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Physical and Thermal Properties of Zirconium Tungstate Nanoparticles with Different Morphologies from Hydrothermal Synthesis

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Physical and thermal properties of zirconium tungstate nanoparticles with different morphologies from hydrothermal synthesis

By: Hongchao Wu

A thesis submitted to the graduate faculty
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Program of Study Committee:
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Mufit Akinc
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Table of Contents

Acknowledgements ................................................................................................................. iv
Abstract .......................................................................................................................................... v

Chapter 1. Introduction ................................................................................................................ 1
  1.1 Negative thermal expansion materials .............................................................................. 1
  1.2 Phase transition and NTE behavior in ZrW₂O₈ .................................................................. 2
  1.3 Synthesis of ZrW₂O₈ ........................................................................................................ 5
  1.4 Hydration phenomena of nano-sized ZrW₂O₈ ................................................................. 6
  1.5 ZrW₂O₈ composites .......................................................................................................... 7
  1.6 Research objective .......................................................................................................... 9

Chapter 2 Experimental techniques .......................................................................................... 10
  2.1 Materials .......................................................................................................................... 10
  2.2 Synthesis ........................................................................................................................ 10
  2.3 Characterization .............................................................................................................. 12
    2.3.1 X-ray diffraction (XRD) .......................................................................................... 12
    2.3.2 Isothermal X-ray diffraction .................................................................................. 14
    2.3.3 Scanning electron microscopy (SEM) ..................................................................... 15
    2.3.4 Thermogravimetric analysis (TGA) ....................................................................... 15
    2.3.5 Brunauer-Emmett-Teller (BET) surface area analyzer ........................................... 16

Chapter 3 Study on controlling morphologies and crystallite sizes of ZrW₂O₇(OH)₂·2H₂O nanoparticles ................................................................................................................ 21
  3.1 X-ray diffraction results of nano-scaled ZrW₂O₈ and ZrW₂O₇(OH)₂·2H₂O ......................... 21
  3.2 Effects of experimental parameters on morphologies of ZrW₂O₇(OH)₂·2H₂O nanoparticles ............................................................................................................................ 23
    3.2.1 Effect of initial reactants ......................................................................................... 23
    3.2.2 Effect of acid types ............................................................................................... 29
    3.2.3 Effect of acid concentration ................................................................................ 33
    3.2.4 Effect of reaction temperature ............................................................................. 40
    3.2.5 Effect of reaction time .......................................................................................... 47
  3.3 Conclusion ......................................................................................................................... 53

Chapter 4 Characterization of thermal and physical properties of zirconium tungstate nanoparticles ...................................................................................................................... 55
  4.1 Selection of zirconium tungstate nanoparticles for characterization ................................. 55
4.2 Characterization of negative thermal expansion properties ............................... 57
4.3 Hydration of ZrW₂O₈ nanoparticles...................................................................... 61
4.4 Characterization of pore structures of ZrW₂O₈ nanoparticles.............................. 64
4.5 Study on correlation of hydration and pore structures in ZrW₂O₈ nanoparticles ......... 67
4.6 Conclusion.............................................................................................................. 69

Chapter 5. Summary and Future works .................................................................. 70
References...................................................................................................................... 73
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Abstract

Negative thermal expansion (NTE) materials belong to a group of solids that perform contractions in volume under heating conditions, instead of thermal expansion observed in most other solids. Due to this special negative thermal property, NTE materials are gradually drawing research interest for their potential application as fillers in composites used to control thermal stress” generating from mismatch of thermal expansivity and to govern the overall thermal expansion behavior.

Zirconium tungstate (ZrW$_2$O$_8$) is a ceramic material that exhibits strong, isotropic NTE over a wide temperature range from 0.3 to 1050 K. The formation and transition of three phases ZrW$_2$O$_8$ can be achieved under certain temperatures and pressures. ZrW$_2$O$_8$ nanoparticles can be synthesized at lower temperatures by hydrothermal reaction followed by a subsequent heat treatment by converting the precursor ZrW$_2$O$_7$(OH)$_2$·2H$_2$O to ZrW$_2$O$_8$. However, nano-sized ZrW$_2$O$_8$ was reported to display a hydration phenomena when exposed to ambient external conditions. Through the careful selection of experimental parameters such as initial reactant types, acids types and concentrations, as well as reaction time and temperature, the effect of reaction conditions on morphologies and crystallite sizes of ZrW$_2$O$_8$ nanoparticles was characterized using scanning electron microscopy and powder X-ray diffraction. Three types of ZrW$_2$O$_8$ nanoparticles with distinct morphologies and crystallite size-scales were chosen for characterization and comparison. Thermal and physical properties, as well as the hydration problem, were compared using various techniques, including isothermal X-ray diffraction, Brunauer-Emmett-Teller (BET) surface area analyzer and thermogravimetric analysis. It was found that the synthesized ZrW$_2$O$_8$ nanoparticles present more negative CTE values than bulk-scaled in α-phase, and the CTE is dependent on the crystallite sizes of nanoparticles. All three
types of nanoparticles underwent different extents of hydration problem originated from moisture adsorption, which is determined by pores structure formed by agglomeration of nanoparticles. It was observed that ZrW₂O₈ nanoparticles with smaller dimensional sizes tended to form large pores and suffered from most severe hydrations.
Chapter 1. Introduction

1.1 Negative thermal expansion materials

The majorities of solid materials contain a positive coefficient of thermal expansion (CTE) and undergo an expansion in volume upon heating. The simplest level of thermal expansion can be illustrated by the asymmetry of the potential well of a diatomic molecule\(^1,2\): As temperature increases, the gradual population of higher energy vibrational modes gives rise to an increase in the interatomic distances.

However, there are several materials that show the negative CTE values and exhibit a contraction in volume with a rise temperature. Such solids have important applications in composites materials to tailor the overall thermal expansion behavior. They are especially useful for zero expansion composites that can be utilized in high precision optical mirrors, fiber optic systems and the packaging industry\(^2\). The majority of materials that show the negative thermal expansion (NTE) behavior are oxides with a linear metal-oxygen-metal linkage and corner sharing MO\(_x\) polyhedral frame structure as shown Fig. 1-1. The heat absorption will excite the vibrations in the transverse direction of the oxygen atoms and cause a reduction in structure volume\(^3\). The NTE materials can be categorized into the structural families of cubic AM\(_2\)O\(_7\)\(^2,4,5\), cubic AM\(_2\)O\(_8\)\(^6-8\) and orthorhombic A\(_2\)(MO\(_4\))\(_3\)\(^9,10\), whose oxygen atom is connected by two metal atoms to form an open flexible structure. For the cubic AM\(_2\)O\(_7\) structures, the typical example of such materials is ZrV\(_2\)O\(_7\). The origin of NTE behavior is from the rotations of VO\(_4\) tetrahedral and distortion of ZrO\(_6\) octahedral\(^4\). In case of A\(_2\)(MO\(_4\))\(_3\), where octahedral A cationic site can be occupied by a trivalent cation (Sc\(^{3+}\), Al\(^{3+}\)) and a tetrahedral M cationic site can be occupied by Mo\(^{6+}\) and W\(^{6+}\), the transverse thermal vibrations occur in A-O-M linkages giving rise to the NTE
behavior. Cubic AM$_2$O$_8$ (A=Zr, Hf; M=W, Mo) is another well acknowledged structure family of materials that display the negative thermal expansion behavior. The most important and widely studied one is zirconium tungstate (ZrW$_2$O$_8$), which exhibits very strong and isotropic NTE over a wide temperature range from 0.3 to 1050 K$^7$.

Fig. 1-1 A schematic representation of transverse vibrations of Metal-Oxygen-Metal bonds results in the NTE behavior in open framework of oxides$^5$.

1.2 Phase transition and NTE behavior in ZrW$_2$O$_8$

At room temperature, ZrW$_2$O$_8$ is in metastable state since it can only be thermodynamically stable from 1378 to 1530 K. As heating up to 1050 K, ZrW$_2$O$_8$ decomposes into ZrO$_2$ and WO$_3$.$^{11}$ Fig. 1-2 shows a cubic ZrW$_2$O$_8$ structure that consists of corner sharing ZrO$_6$ octahedra (in green) and WO$_4$ tetrahedra (in red). Each WO$_4$ tetrahedron only shares three of its four oxygen atoms and leaves an oxygen atom in free position$^{12}$. Due to the uniquely flexible metal-oxygen-metal linkage, the transvers vibration of the oxygen atom, connected between the Zr and W atoms, excited at a low thermal energy results in small counter-rotations
of WO₄ and ZrO₂ polyhedra. This is the origin of the negative thermal expansion properties of ZrW₂O₈, and is also termed as a “quasi-rigid unit mode” by A. Pryde and coworkers⁵,¹³.

To our knowledge, there are three phases of ZrW₂O₈ existence under certain temperature and pressure conditions. An early study on NTE behavior of ZrW₂O₈ done by A. Sleight and coworkers⁷, revealed that discontinuous changes of expansion at 430 K is observed in the temperature range of 0.3 to 1050 K, which indicates a reversible order-disordered α-β phase transition. Below 430 K, α phase ZrW₂O₈ shows the cubic crystal structure (space group P2₁3) with the CTE value of -8.8 × 10⁻⁶ °C⁻¹. When ZrW₂O₈ is heated above 430 K, α-ZrW₂O₈

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**Fig. 1-2** Polyhedral representation of cubic crystal structure of ZrW₂O₈
transforms into $\beta$-ZrW$_2$O$_8$ with CTE of $-4.9 \times 10^{-6}$ °C$^{-1}$ (space group Pa$\bar{3}$) due to the disordering of WO$_4$ tetrahedra$^7$. The mechanism of the phase transition from acentric to centric cubic also stems from the special flexible structure of ZrW$_2$O$_8$: At low temperatures, since the corner-sharing structure of ZrO$_6$ and WO$_3$ led to ZrW$_2$O$_6^{4+}$, the two free oxygen ions coordinate with the tungsten atom to form WO$_4$ groups. At higher temperatures, the positions of the two terminal oxygen ions become disordered and migrate to the position that bonds with two WO$_4$ tetrahedra groups with equal probabilities$^2$.

Another irreversible phase transition of ZrW$_2$O$_8$ was observed and reported by J. Evans et al in 1997$^{14}$. It is shown that $\gamma$-ZrW$_2$O$_8$ can be obtained under pressures at 0.2 GPa from $\alpha$-ZrW$_2$O$_8$. The $\gamma$-phase with orthorhombic structure (space group P2$_1$2$_1$2$_1$) can be reverted back to $\alpha$-phase under heating at 393 K and ambient pressure. In this irreversible transition process, about 5% reduction in volume is observed, which is caused by the migration of oxygen atoms bonded to the tungsten atom$^{14}$. It is noted that $\gamma$-ZrW$_2$O$_8$ also exhibits negative CTE but one order of magnitude less than cubic $\alpha$-ZrW$_2$O$_8$ due to the lowering of framework flexibility, which is assumed to be contributed to the less pronounced negative thermal expansion characteristic.

When the applied pressure reaches a higher level, an irreversible amorphization of ZrW$_2$O$_8$ is present. C. Perottoni and J. Jornada$^{15}$ reported that orthorhombic $\gamma$-ZrW$_2$O$_8$ undergoes pressure induced amorphization starting from 1.5 GPa to above 3.5 GPa with no Bragg peaks observed. Although the amorphous zirconium tungstate can be preserved after removal of the external pressure, it can be recrystallized into $\alpha$-ZrW$_2$O$_8$ under ambient pressure upon heating above 923 K$^{15}$. In recent years, several studies have been done to understand the ZrW$_2$O$_8$ and
ZrMo$_2$O$_8$’s amorphization mechanism by investigating the changes in microscopic local structure.$^{16-20}$

1.3 Synthesis of ZrW$_2$O$_8$

A wide variety of methods have been reported for the synthesis of ZrW$_2$O$_8$. In 1959, J. Graham and coworkers$^{21}$ first reported the successful synthesis of ZrW$_2$O$_8$ by the traditional solid state reaction followed by quenching to avoid decomposition of ZrO$_2$ and WO$_3$. Due concerns regarding the quality of synthesized ZrW$_2$O$_8$ with this method and the importance of exploring alternative methods, several researches investigated the sol-gel routes to synthesize ZrW$_2$O$_8$.$^{22,23}$ M. Dadachov and R. Lambrecht$^{24}$ revealed that the hydrothermal method facilitated the formation of single crystalline ZrW$_2$O$_8$ at a lower temperature. C. Georgi and H. Kern$^{25}$ reported a ZrW$_2$O$_8$ preparation method by an amorphous citrate process.

