

CHAPTER 2

Preparation and Characterization of Copper Oxide Nanostructures

This chapter presents two morphologies of copper oxide nanostructures consisting of the mixture of CuO and Cu₂O. The copper oxide nanostructures were synthesized by microwave-assisted thermal oxidation as shown in Figure 2.1. There were copper oxide nanofibers and copper oxide nanoparticles

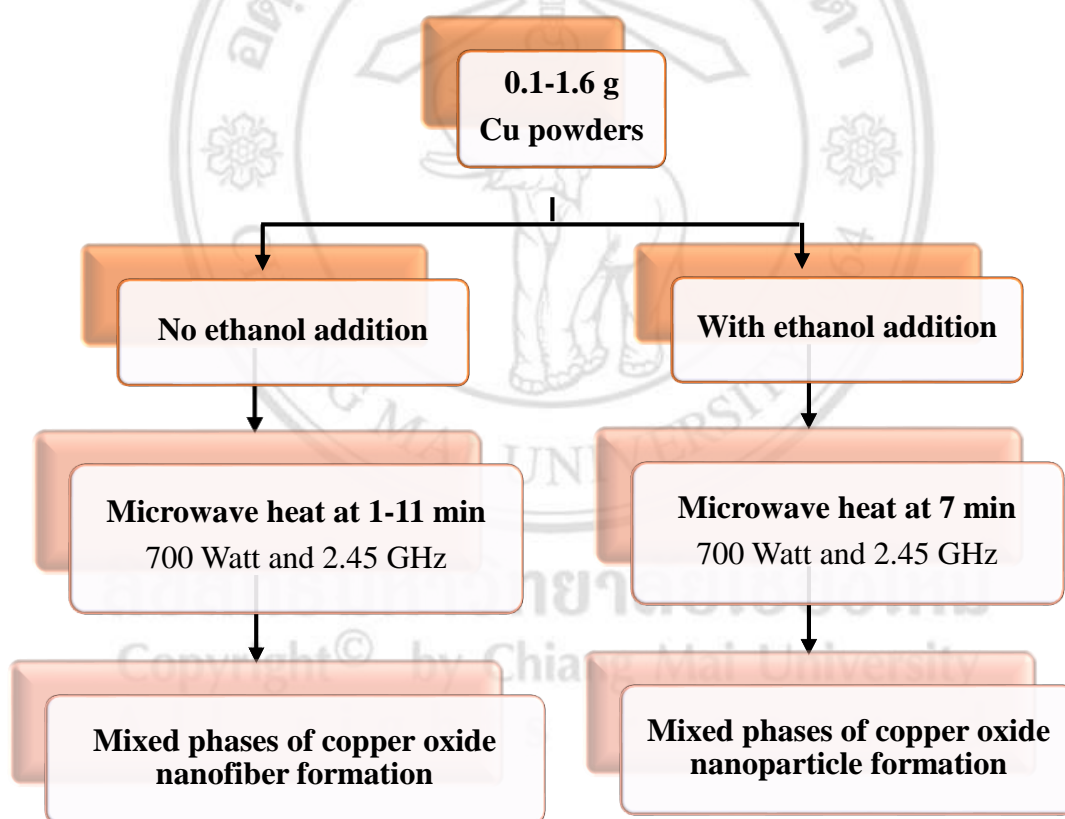


Figure 2.1 The flow chart of copper oxide nanostructures synthesized by microwave-assisted thermal oxidation.

The Cu powders were heated by a microwave at a few minutes. Then, they were oxidized to form mixed phases of copper oxide nanofibers. While, Cu powders with ethanol addition were oxidized to form mixed phases of copper oxide nanoparticles.

Both of nanostructures were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman dynamic light scattering, X-ray diffraction analysis (XRD) and energy dispersive spectroscopy (EDS).

2.1 Synthesis of Copper Oxide Nanofibers

Pure copper powders (99.5%, MW: 63.55 g/mol, 40 μm of particle size) were used as a precursor to synthesize of copper oxide nanofibers. The results showed the mixture of both CuO and Cu₂O. The different masses of the copper powders were varied at 0.4, 0.8, 1.2 and 1.6 g. A quartz rod diameter and length about 2.8 and 10 cm, respectively, was used to be a substrate. The pure copper powders were placed in a quartz rod and heated under microwave radiation (power of 700 Watt and frequency of 2.45 GHz) at room temperature in a normal atmosphere for 7 min. Then, the effective mass yield of the copper oxide nanofibers was measured and the results were plotted as shown in Figure 2.2 (a). The graph showed mass yield of copper oxide nanofibers prepared by different masses of pure copper powders. At 0.5 g of copper powders, only 0.3 mg of copper oxide nanofibers was formed. Then, using 1 g of copper powders can provide a rapidly increase of the nanofiber mass reaching a peak at 2.4 mg. However, it continued to drop to about 1.1 mg, and 0.9 mg after using copper powders at 1.5 g and 2.0 g, respectively. It clearly exhibited that the optimum mass of precursor at 7 min was 1 g. Figure 2.2 (b), showed the nanofiber formation in a quartz rod at the optimum mass, which can be observed obviously with the naked eye.

