuO can be synthesized by using precursors, self-catalytic growth process, sol-vothermal route and hydrothermal decomposition. Recently, various researcher report the growth of CuO by thermal oxidation technique which has the potential to be adapted for large scale quantities and extremely simple. Copper oxide produces using different approaches, materials, concepts and time can have different diameters, lengths, morphologies or even chemical compositions of nanowires. Copper oxide nanowires can be cupric oxides (CuO) or cuprous oxides (Cu_2O) and also can be single-crystalline, bi-crystalline or polycrystalline depend on the methods of choosing the right characteristics (Ji et al., 2010).

In literature, CuO nanostructures can be formed in various shape. One of the methods used in synthesising CuO nanstructures is electrochemical methods. Electrical potential can be used to assist with the redox reactions to speed up the growth process. This method typically used electrochemical cell (two or three electrode) which use a porous template and submerged into a chemical solution as working electrode. To make it conductive, the template can be sputtered on the back side with metal or can be adjusted

on the surface of a copper sheath (Hsieh et al., 2003). The density and diameters of the produced nanowires can be determined by using the density and diameter of the pores in the template. A shaping agent such as polyvinylacetate to have nanowires even thinner than the diameters of the pores (Fillipic and Cvelbar, 2012).

Copper oxide nanowires were grown by Chen et al., (2010) using a three-electrode system for electrochemical corrosion and deposition. The copper tungsten oxide on FTO glass substrates served as the working electrode. A Ag/AgCl electrode with saturated KCl and a Pt sheet with area 10 cm² were used as reference and counter electrodes, respectively. The electrode was submerged into a solution of 3M lactic acid and 0.4M $CuSO_4$ which provided an extra copper source. The deposition bias was fixed as -0.3, -0.4 and -0.5 V vs Ag/AgCl respectively, while high anodic currents at high positive potential were used to monitor the corrosion.

Figure 2.6 shows SEM images obtained from the sample electrochemically deposited at potentials of -0.3, -0.4 and -0.5 V for 2 h. Copper oxide nanowires are clearly seen and appear to emanate from common nucleation sites. It is possible that the sharp tips of the corroded films enhance the electrical field. It also promote the nucleation and growth on neighbouring sites (Chen et al., 2010). The advantage of the electrochemical methods is the ability to control the length and diameter of the nanowires. The phase of copper either copper oxide can be chosen with the right selection of pH value or potential between the working electrode and the reference saturated calomel electrode (SCE) versus a standard hydrogen electrode (SHE). The disadvantage is mostly polycrystallinity of the growth nanowires and slow growth process.
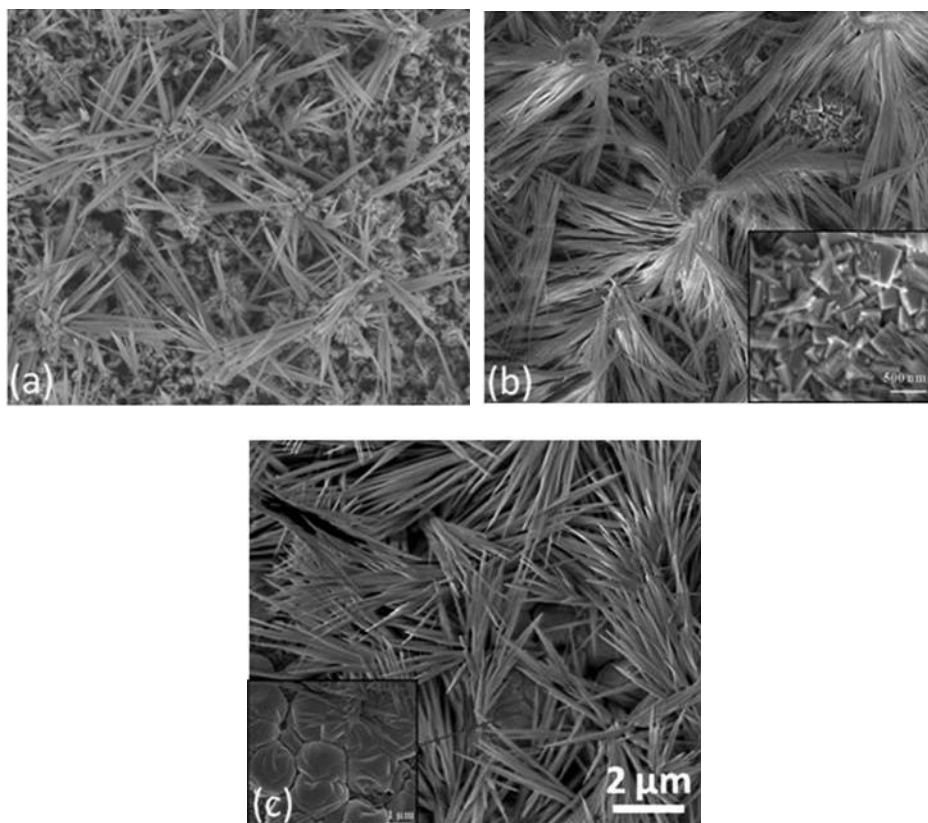
Figure 2.6: SEM images of copper oxide nanowires deposited at potentials of (a) -0.3 V, (b) -0.4 V, and (c) -0.5 V (Chen et al., 2010).

