

Vertically Aligned CuO Nanometre Scale Wires Synthesized by Thermal Oxidation in Atmospheric Air

Gerrard Eddy Jai Poinern¹, Huu Dang¹, Ravi Krishna Brundavanam¹, Derek Fawcett¹

¹Murdoch Applied Nanotechnology Research Group, Department of Physics, Energy Studies and Nanotechnology School of Engineering and Energy, Murdoch University, Murdoch, Western Australia 6150, Australia, Fax: +61 8 9360-6183

Abstract: In this study vertically aligned copper oxide (CuO) nanometre scale wires were synthesized via two thermal oxidation techniques. The first involved the direct heating of an oxygen free copper substrate on a commercial hotplate at 300 °C, while second technique involved heat treating a similar copper substrate in a tube furnace over the temperature range from 400 °C to 600 °C. Both heat treatments were carried out in atmospheric air without the use of any catalysts. The as-grown CuO wires formed using this facile thermal oxidation were found to have high aspect ratios, mechanically stable and firmly attached to the underlining oxide layer. The size, shape, morphology and composition of the wires were investigated using advanced characterisation techniques such as transmission electron microscopy, field emission scanning electron microscopy and X-ray diffraction.

Keywords: nanometre scale wires, thermal oxidation, advanced characterisation

1. Introduction

In recent years there has been a growing interest in the development of one dimensional, (1-D) nanometre scale materials for potential industrial applications such as catalysts, microelectronics, optical devices, energy conversion and sensors [1, 2]. Current research into nanometre scale materials has generally focused on noble metals. On the other hand, an interesting alternative source material is copper, which is abundant, has good thermal and electrical conductivity and costs far less than materials such as gold, platinum and silver. Based on these advantageous facts, there is a current interest in the developing one - dimensional copper nanometre scale structures such as rods, tubes and wires. In parallel, there has also been a significant interest in synthesizing nanometre scale semiconductor materials. In particular, nanometre scale wires offer some unique and interesting properties, which make them attractive for potential applications in sensors, energy conversion and storage applications [3].

There are two oxide forms of copper, the first is cuprous oxide [copper (I) oxide, Cu₂O] and is red in colour. The second form is cupric oxide [copper (II) oxide, CuO] and is black in colour. Cu₂O with time degrades to CuO in the presence of moist atmospheric air. Both copper oxides are semiconductors with band gaps of 2.137 eV and 1.2 eV for Cu₂O and CuO respectively. The band gap of

both copper oxides makes them ideal candidates for potential applications such as solar cells, sensors and optoelectronic devices [4]. Generally, the properties of materials at the nanometre scale are different from the properties of their respective bulk material. The nanometre scale properties are strongly influenced by their size, shape and morphology, which mean that surface interactions and processes largely prevail. It is expected that the synthesis of copper oxide nanometre scale structures of various shapes and dimensional sizes will create some attractive material properties. Copper oxide structures in the form of nanowires (NW) have unique properties stemming from their large surface areas and large aspect ratios which make them ideal for higher light absorption in solar cells [5] and higher species adsorption in chemical sensors [6,7].

Several techniques for preparing copper oxide NWs have been reported in the literature such as wet chemical methods [8-10], hydrothermal [11-13] and template assisted electrochemical synthesis [14-16]. All these synthesis routes generally involve complex reaction processes, expensive equipment and instrumentations and often require the use of many toxic materials. An attractive alternative technique that does not use complex chemical reaction processes is thermal oxidation. In contrast, the thermal oxidation technique uses heat to accelerate the oxidation process over the surface of bulk copper



Gerrard Eddy Jai Poinern (Correspondence)



g.poinern@murdoch.edu.au



+61 8 9360-2892

materials such as gaskets, thin foils and plates [17]. Prior to thermal treatment the copper substrate is cleaned to remove surface contaminants and native oxides. The thermal treatment used to promote oxide growth is carried out at a much lower temperature than the melting point of bulk copper (1085 °C) and its two oxides Cu₂O (1243 °C) and CuO (1326 °C). Generally, the thermal treatment consists of heating the substrate to temperatures ranging from 400 to 700 °C in oxygen rich atmospheres, which tends to actively promote copper oxide NW growth over the whole substrate surface [18]. By controlling the treatment temperature and the atmospheric environment conditions such as gases, moisture content, pressure and flow rates it is possible to influence the oxidation process and formation mechanisms. In addition, by varying the oxidation period from a few minutes to a day or more it is possible to control the length of the NWs formed [4, 17].