Next, the copper oxide nanofibers obtained from 1 g of copper powders were synthesized by using the optimum mass of precursor at the different times of heating. Figure 2.3 showed the percentage of mass yield of copper oxide nanofibers prepared at various time up to 11 min, under microwave radiation. As seen in the graph, the copper oxide nanofibers were observed first after 3 min heating and the percentage of mass yield was only 0.03 before increasing to around 0.05 at 4 min. Next, the percentage of mass yield sharply went up from 0.06 at 5 min to 0.22 at 6 min. Finally, the percentage reached a peak at 0.24 at 7 min. Then, there was a period of stability in the percentage of mass yield.

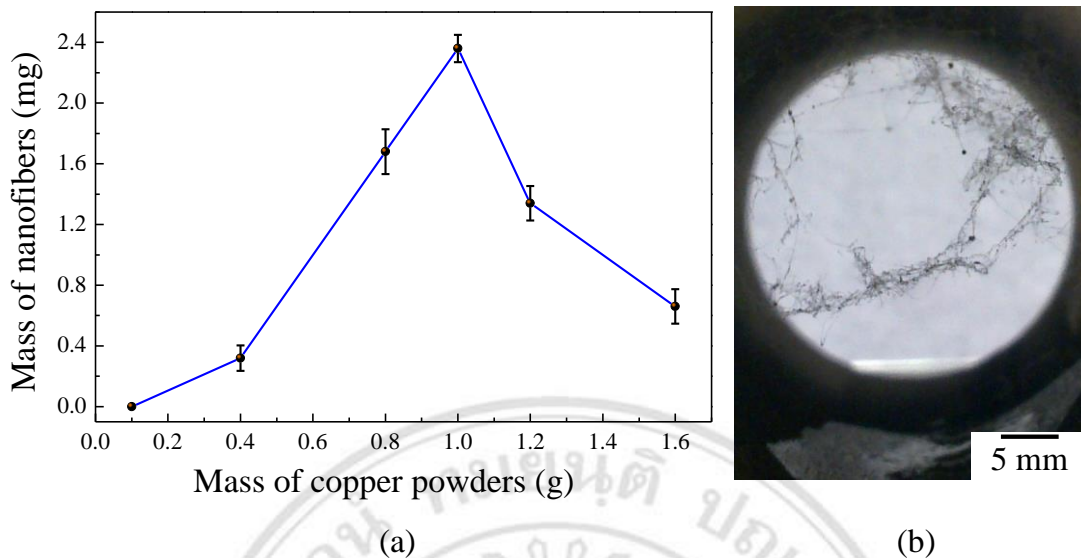


Figure 2.2 (a) The effective mass yield of the copper oxide nanofibers prepared by a different masses of pure copper powders under microwave radiation, at 7 min and (b) copper oxide nanofibers in a quartz rod.

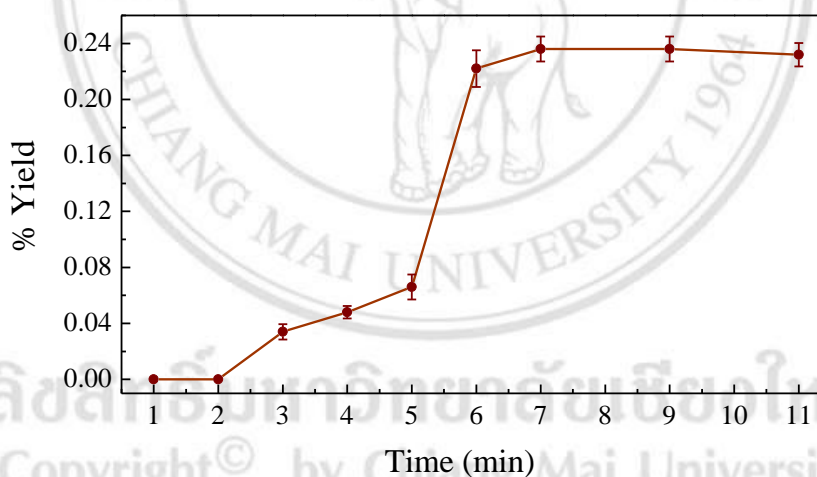


Figure 2.3 The percentage of copper oxide nanofibers obtained from reaction by using 1 g of copper powders at the different heating times.

2.2 Synthesis of Copper Oxide Nanoparticles

Likewise, copper oxide nanoparticles were synthesized by microwave technique. A varying quantity of ethanol, 0-0.4 mL, was added into 1 g of Cu powders. Then, the sample was heated by a microwave at the same power and frequency as the synthesis of copper oxide nanofibers. Finally, the copper oxide nanoparticles were observed in the quartz rod after 2 min heating and gave optimum value of 0.24 at 7 min.

2.3 Characterization of Copper Oxide Nanostructures

2.3.1 Characterization of Copper Oxide Nanofibers

1) SEM images of copper oxide nanofibers

Figure 2.4 (a) showed the images of CuO-Cu₂O nanofibers prepared from 1 g of pure copper powders under microwave radiation at 7 min. It observed that the nanofibers exhibited smooth surface with circular cross-sectional area. The nanofiber diameters were in the range of 500-5,500 nm and their lengths were about 2.5 cm as shown in Figure 2.4 (b). However, time interaction between pure copper powders and electromagnetic wave effected on the diameter ranges of CuO-Cu₂O nanofibers since the nanofibers showed clearly different diameters at different heating times, 4-11 min, as shown in Table 2.1 and Figure 2.5.

