THE ENHANCEMENT OF HYDROPHOBIC AND ELEC--TROCHEMICAL PROPERTIES OF NiO/Ni FOAM BY UV LIGHT IRRADIATION

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การเพิ่มประสิทธิภาพของสมบัติความไม่ชอบน้ำและสมบัติเคมีไฟฟ้าของวัสดุนิกเกิลออกไซด์ด้วยการฉายแสงอัลตราไวโอเลต

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LIGHT IRRADIATION

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การควบคุมสมบัติไฮโดรโฟบิกและสมบัติทางเคมีไฟฟ้าเป็นเรื่องที่มีความน่าสนใจเป็นอย่างมากและยังมีการศึกษากันอย่างกว้างขวาง ซึ่งสมบัติเหล่านี้ยังสามารถไปประยุกต์ใช้งานหลากหลาย โดยในงานนี้เราได้เลือกใช้วัสดุนิกเกิลออกไซด์ด้วยคุณสมบัติที่พิเศษ คือ มีค่าพื้นผิวและความจุไฟฟ้าที่มาก ในงานวิจัยนี้ เราจะนำเสนอถึงกระบวนควบคุมสมบัติความเปียกและสมบัติทางเคมีไฟฟ้าของวัสดุภายใต้เงื่อนไขของอุณหภูมิในการหลอมเหลวและการฉายแสงอัลตราไวโอเลต การเตรียมตัวอย่างนิกเกิลออกไซด์ถูกเตรียมด้วยวิธีการเทอร์มอลออกซิเดชันโดยทำการเผาตั้งแต่อุณหภูมิ 0 °C ถึง 600 °C ในอากาศของสภาพแวดล้อมทั่วไป จากการทดลองนี้พบว่า คุณสมบัติความเปียกของวัสดุจะมีการเปลี่ยนแปลงจาก ไฮโดรฟิลิก (0 องศา) ไปเป็นไฮโดรโฟบิก (120 องศา) เมื่อทำการเพิ่มอุณหภูมิในการเผาไปจนถึง 600 °C นอกจากนี้แล้วภายใต้เงื่อนไขของการฉายแสงอัลตราไวโอเลต เราพบว่า ค่ามุมสัมผัสของหยดน้ำ มีค่าเพิ่มขึ้นจาก 0 องศา ไปถึง 60 องศา และค่าความจุทางไฟฟ้ามีค่าเพิ่มขึ้นจาก ฟาราดต่อกรัม ไปเป็น 35 ฟาราดต่อกรัม พร้อมกับมีสัญญาณการเกิดโครงสร้างทางเคมีแบบใหม่เกิดขึ้น ภายใต้เงื่อนไขของการเผา ยังแสดงให้เห็นอีกว่า ลักษณะความขรุขระของผิวตัวอย่างเห็นการเปลี่ยนแปลงได้มากขึ้นและพบอีกว่าขนาดของรูพรุนมีค่าเพิ่มขึ้นจากขนาดเส้นผ่าศูนย์กลางประมาณ 36±3 นาโนเมตร ไปเป็นขนาดเส้นผ่าศูนย์กลางเท่ากับ 210±11 นาโนเมตร ต่อมาสำหรับการศึกษาการก่อตัวทางเคมีบนผิวของตัวอย่างโดยเทคนิคเอ็กซ์เรย์โฟโตอิมิชชันสเปกโทรสโกปี พบว่ามีการเปลี่ยนแปลงของพีคคาร์บอน ออกซิเจน และ นิกเกิล อย่างชัดเจน ภายใต้เงื่อนของการเผาที่อุณหภูมิต่าง ๆ ในขณะของเงื่อนของการฉายแสงอัลตาไวโอเลต ลักษณะของพีคเหล่านี้มีการเปลียนแปลงน้อยมาก ในการศึกษาโครงสร้างของผลึกพบว่า ยิ่งเผาที่อุณหภูมิสูงขึ้นจะเกิดเฟสของ NiO มากขึ้น สุดท้ายนี้จากการทดลองสามารถสรุปได้ว่า ทั้งการเพิ่มอุณหภูมิในการเผาและการฉายแสงอัลตาไวโอเลตสามารถช่วยเพิ่มประสิทธิภาพของสมบัติความเปียกและสมบัติเคมีไฟฟ้าแต่สามารถอธิบายด้วยพฤติกรรมที่ต่างกัน

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KOMSUN LAPAWEA : THE ENHANCEMENT OF HYDROPHOBIC AND ELECTROCHEMICAL PROPERTIES OF NiO/Ni FOAM BY UV LIGHT IRRADIATION. THESIS ADVISOR : ASSOC. PROF. WORAWAT MEEVASANA, Ph.D. 72 PP.

CAPACITANCE OF NiO/WETTING PROPERTY/UV LIGHT INDUCED SURFACE PROPERTY/CONTACT ANGLE MEASUREMENT/ELEC-TROCHEMICAL PROPERTY

Controlling of hydrophobic and electrochemical properties in materials is very interesting which can be applied in various application. NiO is one of materials composing high surface area and high specific capacitance which is commonly studied in such behaviors. In this thesis, we present how to control the wetting and electrochemical properties as function of annealing temperature and UV light irradiation. NiO were fabricated by thermal oxidation process from Ni foam with temperature ranging from 0 ºC to 600 ºC in air. In the experiment, the result shows that the change of hydrophilic (0º) to hydrophobic (up to 120º) behavior by increasing annealing temperature up to 600 ºC. By UV light irradiation, the water contact angle is increased from 0º to 60º. The specific capacitance was also increased from 15 F/g to 35 F/g with the signature of new chemical species under irradiation measured by cyclic voltammetry. By using scanning electron microscopy (SEM), samples under higher annealing temperature show the increase of surface roughness and porous size (d=36±3 nm) to (d=210±11 nm). By using x-ray photoemission spectroscopy (XPS), the change of C, O, and Ni peaks under effect of annealing temperature is clearly observed. The change of those peaks was not significantly observed by UV light irradiation. By using

irradiation. By using x-ray diffraction, the transformation of crystal structure was observed to change from Ni to NiO phase. Finally, from this result can concluded that both annealing and irradiation can induce the enhancement of wetting and electrochemical properties, however, they possess different mechanism.

School of Physics

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Student's Signature _____

Advisor's Signature _____

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CHAPTER I

INTRODUCTION

1.1 Background and motivation

The wetting property on solid surfaces is a phenomenon that can often be seen in everyday life. The Example of such phenomena is lotus effect. It can be applied as water repelling, easily rolling off and antifouling (P. Zhang and Lv, 2015). This phenomenon attracts much attention in academic and industry. The wetting feature can be applied in a variety of applications such as printing, liquid coating, adhesion, lubrication, self-cleaning and oil water separation (Jerrard, 2008). Using of such materials depends on the specific applications which can be clarified as "good wetness or poor wetness". When a water droplet is placed on the solid surface, the attractive force between them is occurred at the interface which results to the uniform of water droplet. However, the water droplet profile depends on the surface property of solid surface. This surface phenomenon is caused by its surface being covered by liquid. The liquid dispersion is one of the most important physiological phenomena that can be used to describe the wetness of a material. This wetness can be observed by measuring the contact angle and measuring the area of coverage. If the contact angle is low and the area of coverage is very high, the material is hydrophilic. On the other hand, if the contact angle is high and the area of coverage of the liquid is small, indicating that the material is hydrophobic (Kumar and Prabhu, 2007). The principle of this wetting behavior can be explained by the Wetting Model on the flat surface of Young's

equation. They studied the active force between solid and liquid at the 3-phase equilibrium point between air, liquid and solid. The contact angle measurement can be measured directly. This value is related to the surface energy of various phases. This method can be used to describe the wettability of solid surface (Yong, Chen, Yang, Huo, and Hou, 2017). Contact angle measurement can be measured by directly drop the water droplets on the material surfaces or using the standard contact angle goniometer (Lamour and Hamraoi, 2010). In the water contact angle measurement we can clarify the wetting property by using contact angle. If the contact angle at the interface between the liquid and the solid is less than 90º, we determine that the material is hydrophilic and that the angle at 0º is super hydrophilic. If the contact angle is greater than 90º, we give this material a hydrophobic surface and at an angle of more than 150º to a super hydrophobic surface or a hydrophobic material. However, the wetting properties of the solid can be altered depending on two factors. These are the surface structure related to the surface roughness of the nano/microstructure and surface energy related to chemical substance that causes the surface to increase or decrease its energy. In general, the material in the surface is uneven or possesses different roughness. So, the description of the wetting properties of the Young's equation will be modified with the addition of two roughness equations, Wenzel state and Cassie-Baxter state. The Wenzel state is a model that describes the wetting property in the case where a liquid can penetrate into a small gap and cannot easily roll off. However, in the Cassie-Baxter state the fluid can be suspended on the surface and can easily roll off. The contact angle of Cassie-Baxter state is greater than the Wenzel state. The relationship between these two models can be explained by the structure of the surface and surface energy. (P. Zhang and Lv, 2015).

In general, we often see a variety of materials that exhibit hydrophilic and hydrophobic behaviors referring to different wetting properties. In the case of this study, the properties of the sample are related to the sample preparation process, i. e., electrodeposition (Bellanger, Darmanin, Taffin De Givenchy, and Guittard, 2012), plasma etching (Chen et al., 2016), dip coating (Y. Wang, Li, Liu, Xu, and Ge, 2014) hydrothermal process, spin coating (Xu, Karunakaran, Guo, and Yang, 2012), sol-gel process, laser irradiation (Wang, Tzeng, Chen, and Chang, 2012), and alternative current etching method (Liang, Zhu, Li, and Liu, 2015). In addition, these method of sample preparation are also used to study the surface properties of materials. Next, the method is used to study the change or control of wetting properties. The study is based on applying external stimulation on the surface of the material including light exposure, electrical potential, heating, and solvent. As a result, the surface of the material is changed and also the polarity of the material is formed. This change will also result in the wetting properties of the activated material (Caputo et al., 2009).

In the study of wetting property, a variety of materials were used to conduct experiments. In most experiments, the materials are always considered in micro/nano structure especially on the surface which is the tested area. From literature, most of the researches is focused on oxide materials because of their special characteristic of oxygen defect, which makes it an extremely versatile and applicable. So, if wetting property of this material can be revealed, more useful perspective can be achieved. The oxide compounds which were commonly used for the study are ZnO (Khranovskyy, Ekblad, Yakimova, and Hultman, 2012), TiO (Banerjee, Dionysiou, and Pillai, 2015) and NiO foam (Si, Chen, Yang, Guo, and Guo, 2018). However, several studies have been focused on polymer because the fact that polymer materials have been used

extensively in a wide range of applications particularly in coating, texture, and biosensor engineering (Wagner and Theato, 2014).

According to a variety of wetting property studies in various materials, these can be applied in many areas such as energy and environment. One of the most interesting and widely used materials in this field is TiO_2, which is commonly used for coating on other materials because of its transparency. Most applications have been done by coating on the glass giving self-cleaning property under sunlight irradiation. This property is known as photocatalysis which can change the wetting property. When sunlight is shining on the TiO_2 coated glass, the photocatalysis process takes place. This process can destroy organic dirts on the glass surfaces. At the same time, this illumination will increase the wettability of solid, which means that it will have better hydrophilicity. That is, it will stick to water well. Finally, the dirt on the glass will be washed away with water (Parkin and Palgrave, 2005). In addition, light irradiation can not only change the surface properties but also electrical properties of the substance. The study of electrical variation upon light irradiation is one of the tasks. It has been of interest to many research fields of energy storage which energy storage is the device that use to store the electricity.

In the field of energy conversion, several research groups attempt to develop new energy conversion technology to replace petroleum. Nowadays, most energy conversion applications are based on batteries (González, Goikolea, Barrena, and Mysyk, 2016). However, batteries possess a limitation of a cell lifetime and slow charging process when connecting to the device. To overcome this problem, much effort for developing a new type of energy storage called “electrochemical capacitor or supercapacitor” which possesses long lifetime and the fast charging process is now an

attractive issue. Especially in the study of capacitor which gains much attention in research areas because the capacitor is widely used as an integral component in electronics. So, if we can increase the performance of the capacitor, it will result in the development of computer technology as well. A capacitor is a device that is used as a basic circuit. It can store energy in order of microfarads and also act as a filter to select the appropriate signal. This device is similar in structure to the battery, but its electrodes are made of the same material and use solid/liquid electrolyte as the separator between electrodes (Jayalakshmi and Balasubramanian, 2008). The application of supercapacitor can be applied in many fields including electronic devices, solar cells, and energy storages. It has been selected as the next generation capacitor. This device has many advantages such as high-power densities, short charging time, and long-life time. The type of electrolyte impingement at the interface between the electrode and the electrolyte, which has the potential to weld over a conventional capacitor. The unique property such as it can store energy as large as 10^{10} Farad and has a high specific power (~500-10,000 W/kg) and long-life cycle (>100,000 cycles) (Kalasina et al., 2017). In practice, the use of supercapacitors is still limited in the electrode materials that need to improve performance and price. There are a variety of materials which have been study as the electrode of this device, especially oxide materials.

Metal oxides such as MnO_2, RuO_2, and NiO were used for fabricating the supercapacitor due to their high specific capacitances (G. Wang, Zhang, and Zhang, 2012). The application of supercapacitor can be applied in many fields including electronic devices, solar cells, and energy storages. Most of the material's electrical properties in field of energy strorage are described by specific capacitance and specific energy (Simon and Gogotsi, 2008). These properties can be carried out by cyclic

voltammetry measurement. Recent progress on device development such as supercapacitor is still at the research level. There are just a few devices is being commercialized. There are several ways to improve capacitive performance. Light irradiation is one of the way to improve capacitance. This is an interesting new method because light is cheap and abundance. So, if we can enhance the properties of any devices by using sun light as a stimulus, it could be a good option to reduce the cost of production. The increased efficiency of device resulting from light irradiation could be described by the stimulation of electrons at the valence band to the conduction band in the substance. This mechanism results in electron and hole pairs. Holes will react with other substances, and electrons result in material conductivity enhancement. As such, it will make the device good electrical property which result to more capable of charging and with more stored energy (Kalasina et al., 2017).

One of the most interesting and widely studied materials in the field of energy storage is the NiO material. This material has many advantages of being lightweight and flexible, which is suitable for developing and producing a portable electronic device (Yan et al., 2014). NiO is an exciting material with excellent properties, easy fabrication, and a wide range of application (Y. Zhang et al., 2009). It has a high theoretical specific capacitance (2584 F/g), robust chemical-thermal stability, and low cost. NiO can be fabricated by various method such as facile solution method and thermal oxidation process. Most of them is to grow NiO on Ni foam. Therefore, the use of NiO has applied not only the field of energy storage but also the self-cleaning application. In term of self-cleaning material, it requires high porous structure e. g. NiO foam (Gao et al., 2014). This porous structure can lead to a high surface area which can be applied in surface science research. Self-cleaning property is strongly related to the

wetting property (Yan, Gao, and Barthlott, 2011). This property refers to the solid surface which can either absorb or repel liquid droplets known as the Lotus effect. This effect has been attractively studied in various fundamental researches such as thin film technology, textile self-cleaning surface, and micro-fluid of biotechnology. NiO has been developed for environmental protection application, i.e., to solve the oil spill problem in the ocean ecosystem. This application relies on the wetting property of NiO grown on the Ni foam (NiO/Ni foam). NiO/Ni foam can be fabricated by various techniques such as sol-gel, plasma process, spinning method, chemical etching, thermal oxidation method, and light irradiation process (Lu, Hwang, Yang, and Chuang, 2002; Liang, Wang, Wang, and Lu, 2016). The change of wetting and capacitance properties can be occurred by light irradiation while the intrinsic mechanism has not yet been fully explained.

In this work, wetting and electrochemical properties of NiO/Ni foam have been studied. NiO/Ni foams were fabricated by the thermal oxidation process. The properties of NiO/Ni foams were characterized by contact angle measurement (CAM), scanning electron microscopy (SEM), x-ray diffraction (XRD), cyclic voltammetry (CV) and x-ray photoelectron spectroscopy (XPS). The wetting property under UV light illumination (3.05 eV photon energy and 405 nm wavelength) of NiO/Ni foam as a function of time and light intensity was investigated by contact angle measurement. The crystal structure and the surface morphology were characterized by x-ray diffraction and scanning electron microscopy. The specific capacitance of NiO/Ni foam was studied by cyclic voltammetry measurement. The chemical forming on sample surface was examined by x-ray photoelectron spectroscopy. In our experimental results, we found that by increase an annealing temperature, this can effect to the changes of

surface morphology, NiO structure, wetting and electrochemical properties. We found an increase of contact angle and specific capacitance of Ni/NiO foam under UV light irradiation. This could be described by the creation of charge carriers and the modification of surface morphology induced by light. Finally, we believe that the changes of wetting and capacitance properties under UV light irradiation are related to each other. Our findings should help to explain the mechanism regarding the changes of Ni/NiO foam properties as well as apply for future applications.

1.2 Objectives of research

1) To prepare the NiO/Ni foam for studying the surface properties.
2) To examine the wetting property on NiO/Ni foam surface under UV light exposure.
3) To investigate the electrochemical property of NiO/Ni foam surface under UV light exposure.
4) To understand the mechanism of NiO surface under UV light exposure.

