Photocatalytic Activity of Zinc-Doped Titanium Dioxide Nanostructures Prepared by Spray Pyrolysis

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Abstract
In this work, titanium dioxide nanostructures were prepared by spray pyrolysis method on quartz substrates. These nanostructures were doped with different weight percentages of zinc to prepare Zn-doped TiO_2 samples. The energy band gap of these samples were determined as a function of the zinc dopants weight percentage. It was found that the energy band gap increases with increasing weight percentage of zinc dopants when compared to the undoped titanium dioxide sample. The photocatalytic activity of the Zn-doped TiO_2 samples was introduced and compared. The larger weight percentage of zinc dopants showed higher ability to decompose the organic dye used for photocatalytic activity measurements.

Keywords: Titanium dioxide; Photocatalytic activity; Zinc dopants; Spray pyrolysis
Received: 11 January 2025; **Revised:** 02 March 2025; **Accepted:** 16 March 2025; **Published:** 1 April 2025

1. Introduction

Photocatalysts are materials that accelerate chemical reactions under light irradiation without being consumed. They play a vital role in environmental and energy applications, such as water purification, air detoxification, and hydrogen production [1-4]. Titanium dioxide (TiO_2) and zinc oxide (ZnO) are widely used due to their stability and efficiency [5,6]. Photocatalysts enable pollutant degradation by generating reactive oxygen species, breaking down harmful chemicals [7,8]. In solar energy conversion, they assist in water splitting to produce clean hydrogen fuel [9]. Advances in doping and nanostructuring enhance their efficiency, broadening applications in sustainable energy, self-cleaning surfaces, and antimicrobial coatings, contributing to a greener future [10-13].

Photocatalytic activity in semiconductors is a crucial process in environmental and energy applications, such as water splitting and pollutant degradation [14]. When a semiconductor absorbs photons with energy equal to or greater than its bandgap, electron-hole pairs are generated. These charge carriers participate in redox reactions, facilitating the degradation of organic pollutants or hydrogen evolution from water [15-18]. Titanium dioxide (TiO_2) is a widely used photocatalyst due to its stability and efficiency [19]. Modifications, such as doping or heterojunction formation, enhance photocatalytic performance by reducing charge recombination and extending light absorption. This technology holds promise for sustainable energy and environmental remediation [20-22].

Zinc-doped titanium dioxide (Zn-TiO_2) is a modified photocatalyst with enhanced optical, electronic, and catalytic properties. Doping TiO_2 with zinc improves charge separation, reduces recombination rates, and extends light absorption into the visible spectrum [23,24]. Physically, Zn-TiO_2 retains TiO_2's high surface area and stability, while chemically, zinc alters the band structure, enhancing photocatalytic efficiency [25,26]. It is prepared via sol-gel, hydrothermal, or co-precipitation methods [27]. Zn-TiO_2 is applied in water purification, air detoxification, hydrogen production, and self-cleaning surfaces [28]. Its superior photocatalytic activity makes it a promising material for environmental and energy applications, including solar-driven pollutant degradation and antimicrobial coatings [29,30].

Spray pyrolysis is a simple and cost-effective method for preparing thin films and nanostructures with controlled morphology and composition [31]. It involves atomizing a precursor solution into fine droplets and spraying them onto a heated substrate, where thermal decomposition occurs, forming a uniform film or nanostructured material [32,33]. The process parameters, such as precursor concentration, spray rate, substrate temperature, and carrier gas flow, influence the film's thickness, crystallinity, and surface morphology [34,35]. This technique is widely used for fabricating metal oxides, perovskites, and semiconductor materials for applications in photovoltaics, gas sensors, photocatalysis, and transparent conductive coatings [37,38]. Spray pyrolysis allows for large-area deposition, tunable film properties, and easy doping by modifying the precursor composition [39,40]. It is also scalable, making it suitable for industrial applications. Due to its versatility and simplicity, spray pyrolysis is a preferred method for producing high-performance functional materials in energy, electronics, and environmental applications [41,42].

In this work, titanium dioxide nanostructures were prepared by spray pyrolysis method on quartz substrates. These nanostructures were doped with different weight percentages of zinc to prepare Zn-doped TiO_2 samples. The photocatalytic activity of the Zn-doped TiO_2 samples is introduced and compared throughout their ability to decompose the organic dye used for photocatalytic activity measurements.

2. Experimental Part

Titanium oxide thin films, both undoped and zinc-doped, were deposited onto quartz substrates heated to 350°C using the spray pyrolysis technique. The spray nozzle was positioned 30 cm from the substrate. The precursor solution was prepared by dissolving 2 mL of titanium tetrachloride ($TiCl_4$, 99.9% purity, 1.726 g/cm³ density) in 20 mL of 96% ethyl alcohol. Filtered air served as the carrier gas, with a deposition duration of 5 seconds. The samples were then annealed in air at 550°C for 120 minutes. Zinc doping in TiO_2 films was achieved using $ZnCl_2{\cdot}6H_2O$, with dopant concentrations of 1, 3, 5, and 7% by weight.