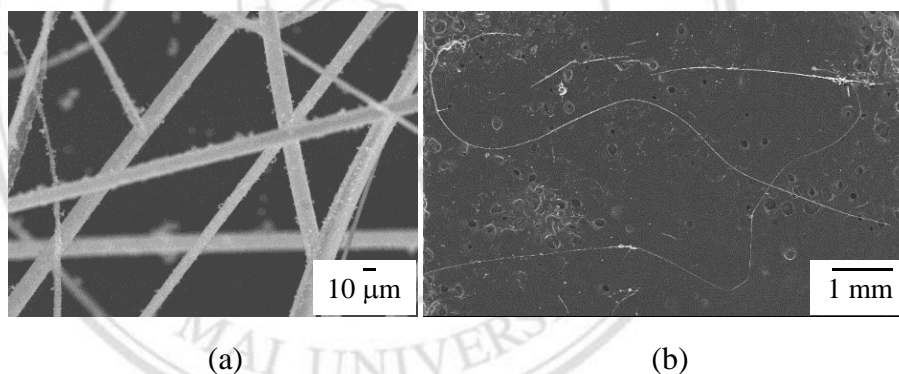
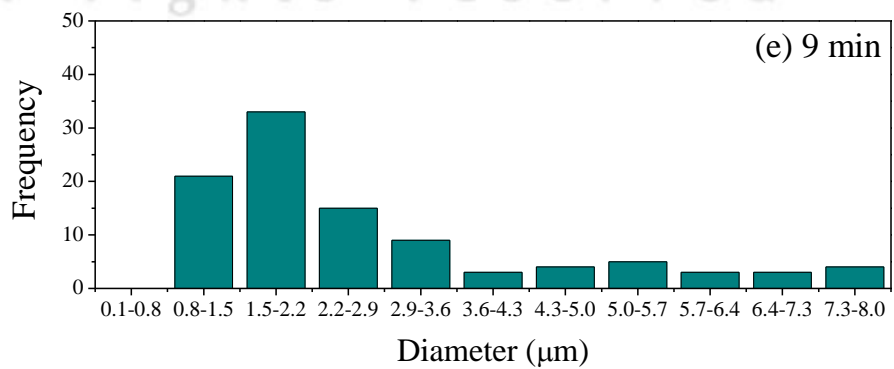
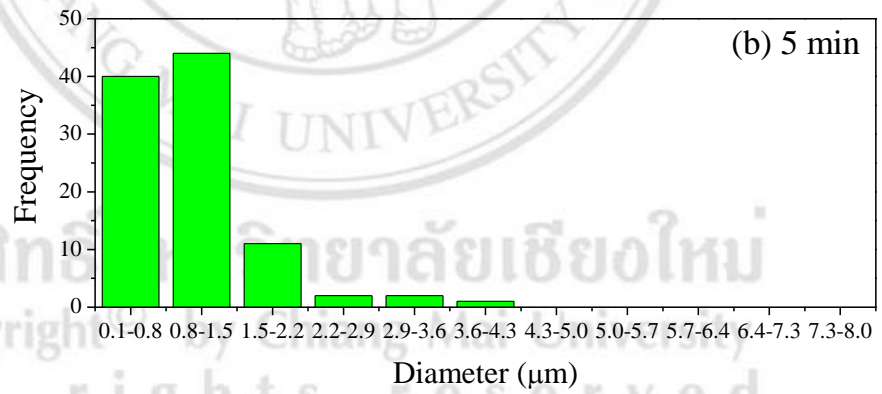
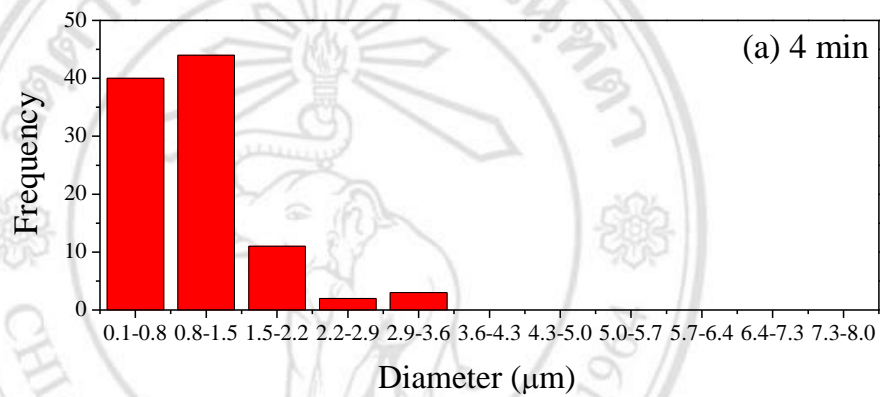


Figure 2.4 SEM image of (a) CuO-Cu₂O nanofibers and (b) average lengths of CuO-Cu₂O nanofibers prepared from 1 g of copper powders under microwave radiation.

According to the SEM images, size distribution of the copper oxide nanofibers at the different heating times was measured by program of Image J. The results were shown in Table 2.1 and plotted as shown in Figure 2.5. Moreover, the SEM images showed diameter ranges of copper oxide nanofibers at a various heating time, 4-11 min, as shown in Figure 2.6.

Table 2.1 Diameter ranges of copper oxide nanofibers at various heating times.

