

CHAPTER 1

Introduction

1.1 Motivation

The DSSCs (Dye Sensitized Solar Cells) are electrical devices that convert solar energy to electricity by using wide band gap metal oxide together with dye. To generate electricity from the DSSCs, firstly, dye molecules absorb visible light, and then inject excited electrons from the dye to the conduction band of the semiconductor before moving through to transparent conductive oxide substrates (TCO) and later external circuit [1]. Due to their attractive properties, low cost, nontoxic and easy manufacturing process, the DSSCs have been active studied for more than 15 years as shown in Figure 1.1.

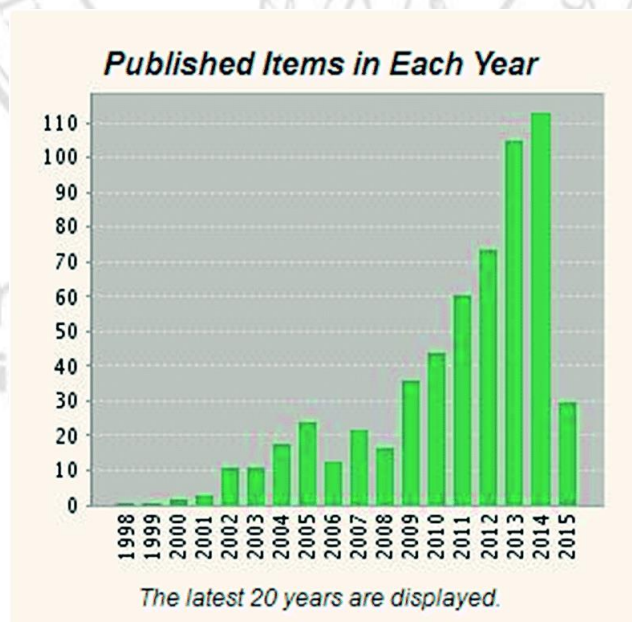


Figure 1.1 Number of DSSCs publications in recent years [2].

The number of DSSCs publications continues to increase between 1998 and 2014 and began to decline in 2015 because its efficiency is quite stable. However, the DSSCs improvement is still a challenge for researchers. Significantly, improvement of

photoanode component because there are several developing methods such as fabrication of various structures [3-6], doping with ions[7-9], coating with conversion materials[10], decoration with noble metals [11, 12] and modification with metal oxides. [13-16]. Among these methods the modification with metal oxides is a popular way to enhance the DSSCs efficiency. Especially, ZnO nanoscale modification as a working electrode in the DSSCs (ZnO DSSCs) have been widely used because it has suitable energy band structure (~3.3 eV at room temperature) for visible light reaction and has high electron mobility. As a result, it can achieve promising power conversion efficiency up to 8.03% [17-20]. However, electron recombination in the ZnO DSSCs leads to a loss of photocurrent and low efficiency. The recombination occurs with some injected electrons in the conduction band, which go back to recombine with I_3^- in electrolyte solution, resulting in current loss and low efficiency of the DSSCs [21-25]. Therefore, the electron recombination needs to be considered. The semiconductor oxides such as TiO_2 , Nb_2O_5 , and CuO are used to serve as a double layer to reduce the electron recombination by coating over a ZnO layer. Recently, copper oxide thin film as a barrier layer can enhance power conversion efficiency of the ZnO DSSCs by recombination blocking [25]. Furthermore, co-working of copper oxide–ZnO DSSCs can improve light scattering and carrier transport properties of the DSSCs [26]. Therefore, efficiency enhancement of ZnO DSSCs by copper oxide modification methods is one of the best effective ways.

Copper oxide compounds, such as CuO and Cu_2O , as p-type semiconductors have been studying since 19th century because many researchers were attracted by their optical and electronic properties [27]. Moreover, there is no toxicity, abundance of the starting material, simple synthesis and low cost [28]. CuO has a monoclinic structure with a lattice constant of $a = 4.6837 \text{ \AA}$, $b = 3.4226 \text{ \AA}$ and $c = 5.1288 \text{ \AA}$. While Cu_2O has a cubic structure with a lattice constant of $a = 4.2696 \text{ \AA}$ having Cu atom in a unit cell coordinated by two oxygen atoms [28, 29]. CuO is an antiferromagnetic material with indirect band gap energy of 1.2 eV and has high carrier concentration with absorption at the spectra band of $0.220 \pm 0.004 \text{ eV}$ corresponding to a low energy photon band and high absorption coefficients at energies above 1.4 eV. Whereas, band gap energy of Cu_2O is about 2.1 eV, which is stable for photovoltaic conversion and owning good carrier. [30]. Furthermore, the copper oxide nanostructures can be easily prepared in several shapes

