Facile Route to Synthesize Zirconium dioxide (ZrO_2) nanostructures: Structural, Optical and Photocatalytic Studies

Sahar Zinatloo-Ajabshir, Masoud Salavati-Niasari*

Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P. O. Box. 87317-51167, I. R. Iran

* Corresponding author. Tel.: +98 361 5912383; Fax: +98 361 5552935;

E-mail address: salavati@kashanu.ac.ir (M. Salavati-Niasari)

Abstract: A facile sonochemical-assisted process has been developed for the morphology-controlled preparation of nanostructured zirconium dioxide (ZrO_2) by using zirconyl nitrate and ethylenediamine for the first time. Effects of concentration of ethylenediamine and several solvents were studied to reach optimum condition. It was found that these parameters play important roles in controlling the morphology and particle size of the final products. The structural and morphological properties of the as-prepared nanoparticles were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, energy dispersive X-ray microanalysis (EDS) spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Moreover, the optical properties of as-synthesized ZrO_2 were examined by Ultraviolet visible (UV-vis) absorption spectroscopy. The photocatalytic behavior of as-synthesized ZrO_2 was also examined by degradation of eriochrome black T dye as a model of water contaminant.

Keywords: ZrO_2 ; Nanostructure; Morphology-controlled synthesis; Optical properties, Photocatalytic activity.

1. Introduction

Among metal oxide materials, zirconium dioxide is a significant metal oxide because of its specific optical and electrical properties [1-3] as well as potential applications, including electrochemical capacitor electrodes and clear optical devices [4], fuel cells preparation [5] and catalysts [6-7]. ZrO_2 has three different crystal phases that are stable at dissimilar range of temperature: monoclinic (below 1175 °C), tetragonal (1175–2370 °C), and cubic (2370–2680 °C) [8]. Until now, numerous methods including microwave irradiation [9], sol–gel [10–12], precipitation [13-15], and sonochemical [16, 17] have been applied to fabricate zirconia. Recently, sonochemical method, as a facile route, has been considerably employed to generate novel nanostructured materials. Ultrasonic irradiations bring about cavitation in a liquid medium where the formation, growth and implosive collapse of bubbles take place. The collapse of bubbles with short lifetimes (less than a nanosecond) generates intense local heating and high pressure. These hot spots can produce high temperature and pressure which are suitable for many chemical reactions [18-23]. As a precipitating agent, ethylenediamine has been frequently reported for synthesis of zirconia by precipitation method [15, 24, 25].

Herein, zirconium dioxide nanoparticles are sonochemically prepared with the aid of the zirconyl nitrate and ethylenediamine. This work is the first successful attempt for the large-scale synthesis of ZrO_2 nanoparticles by using ethylenediamine via a surfactant-free sonochemical-assisted process. The effect of preparation parameters such as concentration of ethylenediamine and solvent on the particle size and the morphology of the final product are also investigated by using scanning electron microscopy (SEM).

2. Experimental

2.1. Materials and experiments

All the chemicals used for the synthesis of zirconia nanoparticles including zirconyl nitrate ($\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (ZN), ethylenediamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$), liquor ammonia solution containing 25% ammonia, methanol, ethylene glycol (EG) and propylene glycol (PG) were purchased from Merck and were used without additional purification. Distilled water was utilized for all the experiments. A multiwave ultrasonic

generator (Sonicator 3000; Bandeline, MS 72, Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 80 W, was used for the ultrasonic irradiation. Hitachi s4160 Japan scanning electron microscope (SEM) was used to investigate the morphological properties of ZrO_2 nanoparticles. Transmission electron microscope (TEM) images were obtained on a JEM-2100 with an accelerating voltage of 60–200 kV. Fourier transform infrared spectra (FT-IR) were recorded with a FTIR spectrometer (Thermo Nicolet Magna-IR 560 spectroscopy, USA) in KBr pellets. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. The X-ray diffraction (XRD) patterns were collected from a diffractometer of Philips Company with X'PertPro monochromatized Cu K α radiation ($\lambda=1.54 \text{ \AA}$). The energy dispersive spectrometry (EDS) pattern was obtained on XL30, Philips microscope. UV–visible spectrum of ZrO_2 nanoparticles was recorded using Scinco UV–vis scanning spectrometer (ModelS-4100).