1.3 Outline of thesis

The thesis is organized as follows. Chapter I is the introduction part. This includes background, research interest and research motivation. Wetting and electrochemical properties are provided. In chapter II, we discuss on literature review related to the study of surface properties of materials and their applications. In addition, the optimization of those properties was also mentioned. The effect of light irradiation to the wetting and electrochemical properties of NiO/Ni foam material was explained. Firstly, basic principles of wetting properties, sample preparation, other related

materials used in this study and the techniques used to measure the values of this property and how light irradiation affected to electrochemical properties. Some research literatures are used to explain how light irradiation taken place to the changes of the wetting property and the electrochemical property. In chapter III, the experimental methods are explained including sample preparation by thermal oxidation process, atomic structure and morphology studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM), the water droplet profile investigated by contact angle measurement, specific capacitance measured by cyclic voltammetry, the chemical forming on sample surface examined by x-ray photoelectron spectroscopy and the effect of light irradiation on their wetting and electrochemical properties. Chapter IV introduces results and discussion of the experiment including the effect of annealing temperature to the surface morphology and NiO crystal structure. The relationship between light irradiation, wetting and electrochemical properties is discussed. In this section, we investigate the wetting property and electrochemical properties of NiO/Ni foam material under UV irradiation. The details of the experimental results will be explained in this chapter. Chapter V stands for conclusion, summary and future plan.

CHAPTER II

REVIEW OF THE LITERATURE

2.1 Wetting properties

Wetting property is a property of solid surface which expresses the behavior of a liquid reaction or wettability of solid. This property can be observed by the distribution of the liquid on the surface of the solid substrate. This property is mostly measured by the contact angle measurements considering by three different phases as solid (substrate surface), liquid, and vapor at the equilibrium state. On the other hand, the liquid distribution may affect to the wetting property of solids which can be considered by the surface absorption property called “inert wetting or non-reactive wetting”. For example, reactive liquid will be absorbed on a substrate resulting to “reactive wetting”. The principle used to describe the wetting property is Young's equation. This equation is related to modeling the solid-liquid spread model. The sample is ideal solid which is physically and chemically inert, smooth, homogeneous and rigid. When the liquid is dropped on the surface of solid, there are two forces emerged; the cohesive force which is the attractive force between liquid molecules giving the fluid with circular appearance. Another force is adhesion force which acts at the interface between the liquid and the solid. This equation will consider the adhesion forces in terms of surface tension or surface free energies (Lamour and Hamraoi, 2010) which produce the contact angle. Thus, the contact angle measurement based on the equation of Young's equation is related to three phases which are solid (S), liquid (L)

and vapor (V) as shown in Figure 2.1 (Kumar and Prabhu, 2007).

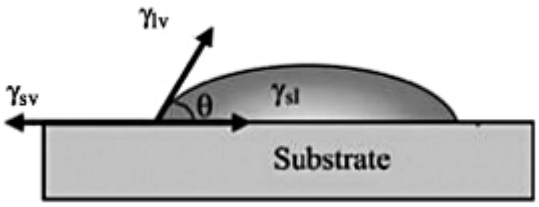


Figure 2.1 A liquid droplet on solid surface (Kumar and Prabhu, 2007).

Considering from the liquid droplets distributed on ideal surface at the equilibrium condition, there is an active force on liquid which is called dynamic driving force for wetting $F_d(t)$ as shown below.

$$F_d(t) = \gamma_{sv} - (\gamma_{sl} + \gamma_{lv}\cos\theta(t)) \quad (2.1)$$

Where γ_{sv} is the solid-vapor interfacial surface tension, γ_{lv} is the liquid-vapor interfacial surface tension, and γ_{sl} is the solid-liquid interfacial surface tension. At the equilibrium, liquid is not spread which means no driving force ($F_d = 0$). The Young's equation then transforms to.

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv}\cos\theta \quad (2.2)$$

The above parameters were defined as adhesion terms between solid and liquid as shown in equation 2.3.

$$W_{sl} = \gamma_{sv} + \gamma_{lv} - \gamma_{ls} \quad (2.3)$$

Substituting eq. 2.3 to eq. 2.1, we will get the equation which is well-known as Young-Dupre equation (Eq. 4) (Kumar and Prabhu, 2007).

$$W_{sl} = \gamma_{lv}(1+\cos\theta) \quad (2.4)$$

The relation between surface tension between each phases will affect differently to the contact angle and wetting property at the interfacial region of liquid and solid. Moreover, the surface tension value of each phases can also be used to describe the adhesive force which reflects to the wettability of solids. Figure 2.2 demonstrates the calculated contact angle and surface tension of three phases which reflects to the liquid profile used to explain the wetting property. As the size of contact angle, the liquid character and behavior on solid surface can be considered as; (1) if the contact angle is in the range of 0º-90º, the solid is called hydrophilic surface or partial wetting, (2) in case of 90º-180º, is called hydrophobic or partial non-wetting. Subsequently, the surface tension can also be calculated by Young-Dupre equation which can be used to explain in other experiments.

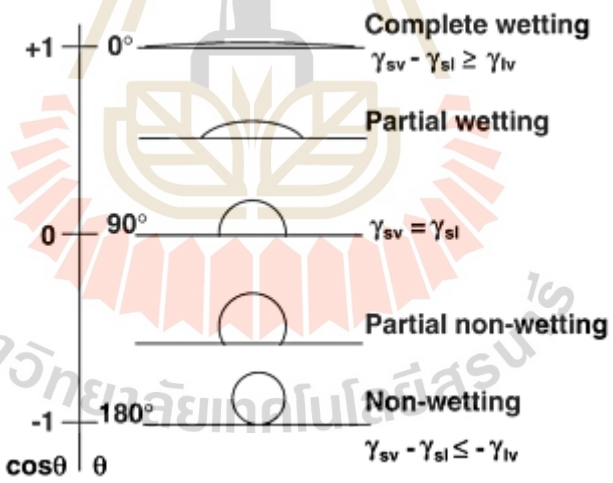


Figure 2.2 The profile of liquid droplet on surface substrate under various wetting condition (Kumar and Prabhu, 2007).

From above explanation, the contact angle was studied only for ideal solids, however, in real experiment is based on real surface which depends on various factors. To explain wetting property of real surface more precisely, some parameters such as

surface roughness and surface energies were implemented (Y. Y. Yan, Gao, and Barthlott, 2011). These extended models are known as Wenzel model and Cassie-Baxter model which are originated from Young's equation. The Wenzel model is used to describe the wetting property related to homogeneous wetting regime. The liquid droplet will contact at the peak and then penetrate to the surface pores as shown in Figure 2.3(b). The equation can be expressed as below.

$$R_f(\gamma_{sv} - \gamma_{sl}) = \gamma_{lv}\cos\theta_W \tag{2.5}$$

Substituting eq. 2.2 to eq. 2.5, we then got.

$$\cos\theta_W = R_f\cos\theta \tag{2.6}$$

Where θ is the Young contact angle, θ_W is the Wenzel contact angle and R_f is the roughness factor which defined by the surface area ratio between the rough surface and its projection on 2D plane. In case of hydrophobic surface ($\theta \geq 90^o$) as (Eq. 2.6), if the roughness factor is increased, it will affect to the decrease of θ_W. This reflects to the surface behavior to be more hydrophilic surface. Similar to hydrophilic surface, more hydrophilic surface is obtained if the roughness factor increases.

The Cassie-Baxter model was used to explain the surface behavior with heterogeneous wetting regime, i.e., the liquid droplet will be suspended on peak and does not penetrate into the valley as shown in figure 2.3(c). The Cassie-Baxter equation is derived from Cassie's law which describe wetting for two component surfaces as expressed below.

$$\cos\theta_C = f_1\cos\theta_1 + f_2\cos\theta_2 \tag{2.7}$$

Where f_1 and f_2 are the area fraction of component 1 and 2 respectively. The variable θ_1 and θ_2 are the contact angle for component 1 and 2 respectively θ_C is the

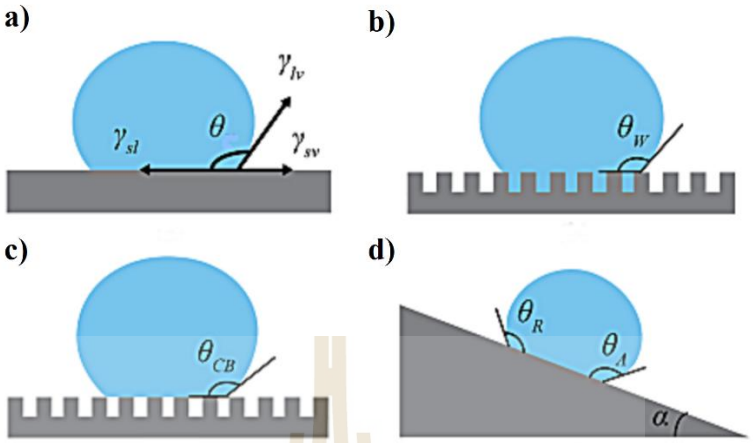


Figure 2.3 The model of liquid droplet (a) Young's model, (b) Wenzel's model, (c) Cassie-Baxter's model, (d) liquid droplet on an incline showing advancing and receding contact angle and sliding angle (Tam, Palumbo, and Erb, 2016).

contact angle of the composite. Air trapped in the valleys between the solid and liquid can be treated as one component with a water/air contact angle of 180º. From this relation, equation 2.7 can be rewritten to be the Cassie-Baxter's equation as below.

$$\cos\theta_{CB} = f_1(\cos\theta_1 + 1) - 1 \qquad (2.8)$$

Where f_1 is the area fraction of the solid surface in contact with the liquid droplet and θ_{CB} is the contact angle of the liquid droplet according to Cassie–Baxter. From the equation, the increase of area fraction will affect to the increase of contact angle and also decrease the adhesion force which result to slippery surface. As a result, hydrophilic surface can be modified to be hydrophobic surface by modifying the surface roughness (Tam, Palumbo, and Erb, 2016). It can be concluded from those two models that the Wenzel model demonstrates the high adhesive surface behavior while the Cassie-Baxter model is used to describe the low adhesive surface (Yong, Chen,

Yang, Huo, and Hou, 2017).

There are several methods to study the wetting property such as in the work purposed by Lamour et al. (Lamour and Hamraoi, 2010) which describe the technique used to measure contact angle and the surface tension of substrate. Surface tension can be obtained from the simplification of Young's equation. Surface tension can be obtained by measuring the contact angle of many liquid with known surface tension. The value of this calculation is based on the Fox-Zisman approximation of the first-order approximation related to the Good-Girifacal equation (Good and Girifalco, 1960). The surface tension of liquid at the critical surface tension of solid can be written as below.

$$\cos\theta = -1 + 2\left(\frac{\gamma_C}{\gamma}\right)^{1/2} \tag{2.9}$$

Using linear approximation from Fox-Zisman approximation, eq. 9 can be rewritten as

$$\cos\theta \approx 1 - \left(\frac{\gamma - \gamma_C}{\gamma}\right) \tag{2.10}$$

From equation 2.10, by plotting graphs between the contact angle of the liquid and the surface tension of the fluid by considering at $\cos\theta = 1$, the value of $\gamma_C = \gamma$ is the surface tension of the solid substrate which is located at the intersection. Figure 2.4(a) shows the setup of the device to perform the experiment. In order to determine the contact angle, the liquid volume $5\ \mu L$ is dropped onto the solid surface and the droplet profile will be analyzed. The contact angle value can be measured by using imageJ program as shown in Figure 2.4(b). After the experiments, the correlation between the contact angle value and the surface tension of the liquid will be plotted and analyzed. As shown in Figure 2.4(c), the surface tension of the glass slide coated with the

monolayer of octadecylsilane shows the values close to its real value. Therefore, if the solid surface has a surface tension greater than the surface tension of the liquid, then the solid surface exhibits hydrophilic behavior. If solid surface is less than the surface tension of the liquid, the solid surface exhibits hydrophobic behavior.

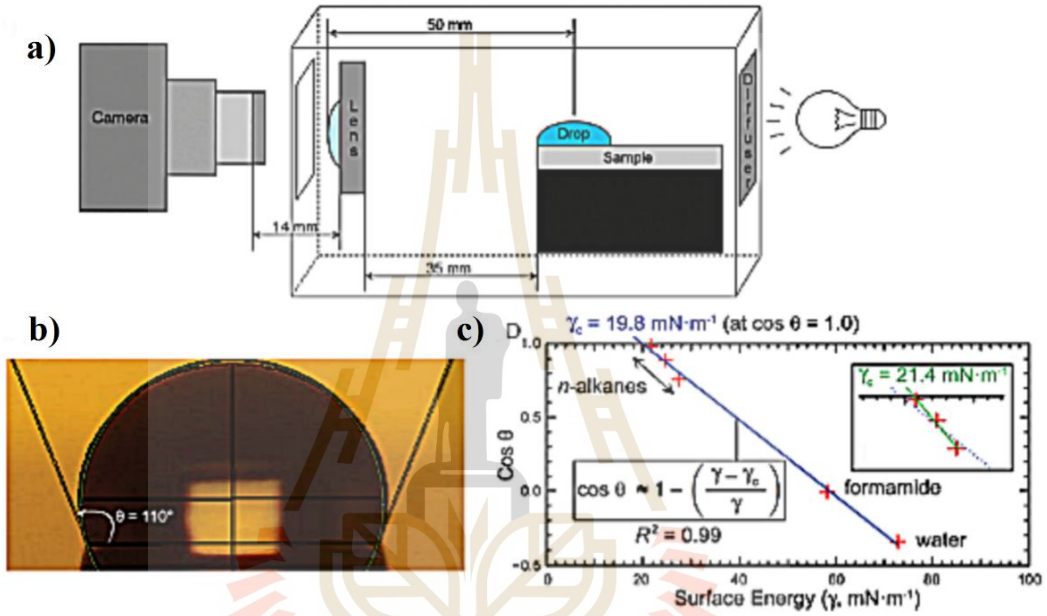


Figure 2.4 Contact angle analysis (a) set up experiment, (b) contact angle of water droplet, and (c) critical surface tension of solid surface. (Lamour and Hamraoi, 2010).

2.2 The effect of surface roughness and surface energy to the wetting properties

There are several factors that affect the wetting properties of solid such as surface roughness, heterogeneity of surface, flux, temperature, atmosphere, and liquid property (Kumar and Prabhu, 2007). Some of them is hard to control. Next, there are also some factors which are related to the surface of solid properties: the chemical composition of the surface and the texture of the surface (surface roughness). These two factors are very important variables which strongly reflect the wetting property of

the solid surface. The phenomenon in nature involving of these two factors is the lotus effect. There are nanoscale surface roughness corroborated with the coating skin on the lotus surface. It depends on how the surface behaves like a hydrophilic surface. In this case, the material must have a surface tension of solid that is higher than the surface tension of the liquid or hydrophobic surface (Li, Liu, Ye, Zhou, and Chen, 2011). This study investigated the relationship between surface morphology and surface roughness of samples coated with a substance. The surface tension is low with the wetting property. Copper plate was used as a substrate. From there, they prepared a sample of copper nanorod structure and microfluids by means of a simple one-step solution immersion process. The mixture between the KOH and $(NH_4)_2S_2O_8$ at different times, then the substance. Fluorescrysilane was used as a low surface energy material. The samples were then taken to see the topography of the surface. It was found that the SEM of the sample at varying time dipped in the strontium would be that the surface structure of CuO would be the change in shape of Figure 2.5 is that the more time it takes to dip, the more likely it is that the structure of the CuO surface will change. CuO samples were then modified by a low surface tension coating. Subsequently, they were subjected to wetting properties by measuring the contact angle and sliding angle as shown in Figure 2.6. CuO sample was modified surface by immerse process and coating. It displays the wetting property of a superhydrophobic surface, which has contact angle values such as, 162º, 160º, 154º and, 162º, respectively. The changes in the immerse time, such as 5 min, 10 min, 15 min, 30 min, and 60 min, respectively, are the same as sliding angle values that increase with immerse time, such as 3º to 12º and then to 90º and finally decrease to 28º. In addition, there is another work on the value of surface roughness that affects the contact angle.

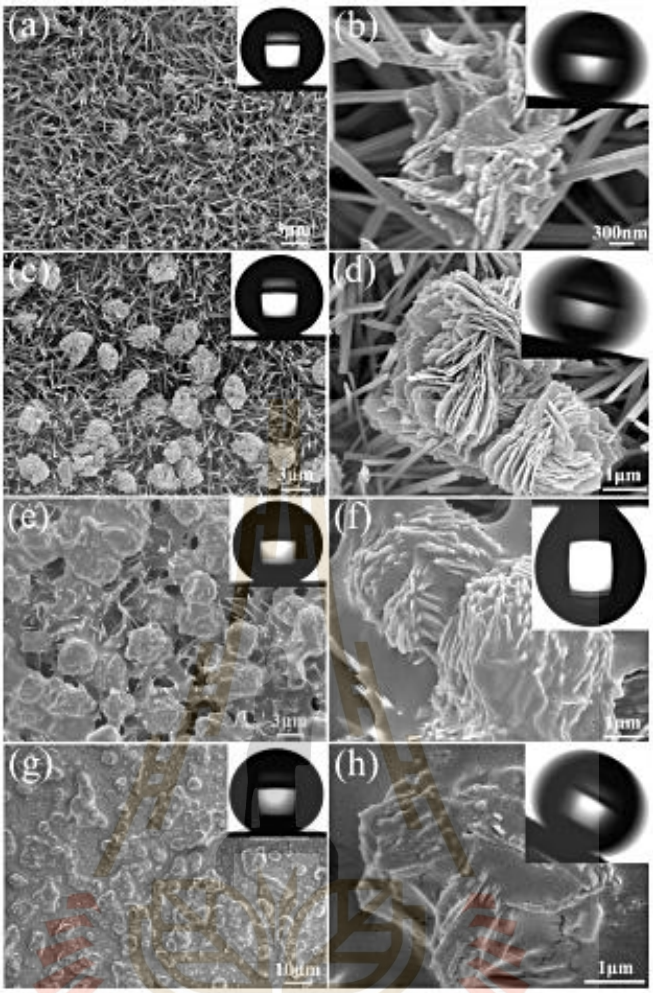


Figure 2.5 SEM image of CuO substrate in difference immerse time (a-b) 5 min, (c-d) 15 min, (e-f) 30 min, and (g-h) 60 min (Li, Liu, Ye, Zhou, and Chen, 2011).

