CHAPTER 1

Introduction

1.1 Introduction

Size dependence of nanoparticles during solid-solid phase transition is one of the most interesting nanotechnology due to different effect of nanoparticles, bridging of bulk materials (250–1000 nm), atomic/molecular structures (50–250 nm) and even quantum-size effect (<50 nm). Physical properties of bulk materials should have constant value but nanosize-dependent properties are generally varied. Basing on the melting point of nanoparticles, the thermal behaviors have inverse size dependence in phase transition temperature due to the direct correlation of volume-surface ratio. In condensed form of fine powder, irregular particle size and shape can lead to non-uniform packing morphology and density. Thus, the properties of materials change as their size approaches nanoscale. The atoms at the surface of a material and phase control are the key step to improve functionality and become significant for industrial and military sectors [1–4].

Zinc Titanium Oxide system has been one of the most important oxides in material science. In the form of zinc titanates has a promising material as a gas sensor [5](for ethanol, NO, CO, etc.), paint pigment [6], catalyst [7] and etc. Also Zn_2TiO_4 has been reported as a material with exceptional electrical properties which could be a suitable contender as microwave resonator [8]. However, zinc titanates are made up of highly compressed grain particles whose sizes range from nano- to micrometers. With nanotechnology, it is expected that some of the application performance can be enhanced because of a large surface-to-volume ratio and symmetry breaking on the surface, nanoscale zinc titanates have shown physical properties different from their bulk counterparts. Driven by this, the preparation and characterization of nanoscale Zinc titanates, in the form of nanoparticles, nanotubes, nanorods and nanowires have been recently receiving much attention.

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ZnO-TiO_2 nanoparticles with high surface area to volume ratio provide the reduction of melting point of a material with reduction in the size. This phenomenon is very interesting in nanomaterials, which melt at a temperature hundreds of degrees lower than the bulk. Melting-point depression can create a large driving force for diffusion, especially at elevated temperature [9]. $ZnTiO_3$, Zn_2TiO_4 and $Zn_2Ti_3O_8$ phases form very readily because of their thermodynamic stability, precisely stoichiometric amounts of ZnO-TiO_2 nanocomposites and the effect of spinel structure. Previously, coarse particles require large energy to produce the titanate. Basing on the ZnO-TiO_2 phase diagram, they require more than 900 °C, which can cause some competition reaction: decomposition of $ZnTiO_3$ into Zn_2TiO_4 + TiO_2 (rutile), and $Zn_2Ti_3O_8$ into Zn_2TiO_4 + TiO_2 (rutile) and interfere the synthesis of pure phase [10–13].

The synthesis of Nanorods of metallic and semi-conducting materials have been studied intensively and drawn a lot of research interest because of their potential applications in fields like nanoelectronics, opto-electronics, sensors and also offer fascinating potential for future technological applications [14]. Nanorods exhibit unique electrical, magnetic, optical, thermoelectric and chemical properties compared to their bulk counterpart [15]. Electronic conduction takes place both by bulk conduction and through tunneling mechanism and quantum confinement effect Nanorods(1-D): particle travel only along the rod direction [16]. The special characteristics of nanorods are high density of electronic state, diameter-dependant band gap, enhanced surface scattering of electrons and phonons and increased excitation energy, high surface to volume ratio and large aspect ratio [17]. Deeper understanding and sufficient control of the growth of nanorods and nanowires are central to the current research interest.

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The fabrication of solid nanorods Zinc titanates is very challenging due to the natural of morphology products always result in irregular morphologies, the uncontrollable agglomerated grains size often results in microstructures or even the purity of products which can forces some researchers aim to build double layer zinc titanates/ZnO or TiO_2 [18]. The controlled synthesis can be realized through various hard or soft template strategies for example, molecules/atoms physically fill up a hollow channel to form nanorod, or they self-organize in 1D manner due to an anisotropic elongation, or they grow with the assistance of a metal catalyst. However, the difficulty for ternary spinel nanostructures is the control of morphology and composition. The structures of titanium dioxide (TiO_2), $Zn_2Ti_3O_8$, $ZnTiO_3$ and Zn_2TiO_4 comprised of TiO_6 octahedra. In rutile and in$ZnTiO_3$, the connection of the TiO_6 octahedra results chains and/or layers. As a result of this resemblance, $ZnTiO_3$ is formed only in thepresence of rutile [19]. Zinc titanates are generally synthesized by characteristic solid state reactions at high temperatures [20]. Due to some confines of solidstate synthesis, such as large grain size and uncontrolled and irregular morphologies, different kinds of alternative techniques have been depicted including mechano-chemical activation [21,22], molten salt synthesis [23], a semi chemical route combined with vigorous micro beads milling [24,25] and sol-gel method. But the sol-gel methods are generally complicated and the reagents used are expensive. So this work will present an easier ones by using the processes for preparing highly quality of powders, better homogeneity, control morphology and smaller particle size are preferred. Moreover, ZnO nanorods were use as the template and high surface-to-volume ratio Anatase-TiO_2 nanoparticles which easily fused to form Zinc titanate under melting-point depression effect. Upon calcinations, the nanoparticles TiO_2 were fused and deposited on ZnO nanorods surface then Zinc titanate nanorods were obtained.