such as tadpole, spindle, sphere, fiber and star-like shapes [24, 31-34]. Controllable morphology of the copper oxide in nanostructure form can lead to changes in band structures. The copper oxides have high electrochemical activity at nanoscale; their band gap energy and surface potential barrier are less than that of the bulk materials [35, 36]. Thus, they are expected to have better interaction in photovoltaic devices leading to use in batteries [37], gas sensors [38], photocatalyst [39], and solar cells [24, 40]. From the wide applications of copper oxide nanostructures, many researchers have paid much attention to develop fabrication methods such as a colloid thermal synthesis [41], plasma decomposition [42], pulsed laser ablation [43], ion implantation [44], spark discharge [45], and microwave [46-48]. Among these methods, the preparation by microwave is a simple one and copper oxide nanostructures are obtained in very short time. Because microwave is absorbed only by the small samples and not by the surroundings.

Microwave is energy in the form of high frequency electromagnetic wave, which the commonly used frequency is 2.45 GHz. The energy efficiency leads to a rapidly heat of samples and giving unpredictable results because of different microwave irradiation power and material-specific microwave pulses [49]. Therefore, the preparation by microwave is mostly intended to use for quality improvement of copper oxide nanostructures. Because the diverse morphologies of copper oxide nanostructures can be obtained. This results in their different orientations and has a distinct effect on their physical properties. Up to date research states, copper oxide nanostructures prepared by microwave techniques have been continuously reported showing many kinds of morphologies such as flower-like and leaf-like nanoparticles and nanowires [25, 50]. Although, this process can be very simple or quite complex, it basically involves a technical process. Since, the preparation of copper oxide nanostructures by microwave has also been using many precursors, which become quite complex chemical process [46-48]. Furthermore, using some additives in the precursor under microwave radiation, also, effect on sample-microwave reaction and the material morphology. Recently, microwave was used together with chemical processes to synthesize Cu_2O and CuO , using such as $\text{Cu}(\text{CH}_3\text{COO})_2$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, NaOH , and $\text{Cu}(\text{NO}_3)_2$ [51, 52]. Although ethanol has never been used with microwave, morphological control of materials by ethanol in previous reports inspired researchers to study its effects on copper oxide morphology under microwave irradiation [53-55]. Since ethanol ($\text{C}_2\text{H}_6\text{O}$) is a clear liquid alcohol made by

the fermentation of different biological materials and can also mix with water. Especially, it has a lower flash point that is a good ignition catalyst and the advantage is used for production of a variety of value-added chemicals [56, 57].

In this study, copper oxides were synthesized by using only pure copper powders as a precursor under microwave radiation in normal atmosphere (open air at a room temperature), in few minutes. The copper oxides were in mixed-phase of CuO and Cu₂O showing nanofiber form. Then, ethanol was added in the precursor as the previous conditions resulting in the formation of mixed-phase copper oxides with nanoparticle form.

The possible formation mechanisms of mixed-phase copper oxide nanofibers formation were investigated. Also, the effects of ethanol on the morphological transformation from nanofibers to nanoparticles were investigated and proposed in a novel idea based on experimental results and theories.

Furthermore, both of copper oxide nanostructures were applied as a thin layer on top of ZnO layer to improve the ZnO DSSCs performance. Thus, the ZnO based DSSCs were investigated in order to understand the physical properties and effect of copper oxide nanostructures on the ZnO DSSCs efficiency.

1.2 Basic Properties of Materials

1.2.1 Cu₂O

Cu₂O (cuprite or cuprous oxide) is a cubic structure with a lattice constant of $a = 4.2696 \text{ \AA}$. Its unit cell contains six atoms, Cu atom in a unit cell coordinated by two oxygen atoms [29]. Thus, it can be viewed as a body-center cubic (bcc) sublattice of oxygen anions and a face-center cubic (fcc) sublattice of copper cations as shown in Figure 1.2. Cu₂O has red to dark red color with melting point and boiling point at about 1,232°C and 1,800°C, respectively.