In this study we report the preliminary results an environmentally friendly process involving the thermal oxidation of copper substrates in atmospheric air to produce strongly vertically aligned CuO NWs without the use of catalysts and complex reaction processes. During the first stage of the study, direct heating of a copper substrate was carried out on a commercial hotplate at 300 °C. In the second stage thermal treatment of the copper substrate was carried out in a tube furnace over the temperature range from 400 °C to 600 °C. Both thermal oxidation methods were carried out in atmospheric air without the use of catalysts. The size, shape, morphology and composition of the CuO NWs formed by both thermal treatment methods wires were investigated using advanced characterisation techniques such as transmission electron microscopy, field emission scanning electron microscopy and X-ray diffraction.

2. Materials and Methods

2.1. Materials

All chemicals used in this work were supplied by Chem-Supply (Australia) and all aqueous solutions were made using Milli-Q[®] water (18.3 MΩ cm⁻¹) produced by an ultrapure water system (Barnstead Ultrapure Water System D11931; Thermo Scientific, Dubuque, IA). Substrates used in this study were made from oxygen free high conductivity ultra high vacuum copper gaskets supplied by VG Scienta[®].

2.2. Substrate pre-treatment

Prior to thermal treatment the copper gaskets (substrates) were removed from the manufacturers sealed package and then cleaned using an aqueous solution containing 20% HNO₃ to remove any surface contaminants and any native oxides. The substrates were washed thoroughly using Milli-Q[®] water, dried

and then stored in airtight containers ready for use. Three sets of substrates were prepared: 1) controls; 2) hotplate set and 3) tube furnace set. In each case, every thermal treatment temperature was investigated in triplicate.

2.3. Thermal treatments

Two thermal treatment methods were investigated, the first used a commercial available hotplate model CH2092-001 supplied by Industrial Equipment and Control Pty Ltd (Australia). The second thermal treatment was carried out in an in-house electrical furnace equipped with a horizontal quartz tube that was 3.8 cm in diameter and 90 cm in length [19]. Once the furnace temperature was stabilized at the respective treatment temperature (from 400 °C to 600 °C), the substrates were introduced into the quartz tube and remained there for the specified oxidation period.

2.4. Advanced characterisation techniques

2.4.1. X-ray diffraction (XRD) spectroscopy

X-ray diffraction (XRD) spectroscopy technique was used to examine and to identify the crystalline size and phases present in the pure copper control and the subsequent oxides formed on the copper substrates. Spectroscopy data was recorded at room temperature, using a GBC[®] eMMA X-ray Powder Diffractometer [Cu K_α = 1.5406 Å radiation source] operating at 35 kV and 28 mA. The diffraction patterns were collected over a 2θ range of 20° to 60° with an incremental step size of 0.02° using flat plane geometry with 2 second acquisition time for each scan. The crystalline size of the particles in the powders was calculated using the Debye-Scherrer equation [Equation 1] from the respective spectroscopy patterns.

2.4.2. Scanning electron microscopy (FESEM) and Energy Dispersive Spectroscopy (EDS)

The SEM technique was used to study the size, shape and morphological features of both the synthesized oxide layer and copper NWs formed during the respective thermal treatments. All micrographs were taken using a JCM-6000, NeoScope[™] with an attached energy dispersive X-ray spectroscopy system. Samples were mounted on individual substrate holders using carbon adhesive tape before being sputter coated with a 2 nm layer of gold to prevent charge build up using a Cressington 208HR High Resolution Sputter coater.

2.4.3. Transmission electron microscopy (TEM)

The size and morphology of the CuO NWs was further investigated using TEM. Sample preparation consisted removing the oxide layer from the copper substrate. The flakes were placed into small tubes containing Milli-Q[®] water. The tubes were then sealed and placed into an ultrasonic bath for 30

minutes. The suspensions were then filtered 2 times, each time using a new Whatman 0.22 μm syringe filter. After filtration a single drop from each sample was deposited onto its respective carbon-coated copper TEM grid using a micropipette and then allowed to slowly dry over a 24-hour period. After sample preparation a bright field TEM study was carried out using a Phillips CM-100 electron microscope (Phillips Corporation Eindhoven, The Netherlands) operating at 80kV.

