

## CHAPTER 2

### Synthesis and Characterization of ZnO Tetrapods Network

Zinc oxide (ZnO) nanostructures have unlimited attention in a wide area of applications because of their unique properties, changeable density of state, quantum confinement effect, and high surface-to-volume ratio [42]. There are many techniques for the preparation of ZnO nanostructures, such as chemical vapor deposition (CVD)[71, 72] (in **Table 1.1**) which has various techniques for example thermal CVD, plasma enhanced CVD[73]), hot filament CVD[74], and control pressure gas oxide CVD[75] etc. These techniques have been in trouble for the preparation such it is unable to prepare a high melting-point metal. This requires a complex and high-cost system. The preparation by microwave-assisted process is an approach to solve the problem. It can be used in CVD processes and has the many advantages. The use of the microwave radiations provides a new, efficient methodology for the synthesis of a number of metal oxide nanostructures of diverse morphologies and size. These radiations have exceptional properties like homogenous volumetric heating, which reasons heating directly inside the specimen, high reaction rate compared with extra physical and chemical methods, selectivity and improved product yield. It is an energy saving procedure.

However, the plasma occurred during the microwave-assisted process requires a system of gas and vacuum systems. These systems require expensive and complex systems and in the vacuum system must be free of dust and dry which cannot be used as substrate material, dusts and wet. In this process, microwave-assisted thermal oxidation technique offers a better approach. It can solve the problem which in the vacuum system of the plasma from microwave-assisted process without using a system of gas and vacuum systems for nanostructure preparation.

**Table 2.1** the techniques process requires [71-75].

Methods	Techniques	The techniques process requires
Chemical vapor deposition (CVD)	thermal CVD, plasma enhanced CVD), hot filament CVD, Vapor phase growth CVD and high pressure gas oxide CVD	It unable to prepare a metal with a <b>high melting point</b> and the process requires the use of <b>high temperature, high power, a long time</b> , requires a system that is complex and costly process.
Microwave-assisted	Chemical Plasma gas systems	Solution process required a system of gas and vacuum systems.
<b>Microwave-assisted thermal oxidation technique</b>	<b>Plasma metal and plasma heat transferred</b>	<b>It can use as substrate material, dusts and wet in atmosphere, In a short time.</b>

**Table 2.2** Microwave techniques for synthesis of ZnO [76-85].

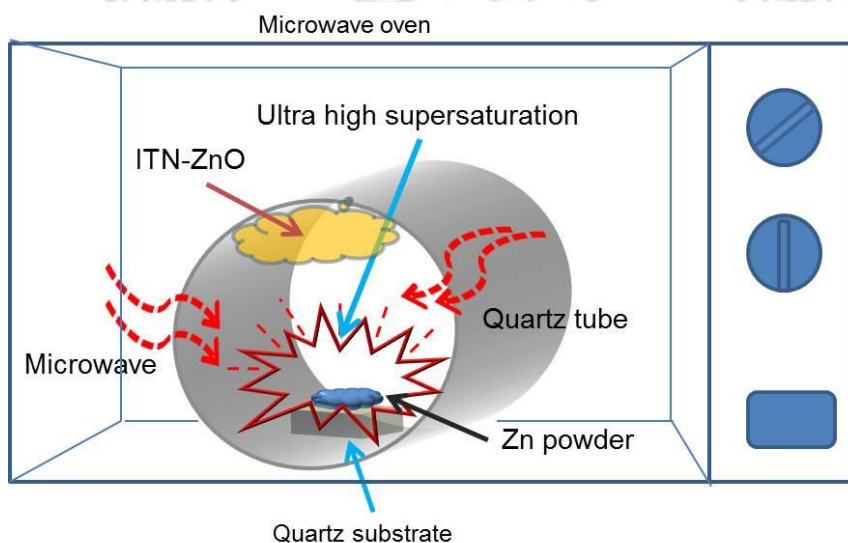
Journals	Use of microwave assistant	plasma assistant	A powder metal substrate	Use of solution metal substrate	Vacuum system	In atmosphere	Growth in microwave field	Time (sec)	Type of nanostructures
M.V. Limayc, et al. (2011)	@			@			@	-	rod
H.Li, et al. (2011)	@			@			@	30	wires
Sharma, et al. (2011)	@			@			@	2	particle
N.F. Homedani, et al. (2011)	@			@			@	2	crystal
ZHU Jian-Yu, et al. (2011)	@			@			@	-	rod
Y.Ni, et al. (2008)	@			@			@	8	crystal
R.Al-Gaashant et al. (2011)	@			@			@	5	Nano structures
R.Al-Gaashani et al.	@			@			@		Nano structures
JH. Kim, et al. (2007)	@	@						-	rod
X-H. Zhaoy, et al (2003)	@	@	@		@			20	Tetrapod
T. Wangenste en, et al. (2011)	@	@	@		@			-	particle
<b>This work</b>	@	@	@			@	@	1-5	Nano structures

Currently, the microwave-assisted techniques are widely used in many systems. In our system, we use a special technique which differs from the other systems as showed in the **Table 2.2**.