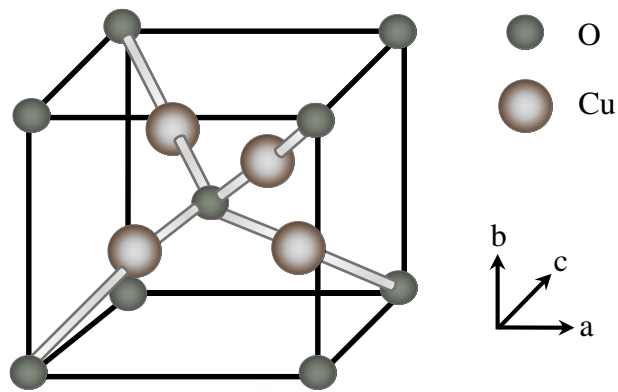


Figure 1.2 Cu₂O cubic structure

Moreover, it is a natural p-type semiconductor having an essentially full *sd* shell ($1s^2 2p^6 3d^{10}$) with band gap energy of 2.17 eV. The amount of cation deficiency of Cu₂O effects on carrier concentration. Moreover, it is stable for photovoltaic conversion [30]. Its high absorption coefficient in easeful light is appropriate for application in photovoltaic devices, especially solar cells. E.de Jongh et al [58] reported that, under photo cathodic condition, long term stability and a high quantum efficiency for the photocathodic were reaction of both oxygen and the methylviologen cation. Therefore, Cu₂O could be a promising material, not for direct photoelectrochemical water splitting, but in conjunction with a suitable redox system as a p-type photoelectrode in an electrochemical photovoltaic cell.

The basic physical properties of bulk Cu₂O are shown in Table 1.1.

ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่
Copyright© by Chiang Mai University
All rights reserved

Table 1.1 A brief overview of the basic physical properties of bulk Cu₂O [27, 59, 60].

Properties	Volume	Unit
Molecular weight	143.09	(g·mol ⁻¹)
Density	6.00	g·cm ⁻³
Melting point	1,505	K
Boiling point	2,070	K
Band gap energy	2.17	eV
Lattice parameters	4.27	° Å
Shortest distances		°
d _{Cu-O}	1.84	Å
d _{O-O}	3.68	Å
d _{Cu-Cu}	3.02	Å
Standard molar enthalpy (298K)	93	J·mol ⁻¹ ·K ⁻¹
Standard enthalpy of formation (298K)	-170	kJ·mol ⁻¹
Cell volume	77.833 x 10 ⁻²⁴	cm ³
Young's modulus	30.12	GPa
Shear modulus	10.35	GPa
Thermal expansion coefficient (283 K)	2.3x10 ⁻⁷	K ⁻¹

1.2.2 CuO

CuO (tenorite or cupric oxide) is a monoclinic structure with a lattice constant of $a = 4.6837 \text{ \AA}$, $b = 3.4226 \text{ \AA}$, $c = 5.1288 \text{ \AA}$, and $\beta = 99.54^\circ$ as shown in Figure 1.3.

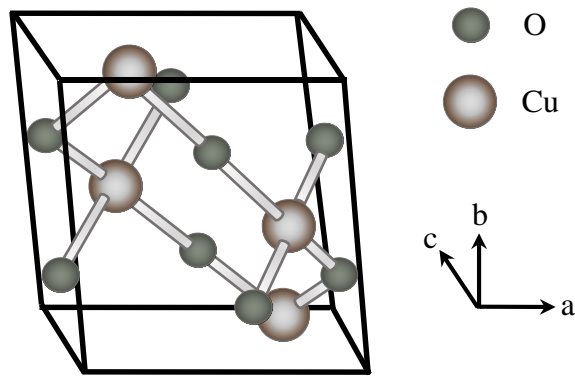


Figure 1.3 CuO monoclinic structure.

CuO has a black color and behaves as an antiferromagnetic material, especially strong antiferromagnetic along the $(10\bar{1})$ direction (231K) [61]. The melting point and boiling point of CuO are higher than Cu_2O which are about $1,559^\circ\text{C}$ and $2,270^\circ\text{C}$, respectively. It is a p-type semiconductors with band gap energy of 1.2 eV, which has high absorption coefficients at above 1.4 eV [28, 62]. Moreover, CuO is also believed to have copper vacancies as acceptors are responsible for hole conduction [60]. The basic physical properties of bulk CuO are shown in Table 1.2.