1.2 Zinc Titanium Oxide System [26]

1.2.1 Zinc Oxide (ZnO)

1.2.1.1 Physical Properties

Synonyms	Zinc Oxide
Molecular formula	ZnO
Molecular	weight 81.38 g/mol
Appearance	White solid
Melting point	1975 °C
Solubility in water	Insoluble

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1.2.1.2 Crystal Structures

Point group 6 mm or C_{6v} hexagonal and space group is $P6_3mc$ or C_{6v}^4. The lattice usually value are $a = 3.25$ Å/ $c = 5.2$ Å; the ratio $c/a \sim 1.60$ is approximate to the flawless amount for hexagonal $c/a = 1.633$. Additionally, in almost periodic table metal II-VI, as in ZnO is enormously ionic (Zn^{2+}–O^{2-}) with the reference radii of 0.074 nm for Zn^{2+} and 0.140 nm for O^{2-}.

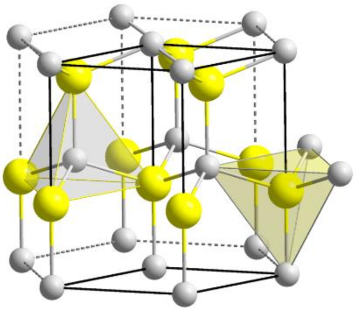

Figure 1.1 the structure of Hexagonal wurtzite ZnO [26]

zincblende structure is called F43m or 216. In FCC lattices there are 2 atom types from interpenetrating. But from rock-salt, there is some different in the structure in two lattices are located corresponding to one another. Tetragonal coordination in zinc blend: The atoms closest up to consist of 4 atoms of the contrast type, located like the 4 vertices of a regular tetrahedron. Furthermore, in zincblende structure has arrangement in the same as cubic structure especially diamond, in contrast, with different types of atoms at the alternative lattice sites.

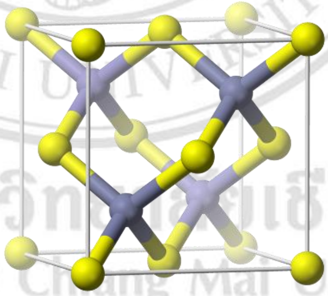

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Figure 1.2 The structure of Cubic Zincblende ZnO [26]

1.2.2 Titanium Dioxide

1.2.2.1 Physical Properties

Synonyms	Titanium (IV) Oxide
Molecular formula	TiO_2
Molecular	weight 79.88 g/mol
Appearance	White solid

Melting point	1975 °C
Solubility in water	Insoluble

1.2.2.2 Crystal Structures

Crystal structures of rutile usually has tetragonal unit cell. The value of cell parameters are a=b and a =4.584 Å and c=2.953 Å. The coordination of cations (titanium) is 6 which have 6 oxygen atoms surrounded. Trigonal planar of oxygen anions have C.N. number of 3. Its octrahedron has an axis screwed in the rutile structure.

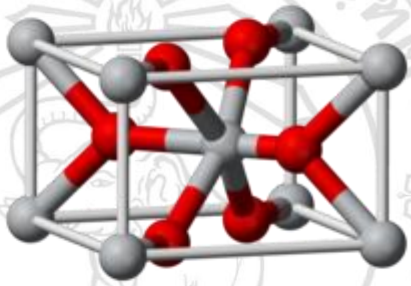

Figure 1.3 the structure of Rutile Titanium Dioxide [26]

Anatase TiO_2 is the rarest shares the same properties as rutile such as luster, hardness and density. Because of structural were differences from rutile in crystal unitcell. But they still share the same symmetry, tetragonal 4/m 2/m 2/m, despite. In anatase TiO_2, four edges hence the four-fold axis were shared in octahedron. Anatase can form the 8 faced tetragonal dipyramids and the elongation is enough to distinguish this structure form from octahedral crystals, but the truth, anatase is faultily called "octahedrite".

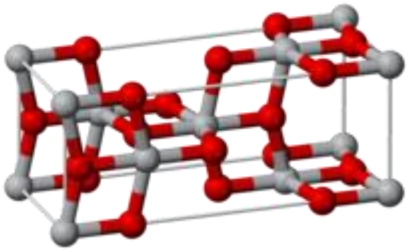

Figure 1.4 The structure of Anatase Titanium Dioxide [26]

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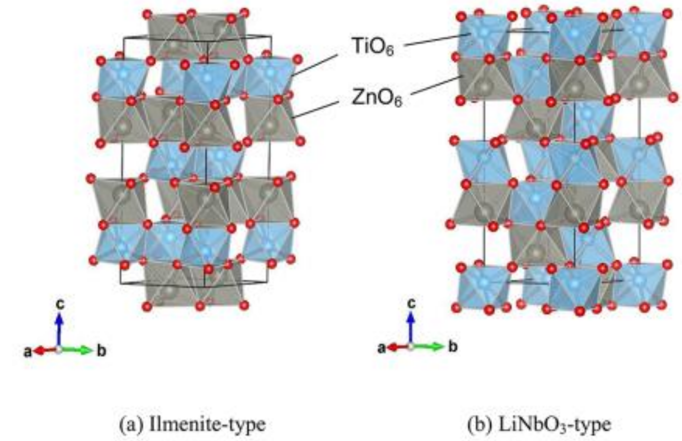
1.2.3 Zinc Titanates