Although several methods are available for synthesis of zirconium tungstate, only two methods are reported to be effective for synthesis of nano-scaled zirconium tungstate. The first method is the combination of sol-gel and reverse micelle methods reported by Sullivan and Lukenhart$^{26}$ in 2005. Yet, there is a small amount of impurity of WO$_3$ in the synthesized ZrW$_2$O$_8$ that restricts its application. The hydrothermal reaction method, is the most widely applied for synthesis of pure and highly crystallized nanoparticles. In this method, the precursor of AM$_2$O$_8$, hydroxide hydrate AM$_2$O$_7$(OH)$_2$·2H$_2$O, can be obtained from a certain combination of reactants reacting in an acidic medium at a high temperature and high pressure; then the cubic AM$_2$O$_8$ can be obtained through a calcination process to dehydrate the precursor. In recent years, several works reported on the synthesis of optimized ZrW$_2$O$_8$ nanoparticles by investigating the experimental variables in the hydrothermal reaction. Q. Xing et al.$^{27}$ and X. Xing et al.$^{28}$ investigated the crystallization and growth of ZrW$_2$O$_8$ nanorods by altering the acidity of the
reaction medium. J. Colin et al.\textsuperscript{29} conducted a more detailed study of the effects of experimental conditions, including acid types and concentration, reaction temperature and time on morphologies via the hydrothermal method. He found that higher concentrations of counter ions with the presence of chloride ions significantly improved crystallization kinetics of nanoparticles in an acidic solution. Kozy and coworkers\textsuperscript{30} reported that the hydrothermal synthesis of ZrW\textsubscript{2}O\textsubscript{8} nanoparticles with width of 10 to 15 nm and length up to 500 nm depended on the reaction conditions. They also reported that non-agglomerated and individual nanoparticles could be produced by using a mixture solution of high concentrations of acids and 1-butanol. The hydrothermal method is a widely studied synthesis method not only for ZrW\textsubscript{2}O\textsubscript{8}, but also for Mo-substituted ZrW\textsubscript{2}O\textsubscript{8} and ZrMo\textsubscript{2}O\textsubscript{8}. In previous works, C. Lind et al.\textsuperscript{6} and S. Allen et al.\textsuperscript{31} reported that synthesized the cubic ZrMo\textsubscript{2}O\textsubscript{8} can be obtained from dehydration of ZrMo\textsubscript{2}O\textsubscript{7}(OH)\textsubscript{2}·2H\textsubscript{2}O in hydrothermal reaction. Besides that, several studies of the nano-sized ZrW\textsubscript{2-x}Mo\textsubscript{x}O\textsubscript{8} were conducted and proved to be effective using the hydrothermal route\textsuperscript{32-34}.

1.4 Hydration phenomena of nano-sized ZrW\textsubscript{2}O\textsubscript{8}

The hydration of zirconium tungstate imposes a potential problem that will limit the practical application of ZrW\textsubscript{2}O\textsubscript{8}. The first study revealing the hydrated cubic ZrW\textsubscript{2}O\textsubscript{8}·xH\textsubscript{2}O synthesized by the hydrothermal method was reported by N. Duan et al.\textsuperscript{35}. Water insertion of ZrW\textsubscript{2}O\textsubscript{8} not only causes the collapse of structure framework and a 10 vol% contraction with no changes in Zr-O or W-O bond length by the increase of tungsten coordination and slight twisting of ZrO\textsubscript{6} octahedra, but also changes in space group from P2\textsubscript{1}3 to Pa\textsubscript{3}. It was reported that , the unit cell parameter changes from 9.15 Å to 8.84 Å followed with CTE for water-inserted ZrW\textsubscript{2}O\textsubscript{8} displayed weakly positive values as 1 mole of water inserted in 1 mole of ZrW\textsubscript{2}O\textsubscript{8} to form ZrW\textsubscript{2}O\textsubscript{8}·1H\textsubscript{2}O\textsuperscript{35}. In the recent study by N. Banek and coworkers\textsuperscript{36} regarding the
autohydration of nano-sized cubic ZrW$_2$O$_8$, indicated that the origin of nano-sized ZrW$_2$O$_8$
hydration was attributed to the increasing defect sites on the surface of nanoparticles which
formed during the synthesis with the addition of alcohol for the unagglomeration of ZrW$_2$O$_8$
nanoparticles. However, no further detailed information was revealed about how the defects and
surface area of nanoparticles effect the hydration reaction.

1.5 ZrW$_2$O$_8$ composites

Due to the significance of NTE, zirconium tungstate can be used as filler integrated into
various materials to produce composites with the controllable CTE. Previously, several research
projects on composites with ZrW$_2$O$_8$ were done by choosing metal and ceramic as the matrix
materials. X. Yang and coworkers$^{37}$ reported that ZrO$_2$/ZrW$_2$O$_8$ composites synthesized with
weight ratio of ZrO$_2$ and WO$_3$ was 2.5:1 showed a nearly zero CTE value (0.67 × 10$^{-6}$ K$^{-1}$). X.
Yan and coworkers$^{38}$ reported that CTE of Cu/ZrW$_2$O$_8$ composites achieved to 4.85 × 10$^{-6}$ K$^{-1}$
when 65 vol% of ZrW$_2$O$_8$ was applied. J. Tani and coworkers$^{39}$ reported that CTE of
Phenolic/ZrW$_2$O$_8$ composites decreased from 46 × 10$^{-6}$ to 14 × 10$^{-6}$ K$^{-1}$ when increased filler
loadings from 0 to 52 vol% were applied.

However, the most applicable ZrW$_2$O$_8$ composites are based on a polymer matrix. These
are the most applicable not only for being inexpensive and their easy processing method, but also
for their ability to facilitate the formation of a homogeneous mixture when combined with
ZrW$_2$O$_8$. Sullivan and Lukenhart$^{26}$ first reported ZrW$_2$O$_8$/polyimide composites that with 22 vol%
micron-sized ZrW$_2$O$_8$ resulted in 30% reduction in CTE. P. Badrinarayanan and coworkers$^{40}$
reported a 92% reduction in CTE of ZrW$_2$O$_8$/cyanate ester resin can be achieved by the
incorporation of 65 vol% micron-sized ZrW$_2$O$_8$. The size of filler may critically influence the
performance and processing of the composite. On one hand, the properties of nano-scale
materials have been shown to be significantly different from bulk properties of the same material. For example, nano-sized copper oxide (CuO) was observed to display a negative CTE value of \(-1.1 \times 10^{-4} \text{ K}^{-1}\) compared with the positive CTE of bulk CuO under the same temperature ranges\(^{41}\). In previous work, Badrinarayanan, P. and coworkers\(^{42}\) observed differences in the \(\alpha\)-phase thermal expansion behavior between bulk ZrW\(_2\)O\(_8\) and ZrW\(_2\)O\(_8\) nanoparticles synthesized through either the sol-gel or hydrothermal method, with the nanoparticles exhibiting greater magnitude of negative CTE values in the \(\alpha\)-phase. On the other hand, due to smaller particles with larger surface areas this facilitates good particle dispersion in polymer matrices. A reduction of particle size to the nano-scale could help achieve optimal performance with lower loadings. For instance, it has been reported that using only 2 wt% of nano-silica in epoxy thin film composites can achieve equivalent mechanical properties and thermal stability as the composite with a micron-silica loading of 15 wt% and 30 wt%, respectively\(^{43}\). Thus, polymer nanocomposites that incorporate nano-sized ZrW\(_2\)O\(_8\) opens a new realm for investigation of tailoring thermal expansion for applications that are widely used in microelectronic devices and aerospace facilities. One of the recent works done by P. Badrinarayanan and M. Kessler\(^{44}\) revealed that a 10 vol% of ZrW\(_2\)O\(_8\) nanoparticles synthesized by a hydrothermal reaction gave rise to a 20% reduction in CTE.

Apart from reducing the size-scale of the filler, it is necessary to perform proper surface treatment to the ZrW\(_2\)O\(_8\) when mixing it with different polymer melts. The hydroxyl groups on the synthesized ZrW\(_2\)O\(_8\) nanoparticles surface may be compatible with epoxy resin, but failed to show promising interactions with polyimides\(^{45}\). The goal of surface functionalization is to improve the compatibility between the modified filler and the matrix, and alter the physical
properties of the composites. Thus, nano-sized unagglomerated ZrW$_2$O$_8$ with proper surface functionalization is the key to produce nanocomposites with superior performance.

1.6 Research objective

The research project includes two sections in this thesis: First, is work focusing on synthesis of zirconium tungstate nanoparticles with different morphologies and crystallite sizes, by controlling the experimental parameters during the hydrothermal reaction; this is discussed in Chapter 3. A systemic study of the comparison of raw materials, types and concentrations of acids, reaction time and temperature on morphologies and crystallite sizes of ZrW$_2$O$_8$ was investigated.

The second part of the research is to study of the effect of ZrW$_2$O$_8$ nanoparticles morphology and crystallite sizes, on negative thermal properties and on the extent of hydration; this is discussed in Chapter 4. Three types of synthesized ZrW$_2$O$_8$ nanoparticles with distinct morphologies and crystallite sizes were chosen for the characterization CTE values. Explanation of the origin of the hydration phenomena was studied by characterizing the pore structure formed in nanoparticles.
Chapter 2 Experimental techniques

2.1 Materials

To synthesize ZrW$_2$O$_8$ nanoparticles, different initial compounds were selected, including: zirconium oxynitrate hydrate (ZrO(NO$_3$)$_x$·xH$_2$O), zirconium acetate (ZrAc) solution in dilute acetic acid (Zr 16%), and zirconium perchlorate hydrate (ZrO(ClO$_4$)$_x$·xH$_2$O), sodium tungstate dihydrate (Na$_5$WO$_6$·2H$_2$O), ammonium metatungstate hydrate ((NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$·xH$_2$O), and sodium metatungstate hydrate (Na$_6$W$_{12}$O$_{39}$·xH$_2$O) was chosen as the tungsten source for all synthesis experiments. All chemicals were purchased from Sigma-Aldrich (St Louis, MO).

2.2 Synthesis

A hydrothermal reaction is a synthesis method for the crystallization of phases of an aqueous solution under a high temperature and vapor pressure. Originally, the term “hydrothermal” was used in the field of geology. Currently, a hydrothermal reaction is a widely used method for the synthesis of crystalline materials where the reaction is often carried out in a Teflon vessel sealed in a stainless autoclave. The major advantage of hydrothermal synthesis is it facilitates the crystallization of a single crystal product with good quality, which is especially advantageous for the crystalline phases that are unstable at their melting temperatures. Besides that, since the reaction proceeds under a high temperature and high pressure, the reactions efficiency can be improved due to the higher solubility of the reactants in the solvents. Based on the merits of hydrothermal synthesis, various kinds of compounds can be synthesized by hydrothermal reaction, including oxides, molybdates, carbonates and silicates, etc.

Zirconium tungstate hydroxide hydrate, the precursor of zirconium tungstate was obtained by a hydrothermal reaction in an acidic solution. The molarity ratio of zirconium to tungstate was 0.08/0.10 for all experiments, as mentioned by Kozy and coworkers$^{30}$ since it...
facilitates the smallest average particle size. In order to synthesize nanoparticles with different morphologies, several reaction variables were attempted including raw reactants, acids types and concentration, reaction time, and reaction temperature. To examine the effect of the initial reactants, different compounds of zirconium and tungstate were selected for synthesis experiments.

The raw material compositions for a typical experiment consisted of 0.259 g ZrO(NO$_3$)$_2$·xH$_2$O (or 0.347 g ZrO(ClO$_4$)$_2$·xH$_2$O or 1.544 g ZrAc solution) and 0.330 g Na$_2$WO$_4$·2H$_2$O (or 0.242 g (NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$·xH$_2$O or 0.2347 g Na$_6$W$_{12}$O$_{39}$·xH$_2$O). Each were dissolved separately in a specific amount of deionized water to prepare the reacting solutions. Both solutions were then combined slowly and simultaneously in a 23 ml Teflon Parr Bomb to form a mixture. The solutions were stirred continuously for several minutes, followed by the slow addition of the acid solution (5 M, 7 M of HCl or 3 M, 5 M of HClO$_4$) where white precipitates formed during mixing. In case of adding HClO$_4$, 2.758 g NaCl was needed to provide a chloride source and to accelerate the reaction kinetics according to previous work$^{30}$. The total solution occupied 41% of the Teflon Parr Bomb’s volume. After fully mixing the solution for several minutes, the Teflon Parr Bomb vessel was sealed and placed in a convection oven to facilitate a reaction at set temperatures (130 °C or 160 °C) and times (12 h or 24 h). After the completion of the reaction, the white precipitates were removed from the Parr Bomb vessel and centrifuged approximately 5 to 6 times with deionized water to remove any residual acids. After drying in a vacuum oven at 75 °C for 24 h, a fine and white powder of the precursor ZrW$_2$O$_7$(OH)$_2$·2H$_2$O was obtained by gently grinding the mixture with a mortar and pestle. The final product of ZrW$_2$O$_8$ powders was obtained by performing the calcination of the precursor at 600 °C for 30 min.
2.3 Characterization

Several techniques were employed for the characterization of prepared zirconium tungstate nanoparticles, including X-ray diffraction (XRD), isothermal X-ray diffraction, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and Brunauer-Emmett-Teller (BET) surface area analysis.

2.3.1 X-ray diffraction (XRD)

X-ray diffraction is an optical characterization technique widely used to characterize crystalline materials due to the nature of the diffraction (i.e. Bragg’s Law: \( n\lambda = 2d\sin\theta \)). A repeating lattice governs the diffraction pattern, where atoms are fixed in periodic positions within crystalline unit cells. In addition, XRD can also be performed on semi-crystalline and amorphous materials to extract useful information about the structure of the samples.

