Synthesis, Characterization, and Morphological Control of ZnTiO₃ Nanoparticles through Sol-gel Processes and Its Photocatalyst Application

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Abstract

In this work, ZnTiO₃ ceramics have been synthesized from the reaction of zinc acetate (Zn(CH₃COO)₂.2H₂O), tetrabutyl titanate (Ti(OC₄H₉)₄) as precursors and ethanol as the solvent, in the presence benzene-1, 3, 5-tricarboxylic acid as a novel chelating agent by sol-gel method. The effect of various parameters such as reaction temperature, pH effect, effect of molar ratio of benzene -1, 3, 5-tricarboxylic acid to tetrabutyl titanate on morphology, size and purity of products was investigated. The as-prepared products were characterized by various analyses such as: X-ray diffraction (XRD), scanning and transmittance electron microscopy (SEM, TEM), X-ray energy dispersive spectroscopy (EDS), UV-Vis and Fourier transform infrared spectroscopy (FT-IR) technique. The photocatalytic degradation was investigated

using methyl orange (MO) under ultraviolet (UV) light irradiation. Application of this product as photocatalyst was investigated through degradation of methyl orange (MO) under UV irradiation and percentage of degradation obtained about 70 % after 60 min.

Keywords: ZnTiO₃; Sol-gel processes; Photocatalyst; Semiconductor; Nanostructures.

1. Introduction

The development of nanomaterials has been strongly pursued due to their unique features such as: electronic, magnetic, optical, chemical, and mechanical properties that differ from bulk materials [1–11]. Size-dependent properties are observed such as quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and superparamagnetism in magnetic materials. Among the different nanomaterials, perception the behavior of ferroelectroinc materials at the nanoscale is importance for the growth of molecular electronics. Indeed, perovskite-phase mixed-metal oxides are significant for their advantageous piezoelectric, dielectronic, electrostrictive, pyroelectric, and electro-optic properties with corresponding applications in the electronics industry for transducers, actuators, and high-k-dielectrics [12, 13]. Among perovskite-phase mixed-metal oxides, ZnTiO₃ has been reported to have superior electrical properties that are sufficient for applications towards microwave dielectrics [14]. Furthermore, ZnTiO₃ is an effective photocatalyst because this compound is categorized in group of the coupled photocatalysts that can help to enhance the photocatalytic activity of TiO₂ through reducing recombination process and change band gap to enhance the optical response in the UV to visible light range [15, 16]. Recently, researchers have reported that three compounds exist in the ZnO–TiO₂ system including: Zn₂TiO₄ with a cubic spinel crystal structure, ZnTiO₃ with a hexagonal ilmenite structure (h-ZnTiO₃), and Zn₂Ti₃O₈ with a cubic defect spinel structure [11–13]. Zn₂Ti₃O₈ has been obtained as a low-temperature form of h-ZnTiO₃ that is produced at $T < 820\text{ }^{\circ}\text{C}$ [17], and only exists based on the Zn₂TiO₄ phase [18]. It is reported that Zn₂TiO₄ and rutile phase of TiO₂ produce from decomposition of h-ZnTiO₃ at $T > 945\text{ }^{\circ}\text{C}$, under the condition of solid-state reactions and it is considered as a metastable phase [19], while single-phase compound has been obtained by zinc oxide and rutile hydrate at $T = 850 \sim 900\text{ }^{\circ}\text{C}$ [20]. Pure h-ZnTiO₃ represents superior

dielectric properties in the microwave range. Many reports have been made to produce pure ZnTiO_3 powders and ceramics. Although Zn_2TiO_4 can be synthesized by conventional solid state reaction between ZnO and TiO_2 with molar ratio 2: 1 [19], but synthesis of pure ZnTiO_3 from a mixture of ZnO and TiO_2 with molar ratio 1: 1 was not successful. There are various problems for synthesis of pure ZnTiO_3 powders by the solid state reaction method such as: high temperature, long range of diffusion distance, large particle size, and limited degree of chemical homogeneity. In the past two decades, sol–gel route has been successfully used for preparation of ceramics, glasses, fibers, and thin films; this method has various advantages such as: chemical homogeneity, easy component adjustment, low calcination temperature and low cost. Besides, sol–gel route is one of methods for synthesis of nanomaterials [21, 22]. Here, ZnTiO_3 nanostructures were synthesized by an unusual sol–gel method. Utilizing novel and less chemical materials in addition to simple procedure is the characteristic benefit of this method in comparison to the other reports [23, 24]. In this paper, ZnTiO_3 nanostructures were successfully synthesized by sol–gel-method. It is found that the amorphous gel can be transformed into pure ilmenite-type ZnTiO_3 through calcinations at 700 °C. The products were characterized by various analyses such as: SEM, TEM, XRD, EDS, FT-IR and UV-vis spectroscopy. The photocatalytic degradation of methyl orange (MO) under UV irradiation was investigated in presence of ZnTiO_3 as an effective photocatalyst. The degradation percentage of MO as a contamination agent was calculated about 70 %.