1.2.3.1 Zinc Metatitanate ($ZnTiO_3$)

$ZnTiO_3$ is perovskite structures (ABO_3) which contains 1ZnO and $1TiO_2$ (rutile) in the ratio of 1:1. The crystal structure usually has 2 forms a. Ilmenite-type b. $LiNbO_3$-type



(a) Ilmenite-type (b) $LiNbO_3$-type

Figure 1.5 The crystal structure of Zinc Metatitanate [26]

1.2.3.2 Zinc Orthotitanate (Zn_2TiO_4)

Zinc Orthotitanate is spinel structure (AB2O4) which contains $ZnO:TiO_2$ (2:1). The crystal structure usually has 2 forms a. spinel type b. inverse-spinel type

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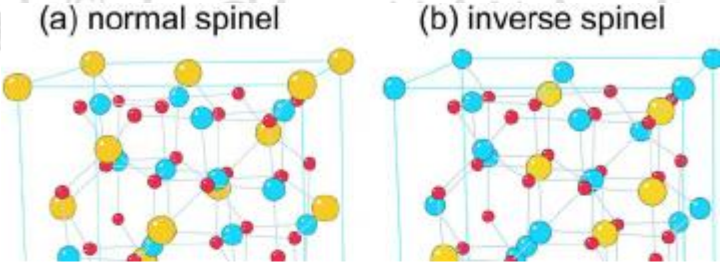

Figure 1.6 the crystal structure of Zinc Orthotitanate [27]

1.2.3.3 Zinc Polytitanate ($Zn_2Ti_3O_8$)

Zinc polytitanate is defect-spinel type structure which contains $ZnO:TiO_2$ in the atomic ratio of 2:3. The defect-spinel structure is one of the most interesting spinel structure due to it might contain some vacancies as regular part of the crystal. Having lots of vacancies as show in the figure 1.7

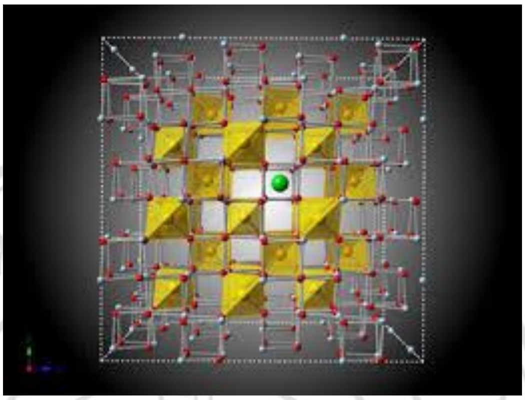

Figure 1.7 the crystal structure of defect-spine [26]

1.3 Hydrothermal synthesis

Hydrothermal synthesis is a procedure of synthesis of powder single crystal that depends on hot water with high pressure helping the minerals solution forming. The autoclave consists of steel pressure vessel which crystalgrowth is froming in a nutrient was support along with solvent (water). The growth chamber is depending upon the temperature. Until the temperature cool down the seed crystal start growing and crystallized until growing the desired crystal. [27]

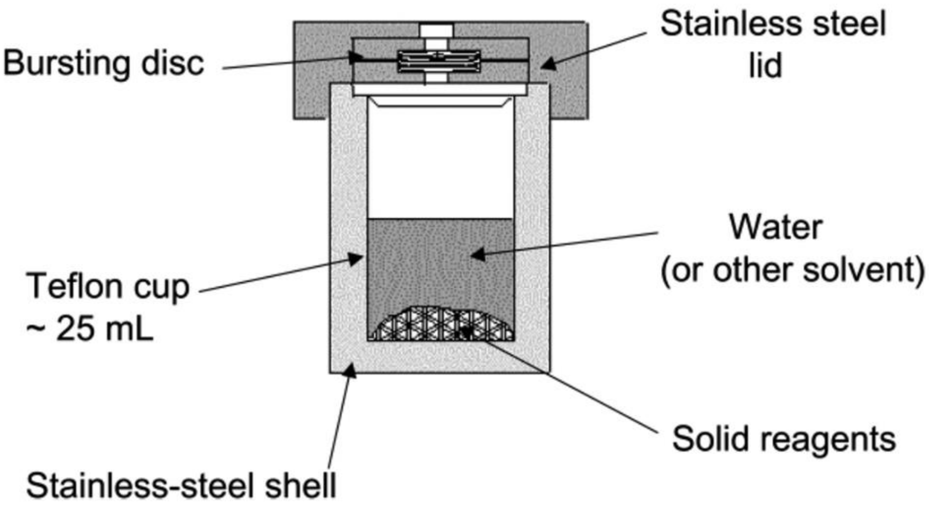

Fig 1.8 Hydrothermal process [27]