Time (min)	Diameters (μm)
4	0.53-3.60
5	0.56-4.29
6	0.29-6.02
7	0.51-5.50
9	1.09-7.43
11	1.11-5.68



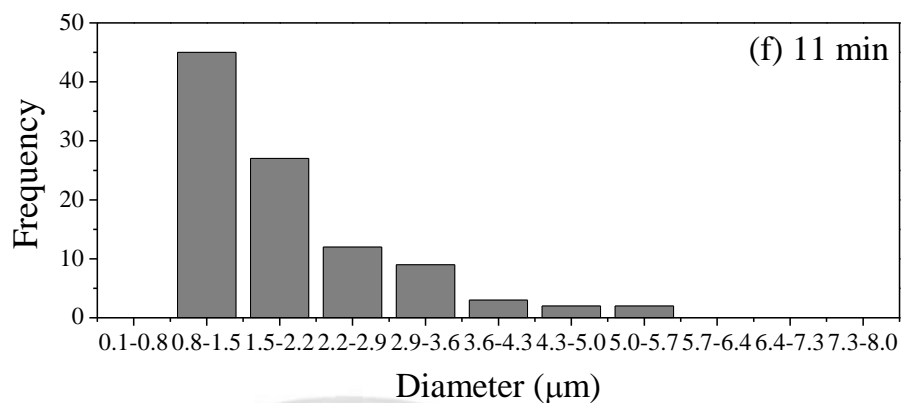


Figure 2.5 Size distribution of the CuO-Cu₂O nanofibers at the different heating times.

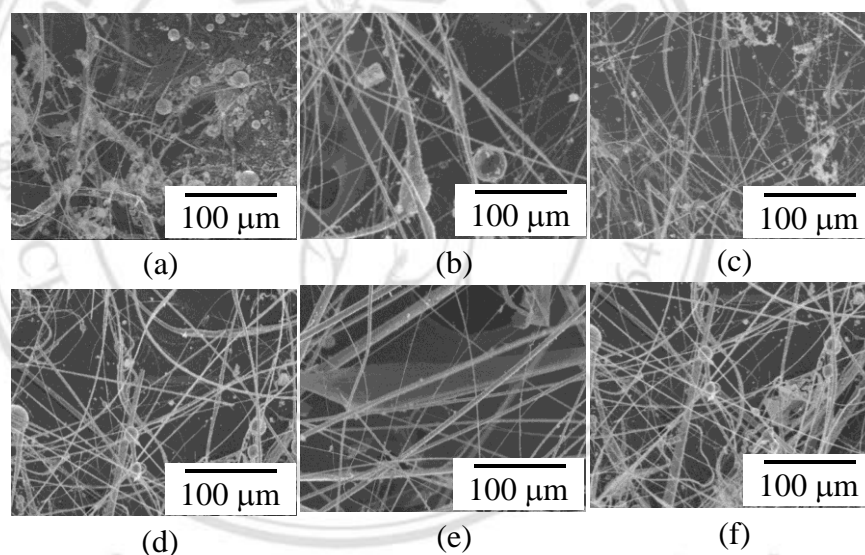


Figure 2.6 SEM image of CuO-Cu₂O nanofibers prepared at (a) 4 min, (b) 5 min (c) 6 min, (d) 7 min, (e) 9 min, and (f) 11 min under microwave radiation.

2) TEM images of copper oxide nanofibers

Some copper oxide nanofibers were stuck by white spots. The TEM images showed white spots on a nanofiber surface with diffraction rings as shown in Figure 2.7. Moreover, the diffraction rings can be identified to the CuO structure.

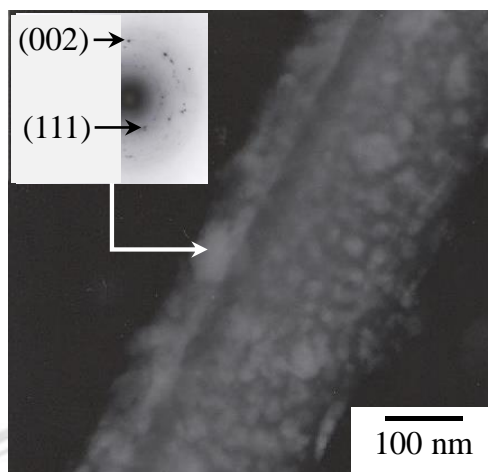


Figure 2.7 TEM images and electron diffraction patterns of CuO spot on a nanofiber.

3) Raman of copper oxide nanofibers

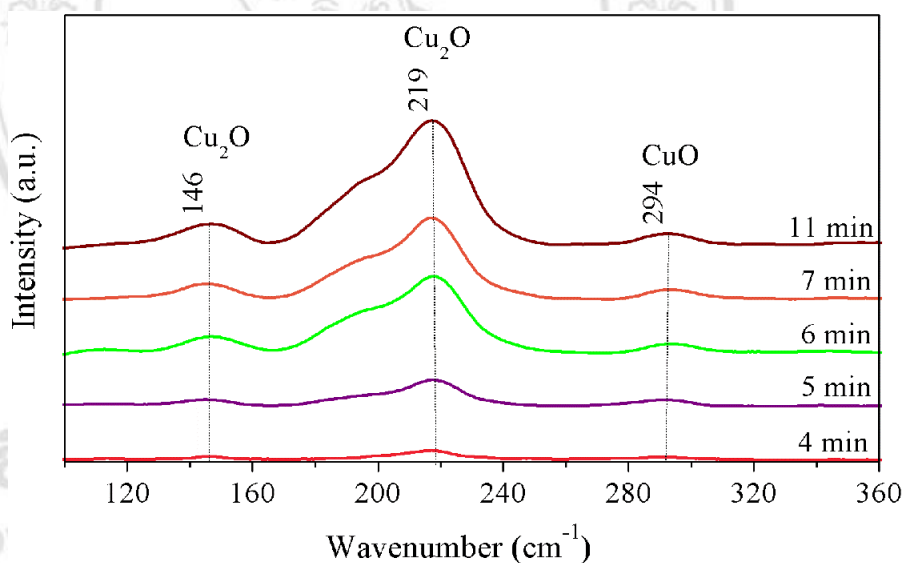


Figure 2.8 Raman spectrum of the CuO-Cu₂O nanofibers synthesized at 4, 5, 6, 7, and 11 min under microwave radiation.

