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Synthesis and Characterization of Tb^{3+}-Activated TiO_2 Photoluminescence Nanomaterials

Tb^{3+} ile Aktive Edilmiş TiO_2 Fotolüminesans Nanomalzemelerin Sentezi ve Karakterizasyonu

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Abstract

As compared to other semiconductor photocatalysts, titanium dioxide has so far been shown to be the most promising material used for both fundamental research and practical applications, because it exhibits a higher photoreactivity and it is cheap, nontoxic, chemically and biologically inert, and photostable. Rare earth ions (RE^{3+}) are preferred as dopant elements due to their high densities and high light yields. Tb^{3+} doped TiO_2 nanoparticles offer several advantages such as broad absorption band, high emission intensity, long lifetime, stability. TiO2: 1%Tb^{3+} nanoparticles, were produced at 550 degrees by the sol-gel method. Particle size analysis, XRD, DTA-TG, FTIR, SEM, and PL analyzes of the synthesized nanomaterials were performed. In the anatase crystal structure, the dimensions of the nanoparticles were measured below 100 nm and were observed in the microstructure where the particles were clustered in places. When the nanoparticles were excited at 275 nm, green emission bands of Tb^{3+} ions at 544 nm and 585 nm were observed. This wavelength is attributed to electronic transitions $^5D_4 \rightarrow {}^7F_5$ and $^5D_4 \rightarrow {}^7F_4$, respectively.

Öz

Diğer fotokatalitik yarı iletkenlere kıyasla, titanyum dioksitin şimdiye dek hem temel araştırmalarda hem de pratik uygulamalarda kullanılan en umut verici malzeme olduğu gösterilmiştir, çünkü daha yüksek bir foto reaktivite sergiler ve ucuz, toksik olmayan, kimyasal ve biyolojik olarak etkisiz ve kararlıdır. Nadir toprak iyonları (RE^{3+}), yüksek yoğunlukları ve yüksek ışık verimleri nedeniyle dopant elementler olarak tercih edilir. Tb^{3+} katkılı TiO_2 nanopartikülleri, geniş emme bandı, yüksek emisyon yoğunluğu, uzun ömür, stabilite gibi birçok avantaj sunar. $Ti0_2$:%1 Tb^{3+} nanopartiküller sol-jel yöntemi ile 550^{o}C' de üretildi. Sentezlenen nanomalzemelerin partikül boyut analizi, XRD, DTA-TG, FTIR, SEM ve PL (photo luminescence) analizleri yapılmıştır. Anataz kristal yapısında, nanopartiküllerin boyutları 100 nm'nin altında ölçülmüş ve partiküllerin yer yer kümelendiği mikroyapıda gözlenmiştir. Nanopartiküller 275 nm'de uyarıldığında, 544 nm ve 585 nm'de Tb^{3+} iyonlarının yeşil emisyon bantları gözlenmiştir. Bu dalga uzunluğu, sırasıyla $^5D_4 \rightarrow {}^7F_5$ and $^5D_4 \rightarrow {}^7F_4$ elektronik geçişlerine bağlanmaktadır.

Anahtar Kelimeler: *TiO_2, Foto Lüminesans, Sol-jel, Nadir Toprak Elementleri*

1. Introduction

Titanium dioxide (TiO_2) nanoparticles are widely used in fields such as pigments, photovoltaic cells, photocatalysis, gas sensors, and innovative surface coating materials due to their photochemical and electrochemical properties [1,2]. Because of its stable and durable structure, wide use area and low cost, studies on the development of TiO_2 are continuously going on [3]. Also, TiO_2 is usually used as a raw material because it can be in both rutile and anatase phase structure [4,5]. Rare earth element activated oxide nanoparticles are of interest because of their tunable and improved optical properties. Lanthanide ions have high density and light output. It increases the UV absorption capacity and emission intensity of photoluminescent and photocatalytic materials. In this way, they make it a more efficient material. The photoluminescence properties can be adjusted by selecting the appropriate host matrix and additive material and determining the stoichiometric additive ratios [6,7]. TiO2 nanoparticles can be produced by different methods such as sol-gel, flame spray pyrolysis, hydrothermal synthesis, solvothermal synthesis, and emulsion precipitation [8]. Tb^{3+} ions are photoluminescen ions that showdown conversion characteristics. Tb-activated oxide nanoparticles absorb high-energy photons and emit low-energy photons, that is, emit in the UV region of the electromagnetic spectrum and propagate through the visible and infrared region. These nanomaterials also exhibit another phenomenon known as quantum cutting whereby a single high-energy photon is absorbed to produce two photons of lower energy [9].