In Kandlikar work (Kandlikar and Steinke, 2002), they studied the wetting properties of materials such as Copper and Stainless steel. In this experiment, the correlation between contact angle and surface roughness was investigated. For contact stainless steel, the contact angle is reduced from 72º to 25º and then increased to 40º, respectively, which changes from smooth to higher surface roughness. This results in the same trend as with copper as in Figure 2.7. When surface roughness has increased, this will cause the contact angle to increase again. This means that the increase in

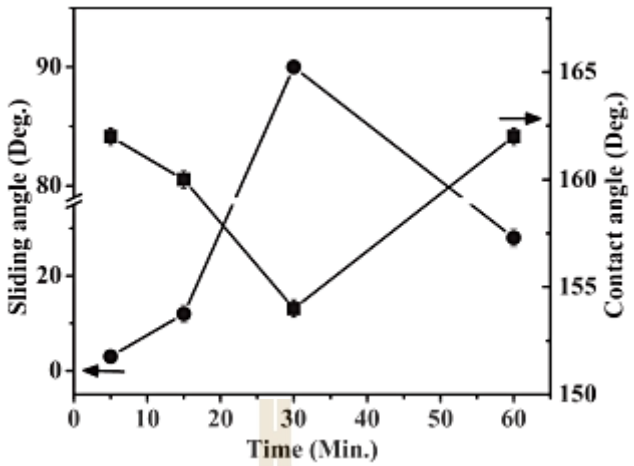


Figure 2.6 Water contact angle and sliding angle on CuO surface in difference immerse time. (Li, Liu, Ye, Zhou, and Chen, 2011).

surface roughness can result in increased contact angle. There is also another study to investigate the effect of surface roughness on the wettability of solids (Huang, Sarkar, and Chen, 2011). Electrodeposition was used to prepare the sample on the aluminum substrate by coating with copper prepared by stearic acid organic molecules. After electrodeposition at voltage from 0 V to -1 V for 30 min, the surface is modified with stearic acid for 30 min at 30 V. The experiment was conducted to study the effect of increasing the negative voltage in the negative direction. As a result, the surface roughness of the sample increases with the negative voltage. The voltage range 0 V to -1 V will increase the surface roughness from 2.39 μm to 7.00 μm , respectively (Figure 2.8(a)). Similarly, the wetting property with the surface roughness was found. The contact angle of the material is increased by the surface roughness from 113º to 157º and it is found that the surface roughness is about 6.00-7.00 μm . This is the point where the material exhibits the superconducting properties of the super hydrophobic surface as shown in Figure 2.8(b).

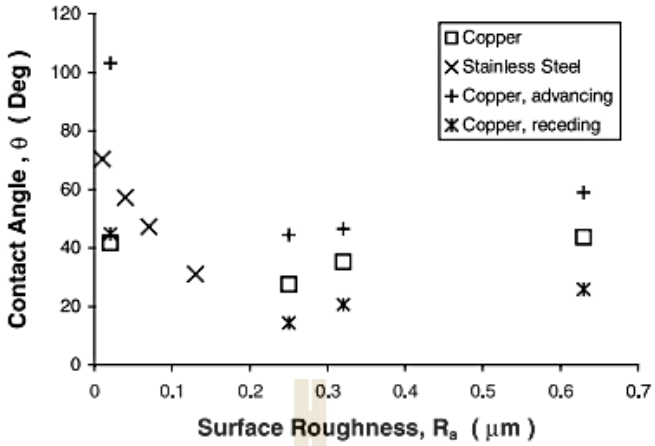


Figure 2.7 Equilibrium contact angle versus surface roughness for copper and stainless steel surface. (Kandlikar and Steinke, 2002)

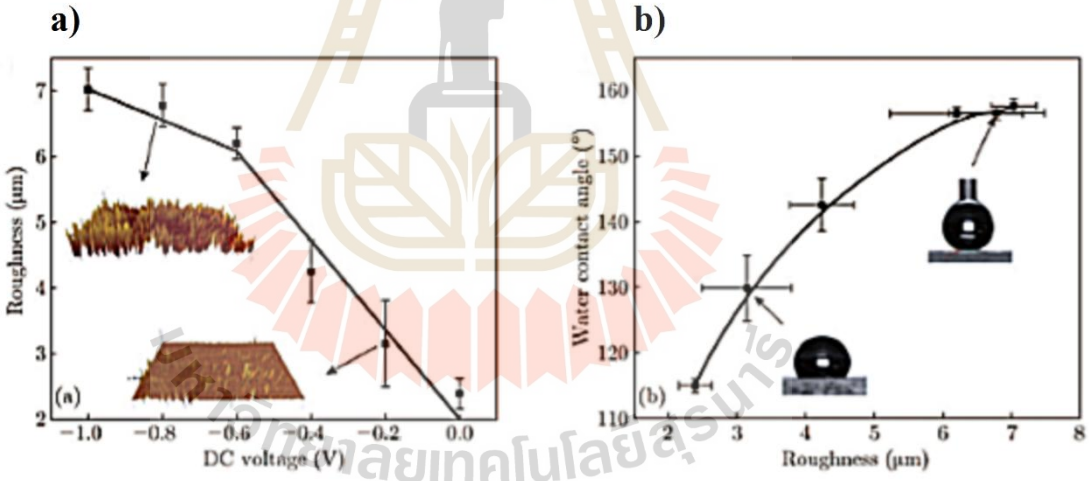


Figure 2.8 The effect of surface roughness to water contact angle (a) the variation of surface roughness versus deposition potential and (b) the variation of water contact angle versus surface roughness after stearic acid modified surface. (Huang et al., 2011).

The principle of wetting phenomena can be described by wetting model on ideal flat surface which has been purposed by Young in 1805. They explain the force between droplets and solid by the three-phase contact line between liquid, air, and solid. At the

equilibrium, the contact angle can be measured as shown in Figure 2.1 (Yong, Chen, Yang, Huo, and Hou, 2017).

2.3 Physical properties and application of Nickel oxide

Nickel oxide (NiO) is an exciting material that can be applied to various fundamental researches. It possesses unique features such as low cost and high specific capacitance (Gonzalez, Sanchez-Herencia, Ferrari, Caballero, and Morales, 2015). NiO can be prepared by various methods under high-temperature process. In general, NiO can be obtained by oxidizing nickel powder in ambient pressure with high heating temperature. For physical properties, NiO has a cubic lattice structure with a ferromagnetic property. It is a p-type semiconductor with a high band gap of 4.0-4.3 eV. The structure density is 6.67 g/cm^3 with the melting point of 1,995 ^oC (De Los Santos Valladares et al., 2014).

2.4 The specific capacitance in NiO/Ni foam

Supercapacitance is a crucial device to store extra energy from energy sources. This device is interesting in fundamental researches and industrials because of their high-power density and long cycling life. The materials used in supercapacitors are based on metal oxides such as NiO and MnO_2 and also the carbon base materials. These materials have unique properties and also low cost. High specific capacitance has been predicted in several metal oxides; for example, NiO was predicted to have relatively high specific capacitance up to 2,584 F/g (H. Yan et al., 2014). It is the promising material which can be used for fabricating the energy storage device. However, in the practical experiment, the specific capacitance of NiO was found to be

quite low due to its low surface area. To overcome this problem, many researchers attempt to grow NiO on Ni foam surface to obtain a high surface area of NiO. In the field of supercapacitors, researchers attempt to increase the specific capacitance of materials by improving the material's structure with various methods. Some methods to fabricate the supercapacitor device are discussed below.

Yan et al. studied the electrochemical properties of NiO nanosheet materials by using hydrothermal process. They tried to improve the specific capacitance of NiO by preparing the NiO nanosheet on Ni foam substrate. In the hydrothermal process, they operate the optimal condition as 400 ^{o}C for 40 min in a vacuum environment. The characterization of their work shows that NiO nanosheet can be formed on Ni foam substrate. Its surface was changed by increasing the surface area. The specific capacitance was investigated by using cyclic voltammetry experiment. The measurement showed an excellent improvement of specific capacitance. The high specific capacitance was measured up to 942.6 F/g at scan rate 2 mV/s. They showed excellent stability of 91.1% over 1,200 charge/discharge cycles at the current density of 5 A/g.

Zhu et al. attempted to study the improvement of specific capacitance in NiO/Ni foam involving metal oxide-based materials as a promising electrode. They prepared NiO/Ni foam by the thermal oxidation process with the optimal preparation of 500 ^{o}C for 2hr in the air environment. The NiO was well formed on Ni foam substrate which is used for an electrode material for the fabrication of supercapacitor device. The morphology of NiO/Ni foam was characterized by x-ray diffraction and scanning electron microscopy. As shown in figure 2.9(a-d), the NiO/Ni foam behaves like a porous structure with a high surface area. By using cyclic voltammetry, they showed that at the optimal scan rate at 5 mV/s, NiO/Ni foam exhibits the high specific

capacitance of 1784.2 F/g which is closed to the theoretical specific capacitance of NiO. This result showed the good stability of 75.8% capacitance retention over 20,000 charge/discharge cycles at 5 A/g which due to the low contact resistance between NiO and Ni foam structures.

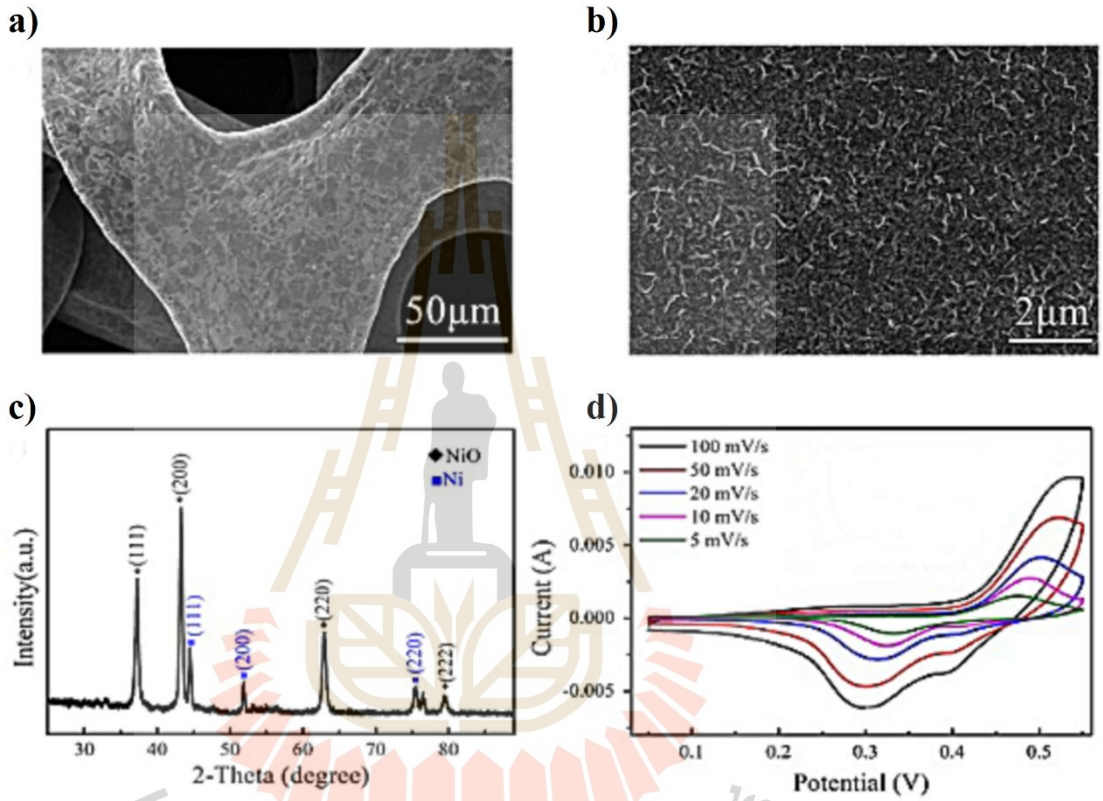


Figure 2.9 The characterization of NiO/Ni foam (a-b) SEM image of NiO/Ni foam, (c) XRD curve of NiO/Ni foam, and (d) CV curve of NiO/Ni foam (Zhu et al., 2015).

2.5 Wetting property in NiO

Wetting property of materials is widely studied in various fundamental researches and industrial applications (Banerjee, Dionysiou, and Pillai, 2015). This property informs about the solid surface behavior. The use of this property can apply in various applications especially the ability to clean its surface called ‘self-cleaning material’. The example of self-cleaning material can be seen on the surface of a lotus

leaf. It can repel water droplets which are known as “lotus effect”. The characteristic of wetting property can be divided into two types: (1) the hydrophilic surface which water droplets can be spread over all surface of the substrate and (2) the hydrophobic surface which water droplets quickly rolls off on the surface of a substrate. The applications of lotus effect have been developed to apply in various fields such as window glass, solar panel, anti-corrosion, and anti-biofouling. From the special application of wetting property, many researchers attempt to develop the surface of material achieving as self-cleaning material. The enhancement of wetting property relies on two main processes which are the control of surface energy and surface roughness. There are various methods to control the wetting property of materials such as electric deposition, plasma process, chemical etching, electrospinning, chemical vapor deposition, and UV light irradiation. Literature reviews of the wetting property based application have been reported in the field of the oil-water separation application which relates to the environment protection and oil spill problem in the ocean ecosystem.

Gao et al. reported the application of wetting property prepared by Ni foam for the oil-water separation. They used high porous-Ni foam as the substrate with a high surface area which is suitable for the oil-water separation application. They grew the cobalt nanowire on Ni foam substrate by a simple template-free ammonia-evaporation-induce method and modified the surface after growth by coating the polymer of fluoroalkylsilane (FAS) on the surface. After sample preparation, they characterized the morphology by SEM technique. In the measurement, they showed that the growth of cobalt nanowire on Ni foam surface could increase the surface roughness. They used the contact angle measurement to obtain wetting property and the result showed that surface behavior of their samples is highly hydrophobic with a high contact angle of

(156±2)º and sliding angle of 2º as shown in figure 2.10(a-b). The oil-water separation treatment is shown in Figure 2.10(c-d). This sample can be used to separate the liquid mixture between oil and water. This is due to the polymer of FAS behaving like hydrophobic material for only water which repels water droplets but hydrophilic material for oil. From these results, this process was served to develop the surface materials as Ni foam which could be applied in various application in the future. Wang and his team have reported the fabrication of Ni foam base on oil-water separation (Wang et al., 2015). They used a simple one-step copolymerization method to modify the surface of Ni foam by coating the organic film on Ni foam surface with dopamine and octadecylamine. In the characterization process, they showed that the water contact angle was (154±2)º and the sliding angle was (4±1)º. In the oil-water separation treatment, it was found that modified-Ni foam sample can fast removed oil from water.

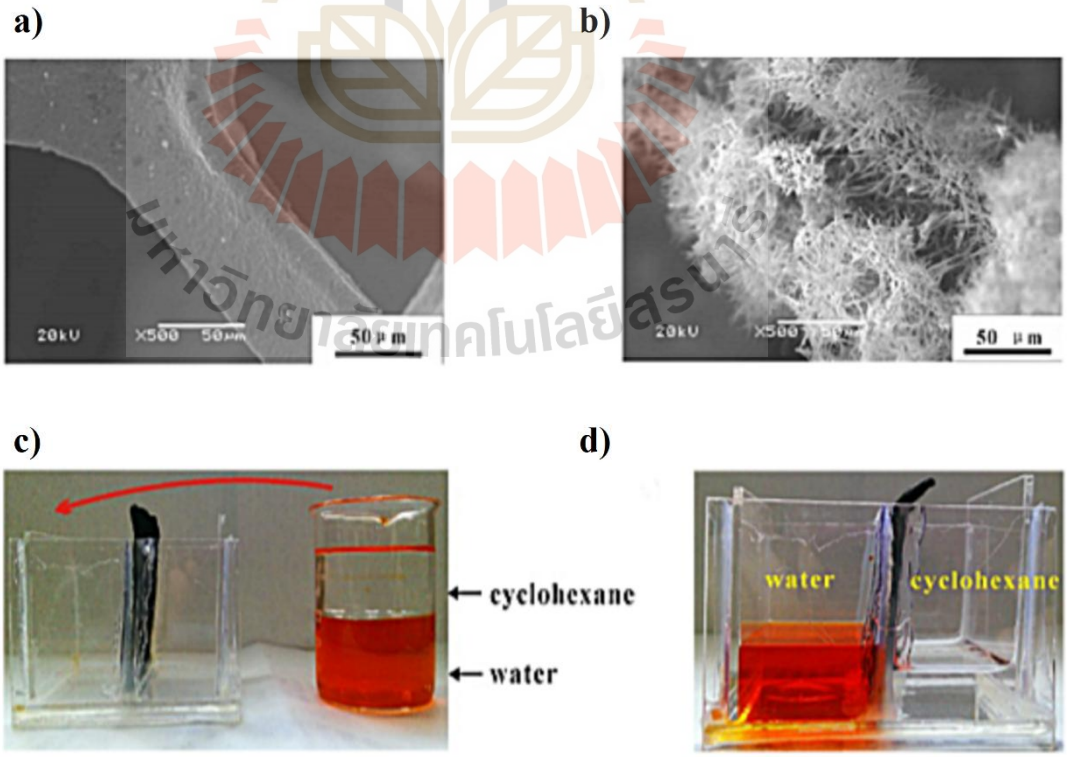


Figure 2.10 Ni foam treatment for oil-water separation (a) the original Ni foam sample,

(b) the Cobalt nanowire growth on Ni foam, and (c-d) the oil-water separation (Gao et al., 2014).