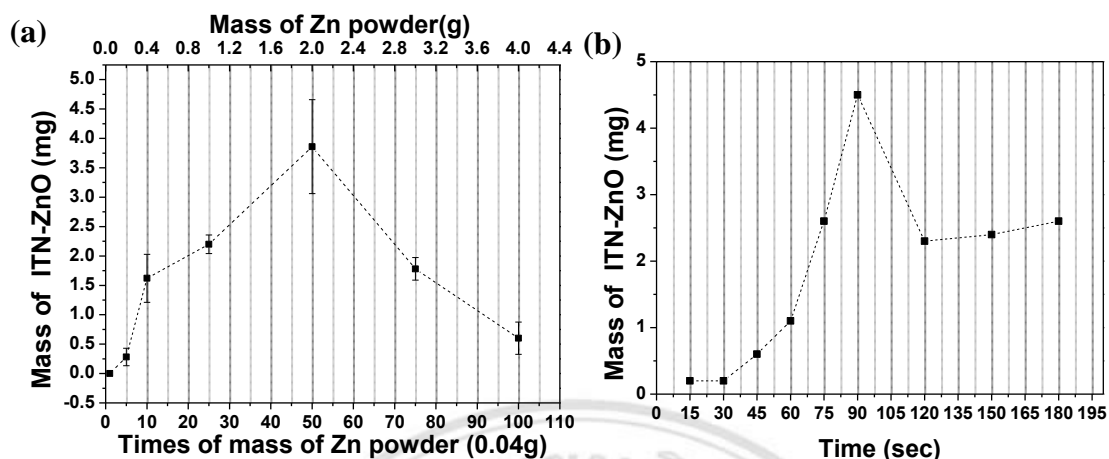
## 2.1 Preparation of the interlinked ZnO tetrapod networks

### 2.1.1 Preparation of ITN-ZnO

Zinc (Zn) powder (0.04-4 g; 99.99%, less than 50  $\mu\text{m}$  particle size) as a precursor loaded on a quartz substrate was placed in a quartz tube with diameter of 2.8 cm and length of 10 cm in a household microwave oven (SHARP model), as shown in **Fig. 2.1** and as shown results in **Fig. 2.2**. The Zn powder was then heated with microwave power of 100-800 W at a frequency of 2.45 GHz for 60 s under atmospheric conditions, as shown results **Fig. 2.3**. Finally, after the system cooled down, the wool-like ZnO structures were observed in the quartz tube and collected for further investigation.

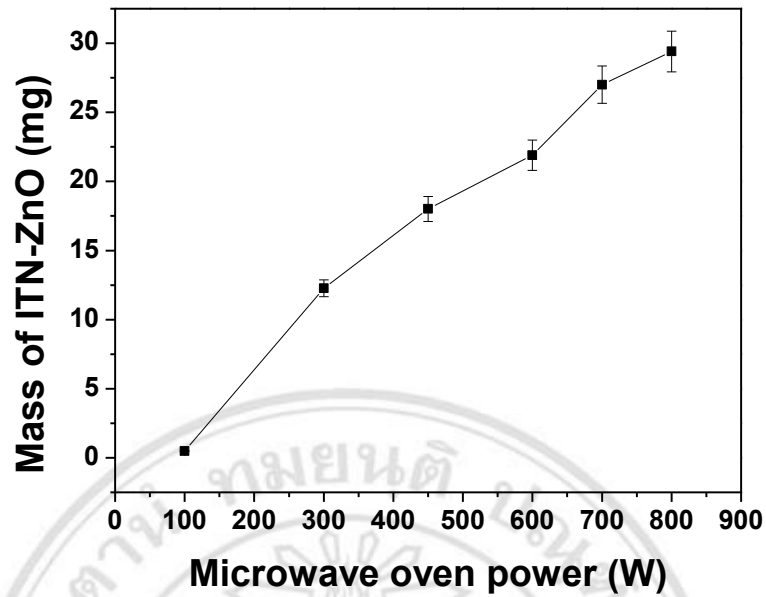


**Figures 2.1** Schematic illustration of the preparation system of ITN-ZnO, this system uses a household microwave oven (SHARP model) with power of 700 W and frequency of 2.45 GHz ( $\lambda= 12$  cm). Zinc powder (2 g) on a quartz substrate was placed in a quartz tube and heated for 60 s. The wool-like products obtained in the quartz tube were collected for further investigation. Reprinted with permission from ref [70]. Copyright (2015) American Chemical Society.



**Figure 2.2** The maximum of mass of ITN-ZnO were synthesized from with Zn powder 2.0 g (50 times of Zn powder 0.04g) (a) and time at 90 sec (b).

