SYNTHESIS AND CHARACTERIZATION OF TRANSPARENT PHOTOCATALYTIC ZTO COATINGS

UDC:628.315.3
Original scientific paper https://doi.org/10.46793/adeletters.2023.2.3.5

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Abstract:
The photocatalytic approach is known to be one of the most promising processes for the tertiary treatment of polluted water. The paper presents studies of Zn_2SnO_4 (ZTO) coatings synthesized by spray pyrolysis of Zn and Sn salt solution with the addition of dispersed Ta_2O_5 powder. The structural, morphological and optical properties of the coatings were investigated. Despite the simplicity and availability, the spray pyrolysis method provides homogeneous coatings. Introducing 0.001 mol/L of Ta_2O_5 into the initial salt solution was found to contribute to a significant change in the surface morphology of the synthesized coatings. The effect of the doped Ta_2O_5 phase on the photocatalytic activity of ZTO for the degradation of methylene blue (MB) has been investigated. An improvement of up to 90% in the degradation of MB has been observed for the Zn_2SnO_4/Ta_2O_5 system after five hours of UV irradiation.

ARTICLE HISTORY
Received: 29 June 2023
Revised: 10 September 2023
Accepted: 28 September 2023
Published: 30 September 2023

KEYWORDS
Spray pyrolysis, ZTO films, specific surface, photo-catalytic application

1. INTRODUCTION

Zinc stannate (Zn_2SnO_4) is a material that has gained attention as a photocatalyst material in recent years due to its unique structural, electronic, and optical properties. Photocatalytic activity is the ability of a material to generate reactive species (e.g., hydroxyl radicals, holes, or electrons) by absorbing light, which then reacts with pollutant molecules or initiates the decomposition of harmful contaminants. ZTO and coatings based on it are among the most popular materials that find application in many branches of engineering [1]. Due to thermal stability and high electrical conductivity, Zn_2SnO_4 can be used in gas sensors [2-4], solar technologies [5,6], and microelectronics as transparent electrodes [7,8]. Despite numerous researches on Zn_2SnO_4, it still finds new applications. For example, the work [9] suggests using Zn_2SnO_4 to convert CO_2 into methane. Another promising application of Zn_2SnO_4 is its use as a photocatalyst in wastewater treatment of food, paper and textile industries [10]. However, the use of Zn_2SnO_4 in photocatalysis is strongly limited by the band gap width (3.6 eV). The development of effective Zn_2SnO_4-based photocatalysts is a difficult but promising task.

Photocatalytic decomposition of organic substances occurs on the surface of a photocatalyst [11-14]. It is known that an increase in the specific surface increases the photocatalytic activity of coatings [15,16]. Therefore, the specific surface is an important parameter affecting the efficiency of photocatalysts.

Despite these promising properties, the photocatalytic performance of ZTO can still be improved. Research has been conducted on doping with other elements, forming heterojunctions with other materials, and optimizing the nanostructure of ZTO to enhance its performance. These efforts aim to further increase the reactivity and stability of ZTO for various photocatalytic applications, such as water and air purification, hydrogen production by water splitting, and CO_2 reduction. Various

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additives are used to modify and change the surface structure of coatings [17-19]. It is possible to control the electron mobility of ZnO through only UV irradiation [20]. The work [21] demonstrates the positive effect of introducing insoluble additives into the precursor on the structure and properties of the coatings.

Dispersing tantalum pentoxide (Ta_2O_5) in the precursor solution can be a helpful approach when preparing a coating via spray pyrolysis, especially for modifying the properties of the resulting material [18]. Ta_2O_5 is known for its high refractive index, wide band gap, and excellent chemical stability, making it suitable for photocatalytic, gas sensing, optoelectronic, and dielectric applications.

Common tantalum precursor choices include tantalum ethoxide ($Ta(OC_2H_5)_5$) or tantalum chloride ($TaCl_5$). Different metal alkoxides or metal salts could be used for the host material depending on the desired composition. In this work, dispersed Ta_2O_5 was used in the precursor solution for coating by spray pyrolysis. This technique is most commonly used in the suspension flame spraying method for the deposition of different coatings [22]. However, it remains unclear to what extent such additives can change the specific surface of Zn_2SnO_4 synthesized by spray pyrolysis. It is assumed that the Ta_2O_5 particles will stimulate the growth of Zn_2SnO_4 crystals, forming a homogeneous coating with a larger specific surface.