Hydrothermal is another method used in synthesising copper oxide nanowires. Heating a solution was found to be beneficial for formation of precursor nanowires, which it can be annealed in an oxygen atmosphere to form CuO nanowires. Copper hydroxide and copper oxalate are examples of precursor nanowires. Next, heating a solution can enable growth of copper oxides directly form the solution, instead of growing copper containing precipitate nanowires first. This method can growth nanostructures freely in solution and the grown nanostructure can be (i) precursor nanostructure that are later transformed to copper oxide nanostructures or (ii) even already copper oxide nanostructures. However, this methods are complicated procedures

which are need complex chemicals and time demanding as well as additional energy for heating. Unless single-crystalline cuprous oxide nanostructure are desirable, all these requirements make them not very favourable technique for growing copper oxide nanostructure (Fillipic and Cvelbar, 2012).

Bhuvaneshwari and Gopalakrishnan (2016) investigated the influence of mixture of aqueous solution of water (H_2O), copper nitrate semipentahydrate ($CuNO_3.2.5H_2O$, 99% purity), sodium hydroxide (NaOH, 99% purity), and ethylene glycol (EG) ($C_2H_6O_2$, 99% purity) on the growth of CuO nanowires. The samples prepared are named as S1 (water as solvent with copper nitrate semipentahydrate), S2 (water as solvent with sodium hydroxide), S3 (10 ml EG with 65 ml water) and S3 (20ml EG with 55 ml water).

Figure 2.7 shows the FESEM micrographs of the mixture of the (a) S1 at 100°C, (b) S2 at 200 °C, (c) S3 at 100 °C and (d) S4 at 100 °C samples. The sample S1 and S2 was maintained in furnace for 12 h while sample S3 and S4 for 6 h. Each snowflake-like structure of S1 are composed of orderly stacked nanosheets with average width while S2 sample can be seen possess a flower-like shape. This flower-like morphology of S2 consists well-oriented petals which are fused at the bottom and spreads towards the top with sharp edges in a trumpet-like pattern. The size of petals increases outward. However, the petals towards inner side of the flower become smaller. S3 shows the hollow sphere-like superstructures and the sphere-like 3D structure consists of voids core surrounded by as assembly of vertically aligned rods. Urchin-like superstructures can been seen at S4 sample. This urchin-like structure are well aligned bundles of several flower-like particles in the inset reveals when closed examination has be done.
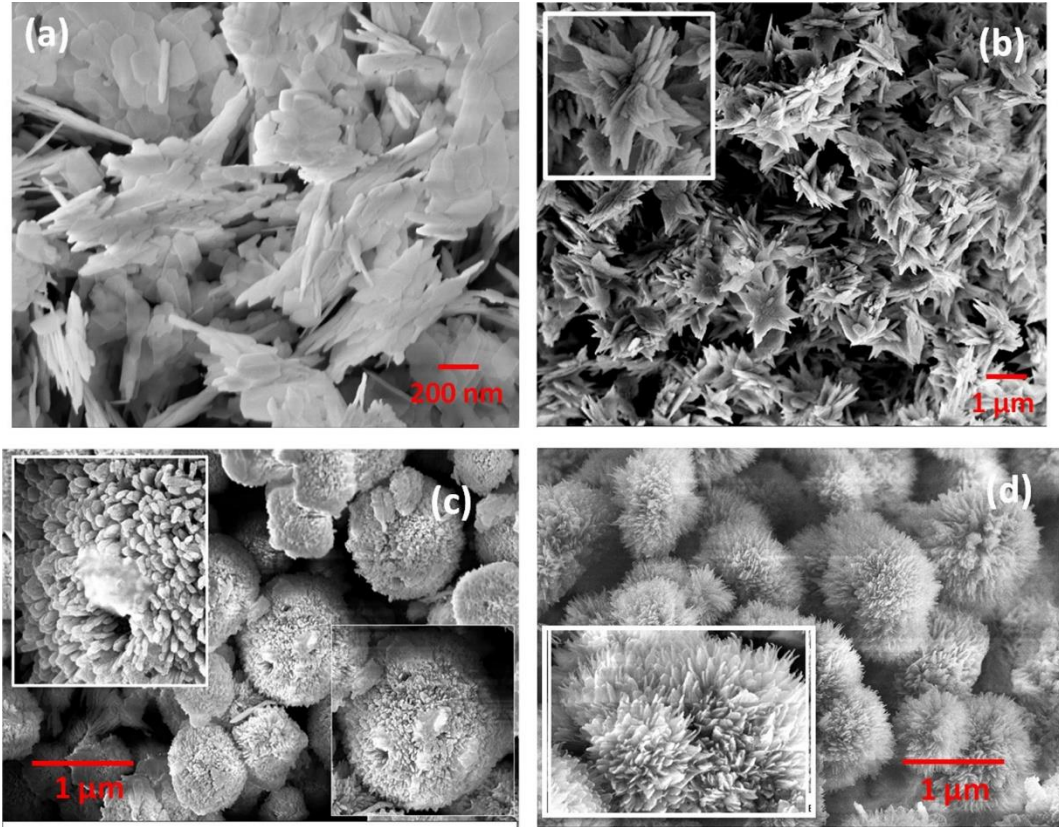
Figure 2.7: FESEM micrographs of CuO nanostructure for (a) S1, (b) S2, (c) S3 and (d)