Initial diffraction patterns are a result of scattering the material’s electron cloud, and then subsequent diffraction occurs due to the interference from the scattered wave fronts. The conditions for maximum diffraction intensity are formulated in Bragg’s law, which is depicted in Fig. 2-1. For an infinitely repeating lattice with spacing \( d \), impinging waves with wavelength \( \lambda \) will scatter and constructively interfere at various angles of incidence, \( \theta \). The order of diffraction, which is the difference of path length between two waves, is given by an integer \( n \).
It is also possible to estimate the crystallite size of sample from XRD pattern by applying Scherrer’s equation:

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$  \hspace{1cm} (2-1)  

where, \(\tau\) is crystallite size, \(K\) is shape factor with the typical value of 0.9, \(\lambda\) is X-ray wavelength, \(\beta\) is full width at half maximum (FWHM) in radians, and \(\theta\) is angle of incident beam. However, it is necessary to make a correction to the FWHM data obtained from XRD due to the instrument’s broadening peak width.

In this experiment, the XRD spectra at room temperature was obtained by using a Scintag Powder XRD instrument with Cu-K\(\alpha\) radiation with a wavelength of 1.5418 Å, scanning range from 10° to 40° at 40 kV/30 mA with scan step of 0.02°. Jade 6 software was used to fit XRD patterns and calculate crystallite sizes for both ZrW\(_2\)O\(_7\)(OH)\(_2\)·2H\(_2\)O and ZrW\(_2\)O\(_8\) based on Scherrer’s equation, with the FWHM values obtained from the diffraction peaks. Silicon
standard data was employed to correct the error from the broadening peaks caused by the instrument.

2.3.2 Isothermal X-ray diffraction

Isothermal XRD measurement is a special XRD technique that can facilitate the characterization of XRD patterns at various temperatures, which provides information about the changes in structure of the sample depending on changes in temperature. In this research, the isothermal XRD was employed to characterize the changes in lattice parameter of unit cells in ZrW$_2$O$_8$ for calculation of CTE values. The measurement was carried out on a PAnalytical instrument together with a temperature controllable hot stage. The procedure for measurement is: first, the samples were heated to 600 °C at a rate of 20 °C/min to evaporate any water residue in the samples and eliminate the effects of adsorbed moisture observed in previous work$^{42}$; then, a cycle of cooling and heating was performed between room temperature and 600 °C in 10 °C temperature steps from 20 to 200 °C, and in 50 °C steps from 200 °C to 600 °C, with heating and cooling rates of 5 °C/min between each measurement temperature. The diffraction data was collected in scan steps of 0.02° from 10° to 90° for 100 second exposure times at each testing temperature. The lattice parameters at different temperatures were obtained by performing Rietveld refinement of each XRD pattern with a General Structure Analysis System (GSAS). In each refinement, a pseudo-Voigt profile of type 2 was employed for fitting the peak profile and 28 histogram variables were refined, including background terms, scaling factors, cell parameters, profile parameters, as well as atomic displacement parameters. The final results for all the refined data were obtained from different temperatures shown as: $\chi^2$ from 2.1 to 5.2 and R-factors (R$_{wp}$) from 4.0 % to 6.7 %.
2.3.3 Scanning electron microscopy (SEM)

Scanning electron microscopy is an important technique providing information about a sample’s surface topography and composition by scanning the sample with a high energy beam of electrons that interacts with the atoms within the sample. Due to the small wavelength of electron beam on the surface, SEM facilitates a high resolution image of the morphologies of a sample.

In this experiment, the nanoparticle morphologies and size scales were characterized by FEI Quanta 250 field emission SEM at 10.00 kV under a high vacuum measurement condition. To prepare the sample, the ZrW$_2$O$_8$ nanoparticles were sealed in 20 ml vials containing an acetone solution and placed in the ultrasonic bath for sonication to get fully dispersed; then two drops of the mixture were placed onto a piece of glass on a carbon black grid. After the solution evaporated and only left nanoparticles on the slide, samples were sputtered a coating layer of iridium with thickness of 2 nm on the surface to inhibit “charging” for non-conductive samples under high energy electron beams in SEM. Nanoparticle sizes were measured by the Quartz PCI viewer V5.1 software.

2.3.4 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a type of thermal analysis measurement used to detect changes in the weight of a material as a function of temperature or time, under a controlled atmosphere. Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C. The technique can be used to characterize materials that exhibit a weight loss or gain due to decomposition, oxidation, or dehydration under a continuous heating environment. In this research, TA Instruments Q50 TGA was used to study the dehydration process in calcination and hydration phenomena of the
synthesized ZrW$_2$O$_8$ nanoparticles by determining the weight loss of their water contents. The procedure of determining dehydration is to weigh approximately 10 mg of a sample in an alumina pan and then heat that sample under Nitrogen gas to 600 °C at rate of 20 °C/min and isothermally for 30 min; For the study of the amount of water hydrates gain during hydration process, 10 mg samples were heated under nitrogen gas to 190 °C at a rate of 20 °C/min and held for 10 min until no further weight loss was observed.

2.3.5 Brunauer-Emmett-Teller (BET) surface area analyzer

A Brunauer-Emmett-Teller (BET) surface area analyzer is a principal technique for the analysis of the surface of a sample such as surface area and porosity of a solid$^{46}$. The mechanism of BET analysis is based on the adsorption and desorption of gases such as N$_2$ onto the sample as a function of relative pressure and can be illustrated in Fig. 2-2. At low pressures, the gas molecules first begin to be adsorbed at isolated random sites on the surface of sample; as the gas pressure increases, the monolayer is formed on the sample and more layers can be built up to form multiple layers if the amount of N$_2$ is increased further, and finally when all the pores are filled at a very high pressure it is called condensation. This can be measured and used to estimate the pore size, volume and distribution. The BET equation is shown below:

$$\frac{1}{v(p/p_0-1)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \left( \frac{p}{p_0} \right)$$  \hspace{1cm} (2-2)

where, $p$ and $p_0$ are the equilibrium and saturation pressure of adsorption, $v$ is the volume of gas adsorption, $v_m$ is the volume of gas adsorbed by monolayer, $c$ is BET constant, expressed as:

$$c = \exp\left( \frac{E_1-E_L}{RT} \right)$$  \hspace{1cm} (2-3)
where, $E_1$ and $E_L$ are the heat of adsorption for first layer and higher layers. The total surface area is described as the external surface area plus the micro-pores area and can be calculated by the following Equation 2-4:

$$S_{BET,Total} = \frac{(v_m N s)}{V}$$

(2-4)

where, $v_m$ is the molar volume of adsorbed gas for monolayer, $N$ is Avogadro’s number, $s$ is adsorption cross section, $V$ is molar volume of adsorbed gas.

Fig. 2-2 Scheme of pore filling during the BET analysis
A porous material is a solid with a pore matrix in its continuous structure, such as Zeolite. However, some other solids can also create pores without these pore structures. For instance, nanoparticles tend to join together under a strong electrostatic force on the surface to form agglomerates, the voids created by the aggregation of the nanoparticles constitute a pore system on the sample. Pore can be classified into three types according to the width of pore system in the solids as shown in Table 2-1. For micropore structures, due to the proximity of the walls, the interaction potential is much higher than in wider pores structures. In mesopores, capillary condensation plays an important role. In macropore structures, pore ranges are very wide.

**Table 2-1** Classification of pores according to width

<table>
<thead>
<tr>
<th>Pore type</th>
<th>Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micropores</td>
<td>$d &lt; 2 \text{ nm}$</td>
</tr>
<tr>
<td>Mesopores</td>
<td>$2 \text{ nm} &lt; d &lt; 50 \text{ nm}$</td>
</tr>
<tr>
<td>Macropores</td>
<td>$d &gt; 50 \text{ nm}$</td>
</tr>
</tbody>
</table>

Adsorption and desorption of isotherms are very important for BET surface area and porosity analysis. They describe the amount of gas adsorbed and desorbed over a wide range of relative pressures at a fixed temperature and can be used to characterize the surface porosity.

There are five typical isotherm types proposed by Brunauer, Demingand Tell as shown in Fig. 2-3. In a type I isotherm, adsorption takes place in the solid’s micropores and no further adsorption is continued. A type II isotherm is often observed in the adsorption of gases into a non-porous solid with pore diameters larger than 2nm. A type III isotherm is regularly observed in nonporous or macropore structures, and adsorption proceeds as the adsorbate interaction with an adsorbed layer is greater than the interaction with the adsorbent surface. Also, type III isotherms show a weak interaction between a gas and solid which causes a small uptake at low pressures. The adsorbate-adsorbate force promotes the adsorption of further molecules once one molecule
is adsorbed. A type IV isotherm with a characteristic hysteresis loops occurs in pores ranging of 1.5 – 100 nm. A type V isotherm takes place in a mesoporous or microporous solid with weak interaction forces between adsorbent-adsorbate, which is similar to a type-III isotherm.

**Fig. 2-3** Different types of adsorption and desorption isotherm

In this experiment, Micromeritics ASAP 2020 Surface Area and Porosity Analyzer was used to examine the surface area and pore structures of the synthesized ZrW$_2$O$_8$ nanoparticles. The procedure for the characterization is: first the same is put into a tube and degased under a high temperature (~300 °C) to eliminate the existing adsorbed matters such as water; then the tube is connected to the analysis station and cools down evacuating the system. After certain amount of nitrogen (N$_2$) is introduced to keep the system in equilibrium, the pressure is measured. Then another amount of nitrogen is added and pressure is measured again. As long as the pressure does not change it means that the nitrogen is adsorbed on the surface of the sample. If
the pressure increases it means that surface is covered completely with nitrogen. When atmospheric pressure is reached, the procedure is repeated in reverse with nitrogen leaving the sample and the pressure is again measured after equilibrium. The measurements are completed when system has returned to its initial vacuum pressure.
Chapter 3 Study on controlling morphologies and crystallite sizes of ZrW₂O₇(OH)₂·2H₂O nanoparticles

In this research, experimental conditions were varied for the synthesis of ZrW₂O₈ nanoparticles with different morphologies and crystallite sizes using the hydrothermal reaction technique. This included different initial reactants such as a ZrAc solution, ZrO(NO₃)·xH₂O, and ZrO(ClO₄)₂·xH₂O for zirconium compounds; Na₂WO₄·2H₂O, (NH₄)₆H₂W₁₂O₄₀·xH₂O, Na₆W₁₂O₃₉·xH₂O for tungsten sources, various acidic mediums (5 M, 7 M of HCl or 3 M, 5 M of HClO₄), and reaction time was varied (12 h and 24 h) as well as temperature (130 °C and 160 °C).

3.1 X-ray diffraction results of nano-scaled ZrW₂O₈ and ZrW₂O₇(OH)₂·2H₂O

The crystal structures of both ZrW₂O₇(OH)₂·2H₂O and ZrW₂O₈ were identified using the X-ray diffraction technique. Tetragonal ZrW₂O₇(OH)₂·2H₂O and cubic ZrW₂O₈ nanoparticles could be obtained without containing any impurities, such as WO₃, under all hydrothermal routes tested in this work, as confirmed by the x-ray diffraction patterns shown in Fig. 3-1.
However, differences in experimental conditions led to diffraction patterns with different Bragg’s peak intensities and different widths due to variations in crystallite sizes of the nanoparticles. The detailed data of crystallite sizes for each experimental batch is shown in Table 3-1. It was found that the crystallite sizes of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O ranged from 20 to 66 nm, depending on experimental parameters. The smallest crystallite size was observed from the system of ZrO(ClO$_4$)$_2$/Na$_2$WO$_4$ and ZrO(NO$_3$)$_2$/Na$_2$WO$_4$ under 5 M HClO$_4$ acidic solution, which were 17 nm and 20 nm, respectively. The largest crystallite size was found in the synthesis condition at 160 °C. The experimental condition played an important role in the nucleation and growth of ZrW$_2$O$_8$ nanoparticles. Under most circumstances, the crystallite size is not always identical to the particles size due to the agglomeration of nanoparticles or multiple crystals.
joining together to form larger particles, thus to have a better understanding of changing in shapes and sizes of nanoparticles, it is practical to use SEM technology to study the effects of experimental variables on morphologies.

3.2 Effects of experimental parameters on morphologies of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O nanoparticles

3.2.1 Effect of initial reactants

Since the morphologies of the precursor ZrW$_2$O$_7$(OH)$_2$·2H$_2$O resemble ZrW$_2$O$_8$ nanoparticles after heat treatment for crystal structure transformation, in this experiment it is possible to characterize the particles of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O for comparison. Various initial zirconium and tungstate reactants were employed in different combinations to study the effect these variations had on the morphologies of synthesized ZrW$_2$O$_8$ nanoparticles.

