Int. J. Bio-Inorg. Hybr. Nanomater., Vol. 3, No. 3 (2014), 175-178

ISSN Print: 2251-8533

ISSN Online: 2322-4142

International Journal of Bio-Inorganic Hybrid Nanomaterials

Preparation and Characterization of ZrO_2/TiO_2 Nanocomposite under Ultrasonic Irradiation by Sol-gel Route

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Received: 2 June 2014; Accepted: 6 August 2014

ABSTRACT

TiO_2/ZrO_2 nanocomposite was obtained by the sonochemical technique. In this method, two separate gels containing zirconium and titanium were prepared and mixed together. The precursor sol of zirconium was prepared from an aqueous solution of $ZrCl_4$. The precursor titanium tetra isopropoxide (TTIP) dissolved in isopropanol. Mixing of Titanium and Zirconium gels was resulted in a yellow TiO_2/ZrO_2 gel. The precipitate was calcinated in the furnace. The obtained nanopowder characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and Fourier transform infra-red spectroscopy (FT-IR).

Keyword: ZrO_2/TiO_2 ; Nanocomposite; Sol-gel; Ultrasonic irradiation; Particle size.

1. INTRODUCTION

Among the various semiconductors employed, titanium dioxide (TiO_2) is known to be good photocatalyst for the degradation of environmental contaminants due to its high photocatalytic activity, absence of toxicity, relatively low cost, availability and excellent chemical stability under various conditions [1, 6]. When illuminated with an appropriate light source, the TiO_2 photocatalyst generates electron/hole pairs to initiate a series of chemical reactions that eventually mineralize the pollutants [7]. Since photocatalytic process is based on the generation of electron/hole pairs by means of band gap radiation, the coupling of different semiconductor oxides seems useful to achieve a more efficient electron/hole pair separation under irradiation and, consequently, a higher photocatalytic activity [8, 9]. Some success in enhancing the photocatalytic activity has been conducted by several methods such as using nanosized semiconductor crystallites instead of bulk materials [10], modifying photocatalysts by doping with ions [11-14], or coupling TiO_2 to other oxides

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[15-18]. There are numerous nano ZrO_2 preparation methods, for example, chemical vapor synthesis [19], flame spray pyrolysis [20], combustion [21], explosion [22], forced hydrolysis [23], hydrothermal precipitation [24], microwave-hydrothermal [25], solvothermal processing [26], sonication [27] and sol-gel precipitation [28].

The composition of nanocatalysts is one of the ways to enhance photocatalytic activity by improving the band gap of the composite powder. Very nanocomposite have synthesized by various methods The sol-gel method with using ultrasonic irradiation has significant advantages compared to other methods such as high purity, good uniformity of the powder, synthesis at low temperature and easily controlled reaction conditions [29, 30].

The aim in this research is to synthesize the nano ZrO_2/TiO_2 composite by using the probe of ultrasonic, and this is very efficient for introducing of ultrasonic irradiation in mixture reaction.

2. EXPERIMENTAL

2.1. Preparation of Titanium gel

1.6 mL of Titanium tetraisopropoxide was diluted with 16 mL of isopropanol and 150 mL of deionized (DI) water. The PH of the solution was adjusted 1.5 by using nitric acid. 25 mL of H_2O_2 solution was added to produce a white suspension. The product was filtrated and washed several times.

2.2. Preparation of Zirconium gel

Firstly $ZrCl_4$ (4.7 g, 0.2 mol) was dissolved in 2-propanol (100 mL) to get a precursor solution A solution of H_2O_2 (6 mL, 30% v/v) was then dropped into the precursor solution under stirring. The pH of mixture was adjusted 9 by adding ammonium solution 2 M, then Zirconium gel was prepared andthe produced gel was stirred for 2 days, and the probe of ultrasonic was introduced in Zirconium gel and it was irradiated for 30 min.

