

Araştırma Makalesi / Research Article

Synthesis of TiO₂ and ZrO₂/TiO₂ Composite Microspheres and Their Photo-Catalytic Degradation of Methylene BlueAli İmran VAİZOĞULLAR¹, Ahmet BALCI², Mehmet UĞURLU², Muhammet Hamdi KARAOĞLU²¹ Medical Lab Program, Vocational School of Healthcare, Muğla Sıtkı Koçman University, Muğla-48000, Muğla TURKEY² Department of Chemistry, Faculty of Sciences, Muğla Sıtkı Koçman University, Muğla-48000, Muğla TURKEY
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Keywords

Semiconductors, Sol-Gel Chemistry, X-ray Diffraction, Transmission Electron Microscopy (TEM), Catalytic Properties

Abstract

TiO₂ and ZrO₂/TiO₂ composite microsphere particles were synthesized using the sol-gel method. Photoactivity of TiO₂ and ZrO₂/TiO₂ were compared. Particles were characterized using X-ray diffraction (XRD), infrared spectroscopy (FTIR), scanning electron microscopy (SEM) of X-ray (EDAX), and transmission electron microscopy (TEM). The study revealed that TiO₂ particles were microspheres. The decorating of ZrO₂ particles on TiO₂ surface was successfully carried out that was proved by SEM and TEM analyzes. The photo-catalytic activity of TiO₂ and ZrO₂/TiO₂ composite microsphere particles was examined using methylene blue (MB) as reference material under UV lamp. Our findings showed that ZrO₂/TiO₂ was more active than TiO₂. These findings suggest a new TiO₂-based catalyst structure to synthesize and to emphasize the importance of the shape of the catalyst.

TiO₂ ve ZrO₂/TiO₂ Kompozit Mikrokürecik Sentezi ve Metilen Mavisinin Degradasyonunda Fotokatalitik Aktiviteleri**Özet**

TiO₂ ve ZrO₂/TiO₂ kompozit mikrokürecik partikülleri sol jel yöntemi ile sentezlendi. TiO₂ ve ZrO₂/TiO₂ partiküllerinin fotokatalitik aktiviteleri karşılaştırıldı. Partiküller XRD, FTIR, TEM, SEM analiz teknikleri ile karakterize edildi. Elde edilen SEM ve TEM bulguları TiO₂ partiküllerinin küresel ve ZrO₂ nin TiO₂ üzerinde dekore edildiğini gösterdi. Fotokatalitik aktiviteleri Metilen Mavisini kullanarak incelendi. Elde ettiğimiz bulgular ZrO₂/TiO₂ partiküllerinin TiO₂ den daha aktif olduğunu gösterdi. Yukarıdaki bulgular TiO₂ bazlı yeni bir materyalin yapısının sentezini ve fotoaktivitede katalizörün yapısal şeklinin önemini vurgulamaktadır.

Anahtar Kelimeler

Yarı iletkenler, Sol- Jel Kimyası, X-Ray Difraksiyon, Geçirimli Elektron Mikroskopu, Katalitik özellikler

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1. Introduction

Environmental pollution is the most important problem of the 21st century due to its impacts on

the living systems (Qu et al. 2014). Water pollution causes numerous diseases i.e. diarrhea, cholera, typhoid fever, E-coli infections, and diphtheria. Azo dyes can also damage human health and environmental health. Some dyes are found to be toxic, mutagenic and carcinogenic (Lutpi et al.

2011). Heterogeneous photocatalysis plays an important role in environmental treatments such as water disinfection, hazardous waste remediation and water purification. Among those photocatalysts, TiO₂ is a well-used performer that degrades various organic dyes (Chala et al. 2014).