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents were used as received without further purification. X-ray diffraction (XRD) patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu K α radiation. The composition analysis was done by energy dispersive X-ray (EDX, KeveX, Delta Class I). Scanning electron microscopy (SEM) images were obtained on LEO. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. Transmission electron microscopy (TEM) images were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 100 kV. Fourier transform

infrared (FT-IR) spectra were recorded on a Shimadzu Varian 4300 spectrophotometer in KBr pellets. The electronic spectra of the complexes were taken on a JASCO, (190-2700 nm), UV-Vis diffuse reflectance spectroscopy analysis (UV-Vis) was carried out using shimadzu UV-Vis scanning spectrometer.

2.2. Synthesis of ZnTiO_3 nanoparticles

The ZnTiO_3 nanoparticles were synthesized by sol–gel method using zinc acetate $[\text{Zn}(\text{CH}_3\text{COO})_2] \cdot 2\text{H}_2\text{O}$, tetrabutyl titanate ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$) as starting materials, and benzene -1, 3, 5-tricarboxylic acid $[\text{C}_6\text{H}_3(\text{COOH})_3]$ (trimesic acid) as a novel chelating agent. At the first, 0.87 mmol from benzene-1, 3, 5-tricarboxylic acid and 0.29 mmol from titanium butoxide were dissolved in ethanol separately then mixed in a round bottom flask. Then, zinc acetate was mixed to the above solution (molar ratio of benzene-1, 3, 5-tricarboxylic acid to metallic cations was constant and equal to 3: 1). The obtained solution was heated and stirred at temperature between 60 °C and 90 °C in an oven to obtain the dry precursors by evaporating the solvent, and then the dry precursors were ground into powders. Finally, the resulted powders were calcined at three temperatures 700 °C, 800 °C and 900 °C for 3h.

2.3. Photocatalytic experimental

The methyl orange (MO) photodegradation was examined as a model reaction to evaluate the photocatalytic activity of the ZnTiO_3 nanostructures. The photocatalytic experiment was performed under ultraviolet (UV) light irradiation. The photocatalytic activity of zinc titanate nanostructures obtained from sample no. 5 was studied by the degradation of methyl orange solution as an organic pollutant. The photocatalytic degradation was performed with 150 mL solution of methyl orange (0.0005 g) containing 0.05 g of ZnTiO_3 as an effective photocatalyst. This mixture was aerated for 30 min to reach adsorption equilibrium. Later, the mixture was placed inside the photoreactor in which the vessel was 15 cm away from the ultraviolet source of 400 UV lamp. The photocatalytic test was performed at room temperature. Aliquots of the mixture were taken at definite interval of times during the irradiation, and after centrifugation they were analyzed by a UV-vis spectrometer. The methyl orange (MO) degradation percentage was calculated as:

$$\text{Degradation rate (\%)} = \frac{A_0 - A}{A_0} \times 100$$

where A_0 and A are the absorbance value of solution at A_0 and A min, respectively.

3. Results and discussion

In order to study the characteristic vibration bands corresponding to different bonds, the FT-IR spectra (Fig. 1) is used in the spectral range of 400–4000 cm^{-1} . It is well known that the characteristic vibration bands corresponding to metal-oxygen bonds be in the range of 400–700 cm^{-1} . As seen from the spectrum, peaks 439 cm^{-1} and 537 cm^{-1} are the characteristic bands of ZnTiO_3 , corresponding to the stretching vibration of Zn–O and Ti–O bond [25]. Also the bonds at 3438 and 1633 cm^{-1} were refer to (–OH) groups. So, according to appeared peaks, the FT-IR spectrum confirms that ZnTiO_3 nanostructures were produced.