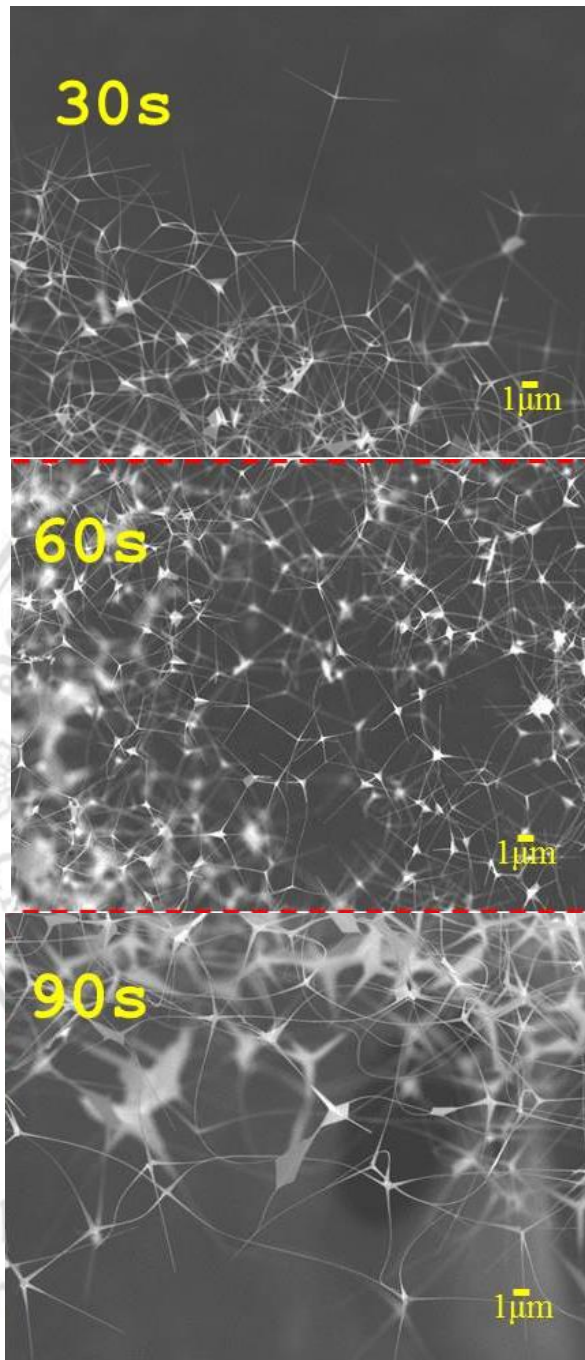
The optimal condition for ITN-ZnO preparation of the produce volume of mass, irradiation with microwave for varying weight of Zn metal powder for 0.04 - 4 g and time synthesis irradiation with microwave for 15 – 180 sec was performed. The mass of ITN-ZnO products were shown in **Fig. 2.2**. It was seen that 2 g and 90 sec of microwave irradiation is the optimal condition for maximum of mass volume. After that, ITN-ZnO was synthesized under a household microwave oven with microwave power irradiation has 100-800 W. The mass of ITN-ZnO products were shown in **Fig. 2.3**. It was seen that the weight of ITN-ZnO directly proportional to microwave power irradiation.



**Figure 2.3** Mass of ITN-ZnO was prepared by increasing microwave power as 100, 300, 450, 600, 700 and 800 w.

In order to obtain the optimal condition for ITN-ZnO preparation, irradiation with microwave for 30, 60, and 90 s was performed. The FE-SEM images of the ITN-ZnO products were shown in **Fig.2.4**. It was seen that 60 sec of microwave irradiation is the optimal condition for obtaining large volume of the ITN-ZnO with homogenous morphology. Irradiating microwave for only 30 seconds provides smaller amount of ITN-ZnO. Longer irradiation up to 90 seconds gives inhomogeneous morphology. Therefore, the sample irradiated with microwave for 60s was further investigated and selected for sensor fabrication.

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**Figure 2.4** Morphologies of ZnO products obtained from microwave-assisted thermal oxidation: FE-SEM image of ITN-ZnO was synthesized under microwave oven at 30-90s. Reprinted with permission from ref [86]. Copyright (2016) Elsevier.

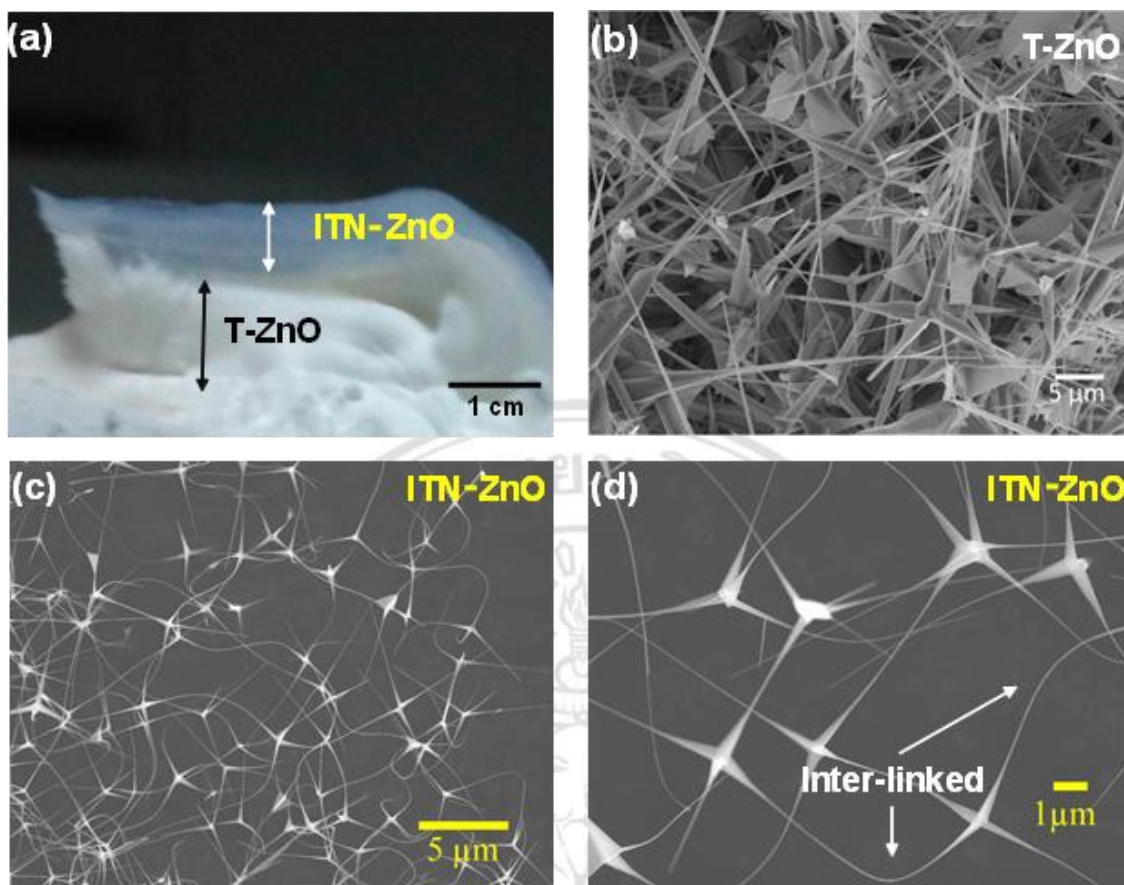
### 2.1.2 Characterization and morphology of ZnO