2.4.4. UV-visible spectrum analysis.

Samples of the copper oxides produced during the respective thermal treatments were examined using the UV-visible spectrum technique. Samples for UV-visible analysis were taken from the suspensions previously prepared for TEM as described above. The UV-visible spectra of each of the samples was then measured using a Varian Cary 50 series UV-Visible spectrophotometer version 3, over a spectral range

from 200 to 1100 nm, with a 1 nm resolution over the first hr at room temperature of 24 °C.

3. Results and discussions

3.1. Pre-treatment of substrates

To ensure that the copper substrate surfaces were free from contaminants and native oxides, all the substrates were cleaned using an aqueous solution containing 20% HNO_3 . After cleaning the substrates were thoroughly washed and rinsed using Milli-Q® water. The dried substrates were then used in subsequent thermal treatments. Figure 1 presents a representative EDX analysis used to examine the substrate prior to the thermal treatment. The spectrum clearly shows that there are no surface contaminants or oxides present. The inserted SEM image shown in Figure 1 is a representative micrograph of faceted surface features present on the copper substrate.

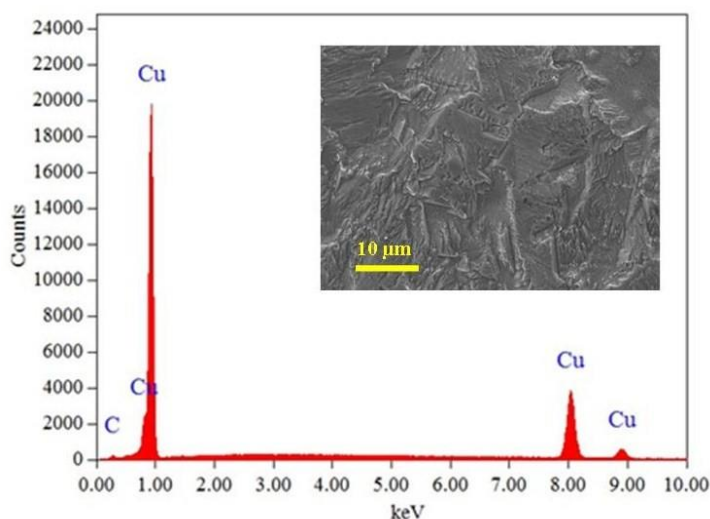


Figure 1 Energy Dispersive Spectroscopy, (EDS) analysis of a representative cleaned copper substrate prior to thermal treatment. Insert presents a typical SEM micrograph of a cleaned surface.

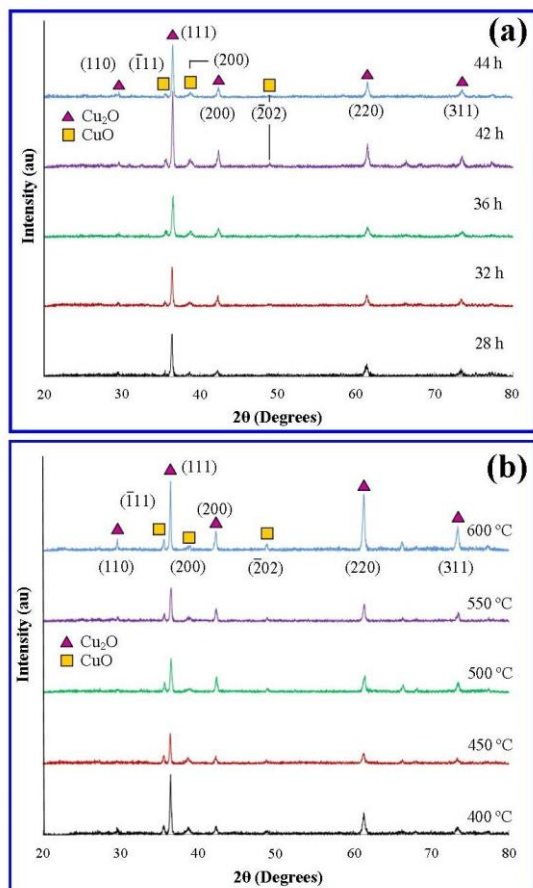
3.2. X-ray diffraction (XRD) spectroscopy