Table 1.2 A brief overview of the basic physical properties of bulk CuO [27, 61].

Properties	Volume	Unit
Molecular weight	79.54	(g·mol ⁻¹)
Density	6.31	g·cm ⁻³
Melting point	1,599	K
Boiling point	2,270	K
Band gap energy	2.1	eV
Lattice parameters		
a	4.6837	Å
b	3.4226	Å
c	5.1288	Å
β	99.54	degree
Shortest distances		
d _{Cu-O}	1.84	Å
d _{O-O}	3.68	Å
d _{Cu-Cu}	3.02	Å
Cell volume	81.08	(Å) ³
Standard molar enthalpy (298K)	43	J·mol ⁻¹ ·K ⁻¹
Standard enthalpy of formation (298K)	-156	kJ·mol ⁻¹
Index of refraction	2.63	

1.2.3 ZnO

ZnO is an II-VI group of compound semiconductor. ZnO crystallizes in 2 forms. There are hexagonal wurtzite and cubic zincblende. The wurtzite structure has a hexagonal unit cell with two lattice parameters a and c in the ratio of $c/a = \sqrt{8/3} = 1.633$ as shown in Figure 1.4(a) [63]. While, zincblende structure crystalline is cubic as shown in Figure 1.4(b).

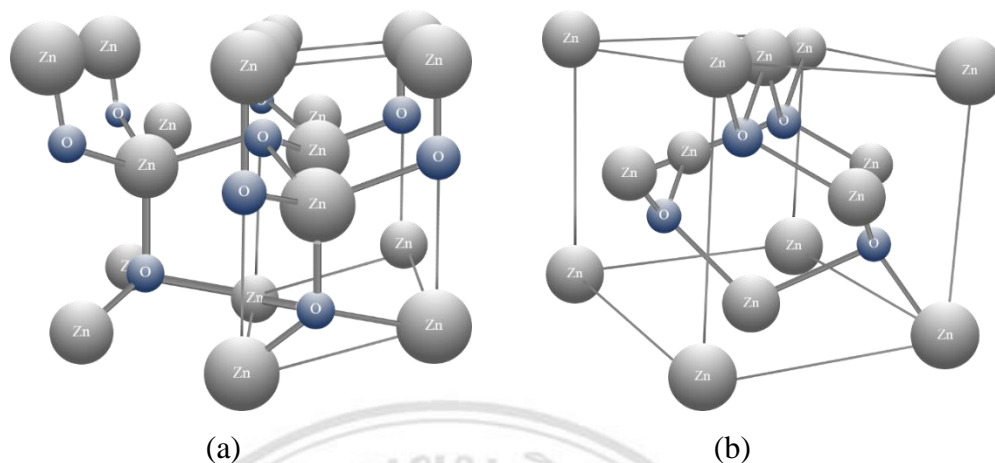


Figure 1.4 ZnO structure of (a) hexagonal wurtzite and (b) cubic zincblende.

ZnO has a white color. It has a wide band gap about 3.3 eV. At a room temperature, ZnO has a large excitation binding energy of 6 eV, which is important for blue and ultra-violet optical devices [64]. The basic physical properties of bulk ZnO are shown in Table 1.3.

Table 1.3 A brief overview of the basic physical properties of bulk ZnO [65, 66]

Properties	Volume	Unit
Molecular weight	81.38	(g·mol ⁻¹)
Density	5.606	g·cm ⁻³
Melting point	2,248	K
Boiling point	2,248	K
Band gap energy (direct)	3.3	eV
Lattice parameters		
a	3.25	Å
c	5.2	Å
Standard molar enthalpy (298K)	43.9	J·mol ⁻¹ ·K ⁻¹
Standard enthalpy of formation (298K)	-348.0	kJ·mol ⁻¹
Flash point	1,709	K
Solubility in water (17.8°C)	0.0004	%

1.2.4 Ethanol

Ethanol known as ethyl alcohol or hydroxyethane can be produced from many raw materials like sugar, barley, and corn [67, 68]. It is no color liquid with a low toxicity. Its chemical formula is C_2H_6O as shown in Figure 1.5.