Figure 2.8 showed Raman scattering spectrum of the CuO-Cu₂O nanofibers preparing from 1 g copper powders under microwave radiation at different heating times of 4, 5, 6, 7, and 11 min. It can be seen that the Raman spectrum contained both CuO and Cu₂O peaks. The CuO represented its characteristic peak at 294 cm⁻¹. While, the Cu₂O exhibited its characteristic Raman bands at 146 and 219 cm⁻¹.

Significantly, the CuO and Cu₂O peaks became stronger and sharper after 7 min, which the nanofibers completely formed. Moreover, these peaks were slightly shifted to higher wavenumber. For example, the peak at 218.02 cm⁻¹, at 4 min, shifted to 218.48 and 219 cm⁻¹ at 6 and 11 min, respectively. The higher wavenumber might be caused from their size effects due to the increased crystal size [89, 90].

4) XRD of copper oxide nanofibers

Figure 2.9 showed XRD patterns of the CuO-Cu₂O nanofibers prepared from 1 g copper powders under microwave radiation at different heating times of 4, 5, 6, 7, and 11 min. All of the nanofibers exhibited a very strong diffraction peak around 2θ angle of 36.34, which represented the (111) of the cubic phase Cu₂O. Especially, at 4 min, only the (111) crystallographic plan was clearly observed. While, peak positioned at 35.25° and 38.60° were firstly observed after 5 min heating corresponding to the (002) and (111) crystalline planes of the monoclinic phase CuO. After 6 min, the peaks at 2θ positions, 42.28, 61.27 and 73.49 were observed and ascribed to (200), (220) and (311) planes of the Cu₂O. Importantly, no impurity peak was detected, indicating that the copper oxide nanofibers were composed of pure crystalline CuO and Cu₂O.

5) EDS of Copper Oxide Nanofibers

The EDS can separate the characteristic x-rays of different elements into an energy spectrum and determine the abundance of specific elements. The EDS spectrum result confirmed that the copper oxide nanofibers composed of copper and oxygen as shown in Figure 2.10.

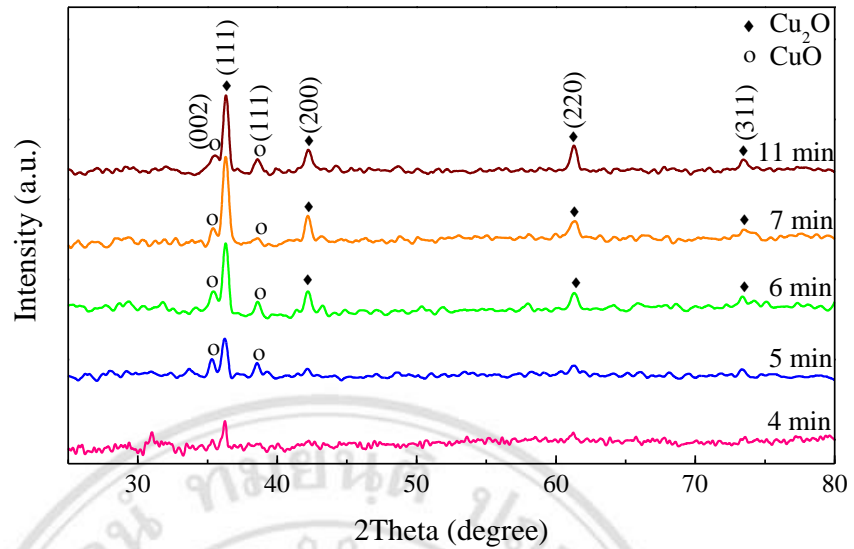


Figure 2.9 XRD patterns of the CuO-Cu₂O nanofibers prepared at 4, 5, 6, 7, and 11 under microwave radiation.

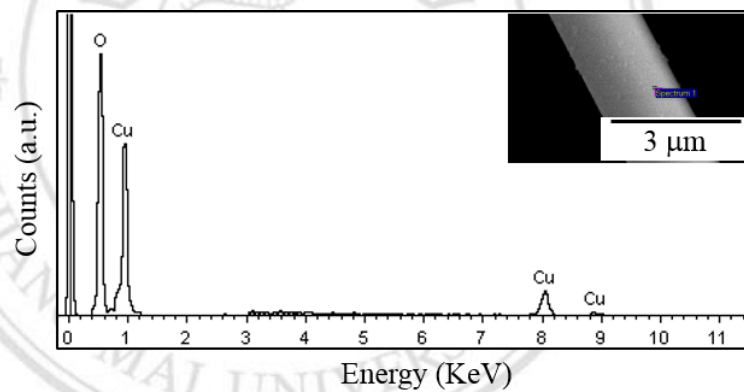


Figure 2.10 EDS spectrum of CuO-Cu₂O nanofibers at 7 min heating.