Some researchers reported that bulk and nanostructure anatase phase in TiO₂ has different chemical properties, catalytic reactivity, and surface acidity based on their different surface planes (Hua et al. 2012, Engates et al. 2011, Martra. 2000). However, there are some problems that inhibit its applications. First, TiO₂ particles absorb_{max} 385 nm; second, its electron-hole pairs can easily be recombined (Aman et al. 2012). Some modifications on TiO₂ structure overcome these difficulties e.g. metal deposition (Fahim et al. 2009), or synthesis of the composites such as TiO₂/ZrO₂, TiO₂/Fe₃O₄, TiO₂/ZnO (Tokmakçı et al. 2009, Shi et al. 2012, Benkara et al. 2013). It carries certain advantages to environmental applications for example enhancing high oxidation power and long durability against photo- and chemical corrosion (Lin et al. 2010). Zirconia (ZrO₂) nanoparticles are interesting due to their enhanced optical and electrical properties (Manirahulan et al. 2013). ZrO₂ is an n-type semiconductor having similar physicochemical properties with that of TiO₂ (Vishwanathan et al. 2004). But in the photocatalytic reactions, the activity of ZrO₂ is generally much lower than that of TiO₂.

There is no much information and research on composite ZrO₂ particles synthesis. Manirahulan et al. (2013) synthesized shell type ZrO₂@SiO₂ nanoparticles through the combination of chemical precipitation and seeded polymerization. Lucky et al. (2010) synthesized ZrO₂/TiO₂ nanoparticles and studied their solvent effects on the crystal growth. In most studies, ZrO₂/TiO₂ particles were synthesized as a powder or thin film. However, some problems are observed in this synthetic procedure. If it is

synthesized as powders, separation from suspended solution can be very difficult as the interaction between thin films and substrates is weak. This phenomenon can be limited to their applications in the photo-catalytic degradation of pollutants (Lucky et al. 2010).

This study aimed to synthesize TiO₂, ZrO₂/TiO₂ microsphere particles and to investigate their photocatalytic degradation of MB (methylene blue). We used composite microspheres phenomenon on photocatalytic for the first time.

Nomenclature

| | |
|----------------|--|
| TBT | titanium tetra propoxide |
| TBOZ | zirconium tetra butoxide |
| MB | methylene blue |
| k | rate constant for pseudo-first order kinetic equation (min ⁻¹) |
| C | the concentration in solution at time t (mg L ⁻¹) |
| C ₀ | initial concentration of MB |
| t | time |
| r ² | linear regression coefficient |
| IEP | isoelectric point |

2. Materials and Method

2.1. Preparation of TiO₂ and ZrO₂ particles

The TiO₂ core was prepared using the sol-gel method. 10 mL TBT and 25 mL absolute ethanol were mixed into 50 mL deionized water. The mixture was stirred for 4 h and centrifuged. Particles obtained were washed several times with deionized water followed by ethanol, dried at 80 degree for 4 h, and calcined at 600 degree for 3 h. For ZrO₂ particles, 10 mL TBOZ was dissolved in 150 mL ethanol and H₂O mixture. Ammonia solution was added dropwise to the mixture. pH was adjusted to 6 and aged for 12 h. Solution was filtered and calcined at 500 degree for 3 hours.

2.2. ZrO₂/TiO₂ particles

To synthesize ZrO₂/TiO₂ composite microsphere particles, 1 g TiO₂ particles synthesized above procedure were added 50 mL ethanol-water

mixtures. 20 mL zirconium (IV) butoxide (TBOZ) and 30 mL ethanol were added into the mixed solution and mixed for 3 h to complete the sol-gel process. Obtained particles were washed three times, dried in an oven at 80 degree for 12 h and calcined at 600 degree for 3 h.

2.3. Characterization

The crystalline phase and the component of the samples were examined by XRD (Rigaku Dmax 350) using copper K radiation ($\lambda = 0.154056$ nm). The IR spectrum analysis of precursor was carried out considering IR measurement system (Thermo-Scientific Nicolet IS10-ATR). The microstructure and shape of the particle were investigated using SEM (JEOL JSM-7600F) and TEM (JEOL JEM 2100F HRTEM). The element was determined with (JEOL JSM-7600F) EDAX analyzer with SEM measurement. Evaluation of photoactivity was performed in section 3.5.