2.3. Preparation of TiO_2/ZrO_2 nanocomposite

The Titanium precipitant was added into Zirconium gel and they were mixed together, themixture was irradiated by the probe of ultrasonic instrument for 2 h. The mixture was stirred for 48 h, then it was filtrated and washed several times. After drying at room temperature, the white precipitated was calcinated at 500ºC for 3 h in furnace.

$$Ti(OC_3H_7)_4 + 6H_2O_2 \rightarrow Ti(OH)_4 + C_3H_7OH + 2H_2O + O_2$$

$$ZrCl_4 + 2H_2O_2 Zr(OH)_4 \rightarrow 2Cl_2$$

$$Ti(OH)_4 + Zr(OH)_4 TiO_2 \rightarrow ZrO_2 + 4H_2O$$

3. RESULTS AND DISCUSSION

3.1. FT-IR analysis

A FT-IR spectrum of the TiO_2/ZrO_2 nanocomposite is shown in Figure 1 in the wave number range from 4000 to 400 cm^{-1}. The peaks at 507, 583 and 756 cm^{-1} can be assigned to symmetric stretching vibration of the Ti–O, Zr-O and Zr–O–Ti respectively. The peak at 1082 cm^{-1} should be due to the Ti–OH bond. The peak at 1628 cm^{-1} resulted from the H_2O molecules bending vibration, which were not removed completelyafter sol–gel synthesis. The wide peak at 3421 cm^{-1} has been assigned to the OH symmetry and asymmetry stretching vibration of surface hydroxyl group.

3.2. XRD Diffraction

The XRD pattern of the TiO_2/ZrO_2 nanocomposite is shown in Figure 2. The distinct peaks corresponding to TiO_2 and ZrO_2 are observed. It is concluded that both

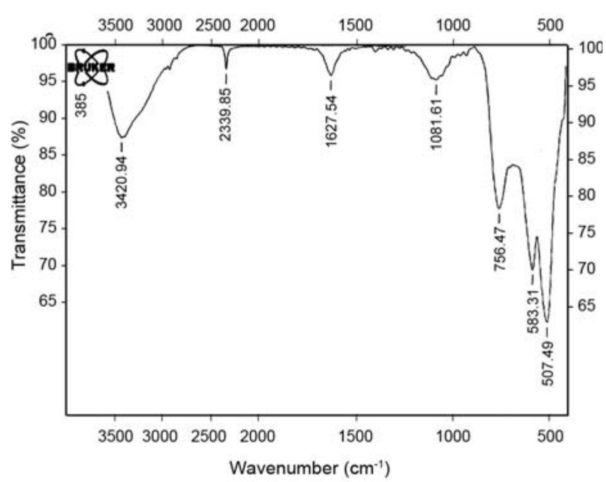

Figure 1: *FT-IR spectra of TiO_2/ZrO_2 nanocomposite.*

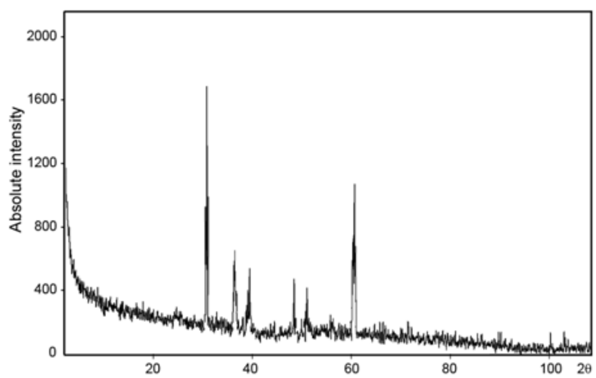

***Figure 2:** XRD pattern of TiO_2/ZrO_2 nanocomposite.*

the materials exist in perfect crystalline phases and retain their physical structure and hence confirmed to form a TiO_2/ZrO_2 nanocomposite (according to card no. 37-1484 for ZrO_2 and card no. 21-1272, for TiO_2 Joint Committee on Powder Diffraction Standards (JCPDS)). The TiO_2/ZrO_2 nanoparticles are seen pure. The crystallite size of TiO_2/ZrO_2 nanocomposite wasestimated to be around 32 nm, by using the Deby-Scherrer equation.

$$Dv = \frac{K\lambda}{\beta \cos\theta}$$

where: Dv is the "volume weighted" crystallite size = ¾ d (crystallite diameter) K is the "Scherer constant" (around 0.9) , λ is the wavelength of the X-rays here is l , CuKα = 1.541 Å, θ is the Bragg angle for the peak at 2θ, β is the "integral breadth" of the peak at 2θ. The β = (π/2) FWHM (full width at half maximum) for a Gaussian shaped peak.