2.6 Light illumination induce wetting properties and specific capacitance

Light irradiation is a technique which is used to modify the surface material as well as the surface property. The material, which possesses the ability to control surface property, is called the smart material or self-cleaning material. The mechanism for light irradiation induced wetting property modification relies on the response of the surface where the energies of light can conduct the surface composition by chemical forming. In the other meaning, the effect of light irradiation can etch the surface of the substrate which results in the surface structure and the changed of its surface property. The light source of most experiments are based on the UV light and the most studied materials are metal oxides. Some oxide materials can respond to UV light irradiation because they have suitable band gap which can conduct and create the oxygen vacancies. The oxygen vacancies can induce the special property in oxides. UV light can be used to control the wetting property which is also called as UV light photo-oxidation method.

Materials were studied for wetting properties under irradiation. In general, they will be semiconductor oxide materials such as TiO_2 and ZnO. Because these materials have the characteristics of the band gap appropriate to respond to light. So when light falls on the material, it will lead to the creation of the electron-hole pair. The electron-hole pair will interfere with the surrounding molecule. This will result in the formation of surface hydroxylation. This will cause the wetting property of the material to change. TiO_2 is a well-known material because it is used in many industrial applications, such as coating materials on the glass, which can be cleaned. In addition, it has special optical

properties: light affects the surface property by causing the light to induce it to become a good hydrophilic state and has contact angle values close to 0º. When it is placed in a dark place, its surface property is reversed, and the contact angle is increased to its original value. (Wang and Hashimoto, 1998) at the work, they studied the wetting properties of TiO_2 under UV light irradiation. They prepared the TiO_2 thin film polycrystalline from anatase sol on glass substrate, which made anneal at 773 K. The contact angle before UV light irradiation is approximately 72º and change to approximately 0º after the UV light exposure.

Moreover, the sample was kept in the dark lead to not transparent. Whereas, when the under irradiation sample is on the same area the sample is covered by water and good transparency. Therefore, irradiation results in the surface of the sample indicate that the sample increase hydrophilicity. On other hand, hydrophilic property can be reversible when the sample is placed in a dark place, the contact angle is increased with increasing time. The effect of UV light irradiation on high performance of hydrophilic property is reported by Banerjee and Dionysiou. There are various models were supposed to understand the mechanism of photo induced hydrophilicity. First, the UV irradiation leads to a structural change. It can be implied that UV irradiation generates oxygen vacancies. Other model, the UV irradiation causes the reconstruction of hydroxyl group at the surface. Mills also reported the self-cleaning action of TiO_2 prepared using chemical vapour deposition technique. Photocatalytic surfaces were irradiated with UV lamps (254 nm wavelength) as a function of time. The contact angle firstly measured had been found to be 67º and then after 60 min irradiation, the contact angle value was decreased to 0º. However, the wettability of TiO_2 coatings after storage in the dark are increased with the increasing time. This

result caused by the oxygen vacancy which induced hole at the surface and deconstruct Ti and O bond. These Ti and O react with H_2O molecule which generates the hydroxyl group at the surface.

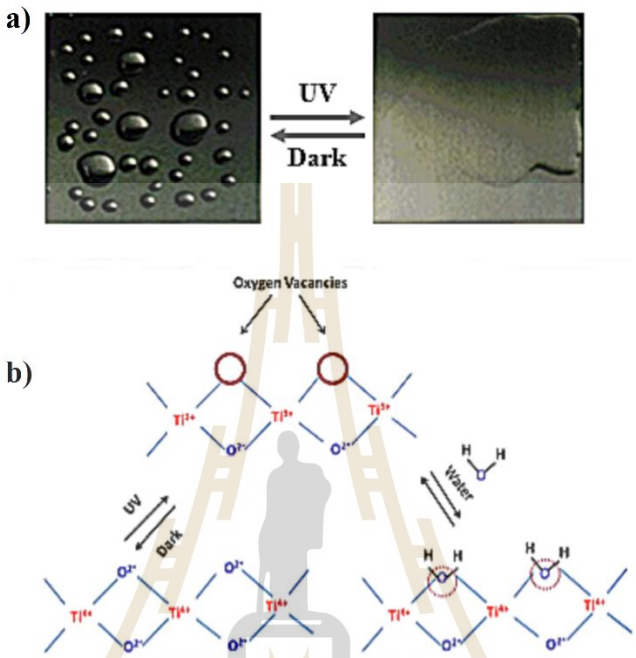


Figure 2.11 UV light exposure on TiO_2 surface (a) the wettability of TiO_2 surface and (b) the schematic of photo-induced hydrophobicity. (Banerjee, Dionysiou, and Pillai, 2015).

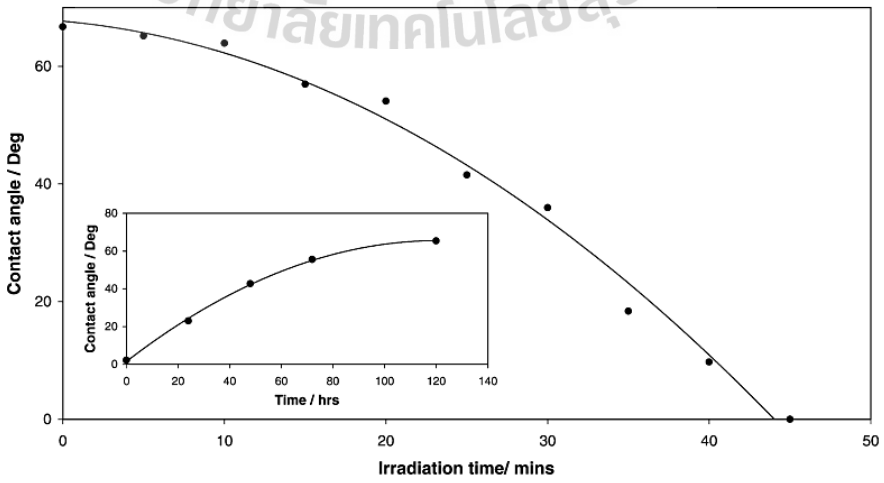


Figure 2.12 The variation of water contact angle as the function of time under UV light

irradiation and the inset diagram observe the dark recovery. (Mills et al., 2003).

Caputo et al. reported the process of UV light switchable the wetting properties. In their work, they studied the wetting properties of TiO_2 which could be changed the surface behavior from a hydrophobic surface to a hydrophilic surface under UV light irradiation. In the experiment, they fabricated the surface substrate of Si wafer by using the photo-lithography as a patterned surface substrate with TiO_2 coating on the top surface. For the wetting property with UV light irradiation experiment, they found that the water contact angle could be changed from hydrophobic surface to hydrophilic surface as shown in Figure 2.13 The explanation of this mechanism could be explained by the UV light irradiation induced some vapor molecules in the air to form the OH^- groups on TiO_2 surfaces by the chemical reaction process. The nature property of OH^- group is to attract to the water molecules which leads to the changing of the surface behaviors. In the opposite investigation without light, they found that the OH^- groups were reduced from TiO_2 surface because it had not enough energies to create the electrons and holes to form OH^- groups with the chemical forming process. In another experiment, Gu and his teams reported the fabrication of superhydrophobic materials by using the UV-photo oxidation method to fabricate the sample (Gu, Qi, Wu, Zeng, and Song, 2014). In the experiment, they prepared the substrate by using the polyimide (PI) film as a substrate. The modification of surface substrate could be achieved by using UV light irradiated on the substrate and the polymer of fluoroalkysilane (FAS) was coated on the surface substrate after UV light irradiation. In the measurement, they characterized the wetting property of the surface substrate

and found that under UV light irradiation the surface roughness of surface substrate was

increased from 1.74 nm to 53.70 nm. Also, to modify the surface after UV light test with FAS, the water contact angle was increased from 105.1º to 159.2º. So this technique of UV light irradiation suited to apply for the fabrication of superhydrophobic surface and various application.

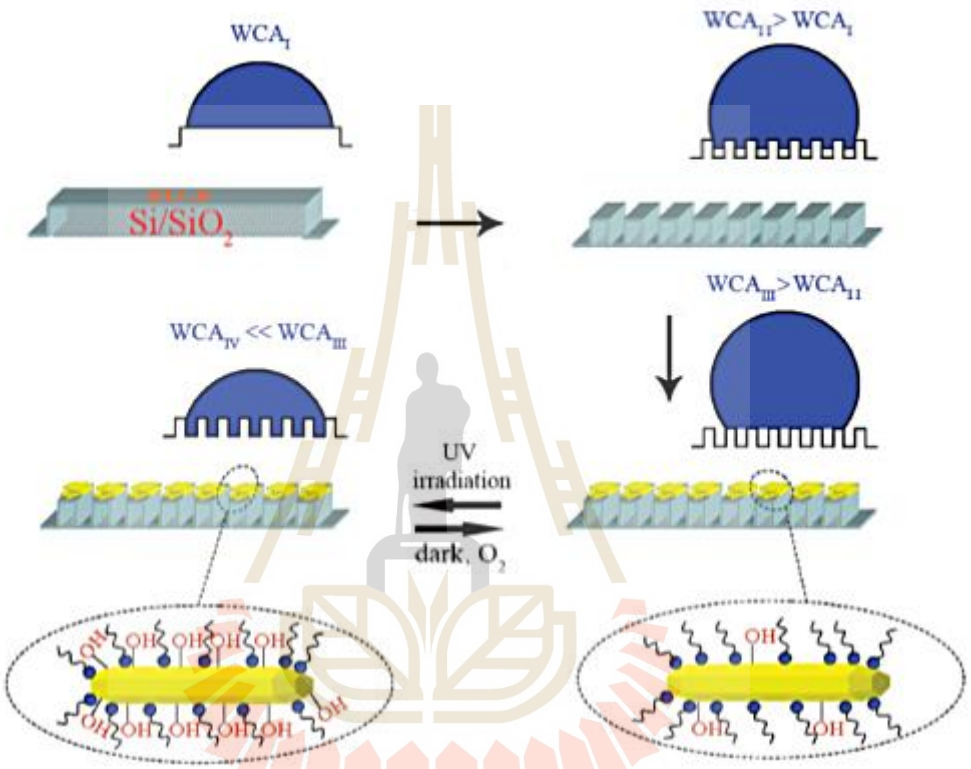


Figure 2.13 The pattern fabrication process and UV light irradiation induce OH^- group (Caputo et al., 2009).

The significance of light irradiation in a field of electrochemical property concerns to the enhancement of specific capacitance of the supercapacitor device. The supercapacitor device is a type of the energy storage which use to collect electrical energy in term of the charge carriers. The potential application of the supercapacitor relies on the material property. It is designed as electrode materials which lead to the development of specific capacitance or areal capacitance properties. The application of

the supercapacitor can be applied in various fields of electrical devices such as mobile phone, power supply, and solar cell. Light irradiation is one method to enhance the electrochemical property without changing intrinsic elements.

Kalasina et al. reported the result of light irradiation to increase the areal capacitance. In this work, they used Cobalt hydroxide material (2.85 eV energy gap) to fabricate an electrode for the supercapacitor device. In the experiment, they prepared the electrode of a device corresponding to the double layer of Cobalt hydroxide substrate by a sheet-like structure. To study the electrochemical property, they irradiated the blue LED on the electrode during the cyclic voltammetry measurement in 6M KOH electrolyte. The result in experiments provided that the areal capacitance of modification device under LED blue light was increasing compared to the original device without blue light treatment as shown in figure 2.14(a-b). The explanation of areal capacitance increasing has been described by the creation of charge carriers with a redox reaction.

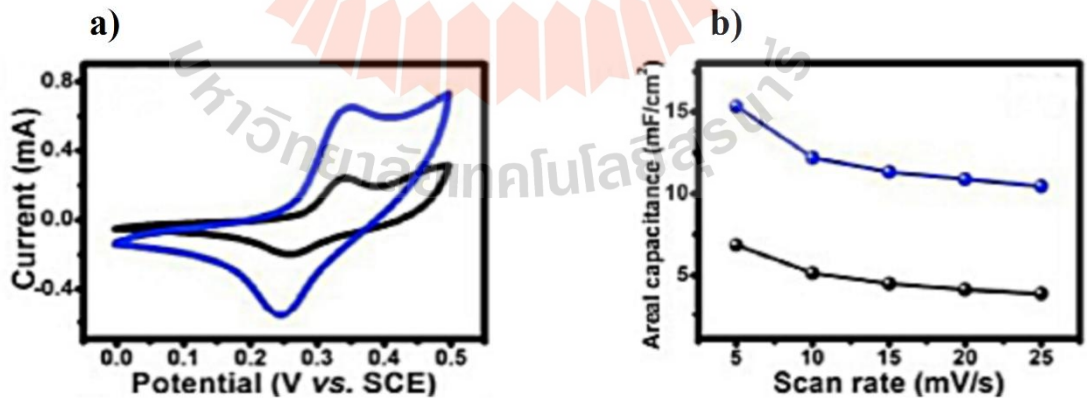


Figure 2.14 Cyclic voltammetry measurement (a) the CV curve of $_2$ $Co(OH)_2$ as a capacitor in 6 M KOH electrolyte and (b) the areal capacitance (Kalasina et al., 2017).

CHAPTER III

RESEARCH AND METHODOLOGY

In this part, we will introduce methods to prepare NiO/Ni foam sample and the process to characterize the surface and electrochemical properties. After the experimental results, the explanation of NiO/Ni foam surface property and the mechanism of NiO/Ni foam under UV light irradiation will be discussed. The procedure of this work can be summarized as below.

3.1 Sample preparation

In this work, we prepared NiO/Ni foam by the thermal oxidation process. Ni foam was obtained from the commercial Ni foam with purity of 99.99% (MTI corp.). Before the experiment, we cleaned the Ni foam in a two-step. First, the Ni foams were cut in size of 3x5 cm^2 as shown in figure 3.1(a), cleaned by ultrasonic method for 30 min in acetone, ethanol and DI water, respectively, to remove their surface contaminants such as oil and an organic compound. Second, these Ni foams were then immersed in HCl acid solution as the concentration 1 M for 1 hr to remove some excessive oxide over layer. The obtain Ni foam, the as-prepared sample was washed several times with ethanol and DI water to remove HCl acid, respectively, and dried in an oven at 50 ^{o}C for 1 hr. After cleaning process, we synthesized NiO/Ni foam by thermal oxidation process. Ni foams were calcined in ambient pressure at 500 ^{o}C for 1 hr with heating rate 5 ^{o}C/min which was the normal condition to form NiO/Ni foam. The sample surface after calcining process was found to change the color from grey to

black color which indicated the formation of NiO films on Ni foam (NiO/Ni foams) as shown in figure 3.1(d). The prepared NiO/Ni foam were then studied the surface property and electrochemical property by using the contact angle measurement and cyclic voltammetry measurement under UV light irradiation.

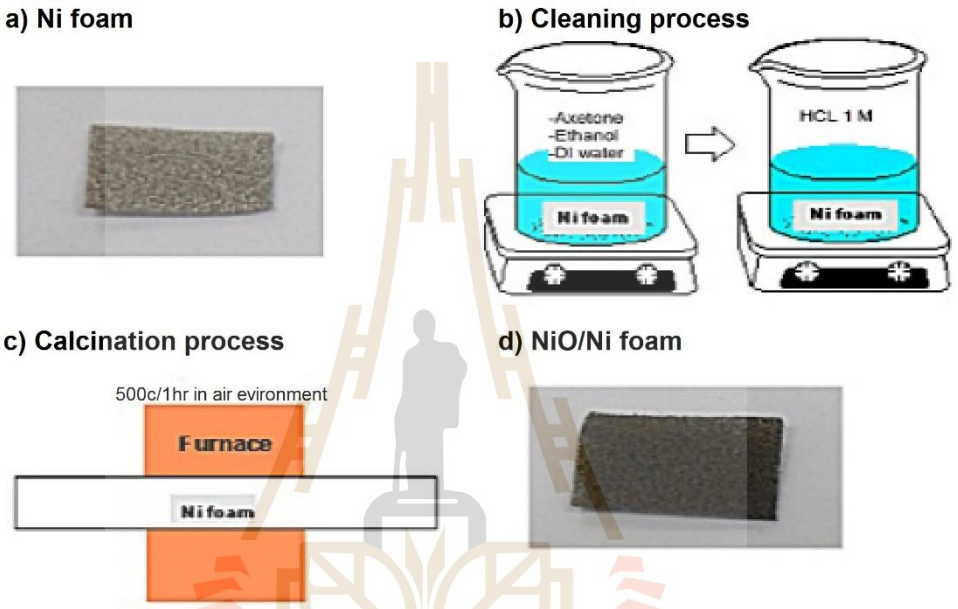


Figure 3.1 The sample preparation process (a) Ni foam before cleaning, (b) Ni foam in cleaning process, (c) calcination process, and (d) NiO/Ni foam.

3.2 Sample characterization

3.2.1 X-ray diffraction: XRD

The x-ray diffraction technique is the method to study the arrangement of atom structure, the identification of the element in the crystalline structure, and the providing information on unit cell dimension. This technique can be classified the difference between amorphous and crystal including to some physical properties of materials. The principle of x-ray diffraction or XRD technique is based on the

constructive interference wave of monochromatic x-rays and crystalline sample. X-ray beam is generated from a cathode ray tube and controlled the energy by monochromatic crystal as shown in figure 3.2(a). In the process of x-ray interaction, when the x-ray beam incident on the sample surface which represents the wave input. It then reacts to the atom of a sample that results in the scattered beam to create the second wave which represents as wave output. This x-ray beam is combined to be the destructive interference and constructive interference that can identify the structure of materials with an explanation by Bragg's law as equation below as shown in figure 3.2(b). As $2d\sin\theta = n\lambda$ Where d is the lattice interatomic spacing in the crystal (m), n is an integer, θ is the diffraction angle (degree), and λ is the wavelength of x-rays bream (m). In the characterization process, the intensity of x-ray bream is directly applied to an incident on the sample surface, and then the detectors detect the bream output as the function of intensity represent I (a.u.) via the scanning rage of 2θ angle (degree). The result is plotted as the diffraction peak of XRD pattern which can be used to identify the atomic element, atomic distance, atomic arrangement structure, etc. This information is achieved by comparison of the standard reference pattern, and it can be applied in many fundamental types of research for studying the structure of materials.