Characterization crystallinity and morphology of wool-like ZnO products were characterized via an X-ray powder diffractometer (Siemens, D-500) with Cu K $\alpha$  radiation, the field emission electron microscope (FE-SEM; S-450 SEM, Hitachi), and the transmission electron microscope (TEM; JEOL FEG-STEM/TEM (2010)).

The morphologies of ZnO products obtained from microwave-assisted thermal oxidation are shown in **Fig. 2.5**. The ZnO products can be distinguished into two regions with two different morphologies as shown as an optical image in **Fig. 2.5a**. In bottom region, tetrapod-like ZnO structure with about 1  $\mu\text{m}$  in diameter at the middle of their legs and 10-30  $\mu\text{m}$  in length is observed as seen as FE-SEM image in **Fig. 2.5b**.

On the other hand, in the upper region, the tetrapod-like structure with leg-to-leg linking together, so-called “interlinked tetrapod network of ZnO” or ITN-ZnO is observed as seen in FE-SEM images in **Fig. 2.5c and 2.5d**. It can be seen that the legs of ZnO tetrapods are inter-linked with the legs of other tetrapods about at the end of the legs and look similar to the shape of neural network. The diameter at the middle of each leg is in the order of 50 nm which is much smaller than those of ZnO tetrapods in the bottom region. This ITN-ZnO is a unique morphology which is definitely different than ZnO tetrapod (T-ZnO) in the bottom region and it is rarely observed elsewhere with other growth techniques.