3. Research Data

3.1. XRD analysis of ZrO_2 , TiO_2 and $\text{ZrO}_2/\text{TiO}_2$ composite microspheres

Figure 1(a,b,c) show that XRD spectrums of ZrO_2 , TiO_2 and $\text{ZrO}_2/\text{TiO}_2$ composite microsphere particles, respectively. In Figure 1a shows characteristic peaks at $2\theta=28.09$, 30.08 , 31.23 , 35.19 , 50.42 , 60.01 corresponding to the t- ZrO_2 and m- ZrO_2 phases (JCPDS78-0047), (JCPDS88-1007). After preparation and calcination process, t- ZrO_2 was dominant in t- ZrO_2 and m- ZrO_2 mixture. The peak intensity of t- ZrO_2 ($2\theta=30.08$) was higher than m- ZrO_2 ($2\theta=28.09$ and 31.23) because of calcination temperature. ZrO_2 particles converted from tetragonal phase to monoclinic phase over at 600°C (Qu et al. 2014). But in this study, synthesized ZrO_2 particles were calcined at 500°C therefore, the peak intensity of t- ZrO_2 phases was higher than m- ZrO_2 . In Figure 1b, the existence of notable peaks of $2\theta=25.23$, 36.94 , 47.96 and 55.00 corresponding to the anatase phase in TiO_2 (JCPDS no. 21-1272). The characteristic peaks appear at $2\theta=25.26$, 28.09 , 30.08 , 36.94 , 47.81 , and 55.01

corresponding to the anatase phase in TiO_2 and tetragonal, monoclinic phase in ZrO_2 .

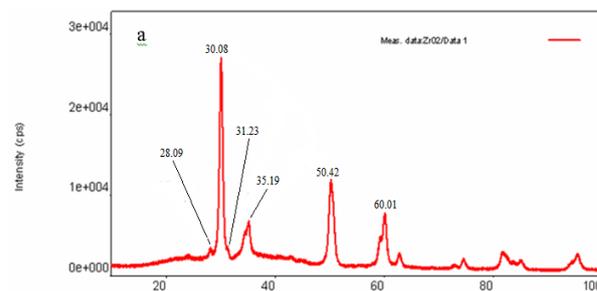


Figure 1a. XRD patterns of ZrO_2 particles

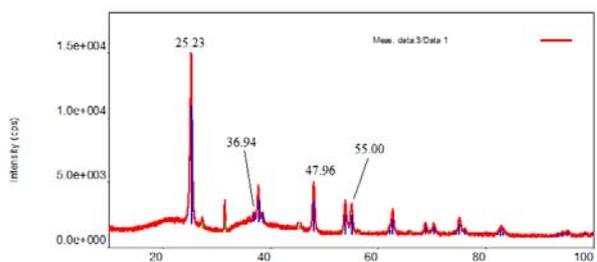


Figure 1b. XRD pattern of TiO_2 particles

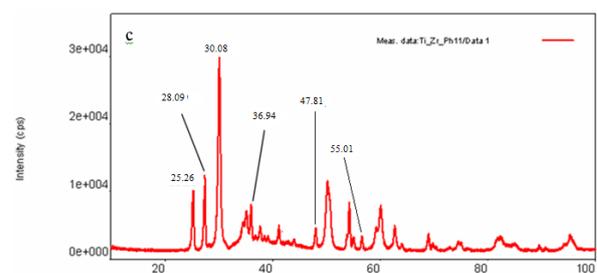


Figure 1c. XRD pattern of $\text{ZrO}_2/\text{TiO}_2$ composite microspheres

3.2. IR analysis

Figure 2a and 2b show FT-IR spectrum of TiO_2 and $\text{ZrO}_2/\text{TiO}_2$ composite microsphere particles respectively. The bands appeared at 3252 cm^{-1} and 1632 cm^{-1} can be attributed to the -OH stretching of water (Figure 2a). Figure 2a shows Ti-O-Ti stretching peak at 798 cm^{-1} . The absorption bands in the range of $1100\text{--}1000\text{ cm}^{-1}$ were attributed to the O-alkyl groups linked to Ti such as $\text{O-C}_3\text{H}_7$, $\text{O-C}_4\text{H}_7$ (Ivanova et al. 2002). In our study, there was no absorption peaks observed between $1100\text{--}1000$ (Figure 2b). This can be related to replacing of alkyl groups with OH groups in water; therefore, whole TTIP was obtained as TiO_2 during the hydrolysis reaction. We observed very small stretching and vibration peaks of $\text{CH}_2\text{-CH}_3$, C-O-H, and C-H at 1383 cm^{-1} , 1465 cm^{-1} , 2922 cm^{-1}