2.2. Synthesis of ZrO_2 nanoparticles

To synthesize ZrO_2 nanoparticles, in a typical procedure, an aqueous solution of ethylenediamine (en) (1 mmol of en was dissolved in 50 mL of distilled water) added into an aqueous solution of ZN (1 mmol of ZN dissolved in 50 mL of distilled water) drop-wise under ultrasound irradiation (at power of 70 W/m^2 for 20 min with utilizing a period cycle including 3s pulse and 1s silent) (sample no. 1). It is worth mentioning that the temperature of the mixture increases during the sonication irradiation [14]. To avoid overheating, the system is externally cooled and temperature was being set at 25°C . The hydroxide precipitate obtained under various conditions was filtered and washed with distilled water three times. The final product was dried at 80°C for 24 h and calcined at 600°C for 4 h. Schematic diagram of formation of zirconium dioxide nanoparticles is depicted in Scheme 1.

To investigate the effect of ultrasound irradiation, a blank test was carried out in the absent of sonication. To study the effect of ethylenediamine on the morphology of the ZrO_2 nanoparticles, blank test1 was performed by NH_4OH instead of en. The effects of concentration of en and solvent on the particle size and the morphology of zirconium dioxide samples were investigated and the results listed in Table 1.

2.3 Photocatalytic measurements

The photocatalytic behavior of the as-prepared ZrO_2 nanoparticles was examined by employing eriochrome black T dye solution in the quartz reactor (the solution including 0.001 g of the eriochrome black T and 0.04 g of the ZrO_2 nanoparticles). After aerating for 1/2 h, the mixture was subjected to the illumination of the UV light. The eriochrome black T photodegradation percentage was estimated as follow:

$$D.P.(t) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_t and A_0 are the measured absorbance quantity of the eriochrome black T solution at t and 0 min by a UV-vis spectrometry.

3. Results and discussion

3.1. Characterization of the nanoparticles

XRD was used to characterize the purity, average crystallite diameter and phase of the as-synthesized products. The XRD patterns of the sample no. 4 after washing and calcination are shown in Fig. 1a and b, respectively. It is clear that the sample prepared by the sonochemical-assisted route (after washing steps) is amorphous (Fig. 1a). As seen in Fig. 1b, nearly all of the diffraction peaks may be indexed to monoclinic ZrO_2 (space group P21/a, JCPDS card 37-1484). Besides, four diffraction peaks in Fig. 1b can be ascribed to tetragonal ZrO_2 (JCPDS 88-1007). The volume content of monoclinic and tetragonal phases of the ZrO_2 was calculated by following equation [14]:

$$V_m = \frac{1.311X_m}{1 + 0.311X_m} \quad (1)$$

where, V_m is volume content of the monoclinic phase and that of tetragonal phase is $V_t = 1 - V_m$ and X_m is given by:

$$X_m = \frac{Im(-111) + Im(111)}{Im(-111) + Im(111) + It(101)} \quad (2)$$

where, I_m (-111) and I_m (111) are the integrated intensities (area under the peaks) of the (-111) (at $2\theta = 28.5^\circ$) and (111) (at $2\theta = 31.5^\circ$) peaks for the monoclinic phase ($m\text{-ZrO}_2$) and I_t (101) is the intensity of the (101) (at $2\theta = 30.5^\circ$) peak for tetragonal phase ($t\text{-ZrO}_2$) of zirconium oxide. The volume content of the monoclinic phase and that of tetragonal phase of the obtained product were 89% and 11%, respectively. To determine the average crystallite size of the prepared sample Scherrer equation [24] was used:

$$\tau = \frac{k\lambda}{\beta \cos\theta} \quad (3)$$

where, τ is the crystallite size, k is the so-called morphology factor, β is the breadth of the shown diffraction peak at its half intensity maximum, and λ is the wavelength of X-ray source applied in XRD. The average crystallite size of the prepared sample was calculated about 23 nm.