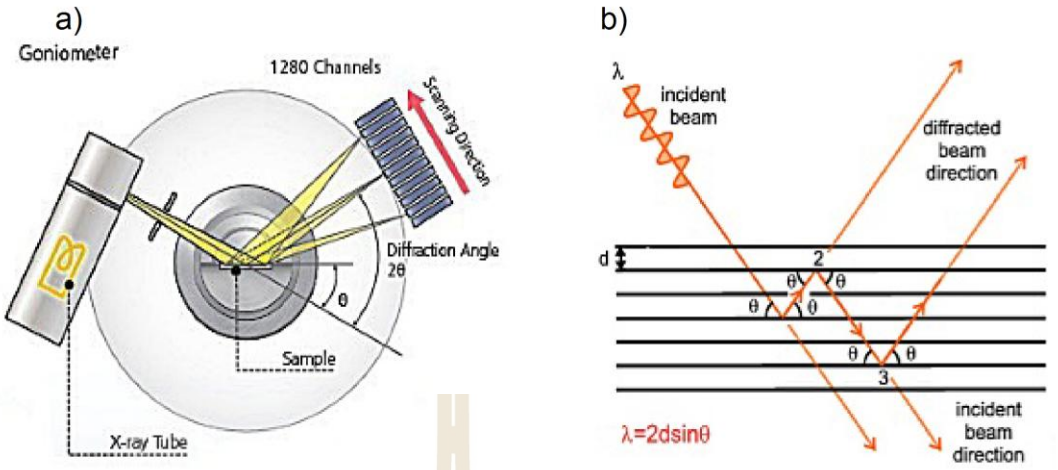


Figure 3.2 The x-ray diffraction principle (a) inside the instrument and (b) procedure of x-ray diffraction process.

3.2.2 Scanning electron microscopy: SEM

Scanning electron microscopy is one technique to characterize the surface morphology of material by using the high energy of electron beams to scan on the sample surface. The principle of scanning electron microscopy relates to the accelerated electron from an electron gun to produce the x-rays beam. Scanning electron microscopy technique relies on the interaction between electron beam and electron around an atom of materials to create the waveform as the signal which can be converted to the morphology of materials surface. During the x-rays beam incidents on the surface material that generate the electrical signals. There are many signals including such as a secondary electron, backscattered electron, diffraction backscattered electron photons, visible light, and heat. These signal can be used to identify the structure of the material. In the morphology and topography images are obtained from the secondary electron and backscattered electron signals. This measurement is non-destructive technique because

it is not damaged the sample surface. In the experiment, when the electron beam from the electron gun incident on the sample surface. This electron will interact with electrons near atomic on the specimen surface that lead to scattering electrons of a sample surface and can be detected by the detector. The electron detector can convert the data of electron signal as an electrical signal to the importance data to be the morphology of the sample surface, crystalline structure, chemical composition, electrical conductivity, and the orientation of materials. In the sample preparation to do SEM, the sample must be conducted electrical or coat with metal materials due to the SEM can detect only an electron. The basic concept of SEM shows in Figure 3.3 below.

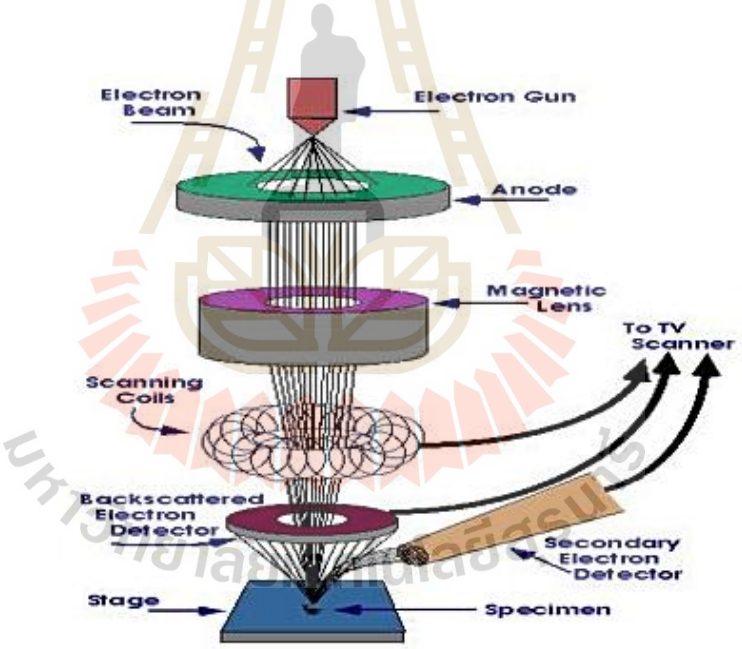


Figure 3.3 The scanning electron microscopy instrument.

3.2.3 Light irradiation setup and Contact angle measurement

The contact angle measurement is the technique to investigate the surface properties of materials. The effect of surface treatment is attractively studies in various part of fundamental research in surface science such as wetting properties, water repellency, and abrasion resistance which can apply in the various field of industrial application.

In this work, we focus on the wetting properties. The definition to study the wetting properties of materials can be explained by Young's equation that concern to the relationship between the contact angle and the surface energies as below.

$$\gamma^{SV} - \gamma^{SL} = \gamma^{LV}\cos\theta \tag{3.1}$$

Where γ^{SV} is the solid surface free energy (J/m^2), γ^{SL} is the solid-liquid interface free energy (J/m^2), γ^{LV} is the liquid surface energy (J/m^2), and θ is contact angle (degree).

These parameters relate to the surface free energy of the system containing between solid, liquid, and vapor. In the ideal of this relationship can be introduced by a liquid droplet which contacts on the solid surface and results to force acting at the interface. There are two forces acting represent to be the adhesive force involve the interaction molecules between liquid and solid at the interface and the cohesive force which relate to the interaction of liquid molecules.

In this work, we attempt to study the surface properties of NiO/Ni foam surface under UV light irradiation. The experimental setup and the characterization process consist of many steps. A 405 nm UV laser was used as a UV light source for the UV light irradiation experimental setup. The laser was connected to the power supply which the intensity of laser can be adjusted by varying applied voltage. The UV light intensity was measured by an Optical power meter (Thorlabs model PM100D). In

the experimental measurement of contact angle, a UV light was exposed perpendicular to the NiO/Ni foam surface at a distance 5 cm away from the sample surface as shown in figure 3.4(a). After UV light irradiation, a contact angle measurement was then immediately performed on irradiated NiO/Ni foam surface. A DI water droplet 10μL was dropped on NiO/Ni foam surface. A high-resolution camera was used to take the snapshot of the water droplet and then conducted to process the black-white image by using ImageJ program. The angle formed between the solid/liquid interfaces is represented to be the contact angle: CA. The process to measure the contact angle relates to the profile of water droplet on a sample surface. The profile of two-dimensional of water contact angle was taking between the solid and the droplet profile as shown in figure 3.4(b). In this work, the contact angle measurement was performed in two conditions such as the function of time exposure (0-30 min with 50mW fixed intensity) and UV light intensity (0-130 mW with 30 min fixed time exposure).

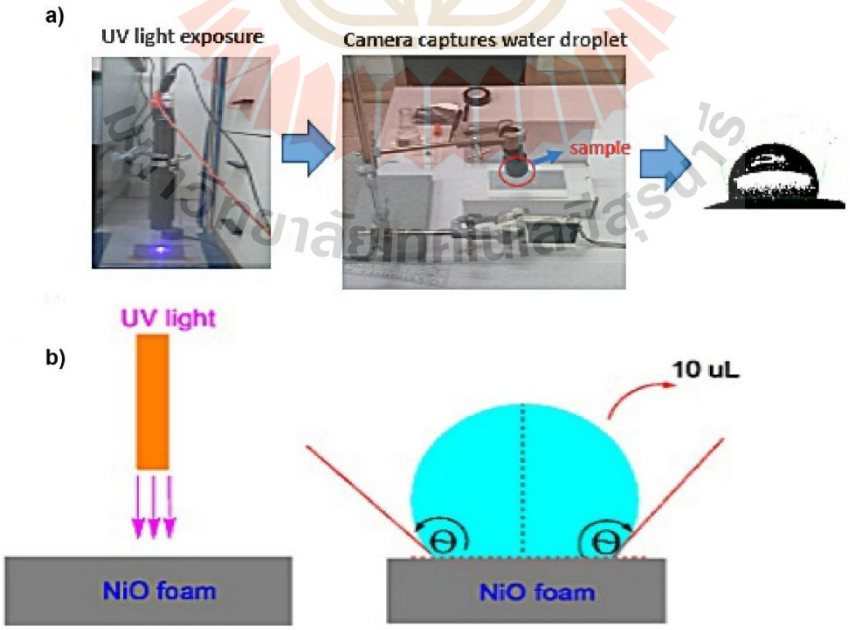


Figure 3.4 The contact angle measurement process (a) setup experiment and (b) contact angle measurement.

3.2.4 Cyclic voltammetry measurement

In the cyclic voltammetry measurement is the technique to characterize the electrochemical properties of the materials for studying the redox reaction on the sample surface. It is widely used various fundamental research to analyze the information about the electrochemical reaction process. In the experiment of my work, we apply the voltage through the electrode cell as varying the scan rate and window potential until the signal is stable while detecting the current signal during the operation. All data from the measurement can be used to plot in function as current vs. voltage curve (CV curve) which leads to explain the electrochemical with the redox reaction process that concern to what the peak of the curve is oxidation or reduction reaction process. The relationship of the peak and CV curve gives the information of the chemical process. This result can be used to indicate the element state of chemical reaction follows with the peak characteristic as oxidation reaction process or reduction reaction process. In the current-voltage curve of measurement can be used to calculate the capacitance of materials that relate to the potential of materials to store charge.

In the calculation, we can bring the data from the experiment input to Igor program and plot c-v curve measurement to calculate the specific capacitance. The capacitance of NiO/Ni foam can be determined and compare between UV light and no UV light. The specific capacitance can be calculated by the equation below.

$$C_s = \frac{1}{mv\Delta v}\int I(t)dt \qquad (3.2)$$

Where C_s is specific capacitance (F/g) of NiO/Ni foam, ΔV is operation potentials windows (V), v is scan rate (mV/s), m is mass of sample (g), and $\int I(t)dt$ is an area of the current-time curve, respectively. And the diagram of cyclic voltammetry as shown in Figure 3.5.

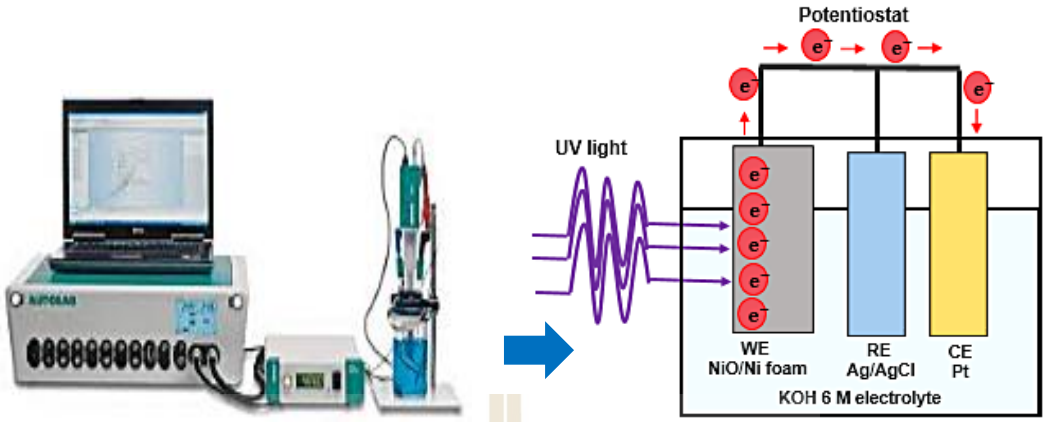


Figure 3.5 Cyclic voltammetry measurement setup.

3.2.5 X-Ray Photoemission spectroscopy

In the studying of the chemical forming on surface of materials, we used the x-ray photoemission spectroscopy: XPS at beam line 5.3 (XPS) of Synchrotron Light Research Institute (SLRI). This technique is the process to analyze the chemical element on the sample surface by using the x-ray beam incident on sample surface. It can be apply in various material such as metal, glass, ceramic, plastic, and semiconductor. The principle of x-ray photoemission spectroscopy technique rely on photoelectric effect show as figure 3.6. When the x-ray beam or photon light with energy hv was incident to atom of sample surface. This atom absorbed the energy until the electron escape from the orbital which had the kinetic energy. It was detected by the instrument of XPS technique which represent to be intensity. From this intensity, it accord to the binding energy of each element which can be used to identify the chemical element of the sample. Also when electron leave from the orbital the nearby electron will stead as same position call relaxation electron. It will emits the energy in form x-ray fluorescence. When this energy collides to valence electron until it escape from the orbital call auger electron. So from the process of electron emits the energy we can used

this technique to measure the kinetic energy of electron. The relation between spectrum of energy or intensity and binding energy can be used to identify the element because these element will give the characteristic spectrum The kinetic energy can be calculate from the equation 3.3.

$$E_k = eV_s = h\nu - W - E_B \quad (3.3)$$

where W is work function (eV), h is Plank's constant,V_s is stopping potential, E_B is binding energy, E_k is kinetic energy of photo-electron, e is the electron charge and ν is the frequency of incident light.

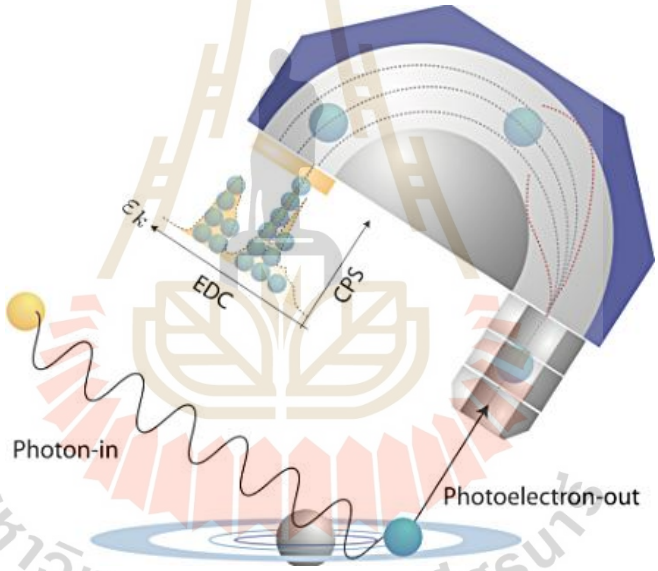


Figure 3.6 X-ray photoemission spectroscopy technique (http://www.slri.or.th).

CHAPTER IV

RESULTS AND DISCUSSION

The contents in this chapter are sample characterization by X-ray diffraction and scanning electron microscopy. The wetting and electrochemical properties were studied by contact angle and cyclic voltammetry measurements. The contact angle was used to study the wetting property which has been applied in two conditions e. g. as a function of irradiation time and light intensity. Surface morphology and crystal structure of the samples annealed with different temperature have been characterized by XRD and SEM. Next, the electrochemical property was measured by cyclic voltammetry which can be used to study the chemical specie changing under light irradiation. The changes of wetting property in NiO/Ni foam under UV irradiation will be discussed in this chapter. Overall results shown in this chapter might be concluded that the wetting property can be modified by the changes of surface roughness and surface energy of chemical forming.

4.1 X-ray diffraction patterns of NiO in different annealing temperature

We attempt to study the formation of NiO on Ni foam by using X-ray diffraction technique. For calcination process of Ni foam, we found that the XRD pattern was changed as shown in Figure 4.1.1 From this result, we can see the Ni peaks which can be labeled by (111), (200), and (220) taken from the standard database in all sample.

The mechanism of forming the NiO film on Ni foam can be explained by the decomposition of thermal reaction due to the oxygen forming reaction. This result shows the change of crystal structure of sample Ni foam calcined at different temperature (0 ºC, 400 ºC, 500 ºC, 600 ºC, and 700 ºC, respectively). From XRD pattern, the pure Ni foam shows only Ni phase emerged at the angle (2θ) equals to 45º, 52º, and 78º, respectively. The XRD pattern of the sample annealed at 400 ºC does not change which can be described that the annealing temperature below 400 ºC cannot change the Ni foam structure. However, at annealing temperature between 500 ºC to 700 ºC, there are some new peaks emerged which is increasing as annealing temperature increases. These peaks refer to the NiO which suggest the formation of NiO on Ni foam upon increasing temperature. Overall, from XRD results, NiO phase can be formed by annealing the Ni foam at temperature higher than 500 ºC. The samples with NiO phase will be later called as NiO/Ni foam.