respectively. It was concluded that all organic species resulted from precursor powder largely disappeared after calcination. Very small and broadening peaks at around 1613 cm^{-1} and at 3381 cm^{-1} were corresponded to the stretching vibration of the hydroxyl (O–H) bonds from water (Figure 2b). The peak of 810 cm^{-1} originated from bending vibration of Zr–O. The peak at around 721 cm^{-1} could attribute to the Zr–O–Ti bonds (Wang et al. 2008).

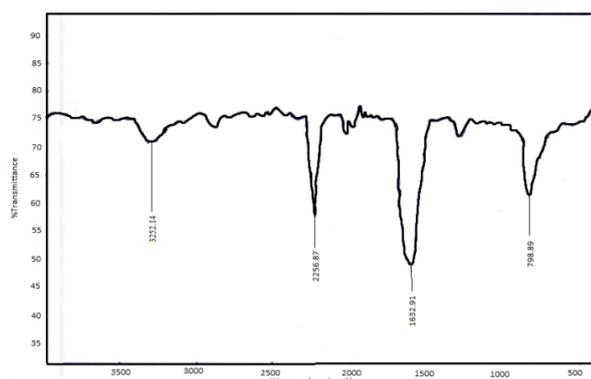


Figure 2a. FTIR spectra of TiO_2 particles

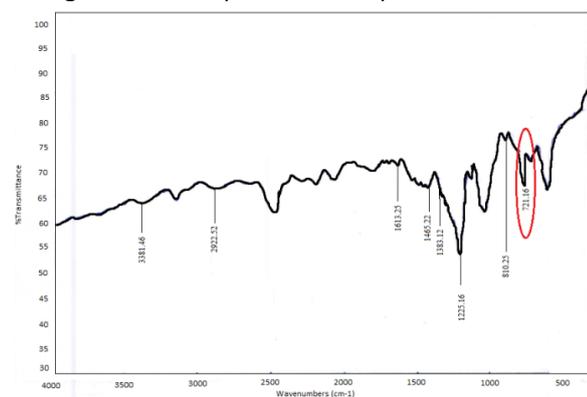


Figure 2b. FTIR spectra of $\text{TiO}_2/\text{ZrO}_2$ composite microsphere particles

3.3. SEM and EDAX

SEM and EDAX analysis reflect the size and shape of the synthesized particles. Figure 3a and Figure 3b show SEM images of TiO_2 and $\text{ZrO}_2/\text{TiO}_2$ particles respectively. Figure 3a shows smooth and co-shape TiO_2 particles with an average diameter of about 400-700nm (Figure 3a). The surface of TiO_2 particles was rough as compared to ZrO_2 on TiO_2 (Figure 3b). After decorating of ZrO_2 on TiO_2 surface, the average diameter of TiO_2 did not increase significantly. Figure 3b describes high

proportional bright particles. This can be attributed to the edge effect on undecorated sample appearing as a bright turbidity. At the same time, the protrusions and the circumferences of the TiO_2 surface led to the large amount of secondary electrons, which causes brighter appearance than other parts. The presence of Ti and Zr atoms were observed by EDAX analysis as a qualitatively (Figure 4). EDAX analysis along the cursor crossing a particle showed Ti located at both and ends and Zr was in the middle because whole TiO_2 surface may not decorate with ZrO_2 .