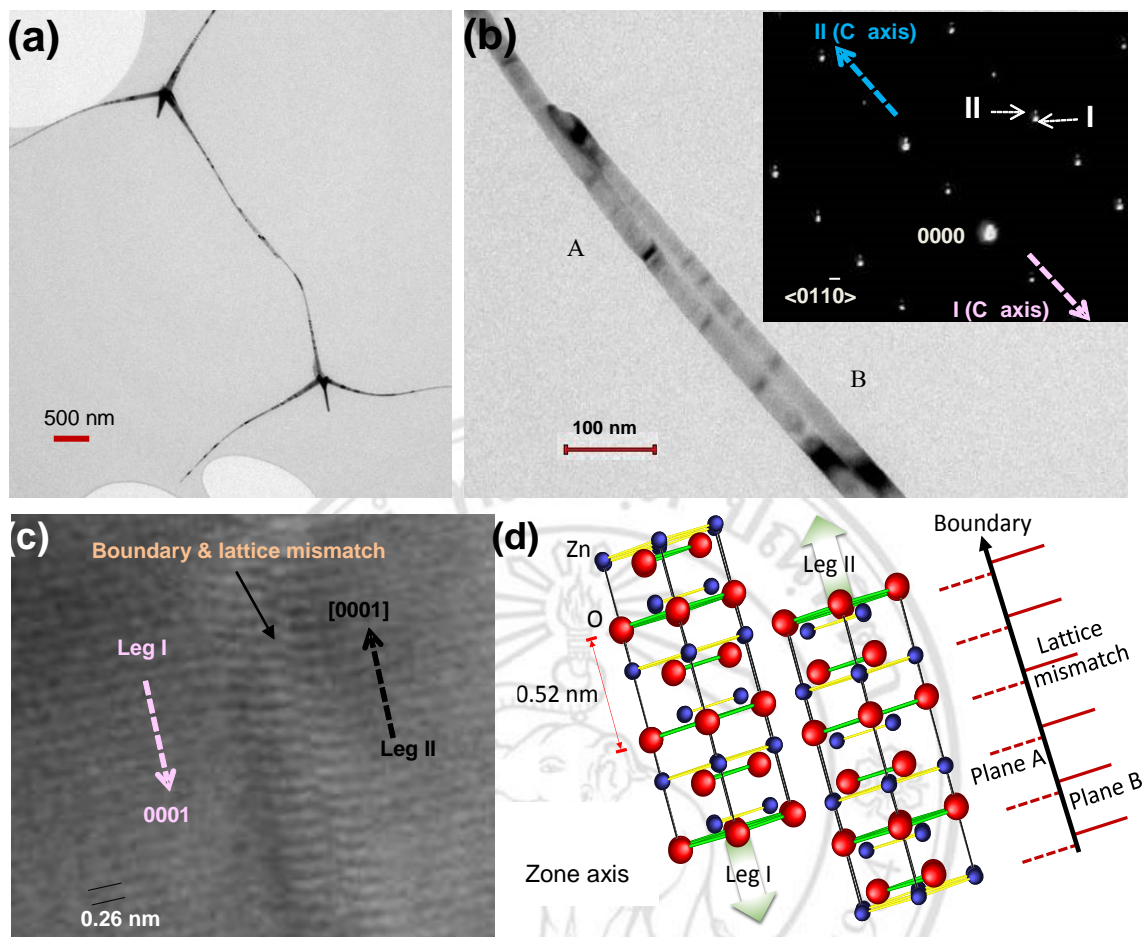


**Figure 2.5** Morphologies of ZnO products obtained from microwave-assisted thermal oxidation: (a) optical image which ZnO products can be distinguished into two regions, (b) FE-SEM image of tetrapod-like ZnO at the bottom region, (c) FE-SEM image of ITN-ZnO at upper region, and (d) high magnification FE-SEM image of ITN-ZnO showing the inter-link between tetrapods. Reprinted with permission from ref [70].

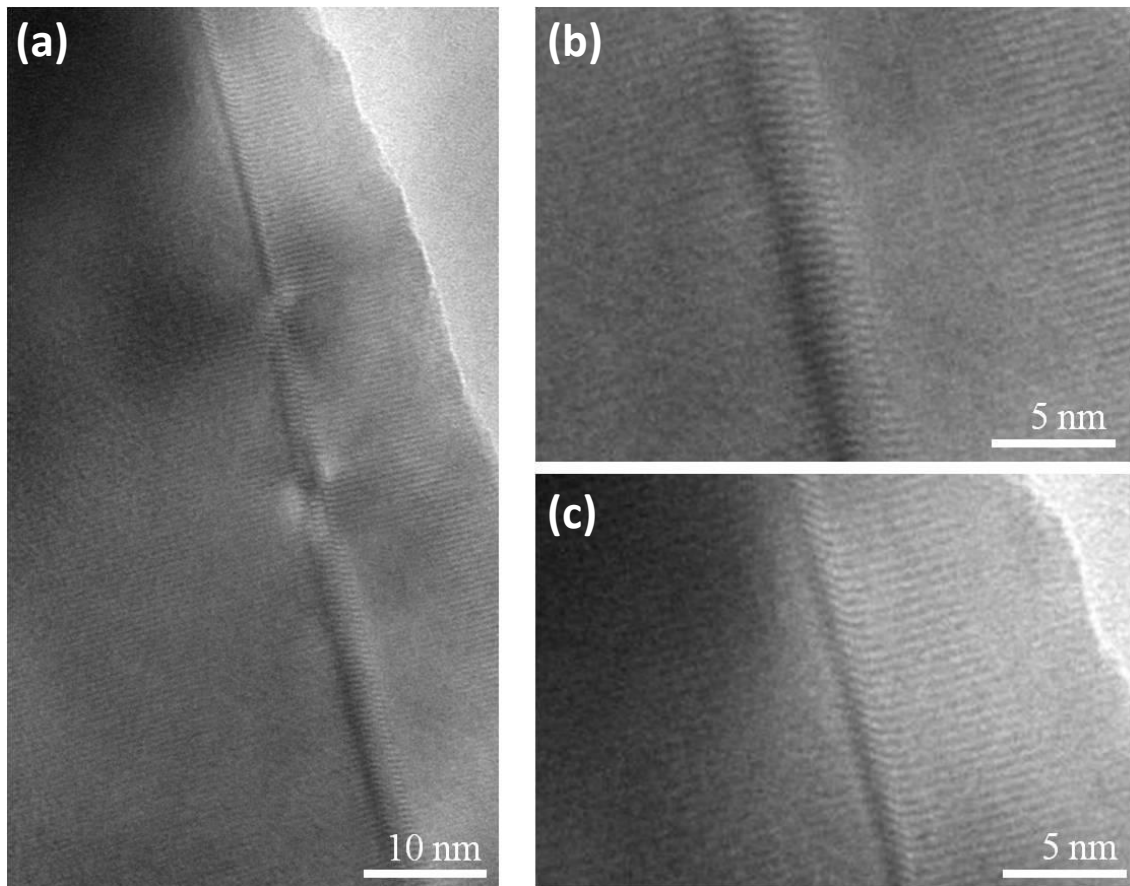
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**Figure 2.6** TEM image of the two ZnO tetrapods network: (a) BF-TEM image of two ZnO tetrapods network (“A” and “B”), (b) high magnification BF-TEM image of the leg marked “I” of the tetrapod “A” connecting with the leg marked “II” of the tetrapod “B”, together with a corresponding selected-area electron diffraction pattern (SADP) from the connected region of these legs. (c) HRTEM image at the boundary between legs “I” and “II”, and (d) schematic plan view of the hexagonal ZnO structure along Zone axes in order to explain small mismatch displacement of about  $c/8$  at the boundary. Reprinted with permission from ref [70]. Copyright (2015) American Chemical Society.



**Figure 2.7** ITN-ZnO was observed several regions for the investigation of lattice displacement (a), (b) and (c). The images are shown below. However, it has selected the clear and meaningful image to put in the manuscript as in **Fig 2.6c**.