2.3.2 Characterization of Copper Oxide Nanoparticles

1) SEM of Copper Oxide Nanoparticles

Figure 2.11 showed SEM images of copper oxide nanostructures transforming from Cu powders to distinct morphologies at 7 min by microwave heating at various ethanol quantities. Cu powders without ethanol represented the copper oxides in nanofiber form as shown in Figure 2.11(a). While, Cu powders with 0.2 and 0.3 mL of ethanol caused copper oxide nanoparticles in spherical shape as shown in Figure 2.11(b) and (c). When the ethanol quantity increased to 0.4 mL, the Cu powders became rough sheet form as shown in Figure 2.11(d).

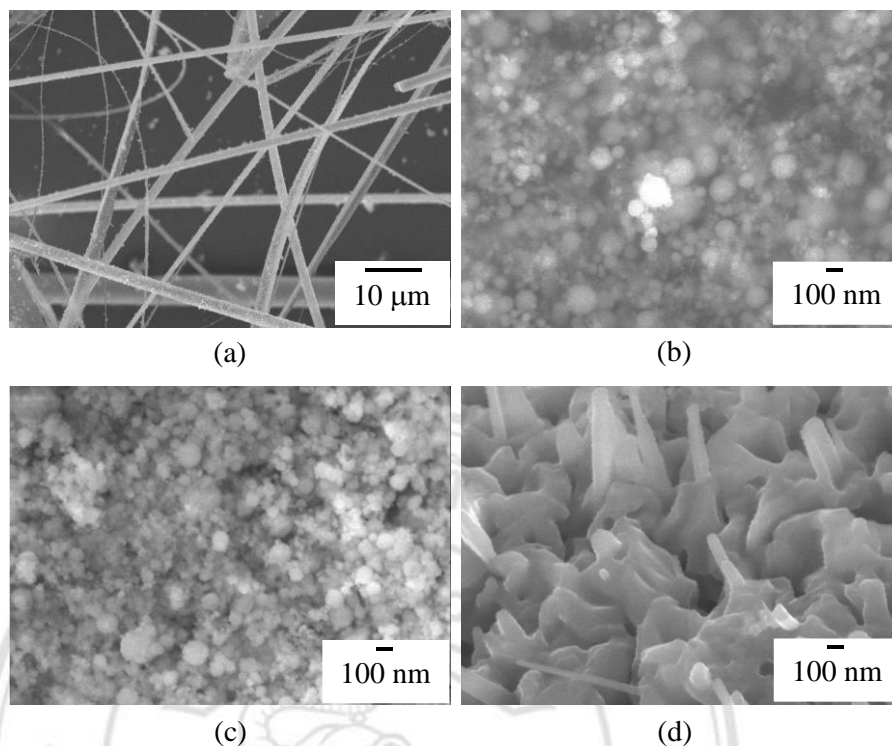
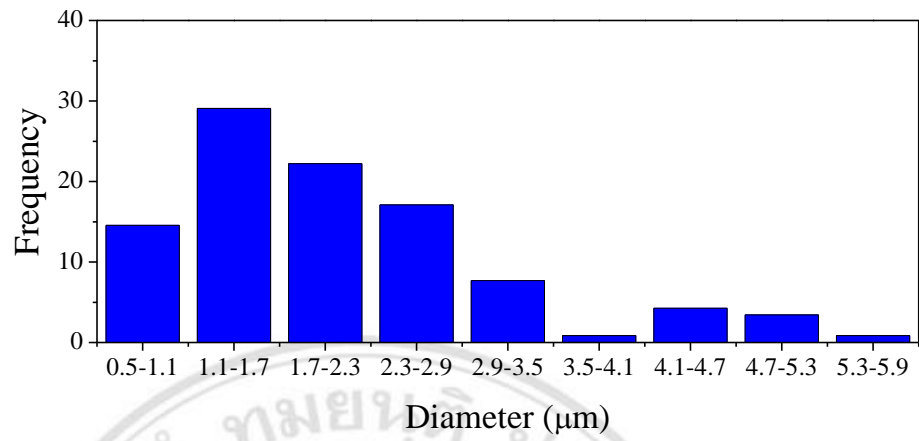
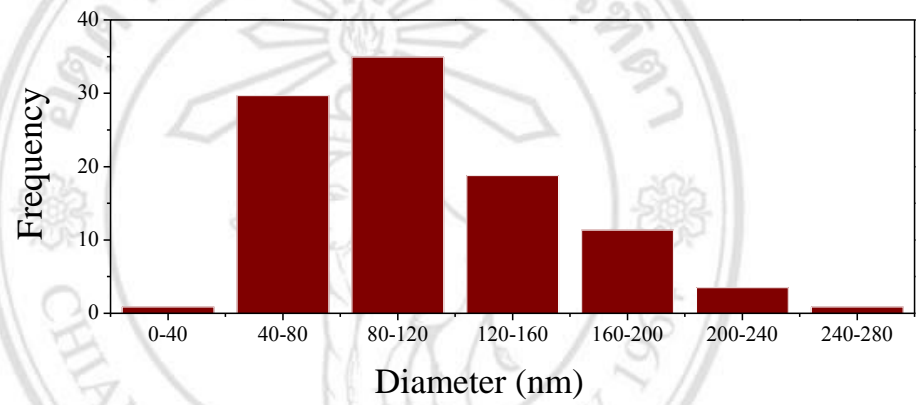


Figure 2.11 The SEM images of the copper oxide nanostructures at 7 min by microwave heating using ethanol additive at (a) 0.0 mL (b) 0.2 mL (c) 0.3 mL and (d) 0.4 mL.