The photocatalytic performance of TiO_2 films was assessed by examining the degradation of methylene blue (MB) during its catalytic breakdown. MB ($C_{16}H_{18}ClN_3S$) is a water-soluble, cationic organic dye commonly found in wastewater and considered potentially toxic. A 100 mg/L aqueous MB solution was prepared in a reactor and continuously stirred. The solution's pH was adjusted to 3 by adding dilute hydrochloric acid. A quartz slide coated with a TiO_2 film (4.5 cm²) was immersed in the solution. Initially, the system was kept in the dark for 30 minutes to achieve adsorption–desorption equilibrium. After stabilization, the TiO_2 film was exposed to UV light with a central emission wavelength of 365 nm. The absorbance of the MB solution was recorded every 30 minutes using a UV–visible spectrophotometer. The photodegradation rate of MB for each film was determined by tracking changes in the intensity of its primary absorption peak at 605 nm.

3. Results and Discussion

Figure (1) presents a plot of $(\alpha h\nu)^2$ against photon energy ($h\nu$) to determine the optical energy gap of films at varying zinc doping concentrations (1%, 3%, 5%, and 7%). The results indicate that the energy gap increases with higher zinc doping levels in TiO_2 films, ranging from 3.8 eV to 3.86 eV, as summarized in table (1).

The photocatalytic reaction is highly sensitive to the surface of the catalyst. It begins with the generation of electron-hole pairs on the TiO_2 surface, triggered by the absorption of photons with energy equal to or greater than the band gap. Under UV irradiation, methylene blue (MB) reacts with the electrons generated on the TiO_2 particles. Figure 2 illustrates the change in absorbance of MB at 605 nm as a function of UV light exposure time on TiO_2 films immersed in the solution. To track the degradation process, spectra were recorded at various time intervals. The experiment was repeated with two sets of films under identical conditions, and the results were consistent. As seen in Figure 2, the absorbance decreases over time, indicating the photodegradation of MB. Notably, films with higher doping concentrations show a more pronounced decrease in absorbance. The reduction of the 605 nm absorbance band suggests strong photocatalytic activity. The results demonstrate that Zn-doped TiO_2 films exhibit enhanced photocatalytic performance compared to undoped TiO_2, likely due to an increased specific surface area.

Table (1) Experimental results of Zn-doped TiO_2

Doping concentrations	E_g (eV)
undoped	3.5
1%	3.8
3%	3.82
5%	3.84
7%	3.86

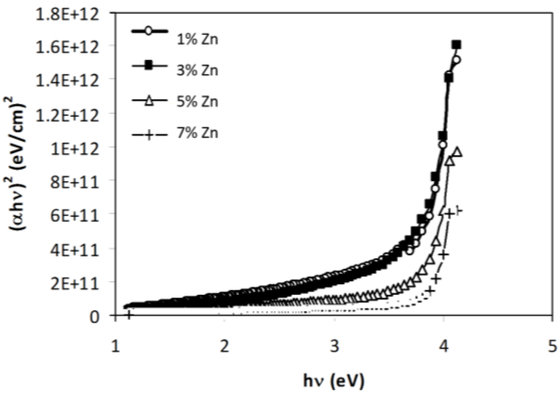

Fig. (1) Variation of $(ah\nu)^2$ with photon energy ($h\nu$) for the Zn-doped TiO_2 nanostructures at different weight percentages of Zn dopants

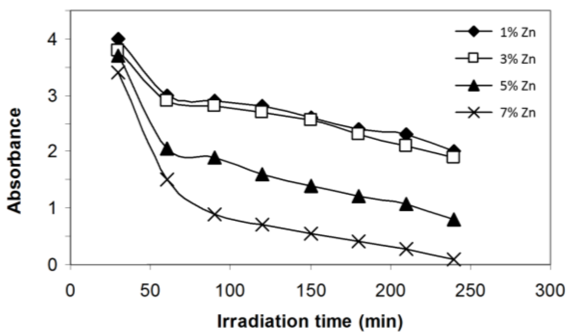

Fig. (2) Variation of absorbance of MB dye containing Zn-doped TiO_2 nanostructures at different weight percentages of Zn dopants

4. Conclusion

In concluding remarks, titanium dioxide nanostructures were prepared and doped with different weight percentages of zinc to prepare Zn-doped TiO_2 samples. It was found that the energy band gap increases with increasing weight percentage of zinc dopants when compared to the undoped titanium dioxide sample. The photocatalytic activity of the Zn-doped TiO_2 samples was introduced and compared. The larger weight percentage of zinc dopants showed higher ability to decompose the organic dye used for photocatalytic activity measurements.

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