To determine the composition of ZrO_2 nanoparticles (sample no. 4), the EDS analysis was employed. As observed in in Fig. 2a, from the EDS, it is clearly identified that the obtained product is composed of Zr and O.

The morphology of the product in the optimum condition (sample no. 4) was further studied by transmission electron microscopy (TEM). As it can be seen, most of the sintered together particles have slightly irregular, round shapes (Fig. 2b). Moreover, the average particle size determined from the SEM image is in relative agreement with the TEM investigations which display the particle's size in the range of 15-25 nm.

FT-IR spectra of sample no. 4 in the range of 500–4000 cm^{-1} after washing steps and after calcination are shown in Fig. 3a and 3b, respectively. The (C-H) bending vibration band at 1383 cm^{-1} and weak (C-N) stretching vibration band at 1340 cm^{-1} indicate the presence of en in the pores after washing steps (Fig. 3a). These bands perfectly vanish after calcination at 600 $^\circ\text{C}$. The presence of physisorbed water molecules linked to ZrO_2 sample was indicated by a weak peak at 1632 cm^{-1} and absorption band centered at 3443 cm^{-1} are ascribable to the $\nu(\text{OH})$ bending and stretching vibrations, respectively [25]. The band at 501 cm^{-1} in Fig. 3b is attributed to Zr–O vibration [15].

3.2. Scanning electron microscopy study

In this work, to study the influence of the en concentration and solvent on the morphological properties of the samples scanning electron microscopy (SEM) was applied.

3.2.1. Effect of en concentration

Different molar ratios of ZN to en were used to examine effect of en concentration on the morphological properties of the products. As already mentioned, in this work, en was used as both precipitating and capping agent. The bifunctional en can precipitate $\text{ZrO}(\text{OH})_2$ from $\text{ZrO}(\text{NO}_3)_2$ and may hinder the aggregation of prepared $\text{ZrO}(\text{OH})_2$ nanoparticles as capping agent. It seems that en with high steric hindrance in the presence of ultrasound irradiation brings about nucleation rather than the particle growth. The schematic illustration of the proposed mechanism for effect of en on synthesis of zirconia nanoparticles is shown in Scheme 1b. Fig. 4a–d displays the SEM images of the samples no. 1, 2, 3 and 4 which were obtained by using 1:1-1:4 molar ratios of ZN:en, respectively. As shown in Fig. 4, by increasing en concentration, the size of nanoparticels is decreased. It seems that when en concentration increases, the chance of collision between $\text{ZrO}(\text{OH})_2$ nanoparticles is decreased owing to the steric hindrance influence of en. Therefore, among the employed molar ratios of ZN:en, very uniform sphere-like zirconium dioxide nanoparticles with small grain size can be formed by utilizing (1:4) molar ratio of ZN to en (sample no. 4). On the other hand, with lower molar ratio of ZN to en, irregular and less uniform spherical nanoparticles can be obtained that were highly aggregated in some places (Fig. 4a-c).

3.2.2. Effect of ultrasound irradiation

To examine the influence of the ultrasound irradiation on the morphological properties of the ZrO_2 , sample no. 5 was synthesized as blank sample without applying sonication at room temperature (25 °C) under vigorous magnetic stirring. It is noteworthy that less sphere-like zirconia nanoparticles with large grain size were formed (Fig. 4e). The result indicates that sonication is favorable to generate uniform sphere-like zirconium dioxide nanoparticles with small grain size (Fig. 4d). It is well known that a lot of energy is created by collapsing of bubbles during ultrasonic irradiation, which can divide large particles to

small ones [26]. Therefore, the production of smaller particles is a benefit of applying ultrasound irradiation.

The reaction mechanism is shown below [14]:

The results have shown that the same reaction in absence of ultrasonic reaction is done in higher reaction time and leads in lower reaction yield. It is reported that higher reaction yield at lower time was obtained by employing ultrasound irradiation [14]. This can be ascribed to the ability of ultrasonic cavitation to create free radicals in solution. The sonolysis of water generates hydroxyl and hydrogen radical in an aqueous system.

where the symbol))) shows ultrasound irradiation.