1.4. Literature and Application Review

In The few decades, synthesis of Zinc Titanate usually required high temperature up to 1000 ^{o}C which can cause the particles and morphology trend to agglomerate into a large particle likes micro scale range. The morphology of the product trend to agglomerated into irregular morphology which is not suitable for using in their applications. For example, catalysts and sorbents for removing sulfur from coal burning gasification should require a large surface area to give more available reaction faster. In addition, the phase purity of zinc titantes products usually affected from using too high temperature calcinations. Commercials grade of the ZnO and TiO_2 would can caused the major problems in the reaction, too because the large particle of commercial grades of precursor needed high temperature for diffusion procedure upon the calcinations process. The particles of precursor should prepare to be ready to diffusion to form titanates during calcinations by using synthesis method that give fine particles, homogenously of nanocomposites and structure flavor to form. [28]

The solutions to solve these major problems are understanding the reaction flavor of each zinc titanates to produce the highest phase purity, reducing the reaction temperature to avoid competition reactions and use the novel methods likes hydrothermal methods to prepared the good precursor. [29,30]

Yang and Swisher [31] reported that the ZnO/TiO_2 phase diagram is well established for a temperature above 1000 ^{o}C. At lower temperature, there is an uncertainty about the range of stability of three zinc titanate compounds, $ZnTiO_3$, Zn_2TiO_4 and $Zn_2Ti_3O_8$. In particular, there is controversy over whether $Zn_2Ti_3O_8$ is stable or metastable. In the research described here, the results of previous investigators confirmed that isothermal treatment gave different phase composition with different starting materials of the same composition. However, by carrying out cyclic chemical transformation experiment, it was found that $Zn_2Ti_3O_8$ is a stable compound at a temperature up to approximately 800 ^{o}C.

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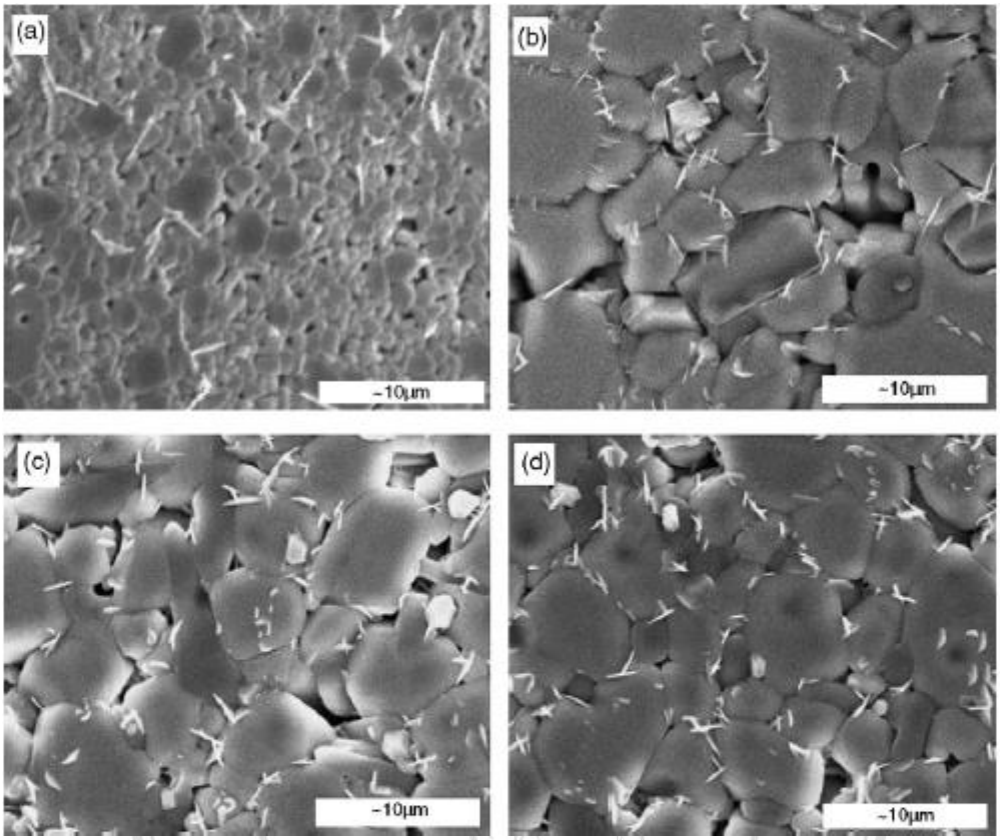

Fig 1.9 the morphology and size problems that occurred in synthesis zinc titanate in the past published by X. Liu and co-worker in 2007. [29]

For the detail gives by phase-diagram, the first region that we should consider for avoid the competition reactions are 945 °C and 800 °C. The decomposition reaction when temperature higher than 945 °C was zinc metatitanate diffusion together to give zinc orthotitanate and rutile which can cause the major problems in phase purity. Next, decomposition reactions of zinc polytitanate into two zinc metatitanates and rutile when the temperature higher than 800 °C. So, the recommended temperature that suitable should at least lower than 800 °C for avoid those competition reactions.

This bring to the method that applied for reduce the temperature was called melting point reduction in nanoscale S.L. Lai [32] reported that melting-point depression in gold nanoparticle is the phenomenon of nanoscale material reduction the melting point up to its size which can helped lower up to hundreds degrees celcius when compared to bulk material. The answers why the reduction occurred in nanoscale material was surface area to volume ratio which can caused react at much faster than bulk materials, high

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surface available to react with the heat up on the calcinations and provides the speed up in thermodynamic processes by driving force to reduce the free energy.