Analysis of the respective XRD patterns was used to identify the copper oxide species present on the surface of the thermally treated substrates. Analysis of the XRD data was also used to estimate the size of crystalline features present in the surface oxide layers that had been formed during the oxidation process. Typical XRD patterns of substrates thermally treated using the hotplate and tube furnace are presented in Figure 2. Inspection of the hotplate substrates [Figure 2 (a)] and tube furnace substrates [Figure (2b)] reveal peaks associated with two forms of copper oxide listed in the ICDD database. The crystalline size, $t_{(hkl)}$, of the oxides formed on each substrate were calculated from the respective XRD patterns using the Debye-Scherrer equation [20]

$$t_{(hkl)} = \frac{0.9\lambda}{B \cos\theta_{(hkl)}} \quad (1)$$

where, λ is the wavelength of the monochromatic X-ray beam, B is the Full Width at Half Maximum (FWHM) of the peak at the maximum intensity, $\theta_{(hkl)}$ is the peak diffraction angle that satisfies Bragg's law for the (h k l) plane and $t_{(hkl)}$ is the crystallite size. Analysis of XRD patterns for both thermal oxidation treatments was carried out and the presence of both copper oxides CuO and Cu_2O were identified. The crystallite sizes calculated for the substrates thermally treated using a commercially available hotplate set at 300 °C ranged from 30.21 nm for 28 h up to 34.26 nm for 44 h. The average was calculated to be 31.72 nm and revealed the variation in crystallite size over the 44 h period was small. A similar calculation was

carried out for the substrates thermally treated in the tube furnace for 2 h at thermal treatment temperatures ranging from 400 to 600 °C. At 400 °C the crystallite size was calculated to be 28.43 nm, while at the highest temperature investigated (600 °C) the crystallite size was calculated to be 37.19 nm. During



the XRD analysis no characteristic peaks of normally associated impurities were detected. This indicated that both copper oxides were obtained under the currently prescribed experimental conditions.

Figure 2 XRD patterns for copper oxides synthesized by thermal oxidation in atmospheric air: (a) hotplate at 300 °C for periods from 28 to 44 h, and (b) tube furnace for 2 h for temperatures ranging from 400 to 600 °C.

3.3. Analysis of SEM and EDS spectroscopy studies. Both thermal oxidation methods used in this study were straightforward routes to grow CuO NWs. During the thermal treatment process, the copper substrate was heated to a specified treatment temperature and as a result both CuO and Cu₂O oxide phases were found on the surface of the substrate as seen in the EDS analysis of the substrates in Figures 3 and 4, and confirm the results of the XRD analysis discussed above. The SEM study identified the growth of CuO NWs from an underlining layer of Cu₂O. Figure 3 presents representative SEM micrographs and their respective EDS analysis for copper substrates thermally treated using the hotplate set to 300 °C for a range of treatment times.

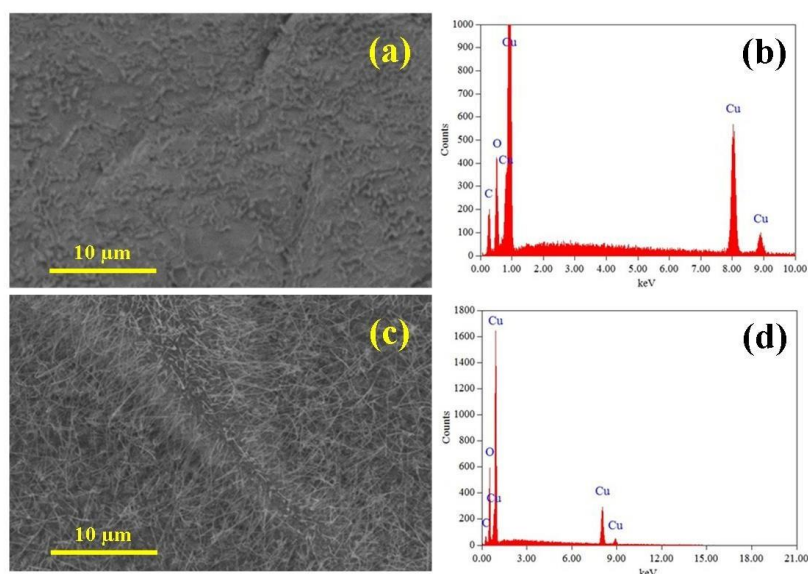


Figure 3 CuO NWs formed during thermal oxidation using a hotplate at 300 °C in atmospheric air: (a) SEM surface micrograph taken after 28 h; (b) EDS analysis after 28 h; (c) SEM surface micrograph taken after 32 h, and (d) EDS analysis after 32 h.