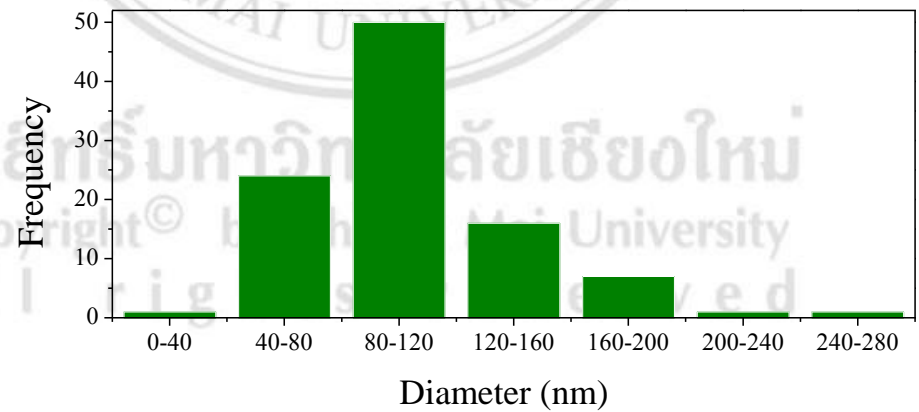
Moreover, the size distribution of nanoparticles was significantly different from nanofibers as shown in Figure 2.12. The diameter of nanofibers were in the range of 500-5,500 nm as shown in Figure 2.12(a). Whereas, Figure 2.12(b) and (c) represented the size distribution of nanoparticles, which were in the range of 80-120 nm. Importantly, nanoparticles had high homogeneous size and shape at optimum quantity of 0.3 mL of ethanol.



(a)



(b)



(c)

Figure 2.12 Size distribution of copper oxide nanostructures prepared against ethanol additive at (a) 0.0 mL (fibers), (b) 0.2 mL (nanoparticles), and (c) 0.3 mL (nanoparticles).

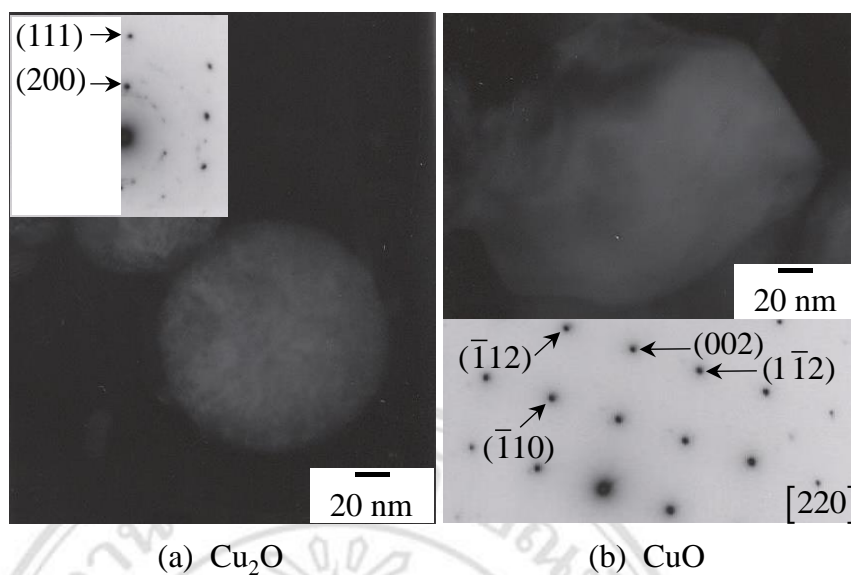


Figure 2.13 TEM images and electron diffraction patterns of (a) Cu_2O and (b) CuO nanoparticles.

2) TEM images of Copper Oxide Nanoparticles

Figure 2.13 showed TEM images and electron diffraction patterns of Cu_2O and CuO nanoparticles synthesized at 7 min under a microwave heating using 1 g Cu powders with optimum quantity of ethanol additive, 0.3 mL. TEM images represented a spherical shape with a smooth surface and diffraction rings, which can be identified as Cu_2O structure as shown in Figure 2.13(a). While, the electron diffraction pattern in Figure 2.13(b) can be indexed to monoclinic crystal structure of CuO and taken at a zone axis of $[220]$ (TEM analysis is shown in APPENDIX A).

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3) Raman of Copper Oxide Nanoparticles

Raman spectroscopy determined modes of vibration and relation of lattices and molecules of sample by laser technique. Figure 2.14 showed the Raman spectra of copper oxide nanoparticles at various ethanol quantities. It was clearly observed that Raman spectra displayed both signals of Cu_2O and CuO . The Raman peaks of Cu_2O were at 146, 219, and 414 cm^{-1} . While, CuO exhibited signals at 296 and 630 cm^{-1} . The results indicated that the mixed phases of copper oxides were formed in all conditions of the synthesis.

