Glycothermal synthesis of nanocrystalline ZrO_2 powders at low temperature without mineralizers

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Zirconia (ZrO_2) nanoparticles were synthesized at temperature as low as 200°C through a glycothermal reaction using amorphous zirconium hydrous gel precursors and 1,4-butanediol as solvent, XRD and TEM data support that glycothermal processing method provides a simple low temperature route for producing highly crystallized ZrO_2 nanoparticles without mineralizers, which could also be extended to other systems. XRD results also showed that ZrO_2 nanoparticles synthesized in glycothermal condition had tetragonal phase with small portion of monoclinic phase, where the tetragonality was confirmed by Raman spectroscopy. The as-prepared ZrO_2 nanoparticles have spherical morphology with an average crystal size of 10–15 nm and agglomerated into bigger spheres with a diameter of about 100 nm. The tetragonal phase begins to transform to monoclinic phase at 600°C when the calcinations of the as-synthesized powder was carried out.

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1. Introduction

ZrO_2 is a functional material with many unique properties. It is the only transitional metal oxide that presents both acidity and alkaline centers, along with the high performance in mechanical, thermal, optical, catalytic properties and high ionic conductivity at elevated temperatures (>1000 K).⁽¹⁻⁴⁾ Therefore, ZrO_2 has been widely used in the fields of industrial materials such as structural ceramics,⁽⁵⁾ solid catalysts,⁽⁶⁻⁸⁾ oxygen sensor,^(9,10) electric materials or oxygen electrolyte for solid oxide fuel cells.^(11,12)

There are many routes for the synthesis of nanocrystalline oxides. In order to prepare ZrO_2 nanocrystalline powder, several methods have been developed, such as pyrolysis,⁽¹³⁻¹⁶⁾ sol-gel,^(17,18) polymerized complex,⁽¹⁹⁻²²⁾ and hydrothermal synthesis.⁽²³⁻³¹⁾ Among these methods, hydrothermal process, in which chemical reactions could occur in aqueous media under the simultaneous generation of heat and pressure, enable the formation of highly crystalline ZrO_2 powder with well-developed surfaces.^(23,27-31) It is also known that organic solvents, especially glycols, play important roles for preventing hard agglomerate formation during hydrothermal crystallization.⁽³²⁾ Combining glycols and hydrothermal treatments is a successful method for preparing well crystallized ZrO_2 nanoparticles with narrow size distribution and low aggregation. However, the reaction mechanisms in nonaqueous solution are complex, and currently there is very limited information regarding the reaction thermodynamics, kinetics, and underlying crystallization mechanisms.

Only a few investigations have dealt with the use of glycol to synthesize crystalline ZrO_2 powders in hydrothermal condi-

tions.⁽³³⁻³⁶⁾ Inoue et al.^(33,34) studied the thermal decomposition of zirconium alkoxides in glycothermal condition. Nanocrystalline ZrO_2 can be obtained directly from glycothermal reaction at 300°C. However, some distinct disadvantages of metal alkoxides make it difficult to use in glycothermal reaction, such as the extreme moisture sensitivity, the tendency to form mixtures of structurally complex species upon hydrolysis, and high cost.⁽³⁷⁾ Also, the reaction temperature for thermal decomposition of zirconium alkoxides is too high because the degradation of 1,4-butanediol to tetrahydrofuran occurs in the temperature range 250–350°C for 48 h without any catalyst.⁽³⁸⁾

The objective of the present work was to examine the possibility of directly synthesizing highly crystallized ZrO_2 nanoparticles using zirconium hydrous gel without inorganic mineralizers in glycothermal conditions. A wet chemical reaction route for the synthesis of ZrO_2 nanoparticles via different glycothermal treatments is described.