The similar SEM study carried out on copper substrates thermally treated in the tube furnace for 2 h over the temperature range from 400 to 600 °C also identified the presence of CuO NWs growing from an underlining layer of Cu₂O. SEM micrographs of substrates treated using the hotplate method revealed that both NW length and density was influenced by the thermal treatment time. The highest treatment period of 44 h produced significantly less NWs, while the 28 h period was only able to form low

densities of NWs over the substrate surface as seen in Figure 3 (a). The most efficient treatment period was found to be 32 h, which tended to form dense arrays of wires that were found to be perpendicular to the surface. Figure 6 shows a typical TEM micrograph of typical CuO NWs formed during the hotplate treatment. The wires have large aspect ratios with lengths ranging from 1 to 5 μm. The micrograph also reveals that the diameters of the NWs are consistent along their full length.

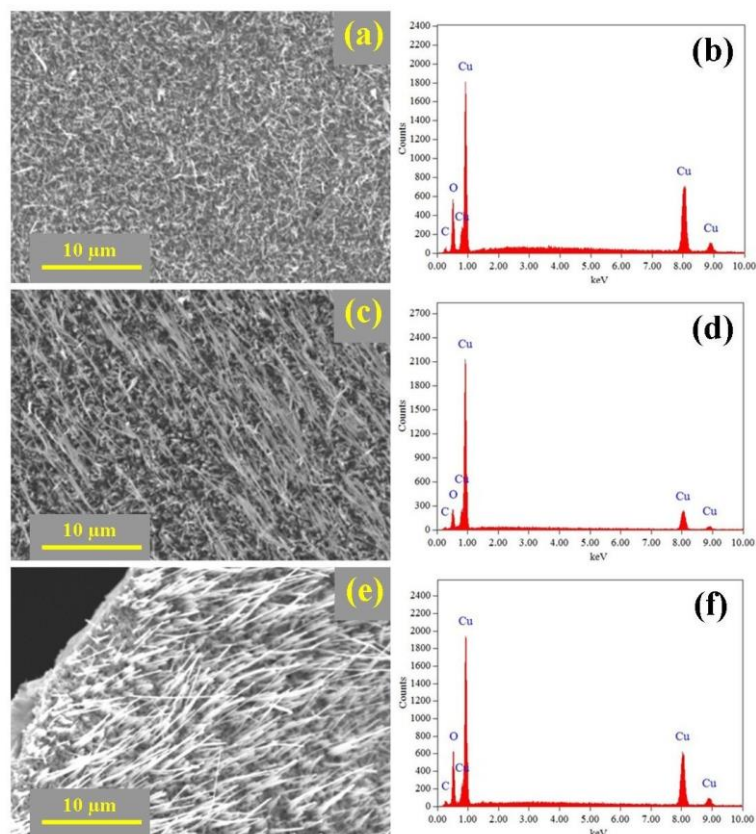


Figure 4 CuO NWs formed during thermal oxidation inside a tube furnace for 2 h at temperatures ranging from 400 to 600 °C with their respective EDS analysis: 400 °C (a) FESEM micrograph and (b) EDS analysis; 500 °C (c) FESEM micrograph and (d) EDS analysis, and 550 °C (e) FESEM micrograph and (f) EDS analysis;

Thermal oxidation in the tube furnace was carried out for 2 h at temperatures ranging from 400 to 600 °C. At 400 °C, NW densities were low and scattered across the substrate, with wires having no apparent alignment and lengths of around 3 μm as seen in Figure 4 (a). The higher temperature of 450 °C produced an increase in regional wire densities and the beginnings of wire alignment. NW lengths at 450 °C had increased in length to a mean value of 5 μm, with the occasional longer wire. At 500 °C, NW

density is high and widespread, with wires ranging in length from 5 to 8 μm in length. Maximum NW growth occurs around just after 500 °C, because at 550 °C a reduction in both wire density and length can be seen and at 600 °C wire density, distribution, length and shape were varied across the surface of the substrate. Figure 5 (a) presents a micrograph image of a typical oxide flake showing the lower density of aligned CuO NWs covering the surface of the flake.

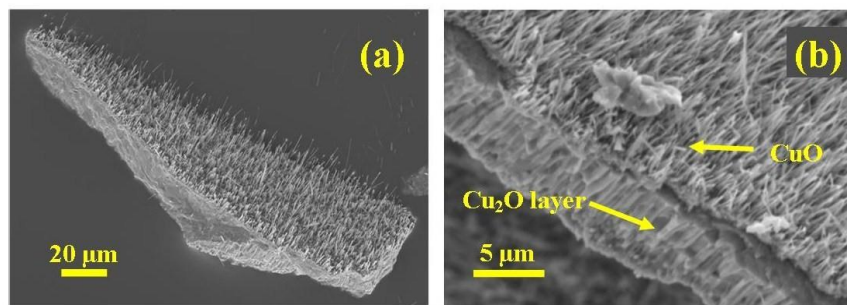


Figure 5 Enlarged SEM micrograph of oxide flake showing the perpendicular alignment of the CuO NWs to the underlining Cu₂O layer. Sample was thermally oxidised in tube furnace for 2 h at 600 °C.