Fig. 2 illustrates the XRD pattern of prepared sample at calcination temperature of 700 °C for 3h. Fig. 2a is related to the witness test (molar ratio of Trimesic acid to tetrabutyl titanate 0:1) and Fig. 2b is related to ZnTiO_3 nanoparticles prepared with molar ratio of Trimesic acid to $\text{Ti}(\text{OC}_4\text{H}_9)_4$ of 3:1. In Fig. 1a due to not having chelating agent, ZnTiO_3 , TiO_2 and ZnO characteristic peaks were observed. While in Fig. 2b zinc titanate with high purity obtained and this pattern matches with ZnTiO_3 with rhombohedral structure (space group R-3 with cell constant $a = 5.0760$, $b = 5.0760$, $c = 13.9200$ Å, JCPDS No. 25-0671). The crystallite size measurements were also carried out using the Scherer equation, $DC = K \lambda / \beta \cos \theta$. Where, K is about 0.9, β is the breadth of the observed diffraction line at its half intensity maximum and λ is the wavelength of X-ray source used in XRD. For prepared ZnTiO_3 in witness test and produced ZnTiO_3 nanoparticles in basic reaction, the mean particle size obtained from the above equation are calculated to be 38.99 nm and 33.47nm, respectively. Clearly, present of trimesic acid in the reaction induces a corresponding decrease in crystallite size, leading to sharper diffraction peaks. Because of, acid provides steric hindrance around Zn^{2+} .

Fig. 3 shows the effect of calcination temperature on the morphology of the products. The SEM images of the as-prepared products at 700 °C, 800 °C and 900 °C for 3h are shown in Fig. 3(a), (b) and (c) respectively. At temperature of 700 °C, nucleation speed is faster than the growth speed of nanostructures, so the products

were composed a large number of separate, small and uniform particles. The growth speed is faster than the nucleation of nanostructures at higher temperatures, so particles which were obtained much more fused to each other and their size is been bigger. These results clearly illustrated that the optimum calcination temperature is 700 °C, and this temperature was used in other experiments.

Fig. 4 depicts scanning electron microscopy (SEM) images of ZnTiO₃ nanoparticles prepared at 700 °C with various pH values. Initial pH for synthesis of the ZnTiO₃ particles was designated in range of 4-5 by pH meter. Fig. 4b shows that the aggregated particles with porosity around them were formed in pH = 4-5. The average particle size is about 62nm, these values are larger than the values estimated from the XRD pattern. Because, the XRD pattern shows crystalline size and SEM images shows particle size, as a result, the nanoparticles are quite small in size. In continuous, the effect of pH on morphology of products was studied, and two other pH were tested. By decreasing pH to 1-2, the particles size of the as-prepared ZnTiO₃ increased and their morphology changed to nanorod-like (Fig. 4a). When pH increased to 9, the gelation process was done quickly, and smaller particles with lower regularity were obtained (adjusting pH of solution were done using NH₄OH and HNO₃).

The effect of the pH on the growth process and morphology of products can be related to the effect of pH on the formation of gel in sol-gel method. The sol-gel method is a chain process for synthesis of nanomaterials that quality and properties of the obtained product (gel) in this method depends on the intermediate steps. The most important steps for formation of gel are pre-hydrolysis, hydrolysis and polycondensation. At low pH the effective density of H⁺ ions in the sol is high and hydronium ions (H₃O⁺) arises from the higher amount of H⁺ ions [26], which prevents the hydrolysis and condensation process in low pH condition. Consequently, at the end of polycondensation process, the gel network resembles only linear polymer structure, which leads to sticking together and larger aggregates. On the other hand, when the pH of sol is raised to 9, the effective density of H⁺ ions reduced, which causes an increase in the OH⁻ ions. The addition of NH₄OH (for increasing pH) too comforts this process. As a result, the hydrolysis and polycondensation rates for the formation of gel are faster when that the precursor sol is in higher pH. So due

to higher effective concentration of OH^- ions, reactions happen in a cyclic manner [27] since the probability of intermolecular reactions are higher than intra-molecular reactions [28]. The higher rate of hydrolysis and condensation in case of higher pH sol, therefore, results in highly branched metal-oxygen polymeric network; which leads smaller and porous particles in nanoparticles deposited from sol having higher pH.