So, more hydroxide species would be generated in solution by applying ultrasound irradiation and therefore, the hydrolysis of the ZN precursor increases.

3.2.3. Effect of en

To study the effect of the en on the morphological properties of the zirconium dioxide, sample no. 6 was prepared as blank test1 using NH_4OH . It can be seen that in the absence of en, irregular ZrO_2 nanostructures with high agglomeration was obtained (Fig. 4f). As already mentioned, when en used as precipitating agent

(Fig. 4d), the probability of collision of $\text{ZrO}(\text{OH})_2$ nanoparticles together decreased because of steric hindrance influence of ethylenediamine, and therefore the size of particles decreased. Thus, very uniform sphere-like zirconia nanoparticles with small grain size can be formed by using en as both precipitating and capping agent under ultrasound irradiation (Fig. 4d).

3.2.4. Effect of solvent

It has been shown that solvent vapor pressure has a great impact on the acoustic cavitation [27]. The intensity of cavitation collapse is increased by decreasing solvent vapor pressure. Such collapse produces high temperature, and therefore the rates of sonochemical reactions increase. In this study, different solvents such as methanol, ethylene glycol (EG) and propylene glycol (PG) with various vapor pressures were applied for the synthesis of zirconium dioxide under ultrasonic irradiation for 20 min by using (1:4) molar ratio of ZN:en. Fig. 5a–c shows SEM images of samples no. 7–9, respectively. Methanol (96 Torr at 20 °C), having higher vapor pressure than water (17.25 Torr at 20 °C), and also water having higher vapor pressure than ethylene glycol (0.0397 Torr at 20 °C). The vapor pressure of propylene glycol is lower than that of ethylene glycol. Application of ultrasonic irradiation to chemical reactions consists of the utilization of ultrasonic cavitation. Ultrasonic cavitation includes the formation of cavities in a liquid medium where the creation, increase in size and sudden collapse of bubbles take place [28]. The sudden collapse of bubbles in liquid creates high energy, which causes mechanical and chemical influences. It is reported that the bubbles with different energies and stabilities were created by different vapor pressures. In the solvents that have high vapor pressure, the sudden collapse of bubbles takes place sooner, and therefore lower energy produces in comparison with those solvents that have lower vapor pressure. This is the reason which can explain why the obtained sample in methanol (sample no. 7) has agglomerated particle-like morphology (Fig. 5a). The created bubbles in methanol medium have low energy and stability, and therefore the large particles cannot be divided to small ones. On the contrary, in the case of propylene glycol (sample no. 8) and ethylene glycol (sample no. 9) with low vapor pressure, bubbles produced by ultrasonic irradiation will collapse later and generate high energy. The particles were coalesced and turned into bulk structures by this

produced high energy (Fig. 5b and c). So, very uniform sphere-like zirconia nanoparticles with small grain size can be obtained by using en and water as solvent in the presence of ultrasound irradiation (Fig. 4d).

3.3. Optical properties of the as-prepared ZrO_2 nanoparticles and band gap analysis

The optical characteristics of the sample no. 4 were investigated by DR-UV-vis spectrum to additional assess their quality. Fig. 6a displays the DR-UV-vis spectrum of the as-prepared zirconia (sample no. 4) and shows an absorption peak at 344 nm. To estimate the band gap from the DR-UV-vis results, Tauc's relationship was utilized [29].

$$(Ah)^n = B(h - E_g)^2 \quad (2)$$

where: A is absorbance quantity, n is 2 or 1/2 for direct and not direct transitions, h is the energy of the photon and B is a substance constant. Extrapolating the linear portion of the plots of $(h)^2$ against h to the energy axis was done to obtain the energy gap (E_g) of the zirconium dioxide nanoparticles as direct semiconductor substance (Fig. 6b). The E_g value of the ZrO_2 is calculated to be 3.44 eV.