Some rare earth doped TiO_2 materials have been studied in the literature. A. Xu et al. have found that rare-earth dopamine increases photocatalytic activity. The increase in activity was due to higher adsorption, redshifts and electron-hole recombination prevention[10]. J. Liqiang et al. investigated the effect of La^{3+} addition on TiO_2. The results showed that La^{3+} dopant had a great inhibition on TiO_2 phase transformation, and did not give rise to a new PL signal, but it could improve the intensity of PL spectra with an appropriate La^{3+} content, attributed to the increase in the content of surface oxygen vacancies and defects [11]. X. Lu et al. investigated the effect of Nb^{3+} addition on TiO_2. After Nb^{3+} doping, the anatase structure was retained and a new absorption peak was observed in FTIR spectrum. The Nb^{3+} doping leads to a significant increase in powder conductivity. As expected, an overall 7.8% energy-conversion efficiency was obtained for Nb^{3+}- dopedTiO2, which was an improvement of 18.2% relative to that of the undoped material [12]. A. Patra et al. investigated the effect of Er^{3+} addition on TiO_2. According to their results, the Er^{3+} ions concentration increases, the emission intensity increases [13]. V. Šteng and his colleaguesproduced different rare earth ions doped TiO_2 particles by sol-gel method. Photocatalytic activity under UV or visible light beams has significantly increased with rare earth ions addition. The increase in photocatalytic activity was due to higher adsorption and electron transfer of rare earth ions to 4f. The highest increase in photoactivity was obtained at 0.5-1% rare earth ion doping, which may be due to the most efficient separation of load carriers. In this study, Tb ion-doped TiO_2 nanoparticles were produced by the sol-gel method. It is expected that the photoluminescence and photocatalytic yield will be very high because the Tb^{3+} element is a lanthanide element with a high number of unpaired electrons in the 4f orbitals. TiO_2 nanoparticles were synthesized at 550°C in the air with a 1% Tb^{3+} ion content and characterized structurally and microstructurally. The size and distribution of the produced particles have been studied. After characterization using XRD, SEM, FTIR, DTA-TG and PL Spectra devices, the results were evaluated.

2. Material and Method

Titanium (IV) isopropoxide (TTIP, $Ti[OCH(CH_3)_2]_4$, 97%), Terbium (III) nitrate pentahydrate $Tb(NO_3)3.5H_2O$ >99%, distilled water, citric acid and polyethylene glycol (PEG) were purchased from Sigma-Aldrich. All of the used chemicals were in analytical grade and used directly without further purification. For the 0.1 molar solution, 0.0099 moll TTIP, 0.0001 moll Tb precursor and 100 mL purified water were prepared. TTIP and distilled water in a balloon jug were mixed mechanically for 30 minutes. A separate beaker Tb precursor was dissolved in distilled water. In another beaker, citric acid solution was prepared in pure water to adjust the solution ph. All the prepared

solutions joined together. The pH of the solution was measured as 3.05. The final solution was added 1.5 grams of PEG and the prepared solution was left to stand at 100 degrees for gelation. After the gelation was completed, drying was performed at 275 degrees.

The obtained gels were characterized by the Fourier Transform Infrared (FTIR) device for the detection of organic bonds. In addition, to determine the calcination temperature of the obtained jellies, thermal analysis was performed using Differential Thermal Analysis/Thermo-gravimetric (DTA-TG) device, which allows to identify endothermic and exothermic reactions. According to the DTA results, the sintering temperature was determined to be 550°C and the dried powders were heat-treated at 550°C in air for 2 hours. After the calcination process was completed, structural and microstructural analyzes of TiO_2:1% Tb^{3+} nanoparticles were performed.