The effect of molar ratio of benzene -1, 3, 5-tricarboxylic acid to tetrabutyl titanate on the morphology of the products are shown in Fig. 5. The SEM images of samples obtained with different molar ratio of chelating agent to titanium source including of 1: 1, 3: 1, and 5: 1 are shown in Fig. 5a–c, respectively. When the amount of chelating agent was 0.29 mmol (molar ratio of -1, 3, 5-tricarboxylic acid: tetrabutyl titanate was 1: 1), formless structures with different size obtained (Fig. 5a). Fig. 5b shows SEM image of as-prepared product with 0.87 mmol of chelating agent (molar ratio of -1, 3, 5-tricarboxylic acid:tetrabutyl titanate was 3: 1). In this value, the small and uniform particles were fused to each other. With increase in amount of -1, 3, 5-tricarboxylic acid to 1.45 mmol, large and fused particles were produced (Fig. 5c). Summary, increasing of the acid amount is caused to form structures with undesired size and morphology, so the lower amount of chelating agent is favorable.

Fig. 6a and b show the FESEM images of the as-synthesized ZnTiO_3 in pure solvent of ethanol and ethanol mixed with minor amounts of ethylene glycol, respectively. As shown in Fig. 7a, ZnTiO_3 nanoparticles calcined at 700 °C in pure ethanol have regular shape and smaller sizes while produced ZnTiO_3 nanoparticles in ethanol mixed with minor amounts of ethylene glycol are erratic with unspecified morphology (Fig. 6b).

Energy-dispersive X-ray (EDX) spectrum (Fig. 7) shows the existence of O, Ti and Zn. we also performed chemical analysis of the sample. The results revealed that the zinc titanate had a Zn/Ti ratio of 1.07, consisting with the EDX analysis.

The room temperature UV–vis absorption spectra of ZnTiO_3 nanoparticles were also measured in the range of 200–700 nm. Fig. 8a shows the diffuse reflection adsorption spectra (DRS) of the ZnTiO_3 nanoparticles calcined at 700 °C. The figure indicates that the ZnTiO_3 nanoparticles shows absorption

maxima at 264nm, the direct optical band gap estimated from the absorption spectra of the ZnTiO₃ nanoparticles are shown in Fig. 8b. An optical band gap is obtained by plotting $(\alpha h\nu)^2$ vs $h\nu$ where α is the absorption co-efficient and $h\nu$ is photon energy. Extrapolation of the linear portion at $(\alpha h\nu)^2 = 0$ gives the band gaps of 3.2 eV for perovskite ZnTiO₃ material. The optical band gap of ZnTiO₃ nanoparticles is smaller than those of the bulk ZnTiO₃ (band gap 3.70 eV) [29], which this red shift may be due to the difference in size of the particles (Quantum size effect) [30, 31].

In Fig. 9 HRTEM images of prepared ZnTiO₃ nanoparticles are shown. As seen, TEM image revealed that the spherical aggregates composed of many tiny grains with 25-40 nm in diameter, which is similar to the size calculated from XRD. Hence the porosity is generated due to interparticle spacing of ZnTiO₃ nanoparticles.

In this work, ZnTiO₃ nanoparticles were synthesized by sol-gel method. First, a solution of benzene -1, 3, 5-tricarboxylic acid (C₆H₃O₆) was mixed with appropriate amount of tetrabutyl titanat (Ti(C₄H₉O)₄) and Zn(CH₃COO)₂.2H₂O. benzene -1,3,5-tricarboxylic acid due to having three functional groups was used as an initiator for polymerization reaction, which allows the predetermined ratio of Zn to Ti to be compatible with the final sample (ZnTiO₃) according to the following reactive formula.

In continuing, a polymeric chain due to reaction between acid and Zn(OOCCH₃)₂ being produced and Zn (II) ions are bound by the strong ionic bonds between the polymeric chains. So, Ti(OH)₄ is distributed randomly within the polymeric chains. This immobility of zinc ions in the polymer chains favors the formation of ZnTiO₃ nanoparticles in the following pyrolysis process.

Furthermore, this route is facile and very suitable for industrial production of ZnTiO₃ nanoparticles. In addition, this process can be versatile to easily synthesize other titanium based perovskite-type oxides. The synthetic pathway is shown in Scheme 1.