S4 samples. Magnified image of a single particle is shown in respective insets

(Bhuvaneshwari and Gopalakrishnan, 2016).

2.4.2   Thermal Oxidation of Copper

Table 2.1 shows the literature surveys on the fabrication of CuO nanowires by

thermal oxidation. Thermal oxidation is usually performed by heating a bulk material

like a copper foil, thin film or nanoparticle to a high temperature (typically between 400

and 600 °C) in an oxygen rich temperature. Normally, the treatment of Cu substrate is

cleaned in order to remove its native oxides and other impurities. The condition for

atmosphere can be in dry, wet air or pure oxygen. Nowadays, many researcher used the

mixture of oxygen with nitrogen, hydrogen, argon, etc. The oxidation atmosphere can be selected gas flow through the oxidation system or be static. Moreover, the pressure can be reduce or static in atmospheric pressure.

Table 2.1: Literature surveys on the fabrication of CuO nanowires by thermal oxidation.

No.	Author/ Year	Thermal Oxidation Conditions			Morphology	Application
		Atmosphere	Temperature °C	Time (hour)		
1	Cowley, 1954	Air	600	25	CuO crystals	-
2	Gulbransen & Andrew, 1961	Hg oxgen pressure	250-450	6	CuO whiskers	-
3	Ali & Wood, 1968	Oxygen pressure	200 & 600	3	Cu_2O whiskers, CuO and Cu_2O nanowires	-
4	Appleby & Tylecote, 1970	Oxygen	900	2 days	CuO	-
5	Shigeji Taniguchi, 1985	Oxygen pressure	600-700	Not stated	CuO nanowires	-

6	Kaito et al., 1986	Air	450	10 min	CuO whiskers	-
7	Jiang et al., 2002	Air	400-700	4	CuO nanowires	Catalyst to convert hydro-carbons completely into carbon dioxide and water
8	Xu et al., 2004	Wet air	800	4	CuO nanowires	-
9	Huang et al., 2004	Water vapour	400-750	0.5, 1, 2, 10, 20	CuO nanowires	-
10	Kaur et al., 2006	Air	675	4	CuO nanowires	-
11	Zhuang et al., 2007	Static air with N_2/ O_2 flow	450	4	CuO nanowires	-
12	Kim et., 2008	Dry air	400	12	CuO nanowires	Gas sensors for air quality control in automative cabin
13	Chen et al., 2008	Air	400	8	CuO nanowires	-

14	Hansen et al., 2008	Mixture of pure O_2 or Ar-O_2	500	2.5	Cupric nanowires	-
15	Goncalves et al., 2009	Air	400-600	3	CuO nanowires	-
16	Liang et al., 2010	Air	500	2	Cupric nanowires	-
17	Vila et al., 2010	Air	380	3, 14	CuO nanowires	-
18	Li et al., 2010	Static air	600	6	CuO nanowires	Conductometric chemical sensor
19	Choopun et al., 2010	Air	600	24	CuO nanowires	-
20	Zhong et al., 2010	Ambient air	400-500	24-96	CuO nanowires	Gas sensors
21	Hsueh et al., 2011	Air	450	5	CuO nanowires	Humidity
22	Mumm & Sikorski, 2011	Air	500	2	CuO nanowires	-
23	Zappa et al., 2011	Oxygen and argon	300	15	CuO nanowires	Chemical sensing
24	Yuan et al., 2011	Air	450	2	CuO nanowires	-