First, Na$_2$WO$_4$·2H$_2$O was chosen as the tungsten source to react with three types of zirconium raw materials in the same HCl acidic medium. The morphologies of three kinds of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O nanoparticles are shown in Fig. 3-2. It was observed that different initial zirconium compounds reacting with Na$_2$WO$_4$ yielded nanoparticles with distinct morphologies. As seen in Fig. 3-2(a) and (d), ZrW$_2$O$_7$(OH)$_2$·2H$_2$O nanoparticles with crystalline sizes of 30 nm exhibit small capsule-like rods with lengths between 200–500 nm and widths of 50–80 nm obtained when ZrAc solution reacted with Na$_2$WO$_4$·2H$_2$O. Upon using ZrO(ClO$_4$)$_2$·xH$_2$O, the ZrW$_2$O$_7$(OH)$_2$·2H$_2$O particles with crystallite sizes of 45 nm were bundle-like rods fused at one end with lengths ranging from 500 to 900 nm and widths between 30 to 80 nm, as shown in Fig. 3-2(b) and (e). Large and long rectangular rods with particles sizes of 0.8–1.5 µm in length and
70–180 nm in width were obtained when ZrO(NO$_3$)$_3$·xH$_2$O was chosen for the reaction, as shown in Fig. 3-2(c) and (f).

Fig. 3-2 SEM images of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O synthesized under the following conditions: 7 M HCl at 130 °C for 12 h with Na$_2$WO$_4$·2H$_2$O and zirconium raw materials of ZrAc in (a) 20000X and (d) 50000X, ZrO(ClO$_4$)$_2$·xH$_2$O at (b) 20000X and (d) 50000X, and ZrO(NO$_3$)$_2$·xH$_2$O at (c) 20000X and (f) 50000X

Then, ZrW$_2$O$_7$(OH)$_2$·2H$_2$O nanoparticles were synthesized using the same reactants under a HClO$_4$ acidic medium with all other conditions fixed. As shown in Fig. 3-3 (a) and (d), rectangular nanorods (ca. 350-800 nm by 40-90 nm) were individually displayed and obtained by a ZrAc and Na$_2$WO$_4$·2H$_2$O in 3 M HClO$_4$ reaction medium. However, the morphologies of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O nanoparticles synthesized when ZrO(ClO$_4$)$_2$·xH$_2$O and ZrO(NO$_3$)$_2$·xH$_2$O were selected for reaction, appeared quite differently compared with the previous combination. Both were nanorods that appeared very thin in width and exhibited an extent of agglomeration to
perform large particles. The crystalline sizes for these two types of nanoparticles were also relatively small, which were 17 nm and 20 nm, respectively. Also, the ZrW$_2$O$_7$(OH)$_2$·2H$_2$O nanoparticles showed distinctively in morphologies obtained from HCl and HClO$_4$ mediums by comparing Fig. 3-2 and Fig. 3-3, the additives of acids exert significant effects on controlling crystallization and growth of nanoparticles, the more systematic experiments on acids types and concentration were carried on and reported in 3.2.2 and 3.2.3.

![Fig. 3-3 SEM images of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O synthesized under the following conditions: 3 M HClO$_4$ at 130 °C for 12 h with Na$_2$WO$_4$·2H$_2$O and zirconium raw materials of ZrAc in (a) 20000X and (d) 50000X, ZrO(CIO$_4$)$_2$·xH$_2$O at (b) 20000X and (e) 50000X, and ZrO(NO$_3$)$_2$·xH$_2$O at (c) 20000X and (f) 50000X](image)

Then, to compare the initial compounds effect on ZrW$_2$O$_7$(OH)$_2$·2H$_2$O nanoparticles on tungsten, Na$_2$WO$_4$·2H$_2$O, (NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$·xH$_2$O and Na$_6$W$_{12}$O$_{39}$·xH$_2$O were selected to react with identical zirconium compounds. First, the ZrAc solution reacted with Na$_2$WO$_4$·2H$_2$O and
(NH₄)₆H₂W₁₂O₄₀·xH₂O respectively, and the produced nanoparticles morphologies are displayed in Fig. 3-4. From observation, the ZrW₂O₇(OH)₂·2H₂O appear as short rods with two sharp ends when the ZrAc and Na₂WO₄·2H₂O mixture reacted in 7 M HCl for 24 h at 130 °C, as seen in Fig. 3-4(a) and (c). Observed from Fig. 3-4 (b) and (d) rectangular nanorods with inhomogeneous sizes can be yielded by using ZrAc and (NH₄)₆H₂W₁₂O₄₀·xH₂O under the same experimental conditions.

![SEM images of ZrW₂O₇(OH)₂·2H₂O synthesized under the following conditions: 7 M HCl at 130 °C for 24 h with ZrAc and tungstate raw materials of Na₂WO₄·2H₂O at (a) 20000X and (c) 50000X, and (NH₄)₆H₂W₁₂O₄₀·xH₂O at (b) 20000X and (d) 50000X](image_url)
In the following experiments, ZrO(ClO$_4$)$_2$·$x$H$_2$O was used as a zirconium source to react with different tungstate materials under the same reaction conditions. It is found in Fig. 3-5(a) and (d) that the synthesized ZrW$_2$O$_7$(OH)$_2$·2H$_2$O nanoparticles appear as bundle-like shape with uniform sizes ca. 500-800 nm in length by ca. 40-80 nm in width when Na$_2$WO$_4$·2H$_2$O was involved in the reaction. However, particles with wide size distributions on both the micron and nano-scales were found from the combination of ZrO(ClO$_4$)$_2$·$x$H$_2$O and (NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$·$x$H$_2$O. The ZrW$_2$O$_7$(OH)$_2$·2H$_2$O also displayed inhomogeneous size-scales and ill-defined shapes when synthesized by choosing Na$_6$W$_{12}$O$_{39}$·$x$H$_2$O as the tungstate raw reactant in Fig. 3-5(c) and (f).

Fig. 3-5 SEM images of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O synthesized under the following conditions: 7 M HCl at 130 °C for 24 h with ZrO(ClO$_4$)$_2$·$x$H$_2$O and tungstate raw materials of Na$_2$WO$_4$·2H$_2$O at (a) 20000X and (d) 50000X, (NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$·$x$H$_2$O at (b) 20000X and (e) 50000X, and Na$_6$W$_{12}$O$_{39}$·$x$H$_2$O at (c) 20000X and (f) 50000X.
Finally, ZrO(NO$_3$)$_2$·xH$_2$O was reacted with Na$_2$WO$_4$·2H$_2$O and (NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$·xH$_2$O under same reaction conditions, respectively, for comparison. As seen in Fig. 3-6, ZrW$_2$O$_7$(OH)$_2$·2H$_2$O appeared as individual rectangular rods with length of ca. 0.5 to 1.2 µm and width of 70 to 160 nm when Na$_2$WO$_4$·2H$_2$O was tested. On the other hand, particles synthesized by Na$_6$W$_{12}$O$_{39}$·xH$_2$O also appeared to lack in uniformity of shape or sizes. Some particles showed long thin rods length up to ca. 2 µm but others as appeared as ill-defined shapes only 300 to 500 nm.

Fig. 3-6 SEM images of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O synthesized under the following conditions: 7 M HCl at 130 °C for 24 h with ZrO(NO$_3$)$_2$·xH$_2$O and tungstate raw materials of Na$_2$WO$_4$·2H$_2$O at (a) 20000X and (c) 50000X, and (NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$·xH$_2$O at (b) 20000X and (d) 50000X
Based on the aforementioned study of how the initial raw materials effected the morphologies and crystallite sizes of ZrW₂O₇(OH)₂·2H₂O, different morphologies and size-scales can be determined using various starting materials. Three types of zirconium compounds when reacted with Na₂WO₄·2H₂O yielded nanoparticles with homogeneous and distinctive shapes and sizes. However, the other two tungstate compounds, (NH₄)₆H₂W₁₂O₄₀·xH₂O and Na₈W₁₂O₃₉·xH₂O, were not successful in the synthesis of ZrW₂O₇(OH)₂·2H₂O nanoparticles due to non-uniform morphologies and wide size distribution. Thus, further research on controlling the morphologies of nanoparticles was based on the ZrAc, ZrO(ClO₄)₂·xH₂O and ZrO(NO₃)₂·xH₂O reaction with Na₂WO₄·2H₂O.

3.2.2 Effect of acid types

Since the hydrothermal synthesis of ZrW₂O₇(OH)₂·2H₂O nanoparticles can only be achieved in an acidic medium, it is important to investigate the effect of acid type and concentration on crystallite size and morphology of the nanoparticles. As reported in prior work, it was found that nanoparticles with different crystallite sizes and morphologies can be obtained by altering the acids used in the reaction. The following studies focus on how the types of acidic mediums influence the formation of ZrW₂O₇(OH)₂·2H₂O nanoparticles in a hydrothermal condition.

First, a ZrAc solution and Na₂WO₄·2H₂O reacted in 5 M HCl and 5 M HClO₄ solution produced ZrW₂O₇(OH)₂·2H₂O nanoparticles which appear to have nearly the same morphologies of rectangular nanorods with size-scales of 0.3-1 µm by 50-100 nm, shown in Fig. 3-7. The crystallite sizes of both nanoparticles were close, 29 and 34 nm respectively. Therefore, it can be concluded that different acid types had little effect on the morphologies of ZrW₂O₇(OH)₂·2H₂O.
Fig. 3-7 SEM images of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O synthesized under the following conditions: ZrAc and Na$_2$WO$_4$·2H$_2$O mixture at 130 °C for 24 h in 5 M HCl at (a) 20000X and (c) 50000X, and 5 M HClO$_4$ at (b) 20000X and (d) 50000X.

In case of ZrO(ClO$_4$)$_2$·xH$_2$O, HCl and HClO$_4$ acids of the same molarity were also tried and an obvious change in morphologies of the nanoparticles was observed, shown in Fig. 3-8. When the reaction was carried out in 5 M HCl, the particles showed as bundle-like shapes with 300-800 nm by 40-70 nm, whose crystallite size was 46 nm. However, the synthesized ZrW$_2$O$_7$(OH)$_2$·2H$_2$O turned into larger peanut-like particles with a width of 90-150 nm that agglomerated with several thin nanoparticles with width of 10-40 nm. Interestingly, the
crystallite size for the latter one was 17 nm, which indicated that crystallite size represents the width of individual particles.

![SEM images of ZrW_2O_7(OH)_2·2H_2O synthesized under the following conditions: ZrO(ClO_4)_2·xH_2O and Na_2WO_4·2H_2O mixture at 130 °C for 24 h in 5 M HCl at (a) 20000X and (c) 50000X, and 5 M HClO_4 at (b) 20000X and (d) 50000X.](image)

**Fig. 3-8** SEM images of ZrW_2O_7(OH)_2·2H_2O synthesized under the following conditions: ZrO(ClO_4)_2·xH_2O and Na_2WO_4·2H_2O mixture at 130 °C for 24 h in 5 M HCl at (a) 20000X and (c) 50000X, and 5 M HClO_4 at (b) 20000X and (d) 50000X.

The same observation was also noticed from using ZrO(NO_3)_2·xH_2O as the zirconium starting materials and reacted with 5 M of HCl and HClO_4 acids shown in Fig. 3-9. The nanoparticles synthesized under HCl were individually present, but the severity of the agglomeration of the nanoparticles made each particle’s edges difficult to identify.
Fig. 3-9 SEM images of ZrW₂O₇(OH)₂·2H₂O synthesized under the following conditions: ZrO(NO₃)₂·xH₂O and Na₂WO₄·2H₂O mixture at 130 °C for 24 h in 5 M HCl at (a) 20000X and (c) 50000X, and 5 M HClO₄ at (b) 20000X and (d) 50000X

The reason for this phenomenon can be explained from the mechanism of crystallization and growth for ZrW₂O₇(OH)₂·2H₂O in a hydrothermal reaction. There are two factors that influence the nanoparticles morphology and crystallite size. One is the crystallization mechanism of ZrW₂O₇(OH)₂·2H₂O nanoparticles in an acidic medium, as referenced by the previous report that a higher concentration of counter ions with the presence of chloride ions significantly improves crystallization kinetics of nanoparticles in an acidic solution²⁹. The other is the
interaction between the nanoparticles induced by the strong electrostatic attraction force on the high energy surface of nanoparticles. In this experiment, the formation and growth of ZrW$_2$O$_7$(OH)$_2$$\cdot$2H$_2$O nanoparticles became faster to overcome the particles’ interaction, this means that individual rods can be synthesized in a HCl acidic medium. However, fewer free Cl$^{-1}$ ions existed in HClO$_4$ solution and the addition of NaCl failed to provide sufficient quantities of Cl$^{-1}$ due to lower solubility in such high a concentration mixture. So the nanoparticles crystallization proceeded at a relatively slower rate. Meanwhile, the strong attractive interaction among the nanoparticles restricted the further growth of ZrW$_2$O$_7$(OH)$_2$$\cdot$2H$_2$O. As a result, the combination of these two factors resulted in the agglomeration of thinner nanoparticles and smaller crystallite sizes in the HClO$_4$ acidic medium.

3.2.3 Effect of acid concentration

Besides acid type, the concentration of the reaction medium is also a significant influence on the crystallization and growth of ZrW$_2$O$_7$(OH)$_2$$\cdot$2H$_2$O. The study of the effect of acid concentration on nanoparticles’ morphologies was investigated in depth.