2. Experimental procedure

The process to prepare ZrO_2 nanoparticles by glycothermal treatment in 1,4-butanediol solution is schematically illustrated in Fig. 1. Zirconium tetrachloride, ZrCl_4 (99%, Aldrich Chemical Co., EP), was used as a source of Zr. Throughout the process, the CO_2 -free deionized water was used in the preparation of all aqueous solution. Modification of zirconium tetrachloride was achieved by adding CO_2 -free deionized water (ice cold water) to prepare aqueous 2M ZrOCl_2 stock solution because ZrCl_4 solution has large vapor pressure at room temperature and is hydrolyzed readily by reacting with water from air. This aqueous ZrOCl_2 stock solution was kept in a stable state without precipitation at room temperature. This stock solution was diluted to obtain a transparent aqueous ZrOCl_2 solution with Zr^{4+}

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Fig. 1. Schematic representation of processing steps for the preparation of ZrO_2 nanoparticles via glycothermal process.

concentration of 0.1 M for precipitation. Amorphous zirconium hydrous gel was prepared by adding 1 M NH_4OH (26%, DC Chemical. Co., EP) dropwise into 25 ml 0.1 M ZrOCl_2 solution until pH is 12 with stirring under N_2 atmosphere to minimize formation of carbonate species. The gel was separated and washed with CO_2 -free water and ethyl alcohol by three cycles of centrifugation for 4 min at 4000 rpm in a centrifuge (Beckman Induction Drive Centrifuge, Model J2-21M, Beckman Instruments, Inc., Palo Alto, CA). Redisperion of gel sediment was performed with a Thermolyne Maxi Mix II, type 37600 mixer (Barnstead/Thermolyne, Dubuque, IA). Excess ethyl alcohol was decanted after final washing and wet precursors were redisperised in 1,4-butanediol solution (99% Aldrich Chemical). Total solvent volume was 70 ml. In all runs, concentration of reactants (i.e. zirconium hydrous gel) is 0.1 M if not specifically mentioned. To investigate the effects of reaction temperature of phase and morphology of ZrO_2 nanopowder in glycothermal condition, reactions were carried out at temperatures from 160 to 220°C. The resulting suspension was placed in a 125 ml stainless-steel Teflon-lined autoclave (Lage Capacity Acid Digestion Bomb, Parr Instruments, Town, State, USA) with a fill factor of 65 vol%. The Teflon-lined vessel was flushed with nitrogen before closing.

The reaction vessel was then heated to the desired temperature (160–220°C) with a rate of 2°C/min. The reaction time at the desired temperature was varied from 6 to 24 h. After glycothermal treatment, the vessel was cooled to $\sim 40^\circ\text{C}$. The recovered ZrO_2 nanopowders were dried at 50°C in a desiccators for 24 h. To investigate the phase stability of tetragonal ZrO_2 nanopowder synthesized in glycothermal condition, as-synthe-

Fig. 2. XRD patterns of ZrO_2 nanopowders synthesized in glycothermal condition at various reaction temperatures for 24 h: (a) 160°C, (b) 180°C, (c) 200°C, and (d) 220°C.

sized tetragonal ZrO_2 nanopoders were calcined from 400 to 1400°C with temperature interval of 200°C in an alumina crucible in air for 4 h.

Phase composition and crystal structure were analyzed using X-ray diffraction (XRD, $\text{CuK}\alpha$, Fine Tube, 30 kV-30 mA, Shimazu, Japan) over the 2θ range from 20 to 80° at a scan rate of 2°/min. The crystallite size of ZrO_2 nanopowder, D , was calculated from the broadening of (101) XRD main peak using the Scherrer formula:³⁹⁾

$$D = 0.94\lambda / \beta \cos \theta$$

where D is the crystallite size, λ ($=0.15406$ nm) the wavelength, β the true full width at half maximum and θ the diffraction angle of the center of the peak (in degrees). The morphology of the synthesized particles was observed using field-emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan) and transmission electron microscopy (TEM, JEM-2100F, Jeol, Japan). High resolution lattice images also were taken to confirm crystallinity. Infrared absorption was measured using Fourier transform infrared (FT-IR) spectrophotometer (Model FT-IR 8700, Shimadzu Co., Kyoto, Japan) for analysis of surface impurities on ZrO_2 nanopowders such as C–O and O–H groups and carbonates using the KBr pellet technique. IR samples were prepared by mixing dry precipitate with dry KBr in 1:100 ratio by weight. The materials were ground by hand in an agate mortar and pestle and pressed in mold for 5 min with holding. Thermal gravimetric analysis (TGA) was carried out to understand the decomposition and synthesis process and to optimize the calcination temperature. Thermogravimetric analysis (TGA) was performed with heating rate of 2°C/min up to 1200°C. Raman measurements of typical glycothermal ZrO_2 nanopowders were performed over the range of 100–1000 cm^{-1} using FT Raman spectrometer (Raman, Model RFS 100/S, Bruker, Germany).