3.4. Photocatalytic properties of the as-prepared ZrO_2 nanoparticles

...Photooxidation of the eriochrome black T dye as a model of water contaminant under UV light was employed to evaluate the characteristics of the as-synthesized zirconium dioxide nanoparticles (sample no. 4). Fig. 6c displays the obtained result. No eriochrome black T was practically deleted after 120 min without employing UV light illumination or as-prepared zirconium dioxide nanoparticles due to the insignificant contribution of the self-degradation. With applying photocatalytic calculations by Eq. (1), the eriochrome black T dye degradation percentage was about 72 after 120 min illumination of UV light. This obtained photocatalytic result indicates that as-formed nanostructured ZrO_2 have very fine capability to be applied as proper and desirable nano-scale substance for photocatalytic utilizations under UV light.

4. Conclusions

In summary, sphere-like zirconia nanoparticles were successfully synthesized by using ethylenediamine (en) as both precipitating as well as capping agent in the presence of ultrasound irradiation. This study demonstrates that using en in presence of ultrasonic irradiation is an appropriate choice for preparation of ZrO_2 nanoparticles without applying any surfactants. The results obtained in the present work show that very uniform sphere-like zirconium dioxide nanoparticles with small grain size can be formed by using (1:4) molar ratio of ZN to en as well as water as solvent. The optical properties of as-synthesized nanoparticles were also investigated. When as-produced zirconium dioxide nanoparticles was applied as photocatalyst, the percentage of the eriochrome black T degradation was about 72 after 2 h irradiation of UV light. This result suggests as-prepared zirconium dioxide nanoparticles as proper and desirable candidate for photocatalytic utilizations under UV light.

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Table 1. Synthesis conditions for all products

Sample no	Precipitating agent	Molar ratio (ZrO(NO ₃) ₂ ·xH ₂ O: Precipitating agent)	Solvent	Ultrasonic irradiation	Morphology
1	en	1:1	H ₂ O	Yes	Irregular sphere-like nanoparticles
2	en	1:2	H ₂ O	Yes	Irregular sphere-like nanoparticles
3	en	1:3	H ₂ O	Yes	Less uniform sphere-like nanoparticles
4	en	1:4	H ₂ O	Yes	Very uniform sphere-like nanoparticles with small grain size
5 ^a	en	1:4	H ₂ O	No	Less uniform sphere-like nanoparticles with large grain size
6 ^b	NH ₄ OH	1:8	H ₂ O	Yes	Irregular nanostructures with high agglomeration
7	en	1:4	H ₂ O/Methanol (25/75)	Yes	Agglomerated particle-like structures
8	en	1:4	H ₂ O/PG(25/75)	Yes	Coalesced particles/bulk structures
9	en	1:4	H ₂ O/EG(25/75)	Yes	Coalesced particles/bulk structures

^a Blank test, in the absence of sonocation.^b Blank test1, in the absence of en.

Figure Captions:

Figure 1. XRD patterns of sample 4 after washing (a), and after calcination(b).

Figure 2. EDS pattern (a) and TEM photograph (b) of the sample no. 4.

Figure 3. FT-IR spectra of sample no. 4 after washing (a), and after calcination (b).

Figure 4. SEM images of ZrO_2 prepared with different molar ratios of ZN to ethylenediamine: (a) 1:1 (sample no. 1), (b) 1:2 (sample no. 2), (c) 1:3 (sample no. 3), and (d) 1:4 (sample no. 4) in the presence of ultrasound irradiation, (e) 1:4 (sample no. 5) in the absence of ultrasound irradiation (blank test), and (f) SEM image of ZrO_2 prepared in the absence of ethylenediamine (blank test1).

Figure 5. SEM images of ZrO_2 prepared with different solvents: (a) Methanol (sample no. 7), (b) PG (sample no. 8), and (c) EG (sample no. 9).

Figure 6. (a) DR-UV-vis spectrum of sample no. 4, (b) plot to determine the band gap of ZrO_2 and (c) photocatalytic eriochrome black T degradation of ZrO_2 nanoparticles (sample no. 4) under UV light.

Scheme 1. Schematic diagram of the preparation of zirconium dioxide nanoparticles (a) and schematic of a mechanism effect of ethylenediamine for formation of ZrO_2 nanoparticles (b).

Scheme 1.

Fig 1.

a

b

Fig 2.

Fig 3.

Fig 4.

Fig 5.

Fig 6.