The EDS spectroscopy studies have confirmed that during thermal oxidation of pure copper substrates two types of copper oxides namely, CuO and Cu₂O are formed. The EDS analysis confirms the results of the XRD analysis and clearly demonstrates the presence of two types of oxides. In conjunction with the SEM and TEM results, it is apparent that each oxide is involved in the formation mechanism that produces the copper oxide NWs. This type of growth mechanism is typical for all copper oxide NWs formed by thermal oxidation and has been identified and confirmed by other researchers [21-23]. In the course of the thermal treatment process the substrate and its surface, transfers energy to oxygen molecules in the nearby atmospheric air and in the process causes the formation of individual oxygen atoms. These oxygen atoms combine with surface copper atoms to form a Cu₂O layer. Thus, the diffusion of copper and oxygen atoms through the forming Cu₂O layer is the first oxide to be formed on the copper substrate. Previous studies in the literature suggest that this initial Cu₂O layer is imperative for the growth of subsequent CuO NWs. This mechanism is also supported in this study since there is a clearly visible delineation between the two oxide structures on the substrates as seen in Figure 5 (b). This is an important factor, since no Cu₂O NWs have been synthesized using thermal oxidations techniques [4]. Furthermore, the EDS analysis confirms the presence of CuO NWs within the 300 to 600 °C temperature range at lower and higher temperatures NWs were not seen on the substrates only Cu₂O. At 550 °C NWs wire densities on all substrates are rapidly declining. However, further studies are needed to investigate the complete formation mechanism behind this decline in NW formation so that the process can be accurately modelled.

3.3. Analysis of TEM and UV-visible spectroscopy studies.

A typical TEM micrograph of a cluster of synthesized CuO NWs formed during thermal oxidation on the hotplate at 300 °C is presented in Figure 6. The high aspect ratios can be easily seen, also seen is the fairly consistent NW diameter along the length of the wire.

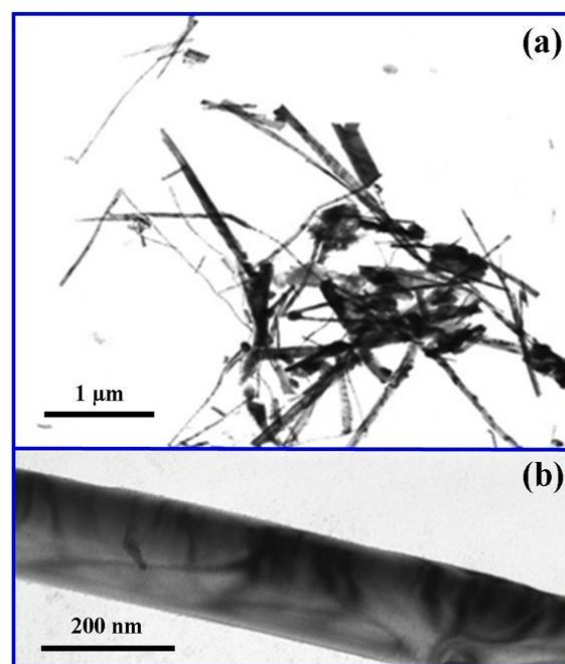


Figure 6 Representative TEM micrographs of CuO NWs produced during thermal oxidation using a hotplate at 300 °C in atmospheric air after 42.5 h.