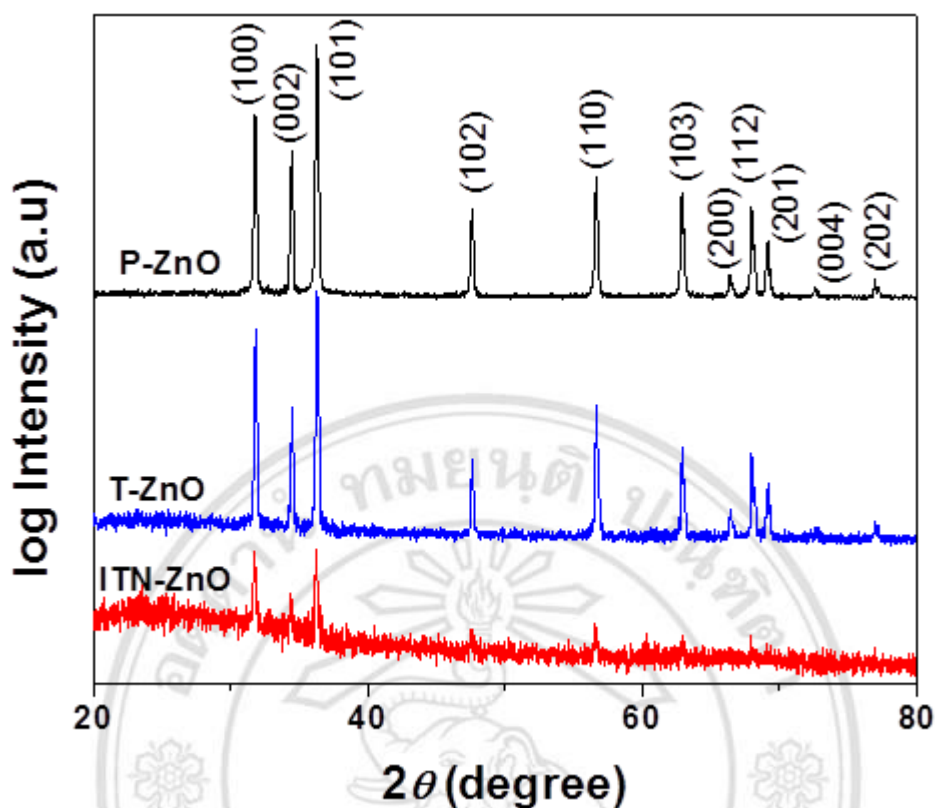
To understand for ITN ZnO formation, TEM is used for further investigation. **Fig. 2.6a** shows a bright-field TEM (BF-TEM) image of the two ZnO tetrapods network and **Fig. 2.6b** shows a high magnification BF-TEM image of the leg marked “I” of the tetrapod “A” connecting with the leg marked “II” of the tetrapod “B”, together with a corresponding selected-area electron diffraction pattern (SADP) from the connected region of these legs. From trace analysis, it was possible that these legs grew along  $\langle 0001 \rangle$  c-axis direction. Normally, each leg of tetrapod had exhibits growth direction along  $\langle 0001 \rangle$  c-axis [26]. Hence, it can be suggested that, at the connected region, these legs grew in the opposite, but equivalent,  $\langle 0001 \rangle$  c-axis directions.

The **Fig. 2.6c** presents a high-resolution transmission electron microscopy (HRTEM) image of the linking between the legs “I” and “II”. The spacing of the lattice

fringes is measured to about 0.26 nm or  $c/2$  where  $c$  is the  $c$ -axis lattice parameter in the ZnO hexagonal structure (0.52nm). It can be seen that at the boundary between the legs, the lattice fringes are continuous suggesting epitaxial linking. However, the lattice fringes of both legs are not fully matched, but a small displacement of about  $c/8$  can be clearly observed.

The lattice mismatch term  $[100-101]$  explain the condition where two materials featuring different lattice constants are exposed together. In general, lattice mismatch will obstruct growth of defect-free epitaxial materials layer unless thickness of the film layer is lower than certain critical thickness. In this case lattice mismatch is continuous suggesting epitaxial linking in both legs of the two ZnO tetrapods.