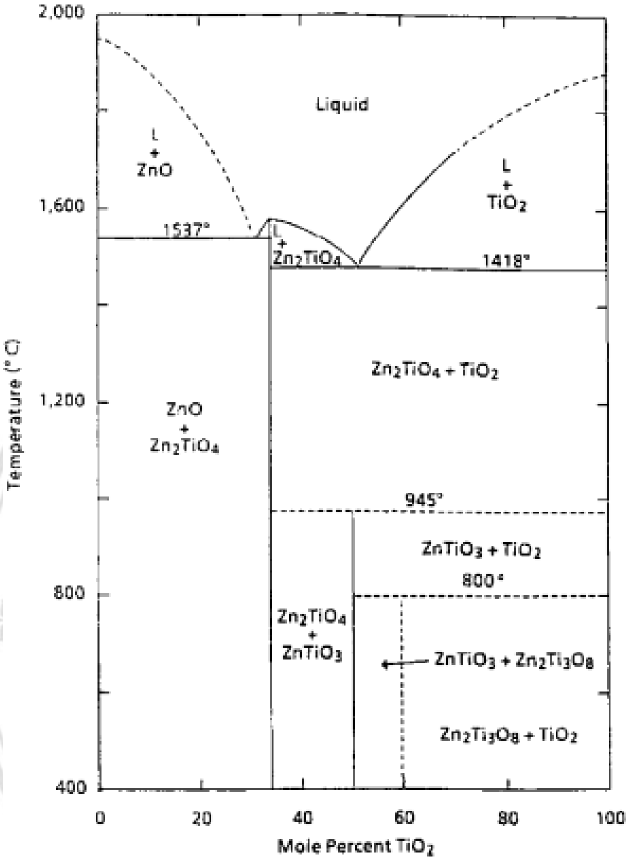

Fig 1.10 ZnO-TiO_2 phase diagram published by J. Yang and J.H. Swisher [31]

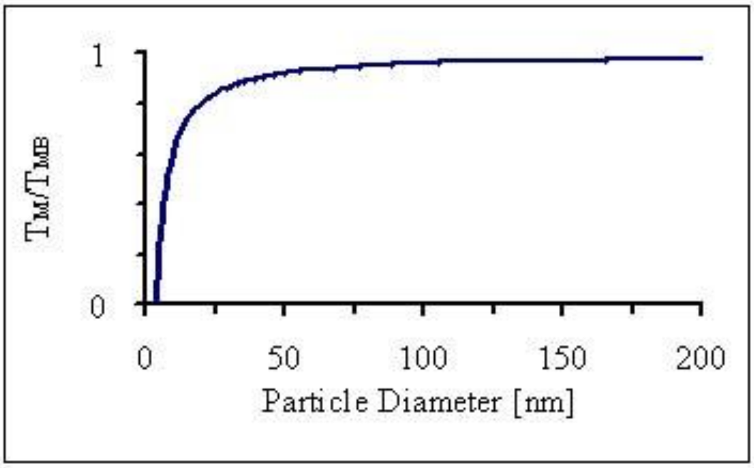

Fig 1.11 melting-point depression in gold nanoparticle [32]

Satoh and coworkers [33] reported that structures of titanium dioxide are the main factors to synthesis each of zinc titanates because of the flavor phase combination which specific to the precursor’s structure. Firstly, anatase is the role play structure to synthesis the zinc orthotitanate and zinc polytitanate and rutile flavor to formed zinc metatitanate.

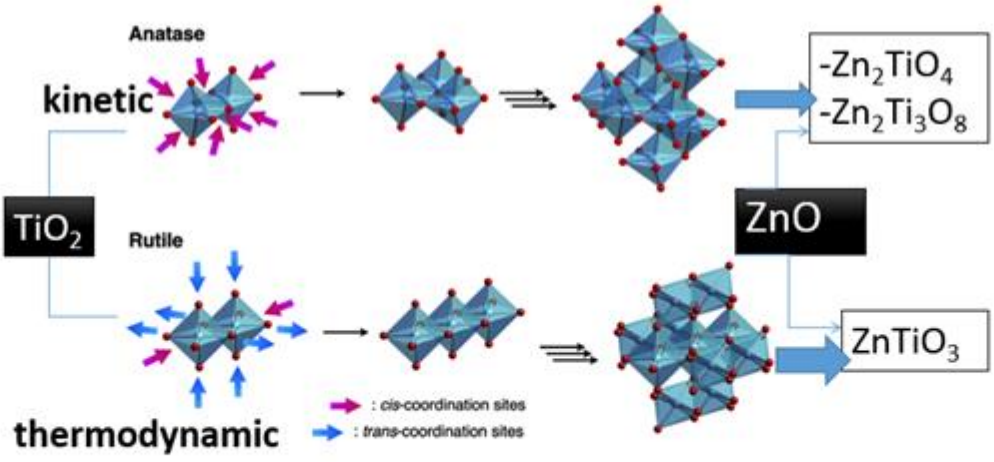

Fig 1.12 schematic images for kinetic and thermodynamic control of the nucleation of rutile and anatase.