The Malvern Zeta Sizer ZS90 nano particle size measurement device was used for particle size and distribution analysis. In addition, phase analysis and crystal structure determination were performed by Thermo-Scientific ARL-Kα X-ray diffractometer (XRD). The microstructures of the nanoparticles were carried out at 100kX magnification and 5kV accelerating voltage using FEI Nova Nano SEM 650. Steady-state photoluminescence (PL) measurements were recorded on a red-sensitive photomultiplier tube equipped with a spectrofluorometer. The instrument was equipped with a Standard 15W Xe lamp and a microsecond flash lamp for steady state measurements.

3. Results

PH value is an important value that determines the acidic or basic character of the solution. The pH value of the solution significantly influences the gelation rate of the solution and the polymeric chain structures formed during gelation. pH is an important factor for many chemical treatments such as the solubility of the compound, the rate of a reaction. The pH of the TiO_2-based solution was measured in the solution state. The solution shows an acidic character due to the pH value of 3.05.

FTIR analysis was performed to gain more insight into the structure and the composition of the synthesized products. Fourier transformed infrared (FTIR) analysis of the sample was conducted in the wavenumber range of 500–4000 cm^{-1}. Figure 1 shows the FTIR spectra of the xerogel and its calcined products, respectively. The sharp peaks seen in the form of vibration between the values of 3856-3639 cm^{-1} wavenumbers are O-H stretches of medium force. The strong and broadband between the values of 3580-3290cm^{-1} wavenumbers are O-H stresses intermolecular connected. The broadband between the values of 2980-1650 cm^{-1} wavelength refers to strong and weak C-H bonds. However, there may be N-H stresses between these values. Between the values of 1450-940cm^{-1} wavenumbers, sharp and strong bonds can be strong bonds of C-O. There may be strong C-N aromatic stresses. Sharp and strong peaks at wavenumbers of 962 cm^{-1} and 839 cm^{-1} can be attributed to C = C bonds. The broadband at 650 cm^{-1} wavenumbers can be attributed to Ti-O-Ti bonds.

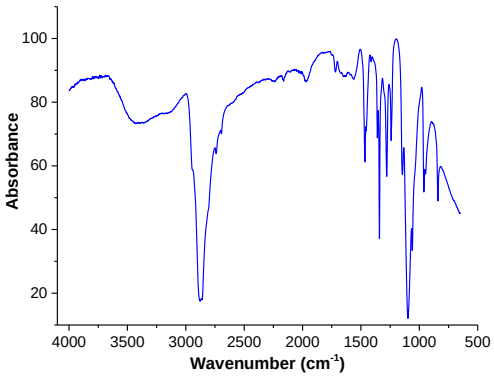


Figure 1. FTIR analysis of TiO_2: 1%Tb^{3+} xerogel

DTA-TGA is an extremely important analysis to see the endothermic and exothermic reactions associated with temperature increase in the material. Weight loss due to temperature increase is also determined by this analysis. In this context, all solutions were dried at 100 ° C for several hours until gelation and xerogels were formed, and then DTA-TGA analysis was carried out in nitrogen gas at temperatures range of 25-800 °C. The DTA-TGA curve of TiO_2-based gels are shown in Figure 2.

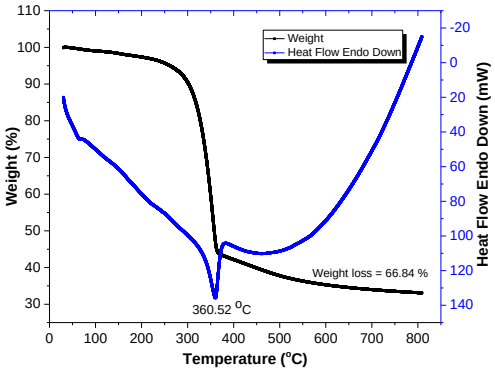


Figure 2. DTA-TG analysis of TiO_2: 1%Tb^{3+} nanoparticles

As can be seen, 66.84 percent of the total mass was removed from the structure. As the temperature increase, the physical water had gone away prior from the structure. The carboxyl and nitrate forms in the precursors are then evaporated. Lastly, the TiO_2 anatase structure has formed at about 360 degrees. DTA analysis is very useful for producing nanoparticles in the smallest possible size since at high temperatures the grain will grow in the microstructure.