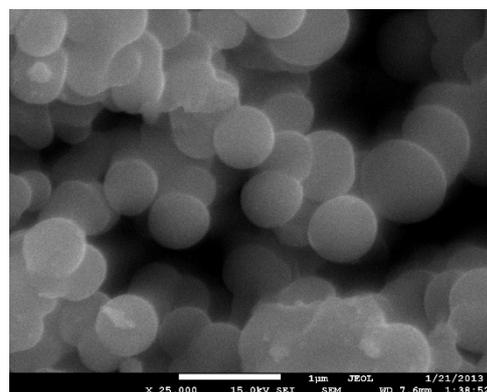


Figure 3a. SEM images of TiO_2 particles

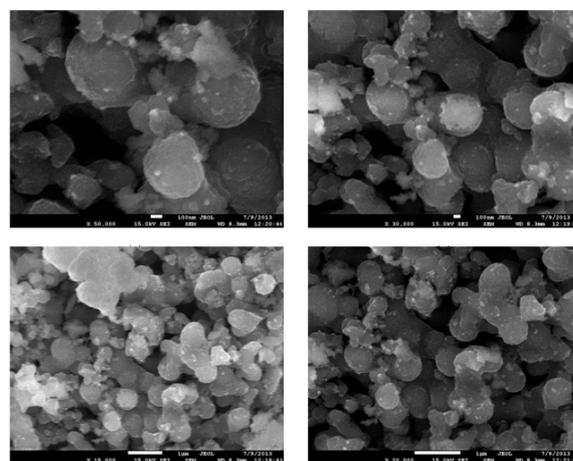


Figure 3b. SEM image of $\text{ZrO}_2/\text{TiO}_2$ composite microsphere particles

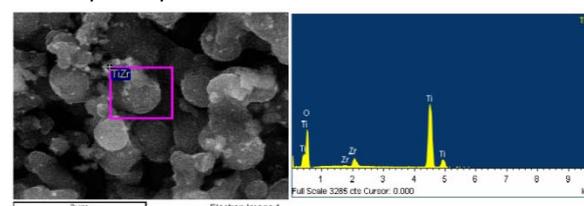


Figure 4. EDAX analysis of $\text{ZrO}_2/\text{TiO}_2$ composite microsphere particles

3.4. TEM analysis

The further investigation of ZrO₂/TiO₂ composite microsphere particles using TEM analysis is given in Figure 5. The surface of TiO₂ particles was multi-layer because of ZrO₂ particles and it's clearly observed with roughness (Figure 5). ZrO₂/TiO₂

| Particles | TiO ₂ | ZrO ₂ /TiO ₂ |
|---|------------------|------------------------------------|
| $k \times 10^3 \text{ (min}^{-1}\text{)}$ | 4,9 | 8,02 |
| r^2 | 0,98 | 0,97 |

particles were irregular and spherical. The dark in the center and luminous in border area confirm the synthesis of ZrO₂/TiO₂ composite microsphere particles (Qu et al. 2014).