3.3. FESEM image

Surface morphology of the synthesized nanocomposite has been studied and their FESEM images have been shown in Figure 3 TiO_2/ZrO_2 nanocomposites have been seen uniform. The average size of nanocomposite according to FESEM images are in the range of 35-45 nm.

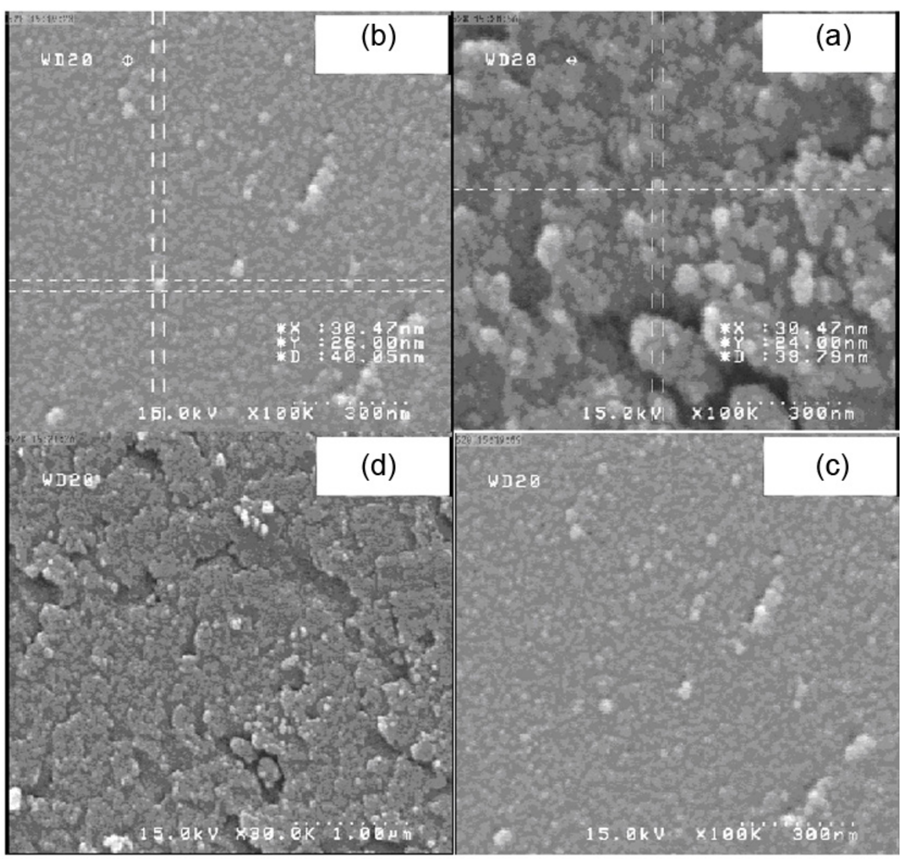

***Figure 3:** FESEM images of TiO_2/ZrO_2 nanocomposite.*

4. CONCLUSIONS

Binary oxide TiO_2/ZrO_2 nanocomposite was prepared from a specific volumetric proportion of ZrO_2 and TiO_2 by sol–gel method by using ultrasonic irradiation. The purity of synthesized TiO_2/ZrO_2 nanocomposite was investigated from FT-IR spectrum. Size, morphology and crystalline phase of nanocomposite were determined by FESEM and XRD analysis. The average diameter of nanoparticles is around 32 nm.

ACKNOWLEDGEMENT

We acknowledge the financial support of this work from section of research and Technology of Islamic Azad University East Tehran Branch.

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