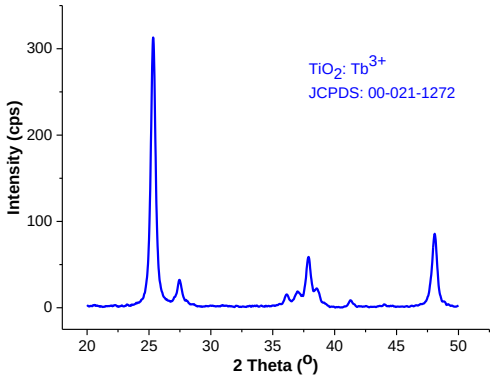


Figure 3. XRD analysis of TiO_2: 1%Tb^{3+} nanoparticles

XRD patterns of the produced TiO_2: 1% Tb^{3+} luminescent nanoparticles are presented in Figure 3. All diffraction peaks are identical to those of the pure anatase phase without the presence of another polymorph. Heat treatment of X-ray diffraction peaks for calcined powder showed the growth of crystals during calcination [14]. In Figure 3, XRD patterns exhibited strong diffraction peaks at 25°, 27°, 37° and 48° indicating TiO_2 in the anatase phase.

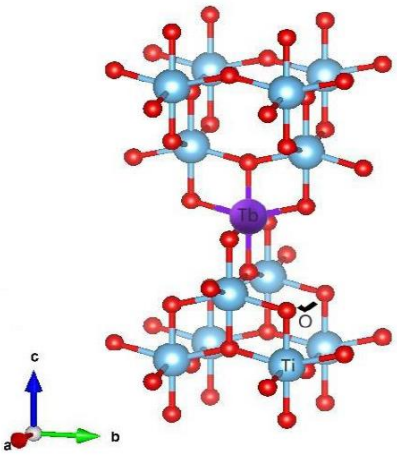


Figure 4. Crystal structure of anatase TiO_2 doped with Tb^{3+}

All the peaks are in good agreement with the standard spectrum (JCPDS no.: 00-021-1272). Also in Figure 4 shows that the Tb doped TiO_2 nanoparticles are identified to have a textured tetragonal anatase crystal structure. The crystal structure is tetragonal and is included in the "I 41/a m d" space group. Also TiO_2 lattice parameters were measured as a= 3,73Å, b= 3,73Å, c= 9,37Å.

SEM was used to further examine the particle size, crystallinity, and morphology of samples. Figure 5 shows SEM images of anatase TiO_2: 1%Tb^{3+} nanoparticles. In these nanoparticles, many anatase agglomerates can be seen by SEM observation.

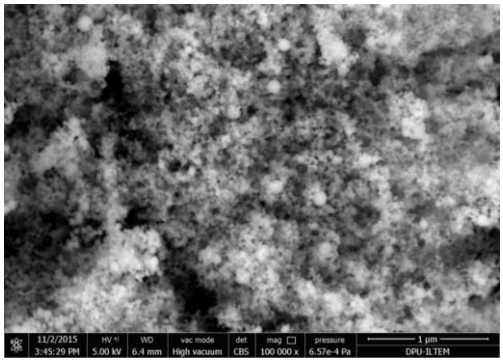


Figure 5. SEM analysis of TiO_2: 1%Tb^{3+} nanoparticles

The particle of TiO_2: 1%Tb^{3+} nanoparticles in anatase phase is mostly spherical morphology. It is believed that the

luminescence efficiency of the particles depends on the particle size. Because, in the literature research, the quantum effect becomes active as the particle size becomes smaller [15].

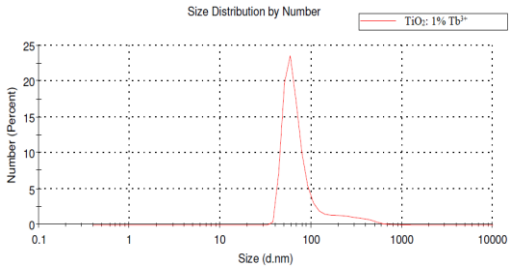


Figure 6. Particle size measurement results of TiO_2: 1%Tb^{3+} nanoparticles

Figure 6 shows the particle size measurement results. Using the sol-gel method, it is observed that the nanosize material is produced successfully. Size is a very crucial factor in developed materials. When the size analysis outcomes are examined, we can distinctly see that the nanoparticles are below 100 nm.