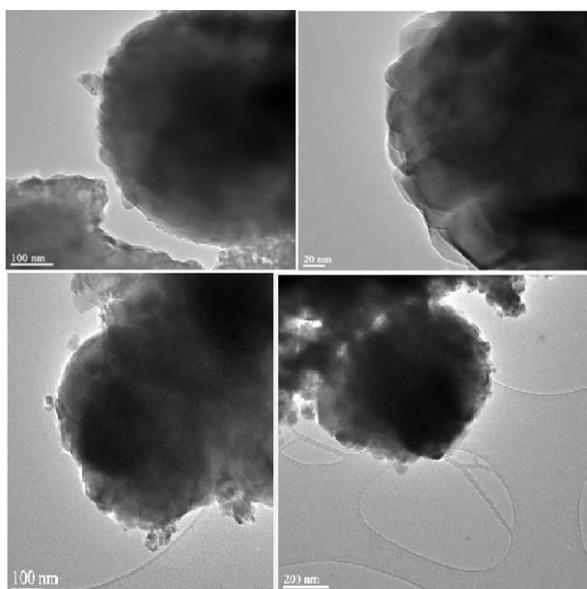


Figure 5. TEM analysis of ZrO₂/TiO₂ composite microsphere particles

3.5. Results and Discussion

The degradation performances TiO₂ and ZrO₂/TiO₂ composite microsphere particles were investigated by degradation of MB in aqueous solution under UV light and the degradation results as shown in Figure 6. Solutions were mixed in dark under magnetic stirring for an hour before illumination. The photodegradation of the MB solution was studied at the λ_{max} 664 nm. The rate of photodegradation of MB by TiO₂ and ZrO₂/TiO₂ was calculated from the change in absorbance during photodegradation in every 30 min. After UV irradiation, the amount of degradation was calculated using C/C₀ ratio, where C₀ was initial

concentration of MB and C was also the concentration in solution at the time. The first order kinetic equation and relationship between $\ln(C_0/C)$ and t was used to investigate kinetic model (Uğurlu and Karaoğlu, 2011) (Figure 7). In this study, pH, catalyst concentration and temperature were constant.

Table 1. Calculated apparent rate constants for TiO₂ and ZrO₂/TiO₂ particles *

* pH adjusted to 9, catalyst concentration (0.5 g/100ml) and temperature (298K) in all experiments

According to the Table 1, pseudo first rate constants are 4.9×10^{-3} and 8.02×10^{-3} for TiO₂ and ZrO₂/TiO₂ respectively. This implied that the reaction rate of ZrO₂/TiO₂ was faster than TiO₂ for MB degradation.

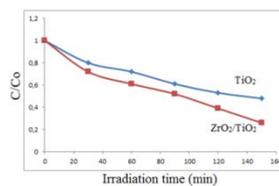


Figure 6. Photo-catalytic degradation rates of MB

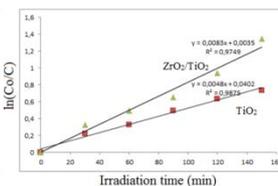


Figure 7. Linear relationship between the $\ln(C_0/C)$ and irradiation time for TiO₂ and ZrO₂/TiO₂ particles

Our experimental data are in good agreement with pseudo-first order kinetic as indicated by plotting $\ln(C_0/C)$ against irradiation time as shown in Figure 7. The removal efficiency percentage of MB in the presence of TiO₂ and ZrO₂/TiO₂ was 51 % and 82 % respectively. ZrO₂/TiO₂ particles were found better photoactive than TiO₂ to remove MB from water solution. The enhancement of photoactivity in ZrO₂/TiO₂ particles can be explained in several ways: (i) ZrO₂ particles dispersed into the TiO₂ and inhibited recombination of e⁻/h⁺ pairs (Pirzada et al. 2015). (ii) ZrO₂ has a high band gap, in this case, both TiO₂ and ZrO₂ electron charges were confined into TiO₂ area. Depending on the ZrO₂ thickness on TiO₂ surface, emission wavelengths decreased and

quantum yields increased resulting in increasing of photoactivity (Schattka et al. 2002). (iii) pH value is an important parameter affecting the photoactivity. If solution pH was lower than that of IEP of ZrO₂/TiO₂, the surface charge of ZrO₂/TiO₂ was positively charged (Aparna et al.2001). When we studied at natural pH (around 5) poor degradation yield was observed for ZrO₂/TiO₂ composite microsphere particles. In contrast, pH value was adjusted to 9, photoactivity of ZrO₂/TiO₂ increased. This can be explained that MB has a special affinity for negatively charged surfaces (Chaudhuri et al. 2001). Therefore increasing of pH in solution increased the number of hydroxyl groups and the number of negatively charged

sites. This caused enhancing attraction between the dye and adsorbent surface resulting in increased the photoactivity (Avena et al. 2001). It has been also reported that addition of small amounts of ZrO₂ into TiO₂ can prevent phase transformation from anatase to rutile; therefore, ZrO₂ enhances the phase stability for the phase transformation of pure TiO₂ (Kim et.al.2009). We described that the formation of a mutual chemical interaction between the pure oxides when they are co-precipitated together (Ti-O-Zr) leading to a profound effect on the photocatalytic properties (Kim et al. 2013).

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