In case that HCL added to ZrW$_2$O$_7$(OH)$_2$$\cdot$2H$_2$O synthesized from the ZrAc and Na$_2$WO$_4$$\cdot$2H$_2$O solution, shows various sizes of nanoparticles depending on the molarity of the acid used in the experiment. It was seen from Fig. 3-10 that the nanoparticles appear similar in size scale (0.3-1 µm by 30-70 nm) when 5 M HCl was involved compared with the ones (300-800 nm by 50-80 nm) obtained from 7 M HCl solution. Also the particles appear as rectangular rods in lower concentration acid mediums, while it was observed that the nanoparticles were characterized as capsule-like shapes at relativly higher concentrated solutions. The phenomenon was opposite the findings by previous researchers$^{29}$, who indicated that the high concentration of
counter-ions in an acid enhanced the growth of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O nanoparticles. The reason for this discrepancy needs further investigation.

![SEM images](image_url)

**Fig. 3-10** SEM images of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O synthesized under the following conditions: ZrAc and Na$_2$WO$_4$·2H$_2$O mixture at 130 °C for 24 h in 5 M HCl at (a) 20000X and (c) 50000X, and 7 M HCl at (b) 20000X and (d) 50000X

Again synthesis was carried in an HCl solution, the bundle-like ZrW$_2$O$_7$(OH)$_2$·2H$_2$O nanoparticles were formed from the ZrO(ClO$_4$)$_2$·xH$_2$O and Na$_2$WO$_4$·2H$_2$O solutions. However, both of the two kinds of nanoparticles yielded from the acidic mediums of different concentrations, looked similar both in particles size (300-800 nm by 40-70 nm) and crystallite
size (46 ± 4 nm). Thus, in this case, the morphologies of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O had a weak correlation with the concentration of HCl acid.

![SEM images of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O synthesized under the following conditions: ZrO(ClO$_4$)$_2$·xH$_2$O and Na$_2$WO$_4$·2H$_2$O mixture at 130 °C for 24 h in 5 M HCl at (a) 20000X and (c) 50000X, and 7 M HCl at (b) 20000X and (d) 50000X](image)

**Fig. 3-11** SEM images of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O synthesized under the following conditions: ZrO(ClO$_4$)$_2$·xH$_2$O and Na$_2$WO$_4$·2H$_2$O mixture at 130 °C for 24 h in 5 M HCl at (a) 20000X and (c) 50000X, and 7 M HCl at (b) 20000X and (d) 50000X

However, the morphology of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O changed slightly when using ZrO(NO$_3$)$_2$·xH$_2$O and Na$_2$WO$_4$·2H$_2$O for the reaction in 5 M and 7 M HCl. As shown in Fig. 3-12, the particles synthesized in 5 M HCl appeared as individual rods with a width of 30-90 nm to
70-160 nm in 7 M HCl, but the particles tended to grow larger in crystallite size from 50 to 63 nm. In addition, the surface roughness was strongly dependent on the concentration of the acid. It was found that the particles present a higher roughness under 7 M HCl than 5 M HCl.

![SEM images of ZrW₂O₇(OH)₂·2H₂O synthesized under the following conditions: ZrO(NO₃)₂·xH₂O and Na₂WO₄·2H₂O mixture at 130 °C for 24 h in 5 M HCl at (a) 20000X and (c) 50000X, and 7 M HCl at (b) 20000X and (d) 50000X.](image)

When HClO₄ was used as the acid for the reaction, it was found that in the mixture of ZrAc and Na₂WO₄·2H₂O the acid concentration was less effective in changing the morphologies of ZrW₂O₇(OH)₂·2H₂O. This yielded similar dimensional sizes of nanoparticles with 0.3-1 μm in
length and by 50-100 nm in width as shown in Fig. 3-13. However, when compared with the
nanoparticles obtained from different raw material systems, acid concentration showed
significant effects on controlling the morphologies of the nanoparticles, especially on the extent
of agglomeration among particles.

**Fig. 3-13** SEM images of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O synthesized under the following conditions: ZrAc and Na$_2$WO$_4$·2H$_2$O mixture at 130 °C for 24 h in 3 M HClO$_4$ at (a) 20000X and (c) 50000X, and 5 M HClO$_4$ at (b) 20000X and (d) 50000X

Fig. 3-14 and 3-15 show the influence of HClO$_4$ molarity on the morphologies of the
nanoparticles. The synthesized ZrW$_2$O$_7$(OH)$_2$·2H$_2$O from the two mixtures (ZrO(ClO$_4$)$_2$·xH$_2$O /
Na$_2$WO$_4$$ \cdot $2H$_2$O and ZrO(NO$_3$)$_2$$ \cdot $xH$_2$O / Na$_2$WO$_4$$ \cdot $2H$_2$O) displayed agglomeration in different degrees depending on the acid concentration that was used. For 3 M HClO$_4$, the nanoparticles got fused together lengthwise and edgewise between each individual particle. However, by increasing the acid to 5 M, the particles showed more severe agglomeration, the individual particles aggregated into large peanut-like particles and were difficult to be identified. Also when comparing the crystallite size of nanoparticles, the ZrW$_2$O$_7$(OH)$_2$$ \cdot $2H$_2$O with smaller crystallite sizes (17-20 nm) were obtained from higher concentrations of acid compared with lower concentrations, whose crystallites sizes were 32-35 nm which were similar to the widths of each individual nanoparticle from the SEM images. Based on the above observations, it can be concluded that when using the acidic HClO$_4$ medium, higher concentrations of counter-ions tended to restrict the growth of the crystals due to the strong agglomeration that occurs between the nanoparticles.
Fig. 3-14 SEM images of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O synthesized under the following conditions: ZrO(ClO$_4$)$_2$·xH$_2$O and Na$_2$WO$_4$·2H$_2$O mixture at 130 °C for 24 h in 3 M HClO$_4$ at (a) 20000X and (c) 50000X, and 5 M HClO$_4$ at (b) 20000X and (d) 50000X.
3.2.4 Effect of reaction temperature

Reaction temperature is another important experimental variable to control the growth of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O nanoparticles in the hydrothermal reaction. In this experiment, two temperatures were studied to determine their effect on synthesis.

In case of the reaction of ZrAc and Na$_2$WO$_4$ solutions, 7 M HCl was used as shown in Fig. 3-16, and it was noted that the obtained ZrW$_2$O$_7$(OH)$_2$·2H$_2$O particles were found to be larger in size (200-800 nm by 50-100 nm) at 160 °C than the ones obtained at 130 °C (200-500 nm by 50-80 nm). This observation indicated that the higher temperature improved the crystallization and growth kinetics of the nanoparticles under a hydrothermal reaction.
Fig. 3-16 SEM images of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O synthesized under the following conditions: ZrAc and Na$_2$WO$_4$·2H$_2$O mixture for 12 h in 7 M HCl at 130 °C (a) 20000X and (c) 50000X, and at 160 °C (b) 20000X and (d) 50000X

Also, the same observation was shown in the same solution reacted in 3 M HClO$_4$. As the reaction was carried out at a higher temperature, the particles became much longer than the ones reacted at lower temperature. The size of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O synthesized under 130 °C was 350-800 nm by 40-90 nm, but both of the length and width were nearly doubled by heating the temperature to 160 °C.
Fig. 3-17 SEM images of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O synthesized under the following conditions: ZrAc and Na$_2$WO$_4$·2H$_2$O mixture for 12 h in 3 M HClO$_4$ at 130 °C (a) 20000X and (c) 50000X, and at 160 °C (b) 20000X and (d) 50000X

In the case of ZrO(ClO$_4$)$_2$·xH$_2$O and Na$_2$WO$_4$·2H$_2$O reacted in 5 M HCl, the same bundle-like nanoparticles appeared at two different reaction temperatures, but the dimensional sizes for the obtained ZrW$_2$O$_7$(OH)$_2$·2H$_2$O varied. To be specific, the particles sizes were characterized as 0.4-1 µm by 40-80 nm when the reaction was carried on at 130 °C. While, the sizes of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O synthesized at 160 °C were measured as 0.8-1.7 µm by 70-180 nm.
Since the width of the particles can be regarded as the crystallite size, reactions at a higher temperature facilitated the growth of crystals in a hydrothermal reaction.

Fig. 3-18 SEM images of $\text{ZrW}_2\text{O}_7$(OH)$_2$·2H$_2$O synthesized under the following conditions: ZrO(ClO$_4$)$_2$·xH$_2$O and Na$_2$WO$_4$·2H$_2$O mixture for 12 h in 5 M HCl at 130 °C (a) 20000X and (c) 50000X, and at 160 °C (b) 20000X and (d) 50000X

When the same reactants reacted in 3 M HClO$_4$ for temperature comparison, a similar trend of increased nanoparticle size was shown, Fig. 3-19. At relatively low temperatures, particles performed slight agglomeration by joining smaller individual nanoparticles of sizes 200-450 nm by 30-70 nm. These particles were found to be extensively longer in length (1-2 µm)
but the widths were unchanged (30-90 nm). Also based on the comparison of SEM images, the degree of agglomeration was not strongly correlated to the reaction temperature as was the acid concentration.

![SEM images of ZrW₂O₇(OH)₂·2H₂O](image1)

**Fig. 3-19** SEM images of ZrW₂O₇(OH)₂·2H₂O synthesized under the following conditions: ZrO(ClO₄)₂·xH₂O and Na₂WO₄·2H₂O mixture for 12 h in 3 M HClO₄ at 130 °C (a) 20000X and (c) 50000X, and at 160 °C (b) 20000X and (d) 50000X

When switching to the new reaction system of ZrO(NO₃)₂·xH₂O and Na₂WO₄·2H₂O taking place in 5M HCl, the morphologies of the obtained ZrW₂O₇(OH)₂·2H₂O were characterized as individual rectangular rods, as shown in Fig. 3-20. To study the effect of
temperature on the morphologies, 130°C and 160 °C were again tested. As the reaction proceeded at a low temperature, the sizes of synthesized nanoparticles showed a length of 0.4-1.3 μm and a width of 30-90 nm, the crystallite size was 40 nm. Yet, it was noted that the obtained ZrW₂O₇(OH)₂·2H₂O appeared to be 0.3-1.3 μm by 50-170 nm, and the crystallite size became as large as 60 nm.

**Fig. 3-20** SEM images of ZrW₂O₇(OH)₂·2H₂O synthesized under the following conditions: ZrO(NO₃)₂·xH₂O and Na₂WO₄·2H₂O mixture for 12 h in 5 M HCl at 130 °C (a) 20000X and (c) 50000X, and at 160 °C (b) 20000X and (d) 50000X
Interestingly in case of HClO₄, a similar observation of a change in nanoparticle morphology again occurred between different reaction systems of ZrO(ClO₄)₂·xH₂O / Na₂WO₄·2H₂O in 3 M HClO₄ as previously studied. The particles were generated into a slightly agglomerated form at 130 °C, with length of 150-500 nm and width of 30-60 nm for the individual nanoparticles. As the reaction temperature was raised to 160 °C, the slightly aggregated nanoparticles grew larger along the length without changing crystallite size (ca. 20 nm). The dimensional scale of the ZrW₂O₇(OH)₂·2H₂O was measured as 0.5-1.5 μm by 70-180 nm.
**Fig. 3-21** SEM images of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O synthesized under the following conditions: ZrO(NO$_3$)$_2$·xH$_2$O and Na$_2$WO$_4$·2H$_2$O mixture for 12 h in 3 M HClO$_4$ at 130 °C (a) 20000X and (c) 50000X, and at 160 °C (b) 20000X and (d) 50000X

Based on the comparison of the effect of temperature on the morphology of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O, the crystallization and growth of the nanoparticles can be facilitated with a higher temperature, and the particles become larger in size-scale compared with the ones yielded at a lower temperature.

### 3.2.5 Effect of reaction time

After studying the effect of synthetic parameters on the morphologies and crystallite sizes of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O nanoparticles including the variations in initial reactants, acids and reaction temperature, the last variable to be investigated experimentally was the hydrothermal reaction time. Based on all the conducted experiments, the effect of reaction time on the morphologies of the nanoparticles was not as obvious as in the previously studied variables. There were only three batches of experiments that reacted in the 3 M HClO$_4$ solution at 130 °C and displayed observational changes in morphologies. Also, the crystallite sizes of the synthesized ZrW$_2$O$_7$(OH)$_2$·2H$_2$O appeared slightly different when the reaction was proceeded at different reaction times. From general observation, it was concluded that the nanoparticles synthesized at a longer reaction time appeared larger in both crystallite size and nanoparticle size. The reason for this can be explained by Ostwald ripening, which states that small crystals dissolve and redeposit onto other crystals in a solution to form larger particles.

As shown in Fig. 3-22, the ZrW$_2$O$_7$(OH)$_2$·2H$_2$O nanoparticles appeared as individual rectangular shapes obtained from the ZrAc solution and Na$_2$WO$_4$·2H$_2$O mixture reacted at 130 °C. As the reaction proceeded for 12 h, the dimensional scale of the nanoparticles was characterized as 350-800 nm by 40-90 nm. The ZrW$_2$O$_7$(OH)$_2$·2H$_2$O grew slightly longer to a
length of 0.5-1 µm if the reaction time was doubled. However, the crystallite size and average width of nanoparticles was sustained even if the reaction time was varied. This indicated that reaction time merely effected the growth of nanoparticles lengthwise as long as the crystallization was completed.

