

## CHAPTER 5

### Conclusions and Future Work

In the last chapter, the main content in the synthesis of the copper oxide nanostructures is concluded. The results shows the mixture of CuO and Cu<sub>2</sub>O in both morphologies, fiber and particle forms. The formation mechanism is proposed based on experimental results. The effects of the copper oxide nanostructures on the ZnO DSSCs enhancement are discussed. Moreover, the future works are suggested in this section.

#### 5.1 Conclusions

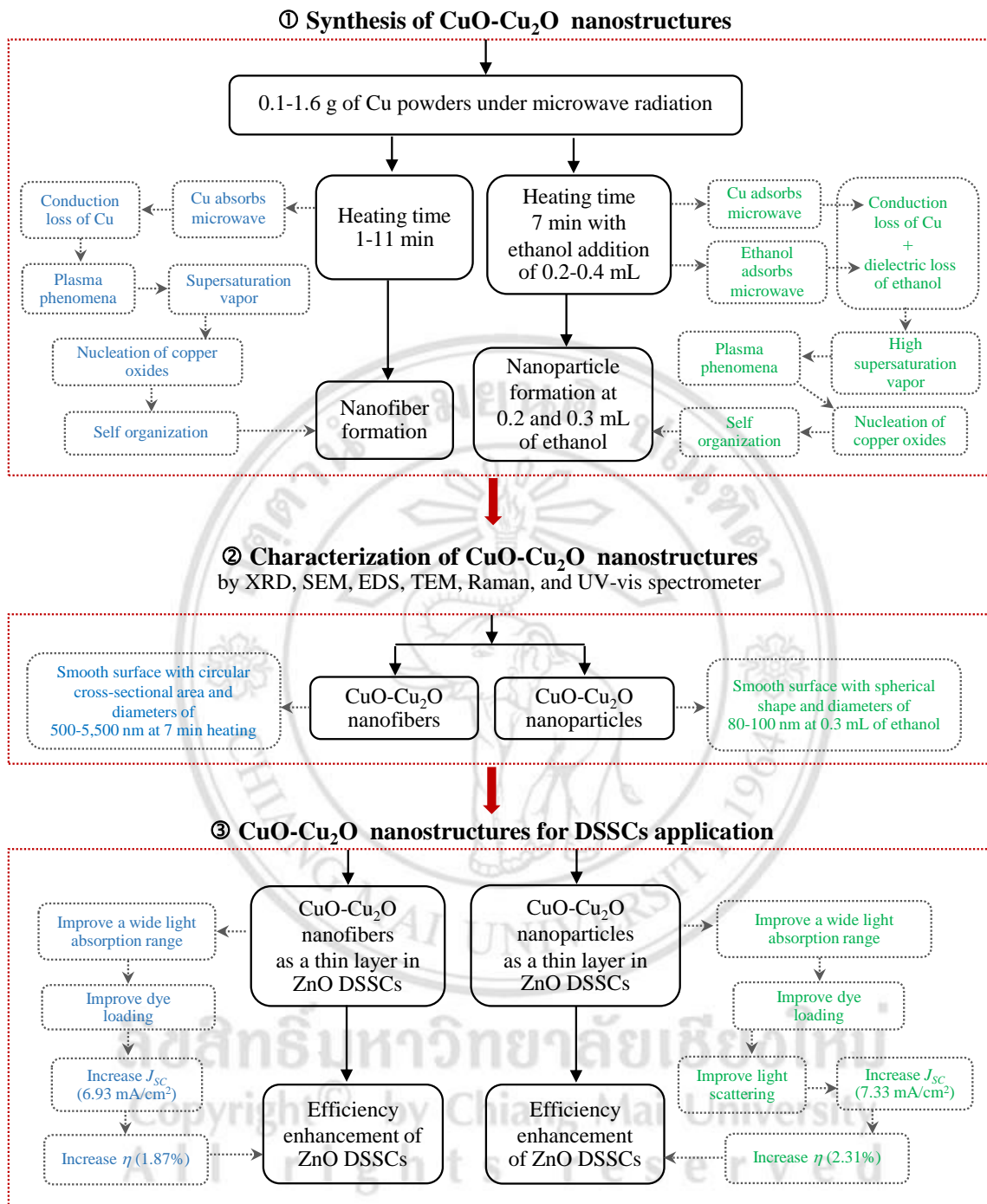
Copper oxide nanostructures, nanofibers and nanoparticles, were successfully synthesized by microwave-assisted thermal oxidation technique. The copper oxide nanostructures were in fiber form consisting of CuO and Cu<sub>2</sub>O with circular cylindrical shape and smooth surface. They have diameters in the range of 500-5,500 nm and have average lengths about 2.5 cm. The conduction loss from microwave-Cu particle interaction at the Cu surface is a major heating, which caused a high vapor pressure of copper oxides and led to the copper oxide nanofiber formation. While, the mixed phases of copper oxide nanoparticles, CuO and Cu<sub>2</sub>O, were synthesized by ethanol addition in pure copper powders. The chemical properties of ethanol (polar solvent, a very low flash point and oxygen composition) encouraged an oxygen increase, generates dielectric heating resulting in higher supersaturation vapor pressure and faster nucleation. This led to the formation of copper oxide nanoparticles in spherical shape in a very short time. The nanoparticles showed homogeneous size about 100 nm at 30 mL of ethanol quantities.