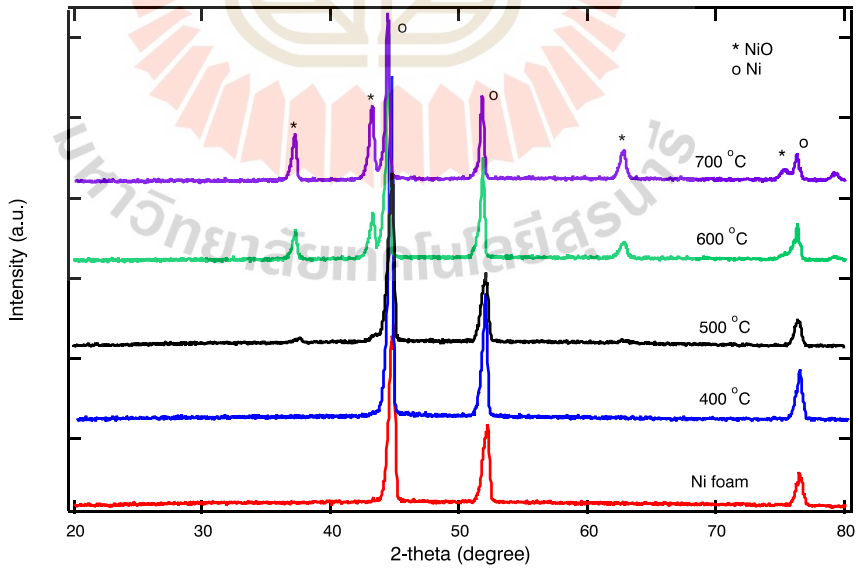


Figure 4.1 X-ray diffraction patterns of Ni and NiO/Ni foam under annealing temperature ranging from 0 ºC, 400 ºC, 500 ºC, 600 ºC, and 700 ºC, respectively.

4.2 Sample morphology characterized by scanning electron microscopy and energy dispersion spectroscopy.

The SEM results of Ni foam and annealed Ni foams at different temperature are shown below. Figure 4.2(a-b) shows the morphology or Ni foam using 100x and 5000x magnifications. From this figure, they show a big pore where the Ni are formed homogeneously. SEM image of pure Ni foam formed as a stacked-porous structure. The zoom-in image of Ni particle (grey area of Figure 4.2(a) shows the smooth surface covered by small dots (Figure 4.2(b)).

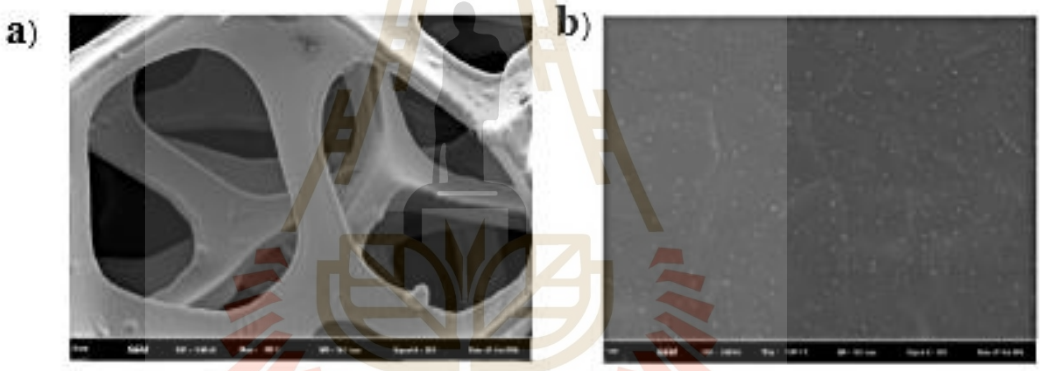


Figure 4.2 SEM of pure Ni foam before annealing (a) 100x and (b) 5000x magnification.

The Ni foam annealed at 400 ^{o}C for 1 and 2 hrs were investigated. As shown in Figure 4.3(a), the Ni foam annealed for 1 hr exhibits some roughness on their surface. At 20k magnification, it shows both rough and small pores on this condition (Figure 4.3(b)). Next, if the sample were annealed for 2 hrs, the surface starts to merge with less pores than the 1 hr annealing condition.

Similarly, we made experiments to study its surface properties by increasing the

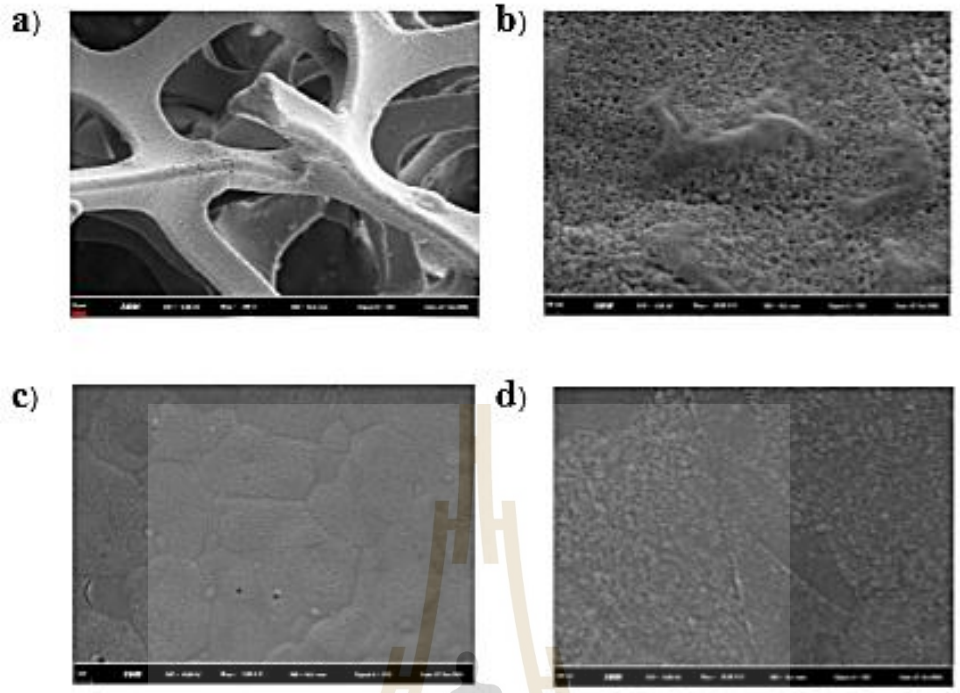


Figure 4.3 SEM images of NiO/Ni foam annealed at 400 ^{o}C (a) for 1 hr, (b) magnification of (a), (c) annealed for 2 hr, and (d) magnification of (c).

annealing temperature and also the annealing time. For example, the samples were annealed at 500 ^{o}C and 700 ^{o}C for 1hr and 2 hr. The SEM image at 5k magnification of the sample annealed at 500 ^{o}C for 1 hr shows the formation of rough surface which was uniformly dispersed as shown in Figure 4.4(a). Later, when zooming this sample at 20k magnification, as shown in Figure 4.4(b), the surface of it is uniformly distributed and has a small porosity. In addition, it was found that if the annealing time were increased to 2hr with 5k magnification, the surface of it is very rough and the formation of the surface is a larger clump as shown in Figure 4.4(c). When zooming with 20k magnification on the surface of this sample, the large clump form with higher porosity as shown in Figure 4.4(d). We can conclude here that in the sample annealed at 500 ^{o}C for 1hr and 2hr, there are several pores have been found and also some large grains are

formed on the surface, indicating coexistence of high porous and surface roughness. Then, when T is increased at T = 700 ^{o}C for 1 hr, the SEM images show uniformly distributed porosity which are very massive compared to other samples. Finally, we can conclude that annealing temperature and time can strongly affect to the surface morphology of NiO/Ni foam especially surface roughness and porosity which are strongly contribute to its surface properties.

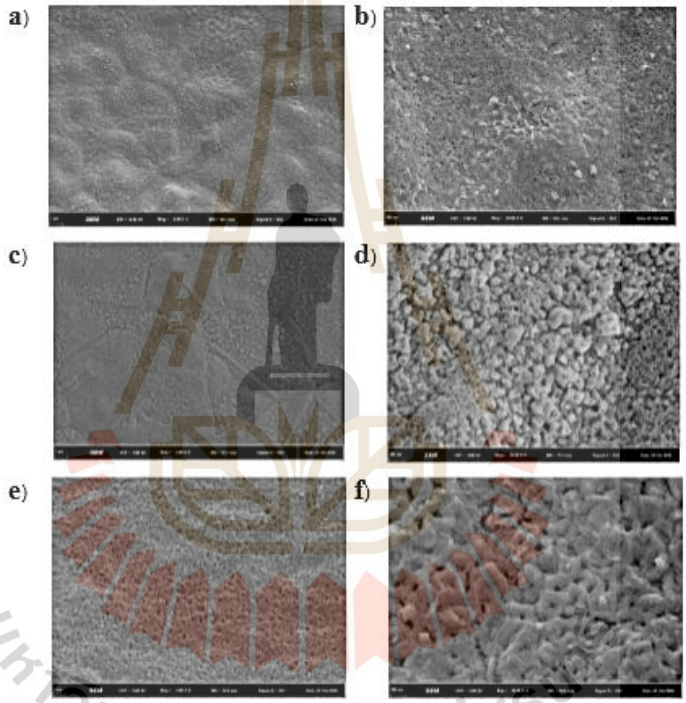


Figure 4.4 SEM of NiO annealed at 500 ^{o}C (a) for 1 hr, (b) magnification of (a), (c) for 2hrs, (d) magnification of (c), (e) at 700 ^{o}C for 1h, and (f) magnification of (e).

We then studied the surface morphology of Ni foam sample as the function of annealing shown as figure 4.5. These sample were calcined as the temperature 400 ^{o}C/1hr, 450 ^{o}C/1hr, 500 ^{o}C/1hr, and 600 ^{o}C/1hr, respectively. The surface morphology of sample surface were characterized by scanning electron microscopy as the electron energy 5kv. We found that the surface morphology changed from small surface roughness (Ni pure)

to high surface roughness and more porous surface according to the increasing temperature. In sample Ni foam 400 ^{o}C/1hr show the morphology of high surface roughness and porous size of (36±3nm) as figure 4.5(b). When the temperature of annealing was increased to 600 ^{o}C/1hr, we found that the porous size was increased to (210±11nm) as shown in figure 4.5(d). In this result to the effect of annealing, the surface roughness and the porous size increasing are effected to water contact angle changing.

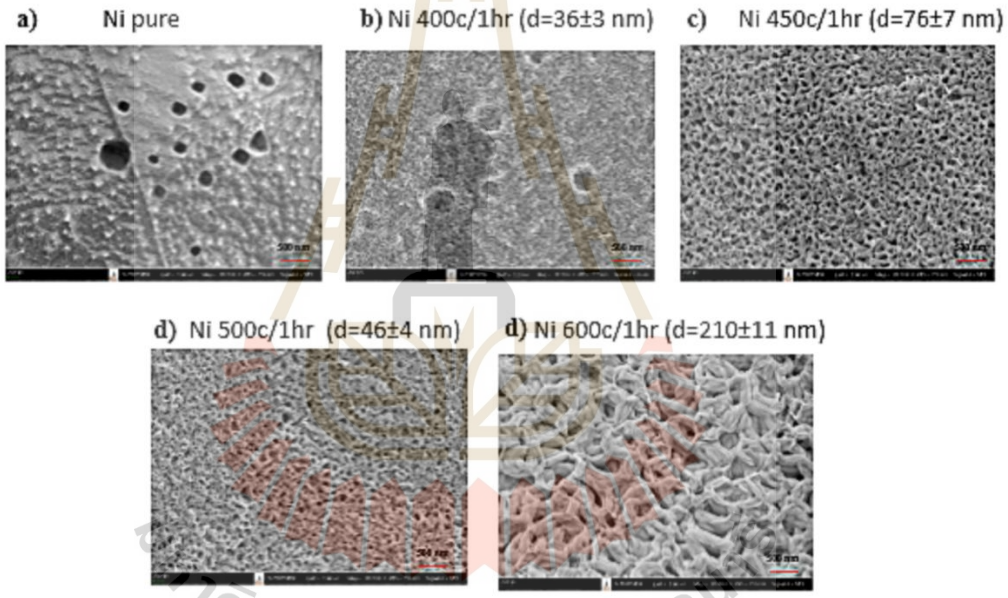


Figure 4.5 SEM of Ni foam as the effect annealed for 1 hr at (a) Ni foam pure, (b) Ni foam 400 ^{o}C, (c) Ni foam 450 ^{o}C, (d) Ni foam 500 ^{o}C, and (d) Ni foam 600 ^{o}C.

Later, we investigated surface morphology of annealed Ni foam sample under UV light irradiation as the function of time. Time duration of UV light irradiation were set as 0min, 30min, and 60min, respectively and fixed intensity of 100mw. Scanning electron microscopy was used to study the surface. The comparison between the surface

morphology and the porous size as the function of time we found that the surface was small changed as shown in figure 4.6(a-d).

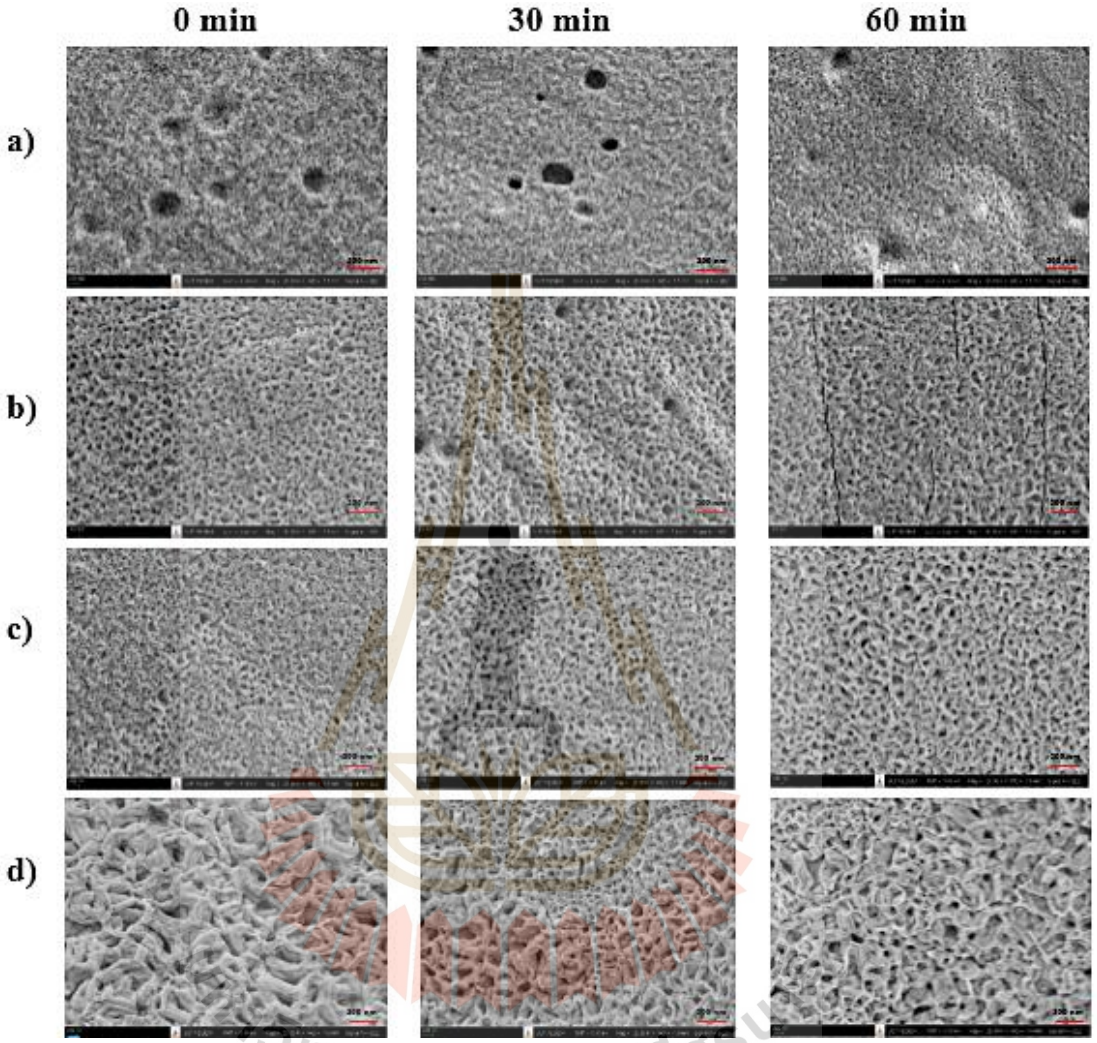


Figure 4.6 SEM of Ni foam as the effect of UV light for (a) Ni foam 400 ^{o}C/1hr, (b) Ni foam 450 ^{o}C/1hr, (c) Ni foam 500 ^{o}C/1hr, (d) Ni foam 600 ^{o}C/1hr.

In the studying of the chemical element in Ni foam as the function of annealing. These sample were characterized by the energy dispersion spectroscopy. The electron as the energy from 0 to 5 keV incident to the sample surface and the chemical element were detected. The result from the figure 4.7 show three peak as Ni peak, O peak, and C peak which peak represent to the atomic percentage of element. We found that the effect of

annealing result to the atomic percentage of chemical element changing such as the Ni peak of Ni foam pure had 77% and reduced to 50% of Ni foam 500 ^{o}C/1hr. The relation of the chemical element changing with the effect of annealing are the once reason to wetting property of Ni foam sample changing.