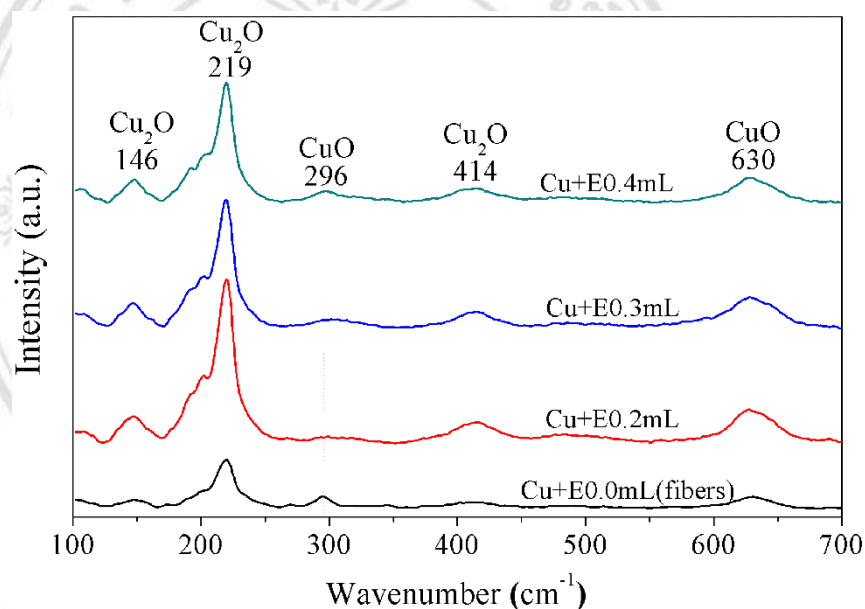


Figure 2.14 Raman spectrum of copper oxide nanoparticles prepared against ethanol additive 0.2, 0.3, and 0.4 mL comparing to no ethanol (fibers).

4) XRD of Copper Oxide Nanoparticles

Figure 2.15 showed the XRD patterns of copper oxide nanoparticles synthesized by microwave heating at various ethanol quantities, 0-0.4 mL. All conditions of the synthesis displayed the sharp peaks of Cu_2O and CuO . The Cu_2O peaks corresponded to (111), (200), (220), and (311) crystal planes. While, CuO was observed at the peaks of (200) and (111). However, a very weak SiO_2 structure, with the peak of (200), was also observed. This is due to a high power induction of ethanol additive at a quartz surface during interaction.

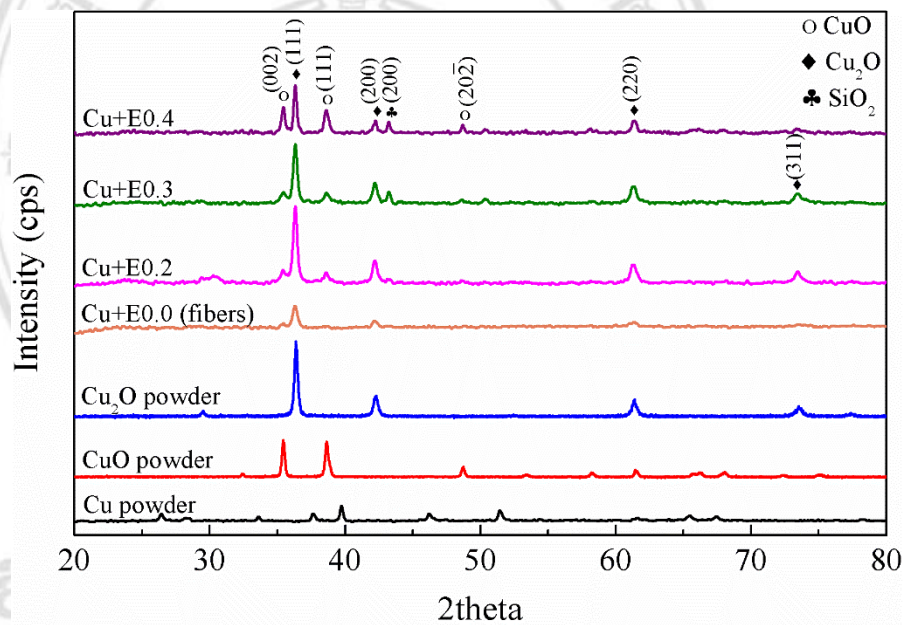


Figure 2.15 XRD patterns of the copper oxide nanoparticles prepared against ethanol additive 0.0, 0.2, 0.3, and 0.4 mL under microwave heating. This results were plotted comparing to pure Cu, CuO, and Cu_2O powders.

2.4 Chapter Summary

The copper oxide nanostructures were successfully synthesized by microwave-assisted thermal oxidation technique. The two morphologies, fiber and particle, were obtained both consisting of two phases, CuO and Cu₂O. Copper oxide nanofibers were synthesized by using only pure copper powders as a precursor and heated under microwave radiation in a few minutes, at room temperature in atmosphere. The 7 min heating was the optimum time for the optimum mass of 1 g copper powders. The components and phase structure of CuO and Cu₂O were confirmed by XRD and RAMAN analysis. The copper oxide nanofibers showed the circular cylindrical shape and a smooth surface. Moreover, the diameters of the nanofibers increased with increasing of heating time in a microwave. At the optimum time, 7 min, the diameters were in the ranges of 0.51-5.50 μm with average lengths about 2.5 cm. While, the pure copper powders with ethanol addition caused copper oxide nanoparticle form. The copper oxide nanoparticles showed the spherical shape with a smooth surface and high homogeneous size. Their diameters were in the range of 80-120 nm at the optimum quantity of 0.3 mL of ethanol. Similarity, the TEM, XRD and RAMAN were characterized to confirm the mixed phases of CuO and Cu₂O. The formation of mixed-phase copper oxide nanostructures, nanofibers and nanoparticles, by simple method in a very short time is an attractive and challenging work. Therefore, the mechanism formations of the both structures will be presented in the next chapter.

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