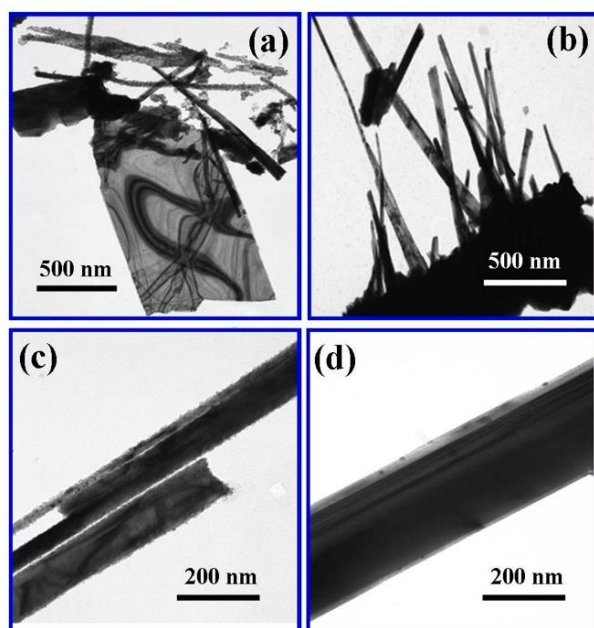


Figure 7 Representative TEM micrographs of CuO NWs produced during thermal oxidation using a tube furnace for 2 h at temperatures of (a) 400 °C, (b) 450 °C, (c) 500 °C and (d) 550 °C.

A similar geometry and morphology can be seen for the NWs synthesized in the tube furnace at various temperatures. Also present along with the NWs are the occasional micrometre scale plate as seen in Figure 7 (a), which was synthesized at 400 °C over a 2 h period. Figure 7 (b) presents a micrograph taken of a small island of CuO NWs. An interesting feature seen is that the NWs tend to gradually taper towards their upper extremities. Typically a NW with a diameter of 120 nm gradually reduces to a diameter around 75 nm at the tip, while other NWs appear to maintain their diameter over the entire length. At 500, 550 and 600 °C the NWs have a solid appearance and have clearly defined boundaries. For example, Figure 7 (c) and 7 (d), which correspond to 500 and 550 °C respectively are clearly rod-like in structure. Also between 550 and 600 °C there was also a shape change in many of the NWs, with the shape more blade-like than circular. This change was not seen in lower furnace temperatures or using the hotplate method. This clearly suggests that blade formation only occurs in the furnace environment at higher temperatures

The preliminary UV-visible spectroscopy studies revealed no significant response, however the authors feel further studies are needed to more thoroughly investigate the UV-visible response of CuO NWs synthesized using the aforementioned thermal oxidation techniques. Both thermal oxidation treatments were able to produce CuO NWs from an underlining Cu₂O layer and confirms the observations reported in the literature. However, further studies are

required to quantify the formation mechanism of the CuO NWs from the oxide layer and the dependence of both temperature and atmospheric gases in forming the NWs. In addition, the dependence of temperature and atmospheric gases on NW diameter and length growth mechanics needs to be fully investigated. Currently, there are several possible growth mechanisms explained in the literature and further studies are needed to identify the growth mechanisms involved in both CuO NW growth and the competing growth of the underlining Cu₂O layer.

4. Conclusion

In summary, we investigated two different thermal oxidation methods to synthesize CuO NWs on a copper substrate. The first involved the direct heating via a hotplate set to 300 °C, while second technique method involved a tube furnace operated over a temperature ranging from 400 °C to 600 °C. Both heat treatments were carried out in atmospheric air without the use of catalysts. Thermal oxidation in the tube furnace revealed that the high temperature range between 500 to 550 °C produced the larger densities of NWs. Above 550 °C the density of NWs steadily decreased. The CuO NWs produced during this study were of fixed diameter (typical around 200 nm) while the length varied between 3 to 15 µm depending on treatment temperature. Blade-like nanometre structures can be of significant benefits in solar cell applications and further studies are needed to investigate the complete growth mechanisms and the interplay between CuO NWs, the underlining Cu₂O oxide layer and the copper substrate.

Acknowledgements

The authors would like to thank Mrs. Mona Shah and Mrs. Sridevi Brundavanam for their assistance in the laboratory and with the SEM micrographs.

Disclosure

The authors report no conflict of interest in this work.

References

1. Shipway AN, Katz E, Willner I. Nanoparticle arrays on surfaces for electronic, optical, and sensor applications. *Chemphyschem* 2000; 1:18-52.
2. De M, Ghosh PS, Rotello VM. Applications of nanoparticles in biology. *Advanced Materials* 2012; 20(22):4225-41.
3. Sunkara M K, Pendyala C, Cummins D, Meduri P, Jasinski J, Kumar V, Russell H B, Clark E L and Kim J H. Inorganic nanowires: a perspective about their role in energy conversion and storage applications. *J. Phys. D: Appl. Phys.* 2011; 44: 174032, 1-9.
4. Filipic G and Cvelbar U. Copper oxide nanowires: a review of growth, *Nanotechnology*, 2012; 23: 1-16. doi:10.1088/0957-4484/23/19/194001.
5. Yin M, Lou Y, Wu C K, Burda C, Koberstein J T, Zhu Y and O'Brien S. Copper oxide nanocrystals. *J. Am. Chem. Soc.* 2005; 127(26): 9506-9511.
6. Zhang J, Liu J, Peng Q, Wang X, Li Y. Nearly monodispersed Cu₂O and CuO nanospheres: preparation and