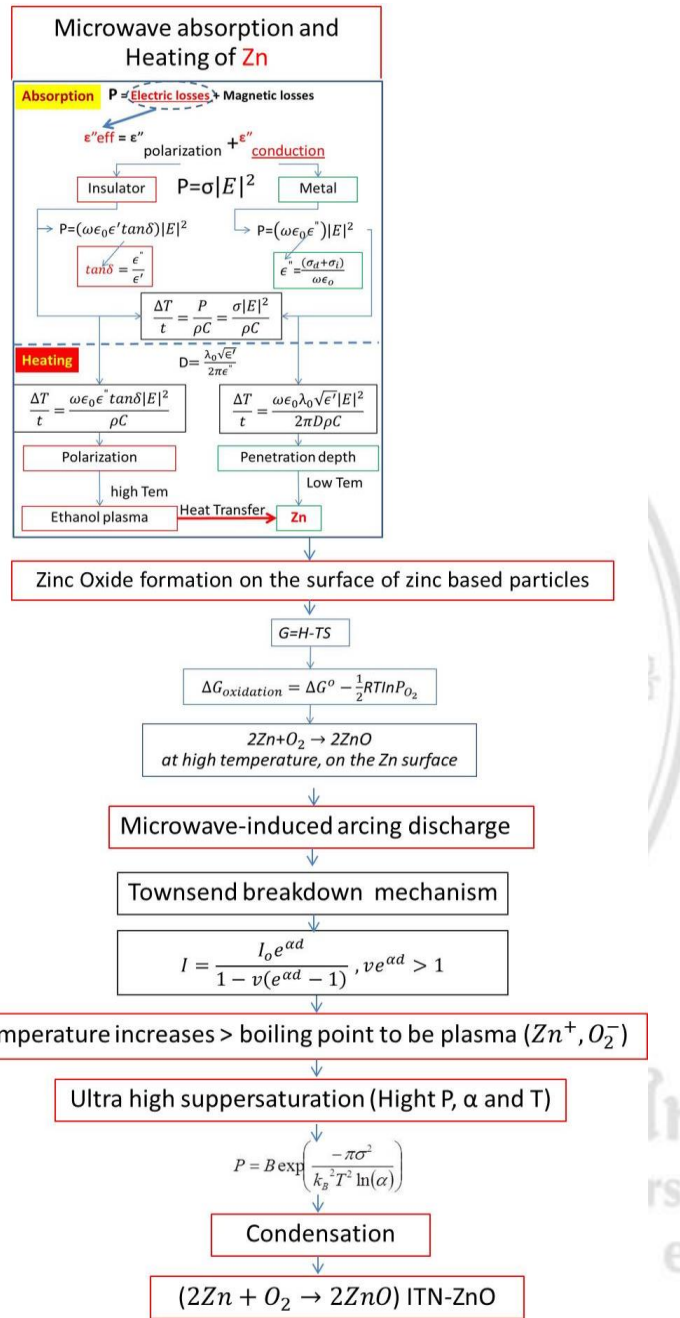
To explain the structural observation above, the schematic plan view of the hexagonal ZnO structure along Zone axes is sketched in **Fig. 2.6d**, composing of alternating Zn and O ion planes stacking along the  $c$ -axis. An O ion plane locates at  $c/8$ , the distance from the second Zn ion plane to the base plane is  $c/2$ , and the next O ion plane locates at  $5c/8$ , and so on. From TEM results, the leg I and leg II are connected with opposite growth directions and must be bonded together via some electrostatic force or ionic bond. So, it is likely that the connection between two legs is performed by chemically bonding between positive charge zinc ions with negative charge oxygen ions due to coulomb charge interaction. Hence, the small mismatch of about  $c/8$  at connection boundary is required for this chemical bonding as observed in TEM. It should be noted that the growth kinetic of ITN-ZnO is composed of two main steps: tetrapod growth and then, connecting and linking growth. The detailed study is our on-going research.



**Figure 2.8** XRD patterns of ITN-ZnO compared with T-ZnO and P-ZnO. The samples were characterized by X-ray powder diffractometer (Siemens D-500) with Cu  $K\alpha$  radiation. It can be seen that all samples have a similar XRD pattern and the diffraction peaks can be indexed as the wurtzite structure ZnO with  $a=b=0.3253$  nm,  $C=0.5213$  nm, which is in good agreement with the JCPDS No.79-2205. Reprinted with permission from ref [70]. Copyright (2015) American Chemical Society.

The crystallinity of the samples has been investigated by using XRD measurements. The XRD spectra of the ITN-ZnO and T-ZnO are compared with commercially available P-ZnO, as shown in **Fig. 2.8**. It can be seen that the XRD patterns of the ITN-ZnO and T-ZnO samples are similar to that of P-ZnO. These diffraction peaks can be indexed as wurtzite structure of ZnO with  $a=b=0.3253$  nm,  $c=0.5213$  nm, which is in good agreement with the JCPDS No.79-2205.

## 2.2 Growth mechanisms of the ITN-ZnO



**Figure 2.9** Schematic diagram explained mechanism microwave assisted thermal oxidation method.

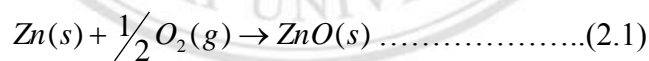
A microwave-assisted thermal oxidation method has critically dependent on several factors including, morphology, size, surface conditions, ionization energy, purity and dielectric of the material [87]. A growth mechanism of ITN-ZnO by microwave-assisted thermal oxidation method is shown in the flow charts of **Fig. 2.9**.

There are three main processes; microwave absorption processes, heating processes and condensation processes. The microwave heating and absorption can be explained by the power equations of the material combining electric losses and magnetic losses by solvent (ethanol) and metal (Zn powder). The power dissipated into or absorbed by the material conversion of electromagnetic energy into heat can be expressed by **Eq. 1.4** from Maxwell's equations [47].

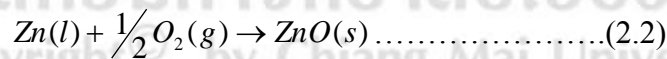
Ethanol is added into the Zn powder metal in the microwave absorption processes due to the Zn powders metal have electric losses only, high penetration depth (**Eq. 1.7**), low conductivity and less ion drift current. Then Zn powders in microwave have the power energy conversion to temperature less than melting point of Zn. Ethanol can be plasma in microwave and transfer heat to the Zn powder then temperature of Zn powder increase. Due to ethanol has high dielectric, the effective relative dielectric loss factor from polarization in **Eq. 1.6** and low boiling point to rapidly conversion to the plasma.

Heating processes; Zn powder gets heat energy due to heat transfer from ethanol plasma. Then, zinc oxide formation on the surface of zinc based particles can be explained by the Gibb free energy.

The oxidation reaction of Zn solid that below melting point can be expressed as[88]:



Even though the chemical reaction of Zn liquid is shown as:



Though, an imperative parameter for the materials feature of thermodynamics potential is Gibb free energy.