So, the reaction in this work should prepare well under the influences between kinetic and thermodynamic by the studied conditions to produce each of anatase and rutile structure by varied the heat and time under the hydrothermal processes. When anatase titanium dioxide was starting to form, the nucleation growth must occur in the cis coordination site. The expansion of crystal structures was in the cis- direction between each titanium ion until the anatase reaction completely forming. In contrast, rutile structure flavored to from under thermodynamic control. Satoh and coworkers explained that the nucleation of rutile structure was expanded in the trans- coordination site because of thermodynamic flavored. Each titanium ion was in the trans- direction each other’s and suitable for applied as the precursor of zinc metatitanate. [33]

The process for applied to synthesis nanoscale rutile and anatase structure is hydrothermal method because of it can synthesis under lower temperature when compare to other techniques. The pressure in the hydrothermal process can achieve in both thermodynamic and kinetic control. The precursor was fine particles and

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homogenously which can reduce the calcinations temperatures. The powder contains of high surface area to volume ratio and high crystallinity to help achieved purity phase and time spent.

Recently, the phase purity cannot achieve and satisfied the properties in each application. The morphology is one of the main factors to improve the applications of the product to highest achievement. For example, the modification in each application demands the control synthesis for specific morphology to improve their applications in both commercial and industry sections. The important of morphology in the materials can show the best results. Firstly, nanoplate was good in the high resistance and multi-stacked material field. Next, nanorods were good in the electron conducting and opto-electric applications. Nanotubes were design for storage, template, transport and devices materials. Nanospheres were used as drug delivery candidate and promising catalysts. Lastly Nanoparticles have high surface area characteristic which suited for catalyst, pigment and photosentisizer applications.

The general method for synthesis controlled morphology was template synthesis. Template synthesis is one of the most promising methods for the nanoscale materials for achieve the desired morphology by direct the formation of the products even it was difficult to prepare. Template based methods can apply in various nanomaterials in large scale and capable of preparing nanostructures with unique morphology, properties and even structure as shown in fig 1.13.

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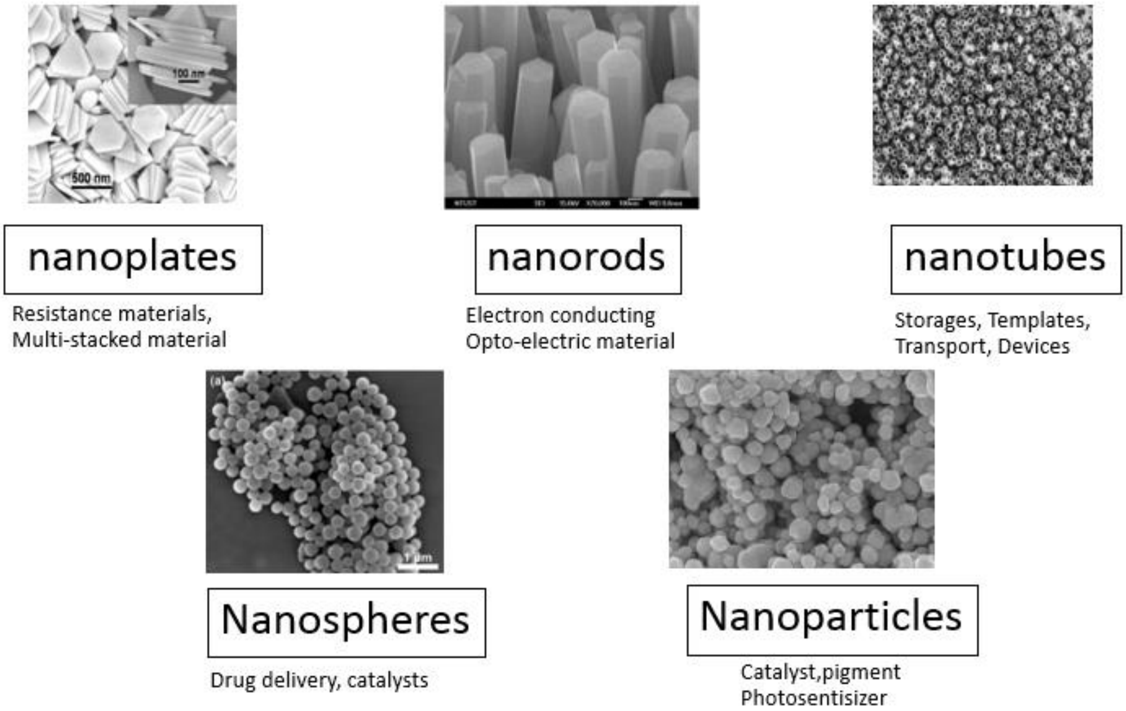

Fig 1.13 various types of morphologies applied in many applications [34]

Template synthesis can be divided into two types. First, soft template is the template like organic molecules for assisting in synthesis formation which can provide good shape of the morphology and size of nanomaterials. The commercial organic molecules generally use in synthesis are SBA-15 [35], MCM-41[36] etc. Next, hard template was the method that applied inorganic material like silica for assisting in synthesis nanomaterials. However, this method was difficult for produce good morphology and required some separation or elimination of the template. The commercial hard template is the mesoporous carbon, CMK-1[37] etc. But in this work, we synthesis at high temperature. So, we developed new template for applied at high temperature without using supporting materials because zinc titanates required high temperature for operated that would affect to supporting materials. Some supporting materials were degraded or can caused melting to the products which hard to elimination or separation from the powders.