![Fig. 3-22](image)

**Fig. 3-22** SEM images of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O synthesized under the following conditions: ZrAc solution and Na$_2$WO$_4$·2H$_2$O mixture in 3 M HClO$_4$ at 130 °C for 12 h at (a) 20000X and (c) 50000X, and for 24 h at (b) 20000X and (d) 50000X

When the reaction time was varied in another system, the same observation occurred, which confirmed the effect of the reaction time on controlling the growth of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O
in a hydrothermal synthetic approach. The nanoparticles obtained from a ZrO(ClO\(_4\))\(_2\)·xH\(_2\)O / Na\(_2\)WO\(_4\)·2H\(_2\)O solution related for 12 h appeared as lightly agglomerated short rods that were 200-450 nm in length and 30-70 nm in width. As expected, the short rods became significantly longer up to 1 µm as the experiment proceeded for a longer reaction time, which can be observed in Fig. 3-23.

Fig. 3-23 SEM images of ZrW\(_2\)O\(_7\)(OH)\(_2\)·2H\(_2\)O synthesized under the following conditions: ZrO(ClO\(_4\))\(_2\)·xH\(_2\)O and Na\(_2\)WO\(_4\)·2H\(_2\)O mixture in 3 M HClO\(_4\) at 130 °C for 12 h at (a) 20000X and (c) 50000X, and for 24 h at (b) 20000X and (d) 50000X
As the reaction system comprised of ZrO(NO$_3$)$_2$·xH$_2$O and Na$_2$WO$_4$·2H$_2$O progressed, the morphologies of the synthesized ZrW$_2$O$_7$(OH)$_2$·2H$_2$O appeared similar to the previously discussed reaction system of ZrO(ClO$_4$)$_2$·xH$_2$O and Na$_2$WO$_4$·2H$_2$O. Observed in Fig. 3-24, ZrW$_2$O$_7$(OH)$_2$·2H$_2$O nanoparticles showed increasing lengths from 150-500 nm to 0.3-1.3 µm as reaction time was prolonged from 12 h to 24 h.

![SEM images of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O synthesized under the following conditions: ZrO(NO$_3$)$_2$·xH$_2$O and Na$_2$WO$_4$·2H$_2$O mixture in 3 M HClO$_4$ at 130 °C for 12 h at (a) 20000X and (c) 50000X, and for 24 h at (b) 20000X and (d) 50000X](image)

**Fig. 3-24** SEM images of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O synthesized under the following conditions: ZrO(NO$_3$)$_2$·xH$_2$O and Na$_2$WO$_4$·2H$_2$O mixture in 3 M HClO$_4$ at 130 °C for 12 h at (a) 20000X and (c) 50000X, and for 24 h at (b) 20000X and (d) 50000X
Table 3-1. Summary of experimental variables and description of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O

<table>
<thead>
<tr>
<th>Materials</th>
<th>Acid</th>
<th>Reaction time</th>
<th>Reaction temperature</th>
<th>Particle shapes</th>
<th>Particle sizes</th>
<th>Crystalline sizes</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrAc/Na$_2$WO$_4$</td>
<td>5M HCl</td>
<td>12 h</td>
<td>130 °C</td>
<td>Individual long rods (fine surface)</td>
<td>0.2-1 µm by 30-70 nm</td>
<td>34±5 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24 h</td>
<td></td>
<td>Individual long rods (fine surface)</td>
<td>0.3-1 µm by 30-70 nm</td>
<td>29±3 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12 h</td>
<td>160 °C</td>
<td>Individual long rods (fine surface)</td>
<td>0.3-1.5 µm by 60-120 nm</td>
<td>46±2 nm</td>
</tr>
<tr>
<td></td>
<td>7M HCl</td>
<td>12 h</td>
<td>130 °C</td>
<td>Individual short rods (rough surface)</td>
<td>200-500 nm by 50-80 nm</td>
<td>30±3 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24 h</td>
<td></td>
<td></td>
<td>300-800 nm by 50-80 nm</td>
<td>26±4 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12 h</td>
<td>160 °C</td>
<td></td>
<td>200-800 nm by 50-100 nm</td>
<td>38±2 nm</td>
</tr>
<tr>
<td></td>
<td>3M HClO$_4$</td>
<td>12 h</td>
<td>130 °C</td>
<td>Individual long &amp; regular rods (fine surface)</td>
<td>350-800 nm by 40-90 nm</td>
<td>30±1 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24 h</td>
<td></td>
<td></td>
<td>0.5-1 µm by 50-100 nm</td>
<td>34±2 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12 h</td>
<td>160 °C</td>
<td></td>
<td>1-2 µm by 60-150 nm</td>
<td>59±1 nm</td>
</tr>
<tr>
<td></td>
<td>5M HClO$_4$</td>
<td>12 h</td>
<td>130 °C</td>
<td>Individual long &amp; regular rods (fine surface)</td>
<td>0.3-1 µm by 50-90 nm</td>
<td>42±4 nm</td>
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<td></td>
<td></td>
<td>24 h</td>
<td></td>
<td></td>
<td>300-800 nm by 50-90 nm</td>
<td>31±4 nm</td>
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<tr>
<td></td>
<td></td>
<td>12 h</td>
<td>160 °C</td>
<td></td>
<td>0.3-1.5 µm by 60-120 nm</td>
<td>47±2 nm</td>
</tr>
<tr>
<td>ZrO(ClO$_4$)$_2$/Na$_2$WO$_4$</td>
<td>5M HCl</td>
<td>12 h</td>
<td>130 °C</td>
<td>Bundle-like rods</td>
<td>0.4-1.5 µm by 40-80 nm</td>
<td>43±1 nm</td>
</tr>
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<td></td>
<td></td>
<td>24 h</td>
<td></td>
<td></td>
<td>300-800 nm by 40-70 nm</td>
<td>46±3 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12 h</td>
<td>160 °C</td>
<td>Large bundle-like rods (fine surface)</td>
<td>0.5-1.7 µm by 70-180 nm</td>
<td>65±2 nm</td>
</tr>
<tr>
<td></td>
<td>7M HCl</td>
<td>12 h</td>
<td>130 °C</td>
<td>Bundle-like rods</td>
<td>300-900 nm by 30-80 nm</td>
<td>45±3 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24 h</td>
<td></td>
<td></td>
<td>300-800 nm by 40-80 nm</td>
<td>50±1 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12 h</td>
<td>160 °C</td>
<td>Large Bundle-like rods</td>
<td>1-1.5 µm by 90-150 nm</td>
<td>66±1 nm</td>
</tr>
<tr>
<td></td>
<td>3M HClO$_4$</td>
<td>12 h</td>
<td>130 °C</td>
<td>Lightly agglomerated</td>
<td>200-450 nm by 30-70 nm</td>
<td>24±2 nm</td>
</tr>
<tr>
<td>Time</td>
<td>Temperature</td>
<td>Material Description</td>
<td>Dimensions</td>
<td>Width</td>
<td></td>
<td></td>
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<td>-------------------------------------------------------------------------------------</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>24 h</td>
<td>160 °C</td>
<td>Agglomerated short and thin rods</td>
<td>0.4-1 μm by 20-50 nm</td>
<td>32±5 nm</td>
<td></td>
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<tr>
<td>12 h</td>
<td>160 °C</td>
<td>Bundle-like thin and long rods</td>
<td>1-2 μm by 30-90 nm</td>
<td>39±1 nm</td>
<td></td>
<td></td>
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<tr>
<td>12 h</td>
<td>130 °C</td>
<td>Thin rods agglomerating into large rods</td>
<td>300-900 nm by 10-40 nm (Individual) to 100-300 nm (agglomeration)</td>
<td>17±3 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24 h</td>
<td>130 °C</td>
<td>Long and thin bundle-like rods (fine surface)</td>
<td>0.4-1.3 μm by 30-90 nm</td>
<td>40±2 nm</td>
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<td></td>
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<tr>
<td>24 h</td>
<td>160 °C</td>
<td>Slightly agglomerated long and thin bundle-like rods (fine surface)</td>
<td>0.4-1.2 μm by 30-90 nm</td>
<td>50±3 nm</td>
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<td></td>
</tr>
<tr>
<td>12 h</td>
<td>160 °C</td>
<td>Mixture of individual and bundle-like various sizes rods (fine surface)</td>
<td>0.3-1.3 μm by 50-170 nm</td>
<td>60±2 nm</td>
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</tr>
<tr>
<td>12 h</td>
<td>130 °C</td>
<td>Individual large rods (rough surface)</td>
<td>0.5-1.5 μm by 70-180 nm</td>
<td>38±1 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24 h</td>
<td>130 °C</td>
<td>Individual multiple-sized rods (rough surface)</td>
<td>0.5-1.2 μm by 70-160 nm</td>
<td>63±1 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 h</td>
<td>160 °C</td>
<td>Lightly agglomerated</td>
<td>150-500 nm by 30-60 nm</td>
<td>26±3 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>Temperature</td>
<td>Reaction Medium</td>
<td>Product Description</td>
<td>Length (µm)</td>
<td>Width (nm)</td>
<td></td>
</tr>
<tr>
<td>------</td>
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<td>----------</td>
<td></td>
</tr>
<tr>
<td>12 h</td>
<td>160 °C</td>
<td>Agglomerated long and thin rods</td>
<td>0.3-1.3 µm by 30-70 nm</td>
<td>35±2 nm</td>
<td></td>
<td></td>
</tr>
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<td>12 h</td>
<td>160 °C</td>
<td>Lightly agglomerated very long rods</td>
<td>0.5-1.5 µm by 70-180 nm</td>
<td>39±4 nm</td>
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</tr>
<tr>
<td>12 h</td>
<td>130 °C</td>
<td>Highly agglomerated multiple undefined shapes</td>
<td>300-800 nm by 30-70 nm</td>
<td>20±1 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24 h</td>
<td>160 °C</td>
<td>Highly agglomerated long and thin rods</td>
<td>0.5-1 µm by 20-70 nm</td>
<td>20±2 nm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*ZrW₂O₇(OH)₂·2H₂O nanoparticles synthesized by Na₂W₁₂O₃₉·xH₂O and (NH₄)₆H₃W₁₂O₄₀·xH₂O were not included due to inhomogeneous of size-scales of nanoparticles

### 3.3 Conclusion

In this chapter, a series of systematic studies on the effects of synthetic variables including different initial raw materials, acid types, acid concentration, reaction time and reaction temperature on morphologies and crystallite sizes of ZrW₂O₇(OH)₂·2H₂O nanoparticles were conducted. Based on these series of experiments, the morphologies of synthesized ZrW₂O₇(OH)₂·2H₂O nanoparticles were found to be greatly dependent on the chosen initial reactants and the particles with the most optimized homogenous size distribution and shape can be obtained by using Na₂WO₄·2H₂O as the tungsten source. The acidic medium played significant role in controlling the nanoparticle’s morphology and crystallite sizes as well. As the reaction proceeded in HCl, the obtained particles appeared as individual well defined shapes and the surface roughness was influenced by the acidic molarity. While the nanoparticles obtained from the HClO₄ solution showed the morphologies as agglomerated forms that aggregated by
several thin individual nanoparticles lengthwise, the extent of the agglomeration was dependent on the concentration of the acid. It was also observed from the experiments that reaction temperature affected the kinetic crystallization of $\text{ZrW}_2\text{O}_7(\text{OH})_2\cdot2\text{H}_2\text{O}$. Higher temperatures tended to accelerate the crystal growth of the nanoparticles and resulted in larger particles’ dimensional sizes and crystallite sizes. Lastly, reaction time had the least apparent effect on the morphologies compared to the other parameters, which inferred that the nucleation of $\text{ZrW}_2\text{O}_7(\text{OH})_2\cdot2\text{H}_2\text{O}$ at a hydrothermal condition was completed within 12 h. However, the Ostwald ripening could give explanation to the observed general increase in crystallite and particles sizes as the reaction proceeded for longer than 12 h. Based on the efforts to control the morphologies of $\text{ZrW}_2\text{O}_7(\text{OH})_2\cdot2\text{H}_2\text{O}$ nanoparticles, the careful selection of experimental parameters is crucial for optimizing the obtained nanoparticles to be used in composite applications.
Chapter 4 Characterization of thermal and physical properties of zirconium tungstate nanoparticles

4.1 Selection of zirconium tungstate nanoparticles for characterization

As the synthesis of zirconium tungstate nanoparticles with different morphologies was discussed in the prior chapter, it is important to study their negative thermal expansion properties and their potential hydration problems which were dependent upon the morphologies and crystallite sizes. Following the previous synthesis efforts, three types of $\text{ZrW}_2\text{O}_7(\text{OH})_2\cdot2\text{H}_2\text{O}$ nanoparticles with different morphologies and crystallite sizes were chosen as the candidates for the characterization of their physical and thermal properties, as specified in Table 4-1. The morphologies of the three $\text{ZrW}_2\text{O}_8$ candidates are shown in Fig. 4-1 (a) through (f). As this table is compared with the morphologies of previous $\text{ZrW}_2\text{O}_7(\text{OH})_2\cdot2\text{H}_2\text{O}$ nanoparticles, it was noted that though the change in crystal form, from tetragonal to a cubic crystal structure during the calcination process, was not accompanied by a change in the nanoparticle morphology.