3. Results and discussion

3.1 Glycothermal synthesis of ZrO_2 nanoparticles

The effect of 1,4-butanediol solution on the formation of ZrO_2 nanopowders under glycothermal conditions was investigated in the current experiments. Tetragonal ZrO_2 nanoparticles have been prepared via precipitation in 1,4-butanediol under autogenous

Fig. 3. FESEM and TEM photomicrographs of ZrO₂ nanopowders synthesized in glycothermal condition at various reaction temperatures for 24 h: (a) FESEM image of ZrO₂ particle synthesized at 200°C, (b) TEM image of ZrO₂ particle synthesized at 200°C, (c) FESEM image of ZrO₂ particle synthesized at 220°C, and (d) TEM image of ZrO₂ particle synthesized at 220°C.

vapor pressure. In order to determine the lowest synthesis temperature for the formation of ZrO₂ nanopowders, precursors prepared at the conditions described above were glycothermally treated for 24 h at different temperatures. Tetragonal ZrO₂ nanoparticles were prepared at temperatures as low as 200°C when the concentration of precursor is 0.1 M. **Figure 2** shows XRD results indicate that the products were amorphous at 180°C and tetragonal ZrO₂ phase started to form from small portion of monoclinic ZrO₂ phase at 200°C. Thus, the transition temperature of the amorphous precursors to the crystalline solid was in the vicinity of 200°C. Tetragonal ZrO₂ phase was transformed into monoclinic ZrO₂ phase with further increasing the reaction temperature higher than 220°C. The average crystallite sizes were determined from XRD patterns according to Scherrer's equations. The main (101) peak is somewhat broadened. The crystallite sizes of ZrO₂ nanopowders were estimated to be changed from 10.1 to 7.4 nm with increasing the reaction temperatures from 220 to 220°C. These sizes agree well with the size determined from TEM images. These observations demonstrated that the highly alkaline conditions as in aqueous solution are not necessary for the formation of ZrO₂ nanoparticles in glycothermal reaction. Therefore, this process eliminates the contamination of the alkaline mineralizer from the final products. Also, the critical size for tetragonal-monoclinic transition is about 10 nm under glycothermal condition using 1,4-butanediol solution.

FESEM and TEM photomicrographs of ZrO₂ nanoparticles synthesized at different temperatures are given in **Fig. 3**. Glycothermally-derived ZrO₂ nanoparticles had a raspberry-like morphology with 50–100 nm as shown in Figs. 3(a) and 3(c). It was found from TEM images that raspberry-like ZrO₂ particles were composed of spherical shaped primary particles with a size less than 10 nm as shown in Figs. 3(b) and 3(d). Raspberry-like shape composed of small primary particles is the characteristic of

hydrothermal ceramic nanoparticles at relatively low reaction temperature (<100°C).⁴⁰⁾ Compositional analysis for tetragonal ZrO₂ nanoparticles synthesized at 200°C by EDS only showed the presence of Zr. This result also indicated that glycothermally-derived tetragonal ZrO₂ nanoparticles are homogeneous, stoichiometric powder.

In inorganic chemistry, ololation is the process by which metal ions form polymeric oxides in aqueous solution. The phenomenon is important to understanding the relationship between metal ions in aqueous solution and metal oxides, which are represented by many minerals. At low pH, many metal ions exist in aqueous solution as aqua coordination complexes.⁴¹⁾ When ZrOCl₂·8H₂O was dissolved into an aqueous solution, tetramer complexes, [Zr₄(OH)₈(H₂O)₁₆]⁸⁺, would form as a major species. The tetramer has 8 hydroxo bridges and 16 coordinate water molecules.⁴²⁾ As the pH increases by strong basic solution, water ligands of tetramer ionize to give the hydroxide complex, which release certain amount of H⁺ ions by deprotonation described in Eq. (1):