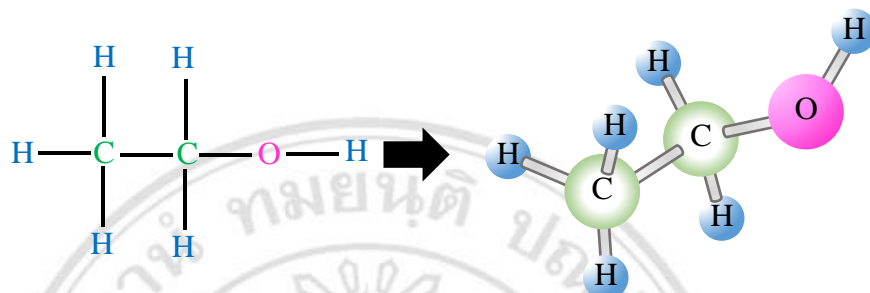


Figure 1.5 Structure formula of ethanol.

Ethanol always uses for cleaning and antiseptics. It has a flash point at only $13.5^{\circ}C$ (286.65 K), thus it is suitable for using as an additive in thermodynamic experiment.

C.B. Wang et al [69] reported that the alcohol (methanol, ethanol, and 2-butanol) oxidation catalytic properties influenced on transformation of three-dimensional bulk metal oxide into surface metal oxide.

M.K. Durka et al [70] studied microwave heating to pervaporation by dewatering of water-ethanol mixtures. They found that dielectric loss of ethanol increased with increasing temperature and thermal gradients were easily induced in microwave.

The basic physical properties of ethanol are shown in Table 1.4.

Table 1.4 A brief overview of the basic physical properties of ethanol [71].

Properties	Volume	Unit
Molecular weight	46.07	(g·mol ⁻¹)
Density	0.789	g·cm ⁻³
Melting point	159	K
Boiling point	351.15	K
Flash point	286.65	K
Self-ignition temperature	693.15	K
Latent heat of evaporation	840	kJ·kg ⁻¹
Kinematic viscosity (313.15K)	1.2	mm ² ·s ⁻¹
Index of refraction	1.316	
Oxygen content	34.8	wt%
Hydrogen content	13.04	wt%
Carbon content	52.18	wt%

1.3 Preparation of Copper Oxide Nanostructures by Various Techniques

Nowadays, synthesis of copper oxide nanostructures, Cu₂O and CuO, were successfully synthesized in several methods. The different sizes and shapes were reported continuously by researchers around the world as shown in Table 1.5.

Table 1.5 Advantages in copper oxide nanostructure preparation by different methods.

Authors	Precursors	Methods	Morphologies	Advantages
P. Raksa et al. [25]	Cu powders	Evaporation and thermal oxidation	CuO thin film and nanowires	Synthesis by simple method and applying as a blocking layer in ZnO DSSCs for efficiency enhancement
M. Kong et al. [72]	Cu ₂ O solid nanospheres Cu ₂ O solid nanospheres	Thermal oxidation	CuO hollow nanospheres CuO hollow nanospheres	synthesis by simple method and applying for ion batteries to improve the batteries performance
L. Peisheng et al. [73]	copper target in PVP	Laser ablation	Cu ₂ O nanoparticles	Synthesis by simple method in a shell layer form of amorphous CuO
A. Ahmeda et al. [74]	Copper nitrate and ethylene glycol	Poly method	Nano crystalline Cu ₂ O flowers, hollow spheres	Various nanostructures of Cu ₂ O applying for photocatalysis
G. Saito et al. [75]	K ₂ CO ₃	Solution plasma	Nanoflowers and nanorods	Reducing CuO nanoparticle sizes by decreasing concentration of K ₂ CO ₃ solution
H. Za et al. [76]	CuCl ₂ - NaOH- SDS- isopropyl alcohol	Gamma irradiation	CuO nanowires and Cu ₂ O crystal	Controlling phases of copper oxide by varying molar ratios of OH ⁻ and Cu ₂

Table 1.5 (continued)

Authors	Precursors	Methods	Morphologies	Advantages
M. Kooti et al. [77]	Copper sulfate	Reduction of Fehling's solution	Cu ₂ O nanoparticles	Synthesis by simple method and low cost
M. Salavati-Niasari et al. [78]	Bis(salicylidiminato) copper(II) and Cu(sal) ₂	Thermal decomposition	Cu and Cu ₂ O nanoparticles	Giving homogeneous sizes of Cu ₂ O with 80-100 nm
X. Liu et al. [79]	Cu(acac) ₂	Controlling the growth temperature	Cu, CuO and Cu ₂ O nanoparticles	Synthesis of CuO and Cu ₂ O by growth mechanism controlling

1.4 Preparation of Copper Oxide Nanostructures by Microwave

Synthesis of copper oxide nanostructures, Cu₂O and CuO, by microwave is a novel method to improve the quality of the nanostructures. The copper oxide nanostructures can be fabricated in few minutes by high frequency electromagnetic energy of microwaves. The energy efficiency results in a rapidly heat of samples and gives variety morphologies. The unpredictable properties of the copper oxide nanostructures depend on the different microwave irradiation powers and precursor properties as shown in Table 1.6.

ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่
Copyright © by Chiang Mai University
All rights reserved

Table 1.6 Characteristics of copper oxide nanostructures preparation by microwave.

Authors	Precursors	Morphologies	Advantages
X. Xu et al. [46]	[BMIM]BF ₄	Leaf-like, chrysanthemum-like and rod shape	High-purity of CuO nanostructure and easy controlling morphologies in short time process
Y. Min et al. [47]	Copper foil	Nanoplate, nanorock, nanotower and nanoflower	Giving various morphologies and pure monoclinic phase of copper oxide
R. Sahay et al [24]	Cu(CH ₃ COO) ₂ and PVA	Nano fibers	Poly-crystalline nanostructure of nanofibers, increased 25% in the current density of DSSCs as a double layer
C. Karunakaran et al [80]	Cu(NO ₃) ₂ , NaOH, (CH ₂) ₆ N ₄ , and C ₁₉ H ₄₂ BrN	Nanoleaves and nanodiscs	Inhibition of bacteria by the copper oxide nanostructure protection
A.V. Nikam et al [81]	Copper acetate	Nnanoparticles	High monocrystalline of Cu ₂ O and CuO, CuO nanoparticles showing good hole mobility
D. Nunes et al [82]	Copper	Nanowires	High monocrystalline of copper nanowires
Hu Meng et al [83]	Graphene oxide and CTAB	Nanorods	Great potential of Cu ₂ O for manufacturing a new generation of low-power and portable ammonia sensors

1.5 ZnO DSSCs

DSSCs are semiconductor photovoltaic devices, which were invented by O'Regan and Gratzel in 1991[84]. The DSSCs can convert solar energy to electrical power. In order to create solar energy, first, the dye absorbs sunlight, and then electrons in ground state are excited to excited state and injected into the conduction band of semiconductor oxide material before passing through the conducting glass to anode and external circuit. Reaching the cathode, the electrons engage in the reduction in electrolyte, and then the iodide reacts with the oxidized dye. Then, electrons return to its ground state, and the cycle is completed [85]. Figure 1.6 shows the principle operation of the DSSC.

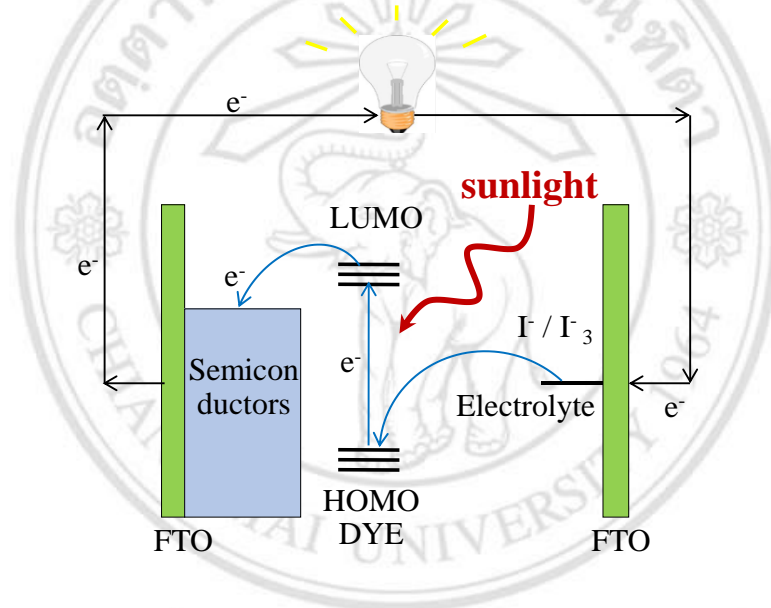


Figure 1.6 The principle operation scheme of the DSSC.