Next, the various masses (0-5.70 mg) of mixed phases copper oxide nanofibers were prepared in viscous solution form and then coated on the top of ZnO layer in photoelectrodes of DSSCs. A high surface area and wide adsorption range of the mixed-phase copper oxide nanofibers can increase charge transport and suppress recombination.

This confirmed by an increase of current density and power conversion efficiency. The current density and power conversion efficiency of the ZnO DSSCs with a surface density of 3.42 mg/cm<sup>2</sup> were rose by 26.2% and 15.4%, over pure ZnO layer, respectively. Whereas, the mixed phases of copper oxide nanoparticles were prepared in viscous solution form with various concentrations, 0-8 mM, and were coated on the top of ZnO based DSSCs. By the large homogeneous size of the nanoparticles compared with ZnO nanopowders, the nanoparticle layer can improve a light scattering. Moreover, the photovoltaic properties of the mixed phases, CuO and Cu<sub>2</sub>O, can improve a wide absorbance in the visible light region. Thus, the current density and power conversion efficiency of the DSSCs with nanoparticle layer at 6 mM were increased by 18.8% and 31.2%, over pure ZnO layer, respectively.

Therefore, this study may provide for a novel idea in the synthesis of metal oxide nanostructures and their application to improve the DSSCs performance.

To see an overview of all important content, the work was summarized in flow chart as shown in figure 5.1.



**Figure 5.1.** Flow chart of the main content in synthesis of mixed-phase copper oxide nanostructures and their application in ZnO DSSCs.

## 5.2 Comparison between this work and other works

Synthesis and application of copper oxide nanostructures in ZnO DSSCs for efficiency enhancement were reported by many researchers. Therefore, this work was compared to other interesting works on the list below.

- P. Raksa et al [25]  
Cu powders were used as a precursor to synthesize CuO thin films and CuO nanowires by evaporation and thermal oxidation methods, respectively. Diameters of CuO thin films were in the ranges of 200-500 nm. Whereas, CuO nanowires had diameters about 50-200 nm with their length of about 10  $\mu\text{m}$ . Both of them were coated on ZnO layer to use as a blocking layer in ZnO DSSCs. the ZnO/CuO thin films can improve current density from 1.40  $\text{mA}/\text{cm}^2$  of pure ZnO layer to 5.10  $\text{mA}/\text{cm}^2$ , which was increase by more than 264%. While, current density of ZnO DSSCs with CuO nanowires increase by more than 6% comparing to pure ZnO layer.
- R. Sahay et al [24]  
Copper acetate (99%), zinc acetate (99%), polyvinyl alcohol PVA, and pure acetic acid were used to synthesize CuO nanofibers by Electrospinning technique. The CuO nanofibers had diameters about 140-269 nm. They were coated on ZnO layer by spin-coating technique to form a blocking layer. The current density of ZnO DSSCs with CuO nanofibers and N719 of dye can improve current density from 0.64  $\text{mA}/\text{cm}^2$  of pure ZnO layer to 0.78  $\text{mA}/\text{cm}^2$ , which was increase by more than 25%.

## 5.3 Future work

This research has shown the synthesis of copper oxide nanostructures and their applications in ZnO based DSSCs. However, some of challenging problems still have many issues to overcome. Thus, the future works were suggested on the list below.

- The sizes of pure copper powders as a precursor should be varied in order to study their particle size effects on formation mechanism of copper oxide nanostructure.