In the resulting [Zr₄(OH)_{8+x}(H₂O)_{16-x}]^{(8-x)+} ion, the remaining water and hydroxo ligands are highly acidic and the ionization and condensation processes can continue. Ultimately the nucleation of ZrO₂ particles occurs when the concentration reaches a critical supersaturation level. This nucleation process depends on the mineralizers in aqueous system. In hydrothermal condition, NaOH is a typical inorganic mineralizer which can lead to the formation of crystalline ZrO₂ at low temperature.³⁰⁾ However, glycothermal method does not need an inorganic mineralizer such as NaOH and KOH for the formation of crystalline ZrO₂ because 1,4-butanediol can complex ions to promote solubility or play a role as oxidizing agent. Avoiding the inorganic mineralizers

Fig. 4. TG-DTA analysis of ZrO_2 nanopowders synthesized in glycothermal condition at various reaction temperatures for 24 h: (a) 160°C, (b) 180°C, (c) 200°C, and (d) 220°C.

prevent contamination by alkalis and/or halides, which are commonly used in conventional hydrothermal process. Also, reaction temperature has a great effect on the tetragonal stabilization in glycothermal condition since phase transformation from tetragonal to monoclinic proceed up to 220°C or higher.

3.2 Surface characterization of ZrO_2 nanoparticles

The as-prepared ZrO_2 nanopowder was investigated by TG-DTA and FT-IR measurements to look for impurities such as water or organic species. **Figure 4** shows TG-DTA analysis of samples synthesized at different reaction temperatures. The total weight losses synthesized at 160, 180, 200, and 220°C for 24 h were, respectively, 25.9, 21, 7.6, and 5.8 wt % at 220°C. The total weight loss between 100 and 800°C is <25.9 wt % for the powder synthesized at 160°C and decreases significantly with increasing synthesis temperature, becoming <5.8 wt % at 220°C. The total weight loss consists of three contributions. The first region (<125°C) corresponds to the loss of physically adsorbed water. The second region between 150 and 350°C corresponds to the loss of physically adsorbed 1,4-butandiol and chemically bound hydroxyl groups. The exothermal peak near 240°C in DTA corresponds with the mass loss of the second regions in TGA. The weight loss of the third regions between 350 and 700°C is attributed to the combustion of carbonized species by 1,4-butandiol chemically bounded inside ZrO_2 nanoparticles and on the surface. The exothermal peak near 420°C in DTA corresponds with the mass loss of the third regions in TGA. From the TGA analysis, it is found that impurities such as water, hydroxyl groups, and organic species decreased with increasing synthesis temperature.

The TGA results were consistent with the FT-IR analysis. FT-IR spectra of samples synthesized at different reaction temperatures are given in **Fig. 5**. There are a strong broad

Fig. 5. FTIR spectra of ZrO_2 nanopowders synthesized at 200°C for 24 h.

absorption centered around 3350 cm^{-1} , which is associated with the O-H stretching vibration of absorbed water and hydroxyl group. The absorption band 1610 cm^{-1} is also due to the bending mode of associated water.⁴³⁾ Bound hydroxyl are invariably found on a surface of solvothermally derived powder due to surface hydration by residual H_2O of precipitated hydrous oxide and are most commonly removed by heating.⁴⁴⁾ The data does reveal weak shoulders near 2945, 2852, 1682, and 1109 cm^{-1} , which are characterized by the adsorption of CH_2 groups. Chemical adsorption and entrapment with the particles of 1,4-

Fig. 6. Typical Raman spectrum of tetragonal ZrO_2 nanopowders synthesized at 200°C for 24 h.

butandiol is believed to be involved in the formation of these peaks through substitution on a surface hydroxyl group.^{45),46)} There are two absorption bands which were only observed in ZrO_2 samples synthesized above 200°C. A sharp absorption band at 550 cm^{-1} corresponds to Eu mode of Zr–O vibration of tetragonal structure.⁴⁷⁾ Another weak shoulder near 745 cm^{-1} could be due to the presence of traces of monoclinic zirconia.⁴⁷⁾ FT-IR analysis suggests that several defects are present in the lattice of ZrO_2 crystallites. Intensities of all absorption bands for these defects decreased with increasing the reaction temperature and have minimums at 220°C.