Importantly, applications of semiconductors in nanostructure forms for photo anode can offer the larger surface area for dye absorption, leading to more injected electrons and a higher of photocurrent [86]. In addition, the semiconductors in nanostructure forms can, also, provide a better electron pathway in transfer process. Thus, various nanostructured semiconductors have been fabricated for improvement in dye loading and electron pathway. Among all of nanostructured semiconductors, oxide semiconductors such as TiO₂, ZnO and In₂O have been widely used for DSSCs because of their suitable properties, wide band gap energy, good chemical stability and non-toxicity. Especially, their band gap energies match the energy of photon, so electrons can be excited to the conduction band [87].

ZnO is chosen for this study with a wide band gap about 3.3 eV, which is appropriate for ultra-violet optical devices. Furthermore, ZnO shows excellent bulk electron mobility and can be fabricated in a great variety of ZnO nanostructures such as nanoparticles, nanosheets, nanowires and tetrapods [88]. The DSSCs based on ZnO nanoscale (ZnO DSSCs) can improve electron injection and can achieve promising conversion efficiency (η) up to 8 % [20]. However, the ZnO DSSCs have a limit performance. A recombination is a main loss of electrons in the transportation process and directly effects on the low efficiency of DSSCs as shown in Figure 1.7 [21, 22]. To enhance the efficiency of the ZnO DSSCs, a loss of photocurrent due to electron recombination needs to be considered.

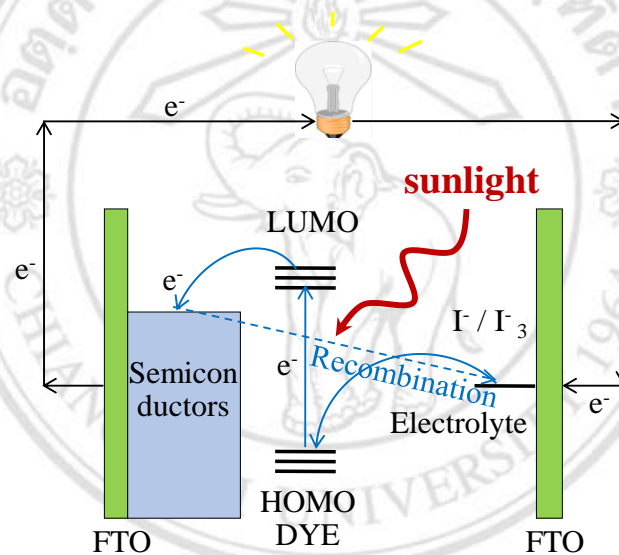


Figure 1.7 The principle operation scheme of the DSSC and recombination.

1.6 Research Objectives and Usefulness of the Research

1.6.1 This work will be accomplished by filling in the following research objectives:

- To synthesize and characterize copper oxide nanostructures by microwave-assisted thermal oxidation.
- To fabricate and investigate photoconversion properties of ZnO based dye-sensitized solar cells with copper oxide nanostructures as blocking layer.

1.6.2 Pursuing a research work will be a challenging and rewarding experience. This opportunity enables us to address the following usefulness of the research:

- The research will provide copper oxide nanostructures by microwave-assisted thermal oxidation and characterization of the prepared copper oxide nanostructures.
- The copper oxide nanostructures can be applied as a blocking layer in dye-sensitized solar cells.

1.7 Thesis Organization

The thesis is divided into five chapters and each chapter contains the following:

- Chapter 1 introduces the motivation, the basic properties of the materials used in this study including copper oxide (CuO and Cu₂O), zinc oxide (ZnO) and ethanol. Also, the literature reviews on copper oxide and ZnO based dye-sensitized solar cells, together with research objectives and usefulness of the research are presented.
- Chapter 2 describes the synthesis of copper oxide nanostructures consisting of mixed-phase CuO and Cu₂O with both nanofibers and nanoparticles, by microwave-assisted thermal oxidation technique. Moreover, the copper oxide nanostructures are characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman dynamic light scattering, X-ray diffraction analysis (XRD) and energy dispersive spectroscopy (EDS).
- Chapter 3 gives formation mechanism of copper oxide nanofibers and copper oxide nanoparticles by ethanol addition under rapid microwave irradiation. Investigation and discussion will be provided.
- Chapter 4 presents the effects of mixed phase-copper oxide nanostructures, CuO-Cu₂O nanofibers and CuO-Cu₂O nanoparticles, on the ZnO DSSCs performance as a thin layer in DSSCs.
- Chapter 5 concludes all contents in this research and suggests possible future works.