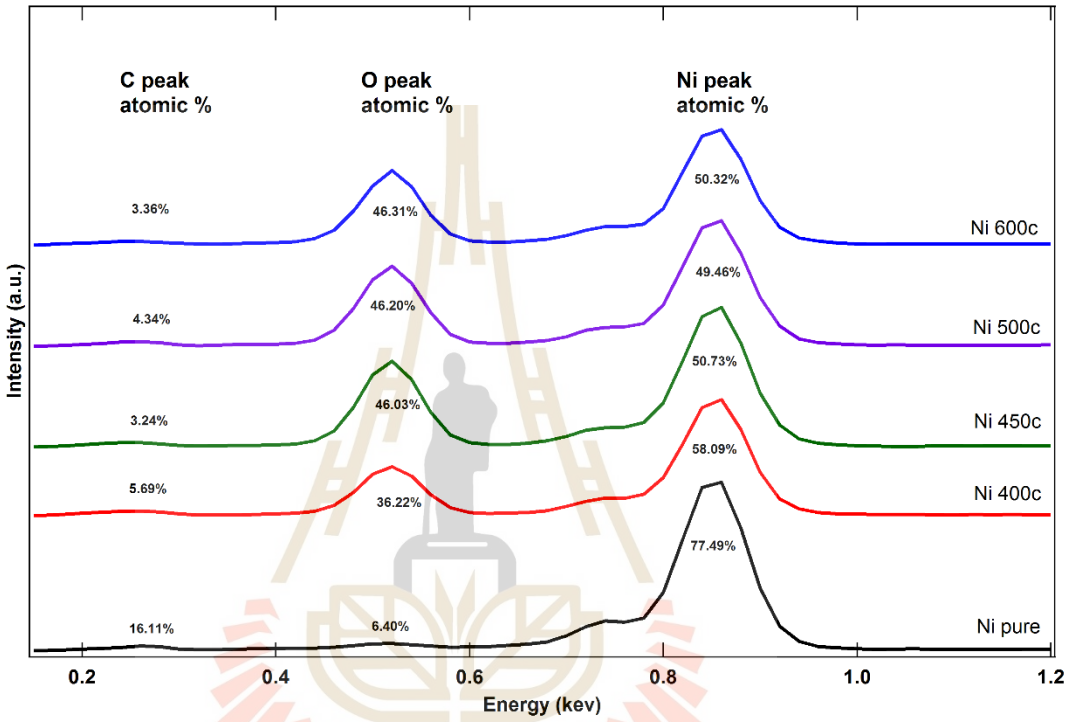


Figure 4.7 EDS of Ni foam as the effect of annealed.

For the studying of the chemical element changing under UV light irradiation, we characterize by comparison between before UV light and after UV light show as figure 4.8-4.11. The result of the experiment shown the peak Ni and peak O under UV light irradiation as 0min 30min, and 60min, respectively for all sample, we found that the atomic percentage of chemical element of Ni peak were small changed than peak O were changed from 33% to 40%. From this result, we know that the effect of UV light can be change the chemical element a little which believe to result the wetting property changing.

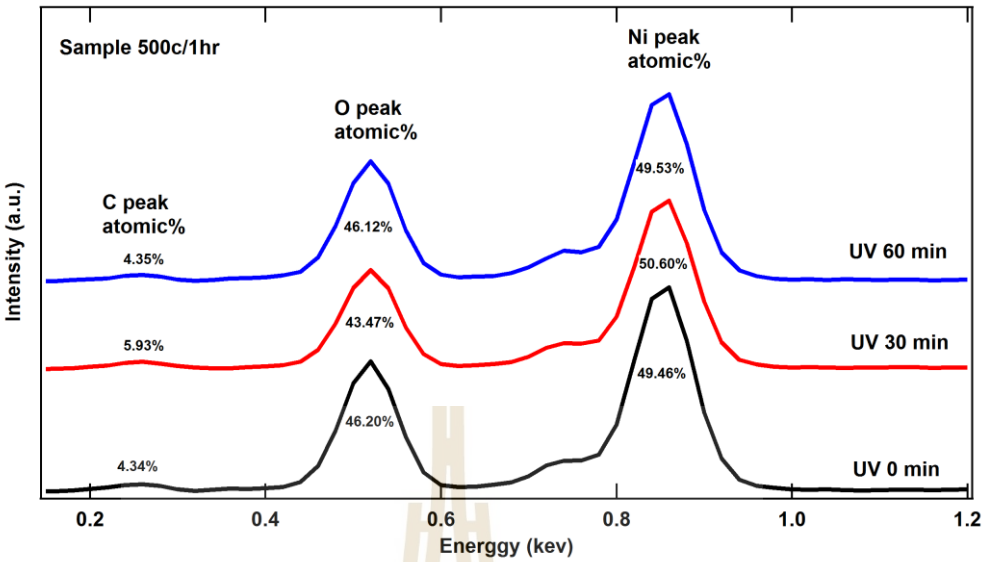


Figure 4.8 EDS of Ni foam as the effect of UV light for Ni foam 500 ºC/1hr.

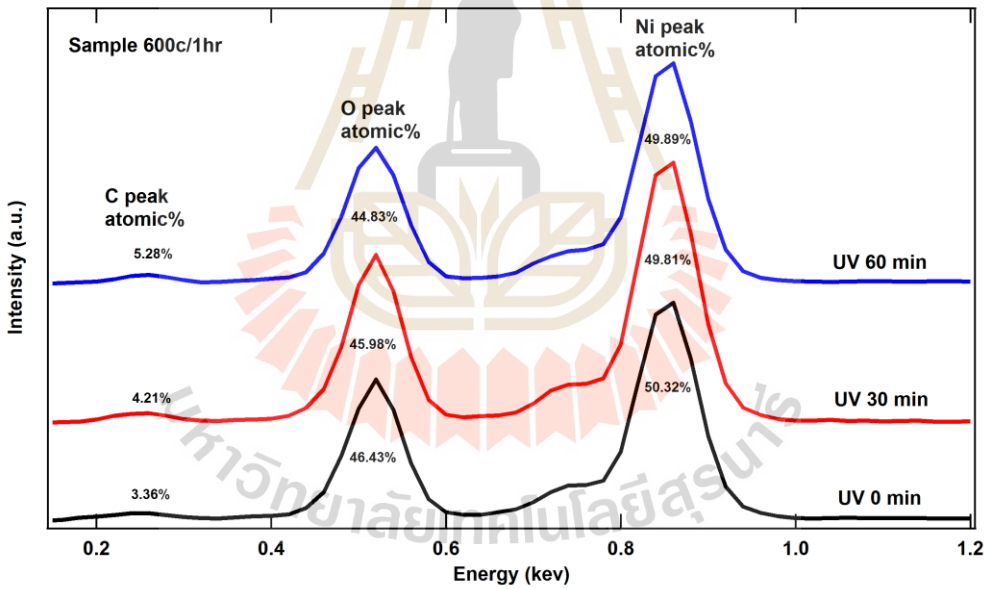


Figure 4.9 EDS of Ni foam as the effect of UV light for Ni foam 600 ºC/1hr.

4.3 Contact angle measurement

4.3.1 Contact angle variation of NiO/Ni foam under violet laser irradiation

The result of contact angle measurement under UV light irradiation is shown in Figure 4.10. In this work, we studied the effect of UV light irradiation in two conditions, as a function of time exposure and UV light intensity. Figure 4.10(a-d) represents the effect UV light as the function of time exposure that the water contact angle is measured with varies of time from 0-30 min and fixed UV light intensity at 50 mW. We can see that the water contact angle is increased from 0º to 60º under UV light irradiation exposure time. Figure 4.10(e) shows the plotting curves between the water contact angle and time exposure that when increase time of exposure the water contact angle will be stable and closely near to 60º. It is seen that the water droplet starts to form on NiO/Ni foam depending on the exposure time of UV light. In the second condition of contact angle measurement concern the function of UV light intensity and fixed the time exposure at 30 min. Figure 4.10(f- i) are the profiles of a water droplet on NiO/Ni foam with different of UV light intensity and we can see that water contact angle is changed as a function of UV light intensity. The contact angle also is increased from 0º to 60º. Figure 4.10(j) give the result of plotting curve between water contact angle and UV light intensity when increase the UV light intensity the water contact angle is stable and closely near to 60º. From these two measurement conditions, we can see that both results are similar which can be concluded that UV dosing plays an important role in the changes of wetting property. We think that the changes of surface roughness as well as some chemical forming on NiO/Ni foam are obtained by UV dosing.

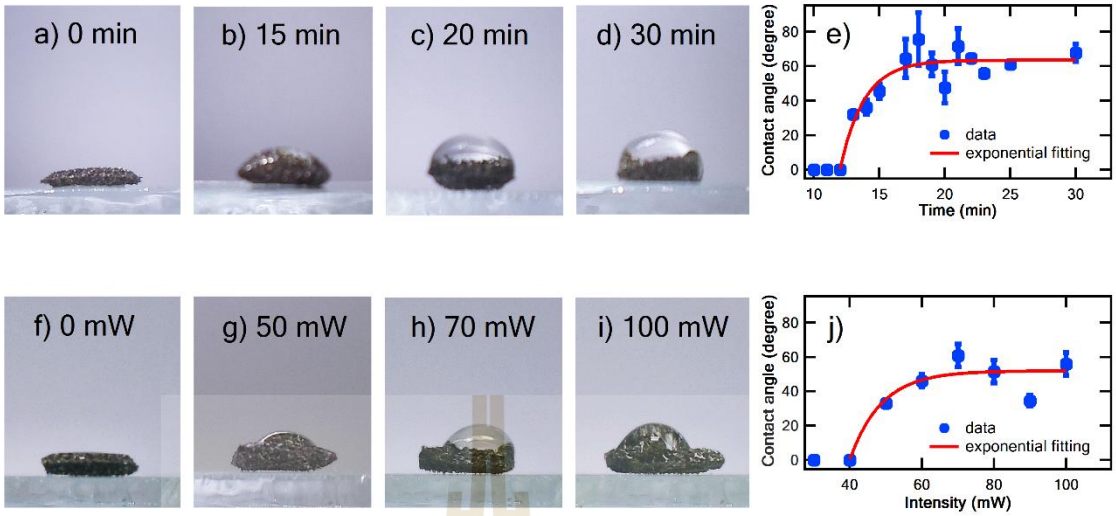


Figure 4.10 Droplet Photographs and contact angle measured in two different conditions (a-e) the different exposure time with fixed intensity (50 mW) and (f-j) the different intensity with fixed time (30 min).

4.3.2 Contact angle at different annealing temperature

To study the wetting properties under UV irradiation based on the temporal relationship of the irradiation and the intensity of light exposure. The previous section shows that the wetting property of the NiO/Ni foam annealed at 500 ^{o}C can be changed. In this section, we have been studying the wetting property of the samples annealed at 200 ^{o}C, 300 ^{o}C, 400 ^{o}C, and 600 ^{o}C for 1 hr, respectively (Figure 4.11). The contact angle of the sample annealed at different temperature compared between the non-irradiated and 30 min of 100 mW light irradiation. The droplets on the sample which are not exposed to the light are shown in Figure 4.11(a) and the exposed sample are shown in Figure 4.11(b). The samples annealed at T in the range of 300 ^{o}C to 400 ^{o}C for 1hr show no formation of water droplet or contact angle (angle=0^{o}), which shows that these samples are very hydrophilic and that their surface is a good hydrophilic

surface. For the sample annealed at T = 600 ºC for 1hr, the contact angle were measured to be 92.6º. When exposed UV light to the sample for 30 min, the contact angle increased slightly to 103.4º. It shows that it has more hydrophobic properties when exposed to the UV light. As a result of this experiment, we can see that the irradiation can result in a wetting property for the sample that is annealed at the temperature higher than 500 ºC. The changes of structural and chemical properties such as surface roughness will cause the wetting property to change.

Figure 4.11 The water droplet profile on difference NiO/Ni foam annealing temperature (a) no UV light irradiation and (b) under UV light irradiation fixed 100mW.

4.4 Cyclic voltammetry measurement

4.4.1 Cyclic voltammetry measurement measurement of NiO annealed at different temperature

In this experiment, we will study the electrochemical property of NiO/Ni foam annealed at 400 ^{o}C and 500 ^{o}C for 1 hr. This study investigated the relationship between capacitance and scan rate values in those samples. In this study, the experiments were carried out using cyclic voltammetry (CV) measurement using the 6 M KOH solution as electrolyte at room temperature. The NiO/Ni foam samples at T = 400 ^{o}C/hr were tested by varying the scanning currents and potentials at various scan rates such as 2 mV, 15 mV, 10 mV, 20 mV, 30 mV, 40 mV, and 50 mV, respectively. We can see that when increasing the scan rate, the larger CV loop is obtained as shown in figure 4.12(a). The larger the loops of the graph reflects to the smaller value of the capacitance. From the results of the capacitance calculation, it is found that the capacitance decreases via increasing scan rate with capacitance values decreasing from 156.7 to 115.1 F/g. In addition, for the CV curve of the sample NiO/Ni foam annealed at T = 500 ^{o}C for 1 hr exhibits the same trend as the sample annealed at T = 400 ^{o}C/hr. (Figure 4.13(a)). Based on the results, the capacitance value is little decreased from 23.3 to 22.5 F/g. Experiments show that the capacitance value decreases with increasing scan rate. At the same time, it is also found that the higher the annealing temperature, the lower the capacitance value which might indicates less chemical ability for the sample with higher annealing temperature.

4.4.2 Effect of light irradiation on specific capacitance

The cyclic voltammetry (CV) measurement is used to understand the electrochemical properties of NiO/Ni foam under UV light irradiation.

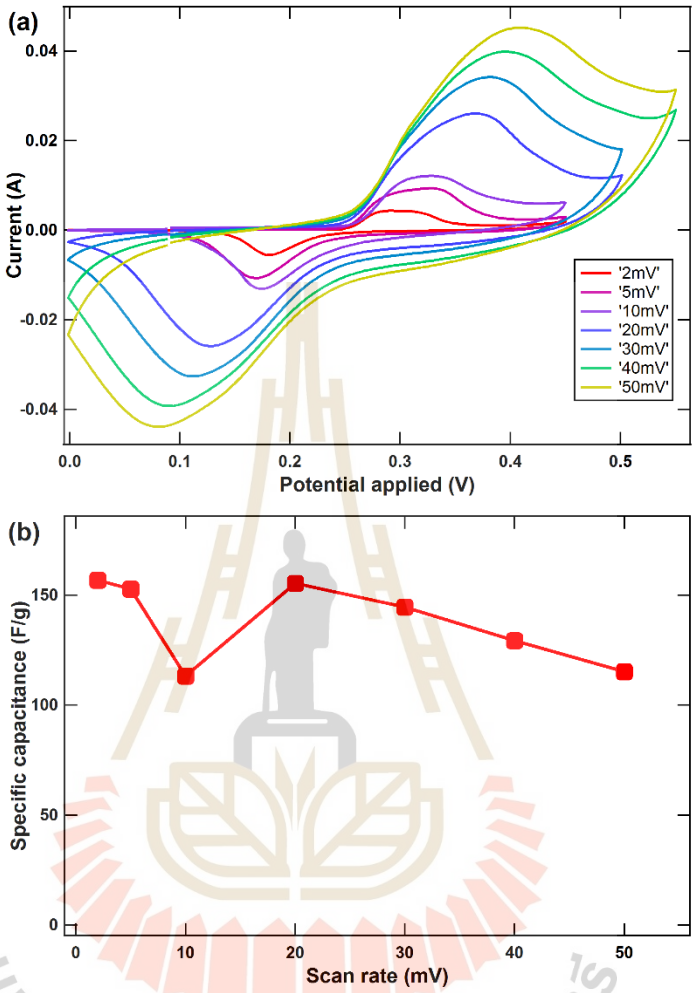


Figure 4.12 CV of Ni foam annealed at 400 °C for 1 hr.

Our measurement was performed with and without UV light irradiation. The experiment was conducted using three electrodes in 6 M KOH solution. Figure 4.14(a) shows the C-V curves between with and without light irradiation. The CV area of irradiated UV light sample was found to be bigger than without UV light. It was seen that the oxidation and reduction peaks of NiO/Ni foam were increased under UV light irradiation. Figure 4.14(b) shows the recovery of C-V curve after the UV light is turning

off. It is precisely seen that the oxidation and reduction peaks are decreased after the light is turning off. The specific capacitance can be calculated by using the area of C-V curve (as shown in equation 2). Figure 4.14(c) shows the changes of calculated specific capacitance under UV light irradiation as under UV light irradiation the specific capacitance is increased from 15 to 35 F/g and no UV light are reduced from 35 to 20 F/g. From this result, the changing of capacitance can be described by the creation of surface oxygen vacancy. It can be implied that such oxygen vacancies on NiO/Ni foam results in more surface charge carriers and hence the increase of specific capacitance is expected.

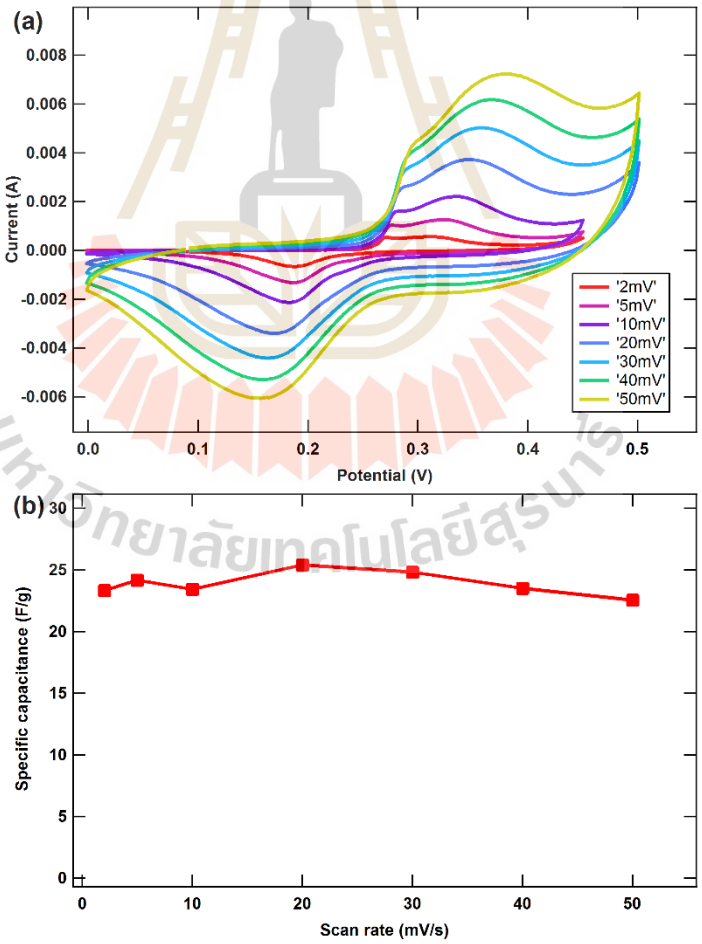


Figure 4.13 CV of Ni foam annealed at 500 ^{o}C for 1hr.