The relatively small atomic scattering factor of oxygen makes it difficult to distinguish between cubic and tetragonal phases with XRD. However, Raman spectroscopy is sensitive to the polarizability of the oxygen ions and it can be used to determine the symmetry of ZrO_2 crystallites.⁴⁸⁾ The Raman spectrum for cubic ZrO_2 phase is characterized by a broad peak near 530–670 cm^{-1} and additional poorly defined structures related to the disordered oxygen sublattice.⁴⁹⁾ Spectrum for tetragonal zirconia is characterized by six relatively sharp bands of the different Raman modes at approximately 147, 266, 322, 464, 606, and 642 cm^{-1} because of its higher symmetry. The band at 147 cm^{-1} is assigned to (O_I –Zr– O_I) and (Zr– O_I –Zr) bending, the band at 266 cm^{-1} to (Zr – O_II) bending; and the band at 464 and 322 cm^{-1} to Zr– O_I / O_II stretching and to the coupling O_I (or O_II)–Zr– O_I (or O_II). The bands at 606 and 642 cm^{-1} are also assigned to (Zr– O_I) stretching.⁴⁸⁾ Monoclinic zirconia has a characteristic spectrum with 18 theoretically determined Raman active modes. Because of their high intensity, the duplet at 180 and 190 cm^{-1} and the band at 476 cm^{-1} are very significant.⁵⁰⁾ Raman spectrum for ZrO_2 nanoparticles synthesized 200°C is shown in **Fig. 6**. ZrO_2 nanoparticles synthesized at 200°C are predominantly tetragonal with sharp bands at 148, 266, 322, 464, 608, 642 cm^{-1} . The broad peaks between 575 and 640 cm^{-1} associated with the cubic phase are not observed. However, weak bands at 182, 383, 476, and 546 cm^{-1} suggest that trace amounts of monoclinic phase exists. These results are in agreement with the XRD results.

3.3 Phase stability of glycothermally-driven tetragonal ZrO_2 nanoparticles

To examine the effects of heat treatment on phase stability of tetragonal ZrO_2 nanoparticles glycothermally synthesized at 200°C, the as-synthesized tetragonal ZrO_2 nanoparticles were

Fig. 7. XRD patterns of ZrO_2 nanopowders calcined at various reaction temperatures for 4 h: (a) as-synthesized tetragonal ZrO_2 particles at 200°C, (b) 400°C, (c) 600°C, (d) 800°C, (e) 1000°C.

Fig. 8. Raman spectra of ZrO_2 nanopowders calcined at various reaction temperatures for 4 h: (a) as-synthesized tetragonal ZrO_2 particles at 200°C, (b) 400°C, (c) 600°C, (d) 800°C, (e) 1000°C, and (e) 1200°C.

heat-treated at various temperatures. The diffraction patterns of ZrO_2 nanopowders heat-treated at various temperatures are given in **Fig. 7**. Tetragonal phase begins to transform to monoclinic phase at 400°C and completely transforms to monoclinic phase at 800°C. **Figure 8** shows the Raman spectra of ZrO_2 nanoparticles after heat treatments. The ZrO_2 nanoparticles calcined below 600°C exhibited several weak peaks at 148, 266, 464, 608, and 642 cm^{-1} that associated with tetragonal phase. Further increasing the temperature above 600°C, the Raman peaks for tetragonal phase disappeared and all Raman peaks are assigned to monoclinic phase. The variation of Raman spectra during heating process is consistent with the XRD analysis stated above. Based on these results, it is suggested that glycothermally synthesized tetragonal ZrO_2 nanoparticles are metastable and easily transform to monoclinic phase with heat treatments.

4. Conclusions

In summary, tetragonal nanocrystalline ZrO_2 particles with trace amounts of monoclinic phase have been synthesized as low as 200°C by glycothermal treatment of amorphous zirconium

hydrous gel precursors without inorganic mineralizers under autogeneous vapor pressures. Reaction temperature has a great effect on the tetragonal stabilization in glycothermal condition since phase transformation from tetragonal to monoclinic proceed up to 220°C or higher. FT-IR analysis suggests that several defects such as H₂O, OH⁻, and CH₂ groups are present in the lattice of ZrO₂ crystallites. Intensities of all absorption bands for these defects decreased with increasing the reaction temperature and have minimums at 220°C. Also, it is suggested that glycothermally synthesized tetragonal ZrO₂ nanoparticles are metastable and easily transform to monoclinic phase with heat treatments.

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