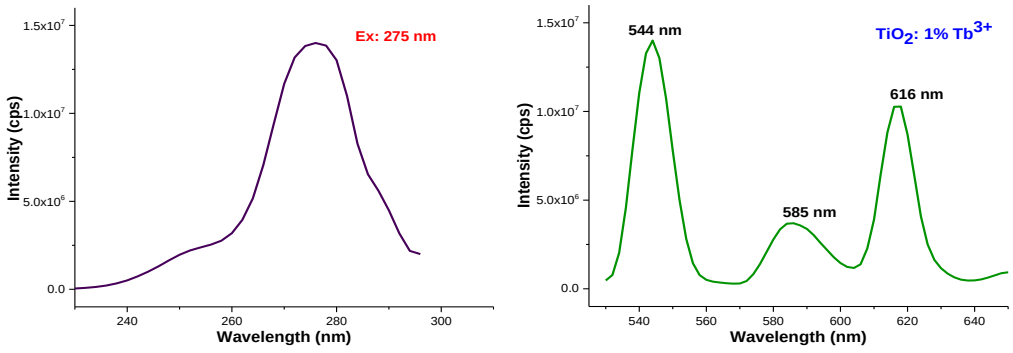
The size of the nanoparticles provides significant efficiency in the chemical and physical properties of these materials. Surface area and surface energy increase. The increase in surface energy and mobility of electrons results in a quantum effect on the material.

This means that the sol-gel method is an optimal method for nanoparticle production. In addition, the size of the calcined nanoparticles can easily be reduced by using nano grinder or by forging processes.

Tb^{3+} ions have a positive effect on TiO_2 luminescence. Transfer of energy to the luminescent centers takes place between the Tb-O-Ti bonds and the Tb-OH bonds acting as extinguishants for luminescence. Tb-doped TiO_2 nanoparticles exhibited green photoluminescence under excitation at 275 nm. The presence of lanthanides in the titanium oxide matrix provides attractive optical properties for long-running multi-band work. They also offer high photostability, a narrow emission band, and a broad absorption band.

Under 276 nm excitation, the emission spectra of Tb^{3+} ions showed dark green, light green and yellow emission at 544 nm, 585 nm and 616 nm, respectively (as shown in Figure 7).

The energy transitions in these regions depend on $^5D_4 \rightarrow {}^7F_J$ (J = 5, 4, 3). The emission spectra have the highest dark green emission band corresponding to the $^5D_4 \rightarrow {}^7F_5$ transition at 544 nm. Then, the light green emission band at 585 nm belongs to $^5D_4 \rightarrow {}^7F_4$, the yellow emission at 616 nm belongs to the $^5D_4 \rightarrow {}^7F_3$ transition. The blue emission peak at about 488 nm of the Tb^{3+} ion was not observed because it was associated with Raman scattering in our study. However, the $^5D_4 \rightarrow {}^7F_6$ energy transition of this blue emission has been repeatedly shown in the literature [16–18].



(a) (b)

Figure 7. (a) Excitation spectrum of TiO_2: 1%Tb^{3+} nanoparticles, (b) Emission spectrum of TiO_2: 1%Tb^{3+} nanoparticles

4. Discussion and Conclusion

In this study, TiO_2 fluorescent particles were successfully produced by the sol-gel method by activating with Tb^{3+} rare earth ions. Structural and microstructural properties of the produced nanoparticles were studied by using XRD, FTIR, DTA-TG, SEM and PL spectra devices. Particle size measurement and morphological analysis showed that the particle size was below 100 nm. The calcination temperature determined by the sol-gel method and DTA analysis was found to be successful in nanoparticle production. Energetic transitions of Tb^{3+} ions were detected by photoluminescence characterization ($^5D_4 \rightarrow {}^7F_J$ (J = 5, 4, 3)). Tb-doped TiO_2 shows the highest activity among all the rare earth doped samples investigated in the literature due to the increase in the electron transfer rate at the interface. This indicates that the photochemical process is dominated by electron-hole recombination.

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