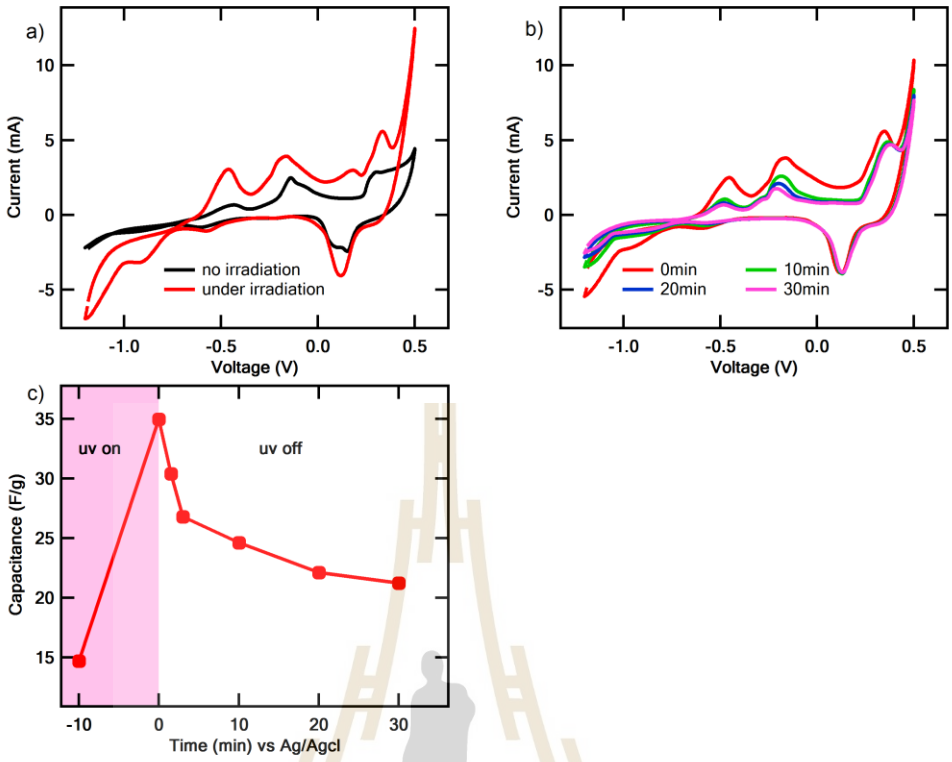


Figure 4.14 The cyclic voltammetry (CV) curves of NiO/Ni foam (a) the CV curves with and without UV light irradiation, (b) the recovery of CV curve after the light is turning off, and (c) the specific capacitance value as a function of time.

4.5 X-ray photoemission spectroscopy measurement

In this section, we try to study the chemical forming on the Ni foam surface which can be changed by the effect of annealing temperature and UV irradiation using X-ray photoemission spectroscopy measurement. This technique can analyze the surface properties of materials with high resolution and high reliability. This can provide the oxidation state of the substance, chemical bonding, and elemental composition on the surface of the material. In this study, we will study the chemical forming properties of the surface under two conditions: the effect of annealing temperature and the effect of UV light irradiation using Al Ka x-rays (1486.7 eV). The

XPS spectrum were measured between 0-1400 eV which can cover both Ni and O peaks.

The XPS spectrum of Ni foam under different annealing temperature is shown in Figure 4.15. Figure 4.15(a) shows XPS survey scans which are very similar for all samples, Based on this measurement, the sample surface is mostly composed of Ni, O, C as marked in the figure. The fine scans near several peaks of C1s, O1s, and valence band are shown in Figure 4.15(b-d). We find that the characteristics of these peaks are markedly different. For C peak, it was found that two peaks firstly occurred and slowly and then disappeared when annealing temperature increased. For O peak, the peak is changed from one to two peaks when is temperature increased which might be related to the new O-Ni bond. The XPS of Ni peak is shown in Figure 4.15(e). For Ni foam, there is only one Ni peak occurred at binding energy around 855 eV. By annealling the sample, there is an extra peak emerged (856 eV) which is assigned as Ni^{2+} (NiO). By fitting the peak between $Ni^{(0)}$ and Ni^{2+}, there is small different in ratio in different annealing temperature. We believe that the difference in the amount of trace elements on the surface of this sample might relate to the wetting property.

Next, we study the surface properties of Ni foam by the effect of UV light irradiation. In this measurement, we focus of the XPS fine scans of C1s, O1s, and Ni peaks, respectively. The XPS results were carried out at 0min, 30min, and 60min time of irradiation, respectively. In the sample annealed at 500 ^{o}C/1hr, it was found that the C peak under UV irradiation are similar. As shown in Figure 4.16, the Ni peak position and ration between peak1 and peak2 does not change under UV irradiation. This behavior is similar for the case of the samples annealed at 400 ^{o}C/1hr, 450 ^{o}C/1hr, and 600 ^{o}C/1hr. From above result, we can say that UV irradiation can slightly change the chemical formation compared with the effect of annealing temperature.

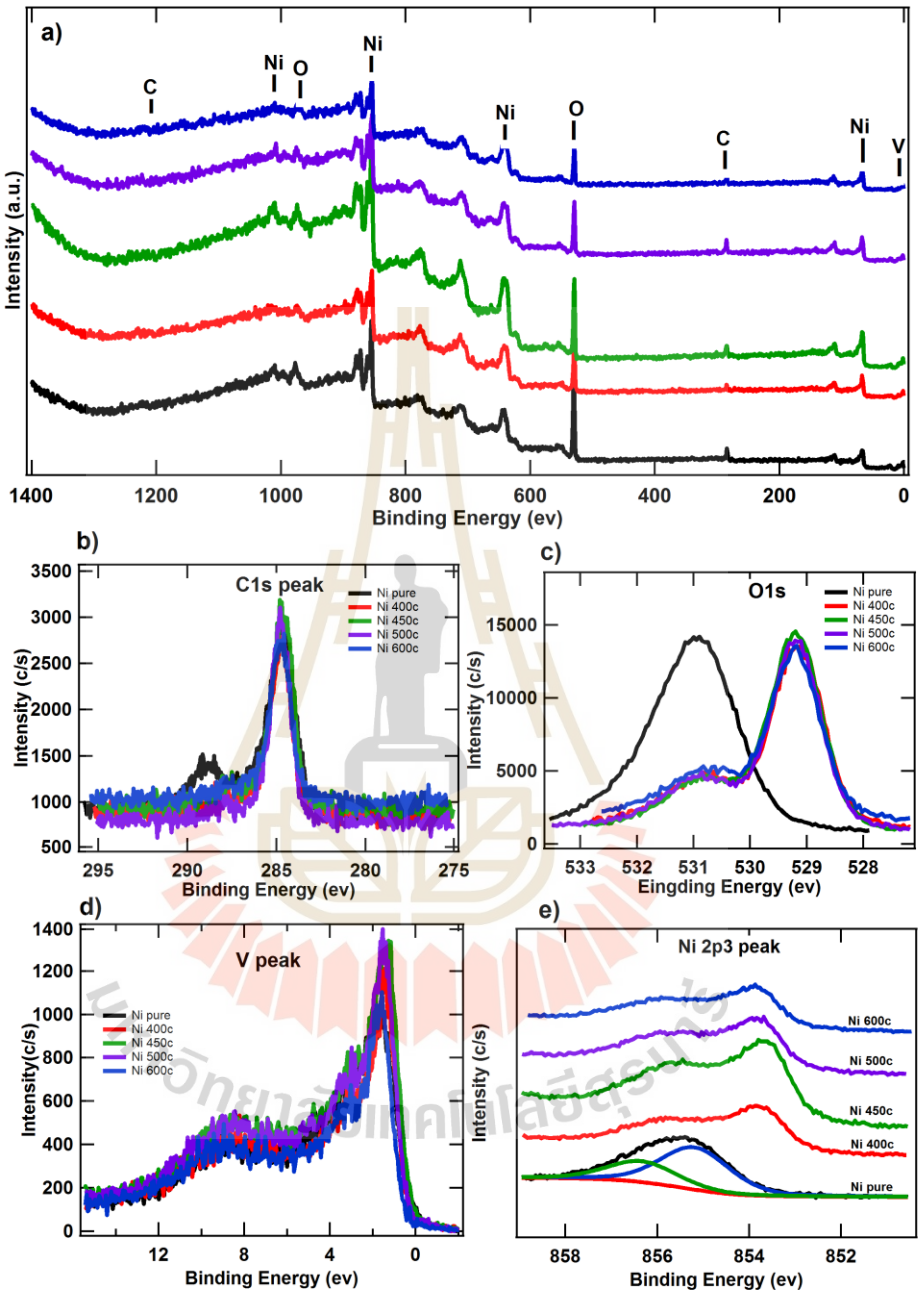
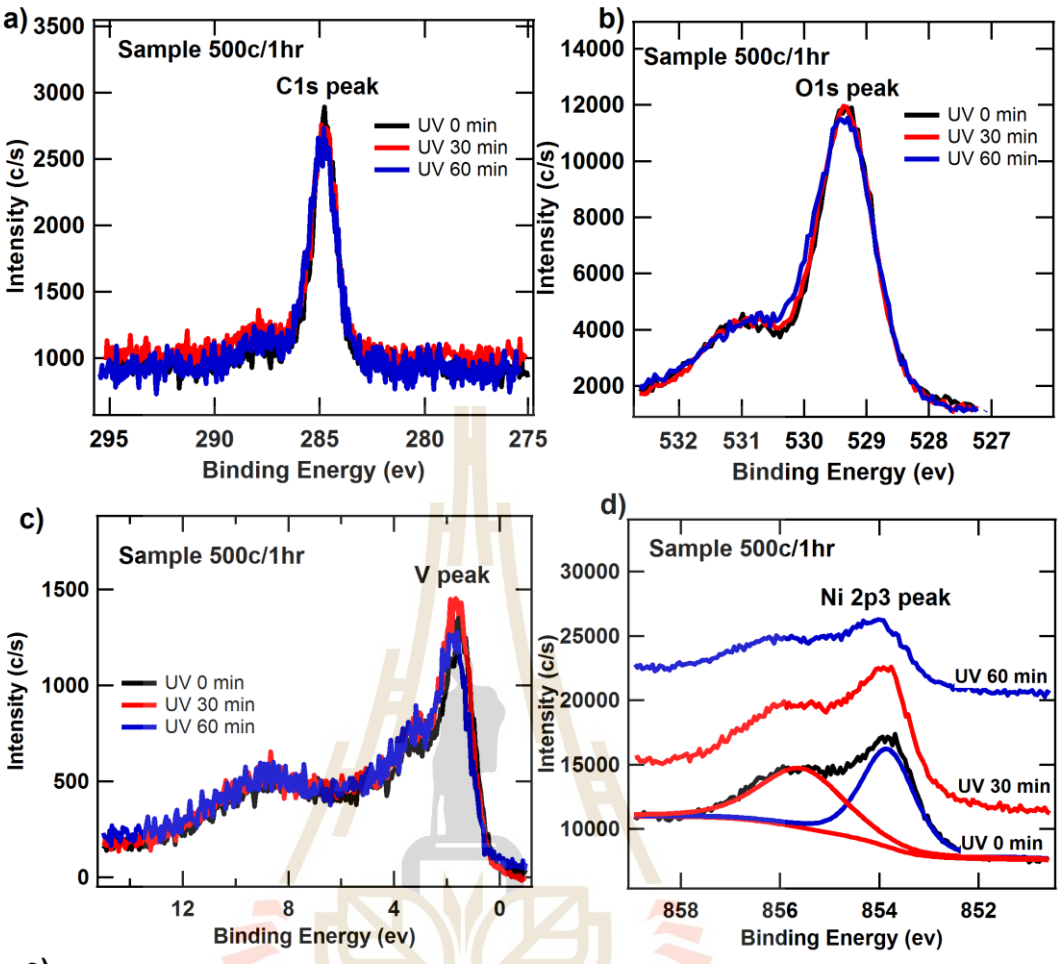


Figure 4.15 XPS of Ni foam as the effect of annealed (a) survey scan, (b) C1s peak, (c) O1s peak, (d) V peak, and (e) Ni 2p3.



e)

Point	Sample_500c	ratio_500c
0	UV 0 min	1.04336
1	UV 30 min	1.13167
2	UV 60 min	1.03777

Figure 4.16 XPS of Ni foam as the effect of annealed 500 ºC/1hr (a) C1s peak, (b) O1s peak, (c) Valence band peak, (d) Ni 2p3 peak as fitting curve, and (e) ratio of Ni peak.

4.6 Discussion

The aim of this research is to study the wetting properties of NiO/Ni foam under UV light, it can be seen that this property changes upon light exposure. This irradiation results in its surface property being changed. This change can also be affected by other factors. From the results above. We find that the Ni foam annealed from 300 ºC for 1

hr to 700 ºC for 1 hr results in a change of the sample surface. This means NiO can be formed on Ni foam and can be increased with increasing annealing temperature. In addition, surface changes can be observed from SEM imaging. We find that the morphology of the sample surface is more rugged and porous. This can be used to indicate that the surface property has changed. This change in surface property can also be tested by examining its wetting properties by measuring the contact angle of the droplets on samples annealing at temperature ranging from 200 ºC to 600 ºC. We can see that the contact angle is increased for samples annealed at T=500 ºC/1hr. In this section we believe that it is related to the increasing of its surface roughness. This is going to make the contact surface of the material and liquid decreased. This is related to the reduction of the adhesive force at the interface of liquid and solid. We also found that UV irradiation results in a change in the wetting property. The contact angle of it increases with the time of exposure and the intensity of light. In addition, the study of the electrochemical properties of NiO/Ni foam was compared with that of light irradiation and non-irradiation. The CV curve and capacitance measurements showed that the capacitance of the samples increased during exposure. When the light is stopped, its capacitance decreases back. This increase or decrease in capacitance values is related to the formation of electrons, holes, and oxygen vacancies. It results in the formation of some species groups occurring at the surface and increasing the species group. These will result in a change in electrochemical reactions and better electrical conductivity. Similarly, the contact angle changes with the exposure. We may be able to explain that, while we were lighting up the UV light on the sample that was airborne around. Light may be stimulated or induced by electrons, holes, and oxygen vacancies, as well as by measuring the CV, and these particles may react with the surrounding air to form another substance. On the sample surface, such as hydroxyl group and

hydrophilic groups, etc., these substances may increase or decrease. Measurement of these phenomena might be done by the XPS technique. From XPS result, we found that all samples have similar elements including Ni, O, and C. Samples with different annealing temperature clearly show the change of XPS curves for Ni and O peaks. Sample with UV light irradiation shows insignificant changes. Here, we might conclude that annealing the sample can change the structural formation while UV light irradiation does not change the structure of the sample surface. So, the occurrence of these substances will result in a change in the wetting properties. Studying the wetting and electrochemical as well as the use of light irradiation to control and modify the properties will be very interesting.

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusions

In this work, we try to study the wetting and electrochemical properties of NiO/Ni foam under UV light irradiation. NiO sample preparation were fabricated by thermal oxidation process as the temperature from 0 ^{o}C to 600 ^{o}C in air environment. The properties of sample surface were investigated by using scanning electron microscopy, contact angle measurement, cyclic voltammetry measurement, energy dispersion spectroscopy, and x-ray photoemission spectroscopy. As the result in our experiment, we found that the NiO/Ni foam can be acquired by calcining the Ni foam at 500 ^{o}C for 1hr confirmed by the x-ray diffraction patterns. In the water contact angle measurement we found that the surface behavior change from hydrophilic (0^{o}) to hydrophobic (90^{o} and 120^{o}) were obtained by increased the annealing temperature up to 600 ^{o}C. So from the attemption to study the change of wetting property of NiO/Ni foam under UV light irradiation using contact angle measurement. We found that water contact angle were increased from 0^{o} to 60^{o}. The contact angle of water droplets is increased depending on the exposure of time and UV light intensity. This means that by introducing UV light on the surface, the wetting property of NiO/Ni foam is changed. Also to the specific capacitance were increased from 15 F/g to 35 F/g. By using cyclic voltammetry (CV) measurement, we found the increase in specific capacitance under UV light irradiation. The specific capacitance decreases close to the

original value after the light is turning off UV. The increase of contact angle and specific capacitance as well as the understanding the intrinsic mechanism of NiO/Ni foam UV light irradiation should help in the development fundamental researches and applications.

The new chemical species group were observed by CV curve measurement which relate to new chemical forming on sample surface. This special group might be effect the changing of surface property. For the morphology of sample under annealing temperature show that the surface roughness increasing and porous size increased from (d=36±3 nm) to (d=210±11 nm). In the studying of chemical forming on sample surface it clearly seen the changing to C peak, O peak, and Ni peak under effect of annealing temperature. For the emergent of C peak, O peak, and Ni peak under UV light irradiation we seen that the chemical forming does not much change. So we might be conclude that the effect of annealing temperature effect to the sample surface properties change. The chemical forming under UV light irradiation does not change the structure of the sample surface. The controllable of annealing temperature and UV light irradiation are good process to optimize the wetting and electrochemical properties.

5.2 Improvement and future plan

In the studying of NiO mechanism under annealing temperature and UV light irradiation have more limitation in the experiment. The understanding of wetting and electrochemical properties, we have to do more experiment and characterization. The investigation of surface properties, the chemical specials group should be characterized by using Raman spectroscopy and Fourier-transform infrared spectroscopy techniques.

Also with the porous size and surface area should be performed by using BET technique. However, the studying of light irradiation effect will be take in various wavelength such as green light and red light. For the investigation of wetting property we will be choose the other liquid to do experiment. So from the addition of understanding, we can control these effect which will be apply to various application in the future.

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