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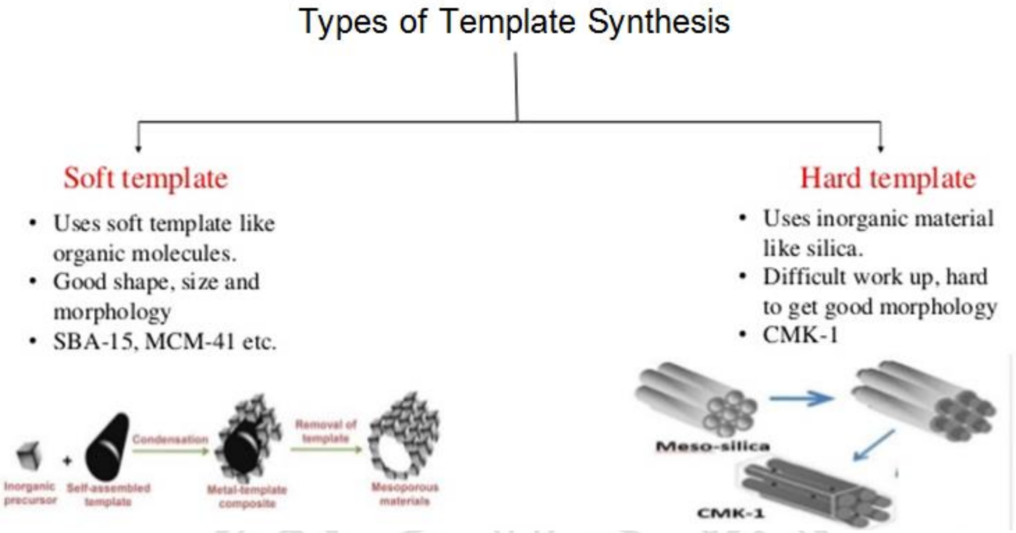

Fig 1.14 Types of template synthesis [38]

The template design in this work was shown in fig 1.15 which composes of (A) Stationary phase and (B) Labile phase. Stationary phase is the controlled morphology phase preferred less reactivity than labile phase, less surface area to volume ratio than labile phase to maintain nanorod morphology and prevent melting [39], slow metal ion diffusion coefficient rate recommended and utility in morphology types to achieve the desire applications. Labile phase is the part of reactively substance which should have high surface area to volume ratio, fast metal ion diffusion coefficient rate, easily melting under calcinations temperature and less than 50nm [40] particle diameter size recommended for this phase. Lastly, labile phase should deposit on stationary phase for better performance up on calcinations processes.

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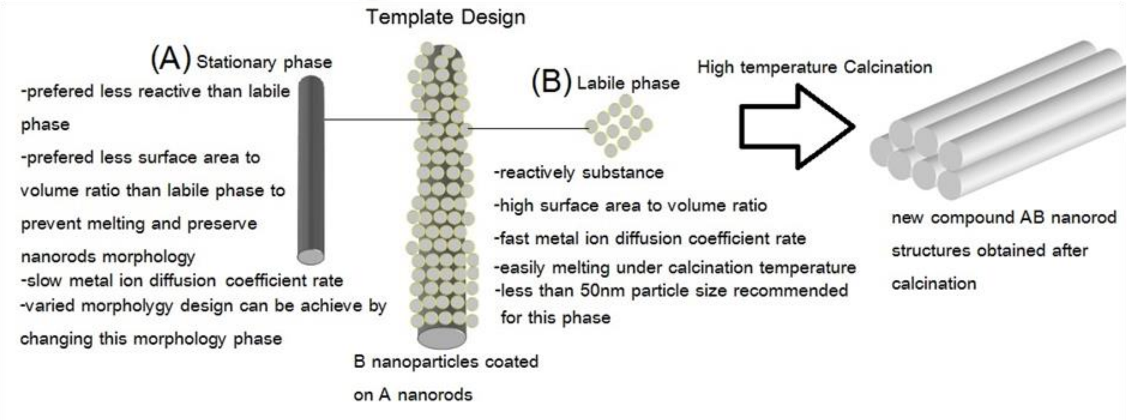
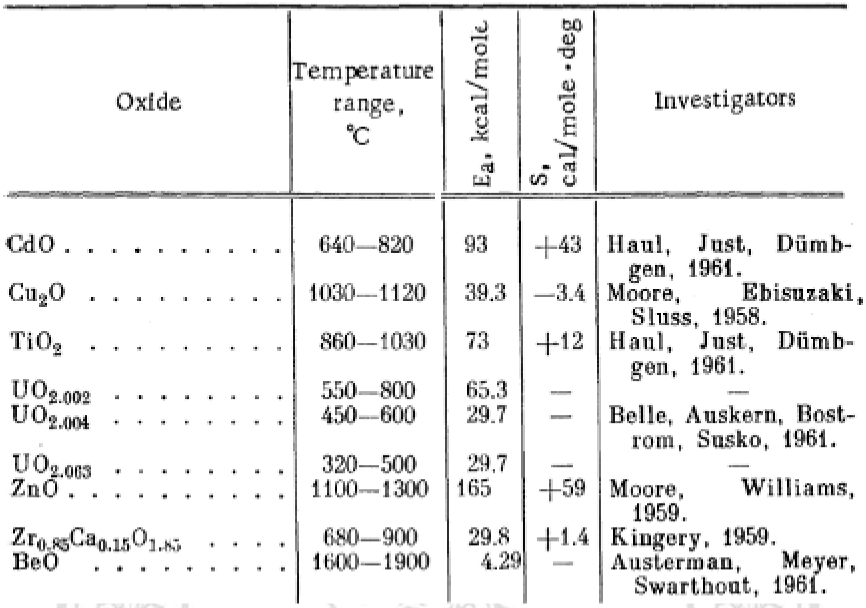