- The various types of chemicals added into the precursor could be considered in order to study their effects on formation mechanism and morphology of copper oxide nanostructures.
- During synthesize process, the oxygen should be flown through the microwave oven in order to increase oxygen quantity. Since the oxygens typically have limited quantities because of the limited volume of a quartz rod. A quartz rod, which has a diameter and length about 2.8 and 10 cm, was used to be a substrate. Therefore, the volume of quartz rod is

$$V = \pi r^2 L . \quad (5.1)$$

This is equal  $\pi (1.4 \times 10^{-2} \text{ m})^2 (0.1 \text{ m}) = 1.96 \times 10^{-5} \pi \text{ m}^3$ . Due to oxygen content in the air, it has only 21%, thus the oxygen in the quartz rod is about  $1.96 \times 10^{-5} \pi \times 0.21 \text{ m}^3 \approx 1.29 \times 10^{-2} \text{ l}$ . Mole of oxygen in the quartz rod can calculate as following:

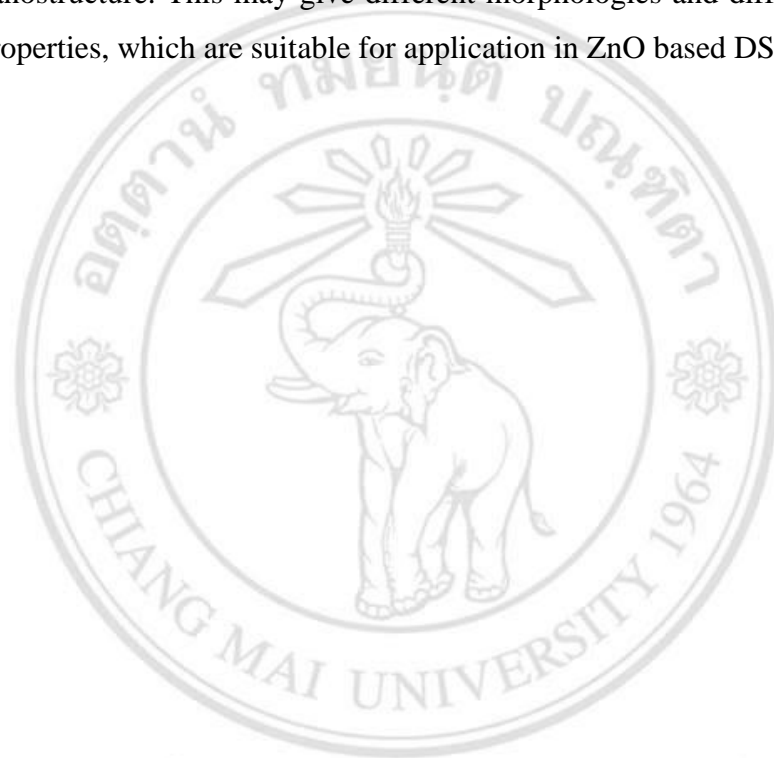
$$PV = nRT , \quad (52)$$

where  $P$  is pressure of oxygen (atm),  $V$  is the volume of oxygen (l),  $n$  is number of moles of oxygen,  $R$  is the gas constant ( $8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$ ), and  $T$  is the temperature in Kalvin. Thus, amount of oxygen ( $n$ ) in the quartz rod is about  $5.2 \times 10^{-4} \text{ mol}$ . Thereby the amount of oxygen can react with  $1.04 \times 10^{-3} \text{ mol}$  of Cu (0.15 g) and generate 1 mol of  $\text{Cu}_2\text{O}$ . Similarity calculation,  $5.2 \times 10^{-4} \text{ mol}$  of oxygen can react with  $5.2 \times 10^{-4} \text{ mol}$  of Cu (0.04 g) and generate 1 mol of CuO.

Therefore, oxygen is essential to form copper oxide. Thus, an increase of oxygen quantity into the microwave may make a better reaction and a greater quantity of the copper oxide nanostructures.

- ZnO based DSSCs with copper oxide layer should be fabricated in a smaller active area ( $< 1 \text{ cm}^2$ ) to save resources. Since its area can affect the effective series resistance of the solar cell and consequently its efficiency.

- The copper oxide nanofibers and copper oxide nanoparticles could be used together as a mixture layer in ZnO based DSSCs. This can provide a new architectural layer for both dye absorption and light scattering in the DSSCs.
- The other additives such as Copper (II) acetate ( $\text{Cu}(\text{CH}_3\text{COO})_2$ ), Copper (II) sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), Sodium hydroxide ( $\text{NaOH}$ ), and Copper (II) Nitrate ( $\text{Cu}(\text{NO}_3)_2$ ) could be considered synthesize copper oxide nanostructure. This may give different morphologies and different physical properties, which are suitable for application in ZnO based DSSCs.



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