Photodegradation of methyl orange under UV light irradiation (Fig. 10 a-c) was employed to evaluate the photocatalytic activity of the as-synthesized ZnTiO₃. No methyl orange was practically broken down after 60 min without using ultraviolet light irradiation or nanocrystalline ZnTiO₃. This observation indicated that the contribution of self-degradation was insignificant. The probable mechanism of the photocatalytic degradation of methyl orange can be summarized as follows:

Using photocatalytic calculations by Eq. (1), the methyl orange degradation was about 70 % after 1 hours under irradiation of ultraviolet light and nanocrystalline ZnTiO₃ presented high photocatalytic activity (Fig. 10a). The spectrofluorimetric time-scans of methyl orange solution illuminated at 365 nm with nanocrystalline ZnTiO₃ are depicted in Fig. 10b. Fig. 10b shows the continuous removal of methyl orange on the ZnTiO₃ under ultraviolet light irradiation. It is generally accepted that the heterogeneous photocatalytic processes comprise various steps (diffusion, adsorption, reaction, and etc.), and suitable distribution of the pore in the catalyst surface is effective and useful to diffusion of reactants and products, which prefer the photocatalytic reaction. In this investigation, the enhanced photocatalytic activity can be related to appropriate distribution of the pore in the nanocrystalline ZnTiO₃ surface, high hydroxyl amount and high separation rate of charge carriers (Fig. 10c).

Scheme 2 illustrates five ways for doping TiO₂ as a well-known semiconductors including: 1) TiO₂/ semiconductor with same band gap, 2) TiO₂/ semiconductor with different band gap, 3) TiO₂/ metal, 4) TiO₂/ graphene and 5) TiO₂/ graphene/ semiconductor. The product of every way has certain application, so doping was done by considering the desired application [32-36].

4. Conclusions

The sol-gel method in comparing to other synthetic methods of nanomaterials preparation has many advantages, for examples: simple, available, and inexpensive. In this work, we have prepared the ZnTiO_3 nanostructures by sol-gel method using $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and tetrabutyl titanate as starting materials and benzene -1, 3, 5-tricarboxylic acid as a novel chelating agent. The effect of various parameters such as reaction temperature, pH effect, effect of molar ratio of benzene -1, 3, 5-tricarboxylic acid to tetrabutyl titanate on morphology, size and purity of products was investigated and the optimum condition for synthesis of desired product was found. A systematic study on the structural, morphological, optical and photocatalytic properties of ZnTiO_3 nanoparticles was carried out using various analyses. SEM images reveal that the ZnTiO_3 -700 °C, ZnTiO_3 -800 °C and ZnTiO_3 -900 °C have a mean particle size of about 36 nm, 187nm and 500nm, respectively, with spherical-like shape. The band gap of this product was estimated by UV-vis spectroscopy and its photocatalytic application was investigated by the degradation MO as an organic pollutant under UV irradiation in presence of ZnTiO_3 . The degradation percentage of MO was calculated about 70 % and confirmed that zinc titanate can be used as a photocatalyst.

In summary and by considering the obtained results can be said that this method can be used to synthesize other titanium-based perovskite type oxides with various morphologies and novel properties.

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Figure captions:

Fig. 1. FT-IR of prepared ZnTiO_3 nanoparticles at calcination temperature of 700°C for 3 h

Fig. 2. a) XRD pattern prepared the witness test at calcination temperature of 700°C for 3h, b) ZnTiO_3 nanoparticles prepared with molar ratio of Trimesic acid to $\text{Ti}(\text{OC}_4\text{H}_9)_4$ of 3:1

Fig. 3. prepared ZnTiO_3 nanoparticles for 3 h at calcination temperature of a) 700°C , b) 800°C , c) 900°C .

Fig. 4. SEM images of prepared ZnTiO_3 nanoparticles for 3 h at calcination temperature of 700°C with pH a) 1-2, b) 4-5, c) 9-10.

Fig. 5. SEM images of prepared ZnTiO_3 nanoparticles prepared with molar ratio of Trimesic acid to $\text{Ti}(\text{OC}_4\text{H}_9)_4$ of a) 1:1, b) 3:1, c) 5:1.

Fig. 6. SEM images of prepared ZnTiO_3 nanoparticles for 3 h at calcination temperature of 700°C with a) pure ethanol, b) mixed ethanol with ethylene glycol.

Fig. 7. EDAX of prepared ZnTiO_3 nanoparticles for 3 h at calcination temperature of 700°C .

Fig. 8. (a) UV–vis absorption spectra of prepared ZnTiO_3 nanoparticles for 3 h at calcination temperature of 700°C and (b) plot to determine the direct band gap of ZnTiO_3

Fig. 9. TEM images of the as-synthesized ZnTiO_3 nanoparticles for 3 h at calcination temperature of 700°C .

Scheme 1. Schematic diagram illustrating the formation of the ZnTiO_3 nanoparticles.

Scheme 2. The various ways to improve the performance of semiconductor compounds.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig.10

Scheme 1

Scheme 2