Fig 1.15 template concept designed for this work

Table 1.1 diffusion processes and kinetics of reactions in the solid state published by N.A. Taranov [41]



Oxide	Temperature range, °C	E_a, kcal/mole	S, cal/mole · deg	Investigators
CdO	640—820	93	+43	Haul, Just, Dümbgen, 1961.
Cu_2O	1030—1120	39.3	—3.4	Moore, Ebisuzaki, Sluss, 1958.
TiO_2	860—1030	73	+12	Haul, Just, Dümbgen, 1961.
$UO_{2.002}$	550—800	65.3	—	—
$UO_{2.004}$	450—600	29.7	—	Belle, Auskern, Bostrom, Susko, 1961.
$UO_{2.063}$	320—500	29.7	—	—
ZnO	1100—1300	165	+59	Moore, Williams, 1959.
$Zr_{0.85}Ca_{0.15}O_{1.85}$	680—900	29.8	+1.4	Kingery, 1959.
BeO	1600—1900	4.29	—	Austerman, Meyer, Swarthout, 1961.

The challenging in this work to find the best candidate for stationary phase and labile phase is the diffusion processes and kinetics of reactions in the solid state published by N.A. Taranov[41] as in the Table 1.1 Titanium dioxide has the melting point in temperature range of 860 – 1030 ^{o}C[42] and activation energy = 73 kcal/mol [43] which were all lower than ZnO. So, ZnO should be considering as stationary phase in this work while TiO_2 consider as labile phase. However, the mentioned temperature of TiO_2 was in the range 860 – 1030 ^{o}C belonged to bulk materials. So, nanoscale materials TiO_2 was recommended for this phase to reduce the temperature to below 800 ^{o}C [44] for avoided competition reaction as shown in the figure 1.16

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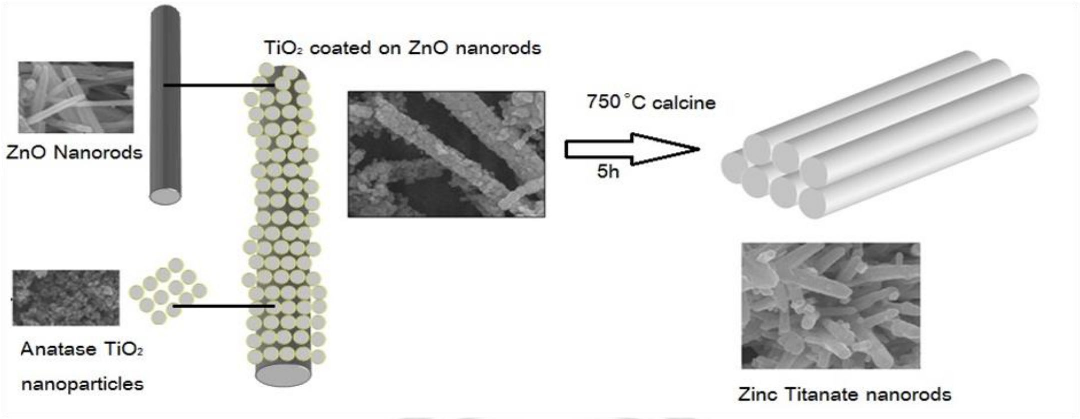

Fig. 1.16 template synthesis designed for zinc titanate nanorods

1.5 Research objectives

1.5.1 To develop the synthesis of one-step ZnO-TiO_2 nanocomposites by hydrothermal method

1.5.2 To study the effect of molar ratio, reaction temperature and holding reaction time on the synthesis of ZnO-TiO_2 nanocomposites by hydrothermal method.

1.5.3 To study the effect of calcination temperature to synthesize $ZnTiO_3$, Zn_2TiO_4 and $Zn_2Ti_3O_8$ by using ZnO-TiO_2 nanocomposites as the precursors.

1.5.4 Tocharacterize the synthesized materials by variety of operation techniques including XRD, FE-SEM, TEM, HR-TEM, FTIR, SAED-TEM, EDX, Raman and Photoluminescence.

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