<table>
<thead>
<tr>
<th>Nanoparticle type</th>
<th>Raw materials</th>
<th>Experimental conditions</th>
<th>Morphology</th>
<th>Size-scales (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{ZrO(ClO}_4)_2\cdot x\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$</td>
<td>7M HCl, 12 h, 160 °C</td>
<td>Large, bundle-like rods</td>
<td>Length: 900-1400 Width: 80-130</td>
</tr>
<tr>
<td>2</td>
<td>$\text{Zr(NO}_3)_2\cdot x\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$</td>
<td>7M HCl, 12 h, 130 °C</td>
<td>Large, rectangular rods</td>
<td>Length: 600-1200 Width: 70-120</td>
</tr>
<tr>
<td>3</td>
<td>ZrAc solution and $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$</td>
<td>7M HCl, 12 h, 130 °C</td>
<td>Small, capsule-like, short rods</td>
<td>Length: 100-400 Width: 40-60</td>
</tr>
</tbody>
</table>
Fig. 4-1 SEM images of ZrW$_2$O$_8$ calcined at 600 °C for 30 min created under different hydrothermal conditions: ZrO(ClO$_4$)$_2$·xH$_2$O / Na$_2$WO$_4$·2H$_2$O in 7M HCl at 160 °C for 12h at (a)20000X and (d)50000X, ZrO(NO$_3$)·xH$_2$O / Na$_2$WO$_4$·2H$_2$O in 7M HCl at 130 °C for 12 h at (b)20000X and (e)50000X, and ZrAc solution / Na$_2$WO$_4$·2H$_2$O in 7M HCl at 130 °C for 12 h at (c)20000X and (f)50000X

The TGA results indicated that the weight loss during the calcination process could be used to estimate the degree of dehydration from the precursor ZrW$_2$O$_7$(OH)$_2$·2H$_2$O to final product ZrW$_2$O$_8$. According to Fig. 4-2, the weight losses of the three chosen candidates under calcination were 10.66 wt%, 10.61 wt% and 10.85 wt%, respectively. Based on the weight loss values, it is possible to quantify the removal of hydrates and to deduce the reaction for the transition from ZrW$_2$O$_7$(OH)$_2$·2H$_2$O to ZrW$_2$O$_8$, which is shown as:

\[
\text{ZrW}_2\text{O}_7(\text{OH})_2\cdot2\text{H}_2\text{O} \rightarrow \text{ZrW}_2\text{O}_8 + 3\text{H}_2\text{O}↑. 
\]
Fig 4-2. Weight loss of calcination to form ZrW$_2$O$_8$ from ZrW$_2$O$_7$(OH)$_2$·2H$_2$O

4.2 Characterization of negative thermal expansion properties

The thermal properties of ZrW$_2$O$_8$ nanoparticles can be characterized by their NTE behavior using the coefficient of thermal expansion (CTE) value. The CTE value ($\alpha$) can be derived from the XRD patterns according to equation (4-1):

$$\alpha = \frac{1}{a_0} \frac{da}{dT}$$  \hspace{1cm} (4-1)

where $a_0$ is the initial lattice parameter and $da/dT$ is the change in lattice parameter with temperature. The dependence of the lattice parameter on temperature for the three chosen ZrW$_2$O$_8$ nanoparticles was obtained from the isothermal XRD measurement shown in Fig. 4-3.
The error bar at each data point indicated the standard deviation of the two separate measurements at a temperature obtained during the first cooling and the following heating procedures. It was found that ZrW$_2$O$_8$ exhibited noticeable reductions in lattice parameters from 9.15 to 9.12 Å with a rise in temperature from 30°C to 600 °C for the three studied samples. This indicated that the unique NTE property of ZrW$_2$O$_8$. Also, as can be seen from the three curves of three types of nanoparticles they exhibited a significant change in slope at temperatures between 160°C and 170 °C for all three candidates. This can be attributed to a phase transition from the cubic α-phase to the β-phase, which was characterized by a disordered cubic lattice as discussed in chapter 1. In addition, when performing the Rietveld refinement of the XRD patterns obtained from 70°C to 160 °C, it was necessary to refine both the α-phase and β-phase simultaneously to improve the quality of fit. This meant that the phase transition of ZrW$_2$O$_8$ does not occur suddenly but in a gradual process within a fixed temperature range. The initial β-phase ZrW$_2$O$_8$ first appears at 70 °C as a minor phase and the temperature is increased the content of the β-phase ZrW$_2$O$_8$ formed from the α-phase, and finally becomes the pure β-phase above 170 °C. The results obtained from the Reiveld refinements of the three types of ZrW$_2$O$_8$ nanoparticles with GSAS are summarized in Table 4-2.
Fig. 4-3 Lattice parameter comparisons of three types of ZrW$_2$O$_8$ nanoparticles

Table 4-2 Rietveld refinements of different types of ZrW$_2$O$_8$ nanoparticles at various temperatures from 30 to 600 °C

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Type-1 nanoparticles</th>
<th>Type-2 nanoparticles</th>
<th>Type-3 nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (Å)</td>
<td>χ²</td>
<td>R$_{wp}$ (%)</td>
</tr>
<tr>
<td>30</td>
<td>9.15052 ± 0.00020</td>
<td>2.4</td>
<td>4.5</td>
</tr>
<tr>
<td>40</td>
<td>9.14946 ± 0.00023</td>
<td>2.1</td>
<td>4.3</td>
</tr>
<tr>
<td>50</td>
<td>9.14846 ± 0.00042</td>
<td>2.2</td>
<td>4.6</td>
</tr>
<tr>
<td>60</td>
<td>9.14748 ± 0.00036</td>
<td>3.5</td>
<td>4.1</td>
</tr>
<tr>
<td>70</td>
<td>9.14635 ± 0.00030</td>
<td>4.1</td>
<td>5.1</td>
</tr>
<tr>
<td>80</td>
<td>9.14522 ± 0.00013</td>
<td>4.5</td>
<td>5.3</td>
</tr>
<tr>
<td>90</td>
<td>9.14414 ± 0.00027</td>
<td>3.7</td>
<td>4.8</td>
</tr>
<tr>
<td>100</td>
<td>9.14329 ± 0.00036</td>
<td>4.2</td>
<td>5.8</td>
</tr>
<tr>
<td>110</td>
<td>9.14224 ± 0.00032</td>
<td>4.8</td>
<td>5.9</td>
</tr>
<tr>
<td>120</td>
<td>9.14126 ± 0.00036</td>
<td>4.8</td>
<td>5.6</td>
</tr>
<tr>
<td>130</td>
<td>9.14014 ± 0.00024</td>
<td>3.9</td>
<td>5.3</td>
</tr>
<tr>
<td>140</td>
<td>9.13922 ± 0.00041</td>
<td>4.0</td>
<td>4.6</td>
</tr>
<tr>
<td>150</td>
<td>9.13818 ± 0.00035</td>
<td>4.6</td>
<td>6.2</td>
</tr>
<tr>
<td>160</td>
<td>9.13707 ± 0.00047</td>
<td>4.2</td>
<td>5.8</td>
</tr>
<tr>
<td>170</td>
<td>9.13630 ± 0.00025</td>
<td>3.9</td>
<td>4.9</td>
</tr>
<tr>
<td>180</td>
<td>9.13572 ± 0.00019</td>
<td>3.0</td>
<td>4.7</td>
</tr>
<tr>
<td>190</td>
<td>9.13511 ± 0.00031</td>
<td>3.7</td>
<td>4.2</td>
</tr>
<tr>
<td>200</td>
<td>9.13452 ± 0.00026</td>
<td>4.5</td>
<td>5.5</td>
</tr>
<tr>
<td>250</td>
<td>9.13224 ± 0.00018</td>
<td>4.2</td>
<td>5.3</td>
</tr>
<tr>
<td>300</td>
<td>9.13003 ± 0.00036</td>
<td>4.8</td>
<td>6.3</td>
</tr>
<tr>
<td>350</td>
<td>9.12790 ± 0.00030</td>
<td>3.2</td>
<td>4.6</td>
</tr>
</tbody>
</table>
The CTE values of three types of ZrW$_2$O$_8$ nanoparticles in their two phases are summarized in Table 4-3. Since the phase transition occurs in the temperature range of 70°C to 160 °C, the CTE value of the α-phase ZrW$_2$O$_8$ could be determined at a temperature between 30 °C to 90 °C. The pure or predominant α-phase existed and the CTE value of β-phase was estimated at higher temperature from 180°C to 600 °C. It was interesting to find that the nanosized ZrW$_2$O$_8$ presented a slightly more negative CTE value than the bulk ZrW$_2$O$_8$ with reported a value of -8.8 × 10$^{-6}$ °C$^{-1}$ in α-phase, while keeping its β-phase consistent with the reported CTE value. In addition, the CTE of α-phase ZrW$_2$O$_8$ was found to be dependent on the crystallite size of the nanoparticles. The type-3 ZrW$_2$O$_8$ nanoparticles with crystallite sizes of approximate 32 nm showed CTE of -9.25 × 10$^{-6}$ °C$^{-1}$. However, it was less negative compared with the CTE of nanoparticles that are type-1 (-11.4 × 10$^{-6}$ °C$^{-1}$) and type-2 (-11.2 × 10$^{-6}$ °C$^{-1}$) with relatively larger crystallite sizes of about 50 nm. Nonetheless, the effect of the crystallite sizes on the CTE values were weakened at higher temperatures after the phase transition, the CTE of the three types of ZrW$_2$O$_8$ in their β-phase exhibited similar CTE values of 4.55 × 10$^{-6}$ °C$^{-1}$, 4.65 × 10$^{-6}$ °C$^{-1}$ and 4.94 × 10$^{-6}$ °C$^{-1}$ as indicated in Table 4-2. Based on the data, the ZrW$_2$O$_8$ nanoparticles with larger crystallite sizes seemed to be more promising in their NTE behavior. On the other hand, the nanoparticles with larger crystallite sizes displayed larger dimensional scales, which reduced the potential of decreased loadings of filler to produce nanocomposites. As a result, further study is needed to learn about which type of the ZrW$_2$O$_8$ nanoparticles can be used as filler and still yield the polymer nanocomposites with superior thermomechanical properties.
Table 4-3 CTE values of different types of ZrW₂O₈ nanoparticles

<table>
<thead>
<tr>
<th>Nanoparticle type</th>
<th>Crystallite size (nm)</th>
<th>CTE value (ppm/°C)</th>
<th>α-phase</th>
<th>β-phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>50±4</td>
<td>-11.4±0.352</td>
<td>-4.55±0.341</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>46±4</td>
<td>-11.2±0.420</td>
<td>-4.65±0.283</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>32±5</td>
<td>-9.25±0.243</td>
<td>-4.94±0.161</td>
<td></td>
</tr>
</tbody>
</table>

4.3 Hydration of ZrW₂O₈ nanoparticles

As the ZrW₂O₈ nanoparticles undergo hydration it could have a detrimental effect of the negative CTE behavior and impact their potential for use as negative CTE fillers\(^\text{36}\). The understanding of the correlations between particle morphology and tendency for hydration was crucial for the synthesis purpose. Hence, in this work three types of ZrW₂O₈ nanoparticles were sealed in ambient conditions and placed in 20 ml vials for two weeks and two months respectively to observe the hydration phenomenon.

The hydration of ZrW₂O₈ nanoparticles could be identified by changes in X-ray diffraction patterns as suggested by previous works\(^\text{35,36}\). The cubic lattice parameter changes from 9.12 to 8.95 Å as the insertion of water into frame structure forms ZrW₂O₈·1H₂O. In this experiment, the hydration of ZrW₂O₈ nanoparticles was also observed in all the samples that were exposed to the ambient atmosphere. Type-3 ZrW₂O₈ nanoparticles were used to compare the changes in the XRD patterns during the hydration process. As shown in Fig. 4-4, the hydrated nanoparticles appeared differently in the XRD patterns from the pristine nanoparticles’.

The particles which underwent hydration for 2 weeks showed broader peaks and as the hydration process continued further, the pattern displayed a shift in all the peaks to higher angles and several peaks disappeared completely. This resulted the cubic phase with a smaller lattice constant.
Subsequently, TGA was employed to quantify the extent of the hydration based on the weight loss by heating samples up to 190 °C. As shown in Fig. 4-5, an increase in storage time from two weeks to two months resulted in a higher degree of hydration due to the greater weight loss. Furthermore, for any given storage time the three types of ZrW₂O₈ nanoparticles displayed different extents of hydration. For example, among the samples stored for 2 months, type-1 nanoparticles showed the lowest weight loss (1.36 wt%) followed by type-2 ZrW₂O₈ with 1.75 wt% weight loss. Type-3 nanoparticles exhibited the most severe hydration phenomena, and exhibited a total weight loss of 2.26 wt%. Banek, N. and coworkers first indicated that the

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**Fig. 4-4** X-ray diffraction patterns of ZrW₂O₈ nanoparticles for (a) newly prepared, (b) hydrated for 2 weeks, and (c) hydrated for 2 months.
origin of nano-sized ZrW₂O₈ hydration was attributed to the increasing defect cites on the surface of nanoparticles. As the recent work done by our research group⁴² shows, moisture adsorption and the surface area of the ZrW₂O₈ particles played a significant role in extent of hydration. The reason for differences in the amount of hydrates in each type of ZrW₂O₈ should be investigated from the physical properties of the nanoparticles.