The Gibb free energy (G) of a phase is given by [47]:

$$G = H - TS \dots\dots\dots(2.3)$$

The free energy of a system is the summation of its enthalpy (H) and the product of the temperature (T: Kelvin) and the entropy (S) of the system.



The activities are approximately one in solid. Even though activity in oxygen is an oxygen pressure in the system can be reduced to:

$$\Delta G = \Delta G^0 - \frac{1}{2} RT \ln P_{O_2} \dots\dots\dots(2.4)$$

In this work, the oxidation reaction of Zn powder surface is related to temperature and pressure in **Eq. (2.4)**. Ellingham has presented a simple process to consider oxidation reaction. The pressure and temperature can oxidize metal to form oxide layer at the equilibrium of oxygen, metal, and metal-oxide ( $\Delta G=0$ ). At the equilibrium, **Eq. (2.4)** can be reduced to:

$$\Delta G^0 = \frac{1}{2} RT \ln P_{O_2} \dots\dots\dots(2.5)$$

For an oxygen molecule 1 mole in chemical oxidation reaction, **Eq. (2.5)** goes to

$$\Delta G^0 = RT \ln P_{O_2} \dots\dots\dots(2.6)$$

The relation between Gibb free energy, the pressure temperature and of oxygen can be schemed in the Ellingham diagram.

Then arcing phenomena in systems of Zn powder metal under microwave irradiation is described by Wen Chen, et al[52]. An electric current of the conducting material is in Fe, Zn, Cu, and Sn. They have negative and positive charges placing on each opposite sides of the metal. The charges are inductive by a field opposing the electric field. In electrostatic equipoise has none electric fields all over the place inside the conductor because of the charges inside the material amount the outside electric field. the electromagnetic field does not vanish directly but decays exponentially inside the material.

Then, Field emission [89]: has the saturation current density enhance using reduction in work function and enhance in temperature.

The microwave oven has high electric field. It is applied among the electrodes at high temperature, the effective work function ( $W$ ) of the cathode reductions and the current density ( $J_s$ ) is then provided by

$$J_s = AT^2 e^{-W/KT} \dots\dots\dots(2.7)$$

The electric charges on the conductor shift completely to the surface of conductor, the shape and material have effect due to Zinc oxide formation on the surface of zinc based particles to be oxide nucleation with the distribution of charging, but then the charge on the surface of material does not spread itself uniformly. So, the manufacturing an electric spark or an electric arc on the Zn powder's surface that is sharp edges or points possibly and sub-microscopic deformation. The surface charge density and the outside electric field may possibly reach very high values. The maximum electric field strength that able to be spark by the material in closed the conductor is determined by its dielectric strength [52].

Microwave-induced arcing discharge that is therefore by Townsend breakdown mechanism [89, 90], as following

$$I = \frac{I_0 e^{ad}}{1 - V(e^{ad} - 1)}, Ve^{ad} > 1 \dots\dots\dots(2.8)$$

where  $I$  imply the current flowing in the system,  $I_0$  imply the current generated at the Zn particle surface,  $V$  imply amount of electrons discharged from the cathode per incident positive ion[90],  $d$  imply the distance between the Zn particles of the system, Townsend's first ionization of coefficient the term  $e^{ad}$  is known as the electron avalanche and it is the amount of electrons created by one electron in travelling from cathode to anode (between zinc particles of Zn powder).

The current in the anode is equivalent to the current in the outside circuit. In theory the current come to be infinitely great within the directly above point out condition but then practically it is limited by the resistance of the outside circuit and in part by the voltage drop in the arc. The condition  $Ve^{ad} = 1$  expresses the condition for start of spark and the Townsend criterion for spark creation or Townsend breakdown measure. The amount of ion pairs created in the gap by the trail of arc electron break down is appropriately great and the bring about positive ions on bombarding the cathode are equal to release one secondary electron and so grounds a repetition of the fall procedure. The discharge is then supposed to be self-sustained as the discharge will sustain itself smooth if the source turn out  $I_0$  is removed. Therefore, the condition  $Ve^{ad} = 1$  defines the inception sparking condition. If  $Ve^{ad} > 1$  Here ionization

created by successive snow slip is increasing. The spark discharge grows more fast the more  $Ve^{ad}$  go above unity. If  $Ve^{ad} < 1$  Here the current  $I$  is not self-sustained on deletion of the source the current  $I_0$  ceases to drift.

However, microwave-induced arcing discharge between Zn particles is corona discharge that in non-uniform fields a number of manifestations of bright and easy to hear discharges are observed long in advance the whole breakdown occurs. These discharges may possibly transient or stable state and are call as 'coronas'. So, it can be heated very fast from power dissipated after those has corona discharge between Zn particle in air and arcing phenomena in metal-solvent and temperature high enough to be change the liquid, gas and plasma of sample in the microwave field[89].

Condensation processes; The saturation of the plasma zinc particles and the difference between the temperatures surrounding the origin combine with oxygen in the air is enough to cause the ultrahigh supersaturation ratio, which resulted in an increase of the nucleation probability in **Eq. 1.1**. Then, the 3D structure able to form by growth and then condensation of ITN-ZnO vapor because of supersaturation conditions with fast growing along c-axis and slow growing in other directions.

### **2.3. Chapter Summary**

ITN-ZnO has been successfully synthesized by using a microwave-assisted thermal oxidation. With this simple and fast process, the ITN-ZnO has been obtained.