- applications for sensitive gas sensors. *Chem. Mater.* 2006; 18(4):867-871.
7. Zhang X, Wang G, Liu X, Wu J, Li M, Gu J, Liu H, Fang B. Different CuO nanostructures: synthesis, characterisation, and applications for glucose sensors. *J. Am. Chem. C.* 2008; 112(43):16845-16849.
 8. Wang W Z, Wang G H, Wang X S, Zhan Y J, Liu Y K and Zheng C L. Synthesis and characterisation of Cu₂O nanowires by a novel reduction route. *Adv. Mater.* 2002; 14(1): 67-69.
 9. Wang W, Zhuang Y and Li L, Structure and size effect of CuO nanowires prepared by low temperature solid-phase process. *Mater. Lett.* 2008; 62(10-11): 1724-1726
 10. Ethiraj AS, Kang DJ, Synthesis and characterisation of CuO nanowires by a simple wet chemical method. *Nanoscale Research letters*, 2012; 7:70, 1-5
 11. Li C, Yin Y, Hou H, Fan N, Yuan F, Shi Y and Meng Q, Preparation and characterisation of Cu(OH)₂ and CuO nanowires by the coupling route of microemulsion with homogeneous precipitation. *Solid State Commun.* 2010; 150: 585-589.
 12. Su Y, Shen C, Yang H, Li H and Gao H, Controlled synthesis of highly ordered CuO nanowires arrays by template-based sol-gel route. *Trans. Nonferr. Met. Soc. China*, 2007; 17: 783-786.
 13. Xiong Y, Li Z, Zhang R, Xie Y, Yang J, Wu C. From complex chains to ID metal oxides: A novel strategy to Cu₂O nanowires. *J. Phys. Chem. B*, 2003; 107: 3697-3702.
 14. Shin H S, Song J Y and Yu J, Templated-assisted electrochemical synthesis of cuprous oxide nanowires. *Mater. Lett.* 2009; 63: 397-399.
 15. Hsieh C T, Chen J M, Lin H-H and Shih H C, Synthesis of well ordered CuO nanofibers by self-catalytic growth mechanism. *Appl. Phys. Lett.* 2003; 82(19): 3316-3319.
 16. Daltin A L, Addad A and Chopart J P, Potentiostatic deposition and characterisation of cuprous oxide wires and nanowires. *J. Cryst. Growth*, 2005; 282 414-420.
 17. Hansen B J, Lu G, and .Chen J. Direct Oxidation Growth of CuO Nanowires from Copper-Containing Substrates, *Journal of Nanomaterials*, 2008; Article ID 830474, 1- 7.
 18. Chen JT, Zhang F, Wang J, Zhang GA, Miaoa BB, Fan XY, Yana D and Yan PX. CuO nanowires synthesized by thermal oxidation route, *Journal of Alloys and Compound*, 2008; 454: 268-273. doi:10.1016/j.jallcom.2006.12.032.
 19. Poinern GEJ, Brundavanam S, Shah M, Laava I and Fawcett D. Photo-thermal response of CVD synthesised carbon (nano) spheres/aqueous nanofluids for potential application in direct solar absorption collectors: a preliminary investigation. *Nanotechnology, Science and Applications*, 2012; 5 (1): 49-59.
 20. Barrett CS, Cohen JB, Faber J, Jenkins JR, Leyden DE, Russ JC, Predecki PK, *Advances in X-ray analysis*, Vol. 29, New York: Plenum Press, 1986.
 21. Jiang X, Herricks T and Xia Y, CuO nanowires can be synthesized by heating copper substrates in air. *Nano Lett.* 2002; 2(12): 1333-1338.
 22. Liang J, Kishi N, Soga T and Jimbo T, The Synthesis of Highly Aligned Cupric Oxide Nanowires by Heating Copper Foil, *Journals of Nanomaterials*, 2011; Article ID 268508:1-8.
 23. Liang JB, Kishi N, Soga T, and Jimbo T, Cross-sectional characterisation of cupric oxide nanowires grown by thermal oxidation of copper coils. *Appl. Surf. Sci.*, 2010; 257: 62-66.