Fig. 4-5 Comparison of weight loss of hydration contents in ZrW₂O₈ nanoparticles synthesized under different experimental conditions
4.4 Characterization of pore structures of ZrW$_2$O$_8$ nanoparticles

To investigate differences in the extent of hydration for the different types of ZrW$_2$O$_8$ nanoparticles and causes for that hydration, it is necessary to understand the differences in their physical properties, such as pore structures.

As a solid is exposed to a gas or vapor it begins to adsorb its surroundings by increasing mass or decreasing its pressure, the amount of adsorbed gas or vapor will reach a final fixed value, which can be quantified in the volume of a solids pores. The adsorbed film formed at lower pressures serves as the nucleus for condensation at a higher relative pressure. However, during the evaporation process, there is no need for nucleation and evaporation occurs as long as the pressure reaches a low level. Due to the processes of condensation and evaporation the hysteresis loop is present as a result. In this experiment, pore structures of ZrW$_2$O$_8$ nanoparticles were characterized by isotherm curves of N$_2$ adsorption-desorption shown in Fig. 4-6. It was noticeable that all three types of ZrW$_2$O$_8$ nanoparticles exhibited similar type IV isotherm curves with a typical characteristic hysteresis loops present for both the adsorption and desorption processes. This type model for isotherm curves was proposed by Zisgmondy, who assumed that the initial part of the isotherm at lower pressures, adsorption is restricted to a thin layer on the surface of sample until at higher relative pressure is reached. Then the N$_2$ starts to push into the surface and fill in voids in the samples, this process is called capillary condensation. As the pressure is continuously increased, more and more pores are filled until the entire system is full of condensation at the saturation pressure. In this case, at low relative pressures (P/P$_0 < 0.8$), the absorption of N$_2$ was restricted to the surface of particles to form thin multilayers resulting in a slow linear increase of N$_2$ adsorption with increasing pressure. At higher relative pressures (P/P$_0 > 0.8$), the N$_2$ adsorption-desorption curves of the three types of synthesized ZrW$_2$O$_8$ nanoparticles
exhibited significant increases in quantity of N$_2$ absorption due to capillary condensation. A significant drop in desorption of N$_2$ from the isotherm curve occurred by evacuating pressure indicated the possible shape of pores, which could be described as ink-bottle type. In addition, it was found that noticeable differences in the extent of the N$_2$ adsorption were displayed among the three types of ZrW$_2$O$_8$. Since the amount of N$_2$ adsorption represents the pore volume in the samples, and type-1 ZrW$_2$O$_8$ showed the lowest quantity of adsorbed N$_2$ it then had the lowest pore volumes, which is followed by type-2 nanoparticles, and type-3 ZrW$_2$O$_8$ exhibited highest level of adsorbed N$_2$ and with the largest pore volumes.

**Fig. 4-6** Comparison of N$_2$ adsorption-desorption isotherms of ZrW$_2$O$_8$ nanoparticles synthesized under different experimental
The pore size distribution curves were obtained by Barret-Joyner-Halenda (BJH) desorption of N\textsubscript{2} isotherms. From the hysteresis of adsorption and desorption, it makes it possible to calculate the pore sizes based on the Kelvin equation (4-2)

\[
\ln \frac{p}{p^0} = -\frac{2\gamma V_L}{RT} \frac{1}{r_m}
\]  

(4-2)

Where, \(V_L\) is the molar volume of the liquid adsorptive, \(p/p^0\) is relative pressure of the vapor in equilibrium, \(\gamma\) is surface tension, and \(r_m\) is mean radius of curvature given by:

\[
\frac{1}{r_1} + \frac{1}{r_2} = \frac{2}{r_m}
\]  

(4-3)

As shown in Fig. 4-7, the three types of nanoparticles exhibited a broad pore size distribution ranging from 10 to 100 nm with majority of pore volumes concentrated at approximately 50 nm. Based on the conventional classification of pores according to their average width, the synthesized three ZrW\textsubscript{2}O\textsubscript{8} nanoparticles are characterized as mesopores. In addition, a significantly higher pore volume was observed for type-1 nanoparticles in comparison to type-2 and type-3 particles, which was in good agreement with the results obtained from Fig. 4-6.
4.5 Study on correlation of hydration and pore structures in ZrW$_2$O$_8$ nanoparticles

Table 4-4 summarized the pore properties and TGA weight loss for the three selected ZrW$_2$O$_8$ nanoparticle types. It was found that size scales of the nanoparticles influenced the pore structures significantly. Type-1 ZrW$_2$O$_8$, exhibited a morphology resembling a large bundle rods, showed the smallest BET surface area (9.96 m$^2$/g), the smallest total pore volume (0.0280 cm$^3$/g), and the smallest average pore size (18.5 nm). In comparison to type-1 particles, type-2 ZrW$_2$O$_8$ were characterized by a morphology resembling long individual rods, and had a greater BET surface area (13.9 m$^2$/g), higher pore volume (0.0541 cm$^3$/g), and higher average pore diameter (25.5 nm). Among the three types of particles, the type-3 ZrW$_2$O$_8$ had the smallest particles sizes,
exhibited the largest values in surface area (20.3 m$^2$/g), total pore volume (0.114 cm$^3$/g), and pore diameter (30.5 nm). The correlation between particles size-scales and the pore structures could be explained by the degree of agglomeration within the nanoparticles. The formation of pore structures in samples was greatly dependent on the dimensional scale of ZrW$_2$O$_8$ nanoparticles. Due to the tendency of nano-sized particles to agglomerate together, caused by a strong electrostatic attraction on their surface, smaller particle tend to create more voids among them thus causing pores with larger volumes and sizes.

Table 4-4 Pore structures and hydrate weight loss of different types of ZrW$_2$O$_8$ nanoparticles

<table>
<thead>
<tr>
<th>Nanoparticles type</th>
<th>Particle size (nm)</th>
<th>BET surface area (m$^2$/g)</th>
<th>BJH cumulative pore volume (cm$^3$/g)</th>
<th>BJH desorption average pore diameter (nm)</th>
<th>Weight loss (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 weeks</td>
</tr>
<tr>
<td>1 Length: 900-1400 Width: 80-130</td>
<td>9.96</td>
<td>0.0280</td>
<td>18.5</td>
<td></td>
<td>1.23</td>
</tr>
<tr>
<td>2 Length: 600-1200 Width: 70-120</td>
<td>13.9</td>
<td>0.0541</td>
<td>25.5</td>
<td></td>
<td>1.43</td>
</tr>
<tr>
<td>3 Length: 100-400 Width: 40-60</td>
<td>20.3</td>
<td>0.114</td>
<td>30.5</td>
<td></td>
<td>1.73</td>
</tr>
</tbody>
</table>

From Table 4-4, it was interesting to notice that the pore volumes and diameters in nanoparticles played a crucial role in the hydration process during storage in an ambient environment. The observation of type-1 ZrW$_2$O$_8$ nanoparticles exhibited the lowest degree of hydration among the three types of samples and could be explained by the fact that the moisture was less likely to be adsorbed by particles with a lower total pore volume and smaller average pore diameter. Type-3 ZrW$_2$O$_8$ nanoparticles showed the largest pore volumes and diameters and consequently underwent greater degrees of hydration. On the other hand, the observed time dependent process of hydration also could be explained by the pore structures effects on moisture
adsorption. As the adsorbed hydrate molecules began to occupy pores, less space was left for further adsorption of the hydrates from the environment. This resulted in fewer amounts of hydrates to be adsorbed as times goes on until finally it reaches a saturation point. Consequently the hydration rate was faster at beginning of the process than in later periods of time as observed experimentally.

4.6 Conclusion

Detailed studies on the analysis of the thermal and physical properties of three types of ZrW$_2$O$_8$ nanoparticles with distinct morphologies and crystallites sizes were investigated in this chapter. First, the morphologies of the nanoparticles can be preserved during the calcination process to transform the precursor ZrW$_2$O$_7$(OH)$_2$·2H$_2$O to cubic ZrW$_2$O$_8$. Regarding CTE values for nano-sized ZrW$_2$O$_8$, it was found that the NTE property effects the crystallite sizes of the synthesized nanoparticles. ZrW$_2$O$_8$ with larger crystallite sizes displayed more negative CTE values in the $\alpha$-phase, but there was no obvious influence on CTE values in the $\beta$-phase. In addition, the hydration of nano-sized ZrW$_2$O$_8$ was studied by characterizing the content of the hydrates using X-ray diffraction patterns and pore structures with different techniques. A possible interpretation of the hydration problem for ZrW$_2$O$_8$ nanoparticles was originated from the moisture adsorption caused by the formation of pores within the nanoparticles. Based on the correlation among the degree of hydration, particle size, and pore size, it was suggested that ZrW$_2$O$_8$ nanoparticles with smaller sizes tended to create larger pores and underwent the most severe hydration problems.
Chapter 5. Summary and Future works

Precursors with different morphologies to the nanoparticulate ZrW$_2$O$_7$(OH)$_2$·2H$_2$O were successfully synthesized with a hydrothermal reaction by controlling various experimental conditions. To study each synthetic variables’ effect on the morphologies of the nanoparticles, a series of systematic research trails comparing the morphologies and crystallite sizes of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O nanoparticles were conducted. This includes different initial raw materials, acid types, acid concentrations, reaction times, and reaction temperatures. Based on the experiments, the ZrW$_2$O$_7$(OH)$_2$·2H$_2$O nanoparticles were synthesized with various morphologies by utilizing different initial reactants, and Na$_2$WO$_4$·2H$_2$O was chosen as the optimized tungsten source for a reaction since the yielded nanoparticles displayed optimized homogenous size distribution and an overall smaller size. The acidic medium was an important factor in controlling the nanoparticles’ morphologies and crystallite size as well. The ZrW$_2$O$_7$(OH)$_2$·2H$_2$O nanoparticles displayed individual and well defined shapes as the reaction proceeded in HCl. Higher concentrations of HCl caused rougher surfaces on the particle than lower concentrations. However, the nanoparticle obtained from the HClO$_4$ solution showed different levels of agglomeration by joining the thin individual nanoparticles lengthwise, and the extent of agglomeration was found to be higher in an acidic medium of a higher concentration. In case of reaction temperature, the larger nanoparticles in both dimensional size and crystallite size were found at higher temperatures indicating that a hydrothermal temperature influenced the kinetic nucleation and crystal growth of ZrW$_2$O$_7$(OH)$_2$·2H$_2$O nanoparticles. The comparison of reaction times in this study suggested that the observation of increasing crystallite sizes in a few systems, was due to the Ostwald ripening phenomena during synthesis. Also there are no significant
changes in the formation of nanoparticles under the hydrothermal condition after 12 h, so the nucleation of nanoparticles was carried on within a 12 h time frame.

The three types of ZrW$_2$O$_8$ nanoparticles synthesized under different reaction conditions, were selected for the investigation of negative thermal expansion behaviors dependent upon their morphologies and crystallite sizes. As expected, all three nanoparticles displayed a phase transition between $\alpha$ and $\beta$-ZrW$_2$O$_8$ at about 170 °C during the measurement. The magnitude of the negative CTE was found to increase with increasing crystallite size of ZrW$_2$O$_8$ in the $\alpha$-phase. It was found that type-1 and type-2 nanoparticles with larger crystallite sizes (~50 nm) present more negative CTE values in $\alpha$-ZrW$_2$O$_8$, which were about -11 ppm/°C. However, the CTE of the three ZrW$_2$O$_8$ nanoparticles in the $\beta$-phase showed nearly identical values the previously reported values at -4.9 ppm/°C, regardless of crystallite size.

In this work, the hydration problems of the three synthesized ZrW$_2$O$_8$ nanoparticles were observed and analyzed. They were identified by the differences in their X-ray diffraction patterns between the pristine and hydrated ZrW$_2$O$_8$ and the weight loss of the contents upon heating. Also hydration can be described as a time-dependent procedure due to longer exposure periods resulting in higher hydration contents, and a hydration rate was found to be faster in the initial period than as the reaction progressed. To understand the hydration problem happening in nano-sized ZrW$_2$O$_8$, characterization of the physical properties of nanoparticles provided considerable evidence to explore the explanation. The origin of hydration for nano-sized ZrW$_2$O$_8$ resulted from the moisture adsorption caused by the formation of pores among the nanoparticles. As nanoparticles exhibited a higher tendency of agglomeration, they tended to aggregate together and create voids among each particle. These voids can be regarded as pores that serve in adsorbing and storing moisture from environment. Also, it was found that the pores dimensions
were greatly dependent on the nanoparticles sizes. In this experiment, ZrW₂O₈ nanoparticles with smaller sizes produced larger pore diameters and total pore volume showed a greater tendency of hydration problems. A candidate with a tendency for hydration problems was not a promising candidate for using as a filler in nanocomposites applications.

Following the efforts on synthesis and characterization of zirconium tungstate nanoparticles, it will be important to investigate the effects of ZrW₂O₈ nanoparticles with different morphologies on the properties of their polymer nanocomposites. The three types of studied ZrW₂O₈ nanoparticles in this work can be applied as nano-fillers to incooperate with different types of polymer matrices, such as epoxy resin and bisphenol E cyanate ester, to study their effects on the thermo-mechanical and dielectric properties of nanocomposites.
References