In some cases, a post-annealing process may be used to optimize film quality, crystallinity, and phase purity after spray pyrolysis. The annealing temperature, time, and atmosphere depend on the material composition and the desired structural and morphological properties.

It is important to remember that this is a general process and the specific conditions for optimal deposition will depend on the precursors, solvents, substrate, and desired film properties. Proper optimization will be required for each particular system.

2. MATERIALS AND METHODS

Zn_2SnO_4 (ZTO)- and Zn_2SnO_4-based coatings with Ta_2O_5 (ZTO-Ta) were synthesized by spray pyrolysis. 0.1 M zinc acetate ($Zn(CH_3COO)_2x2H_2O$) and tin chloride ($SnCl_2$) solution in propanol was used as a precursor for the ZTO coating, with a Zn/Sn ratio of 2:1. For the ZTO-ZnO coating, 0.0001 mol of Ta_2O_5 powder was additionally introduced into the 100 ml precursor solution. The solution was homogenized in an ultrasonic homogenizer for 2 hours. Quartz glasses 20x20x3 mm and 10x5x0.5 mm were used as substrates for ZTO and ZTO-Ta coatings. Precursor solutions were sprayed for 30 s on the surface of quartz glass preheated to 250-300 °C (Fig. 1). The nozzle was placed at a distance of 25 cm to form a more homogeneous coating. After coating, the glasses were annealed for two hours at 450°C in the air atmosphere.

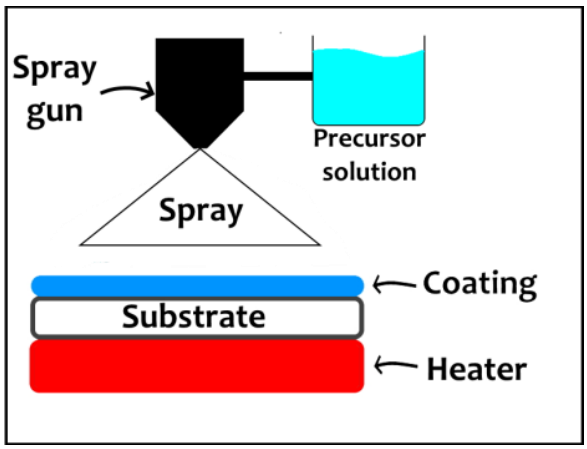

Fig. 1. Schematic of coating deposition

The phase composition was determined using an XRD-7000S diffractometer (CuK_α-radiation, Shimadzu, Japan). The surface morphology was examined with a TM-3000 scanning electron microscope (Hitachi, Japan) at an accelerating voltage of 15 kV, removing the charge from the sample (electron gun: 5×10^{-2} Pa; chamber: 30-50 Pa).

The specific surface and total pores volume of the samples were determined using a SORBI-M device (Russia) by comparing the volumes of adsorbate gas (nitrogen) sorbed by the test sample and a standard sample with a known specific surface. The measurement of the specific surface was performed by the 4-point BET method.

The thickness of the films is calculated using a Stylus Profilometer.

The optical properties of the materials were studied on the Evolution 600 UV-Visible Spectrophotometer (Thermo Scientific, USA) using MgO as the reference standard.

The photocatalytic properties of the synthesized coatings were evaluated by decomposition of the organic dye in an aqueous solution, according to the procedure described in [23]. Methylene blue dye with a concentration of 10 mg/l was chosen as the most commonly used in such works. Quartz glasses (coated and uncoated) were immersed in a quartz cuvette and poured with the dye solution. Then, the cuvettes were

exposed to UV light (15 W, 300-450 nm). The kinetic of the dye decomposition was studied by periodically measuring the spectral properties of the irradiated dye solution using a UV-3600 spectrophotometer (Shimadzu, Japan).

3. RESULTS AND DISCUSSION

Fig. 2 displays the XRD patterns of ZTO and ZTO-Ta coatings. XRD analysis shows that all coatings are naturally polycrystalline, the main phase of both coatings is Zn_2SnO_4 (JCPDS data card no 74-2184). As evident from the patterns, ZTO-Ta shows the characteristic peaks of the orthorhombic - Ta_2O_5 phase (JCPDS data card no. 89-2843). Slight reflexes of the ZnO phase are present in the X-ray diffraction pattern of both coatings. This indicates that ZnO is not completely embedded in the crystal lattice structure of Zn_2SnO_4. Notably, a small addition of Ta_2O_5 into ZTO-Ta enhanced the intensity of ZnO (102) peak (near 2θ=47.4°) in accordance with ZTO coating.

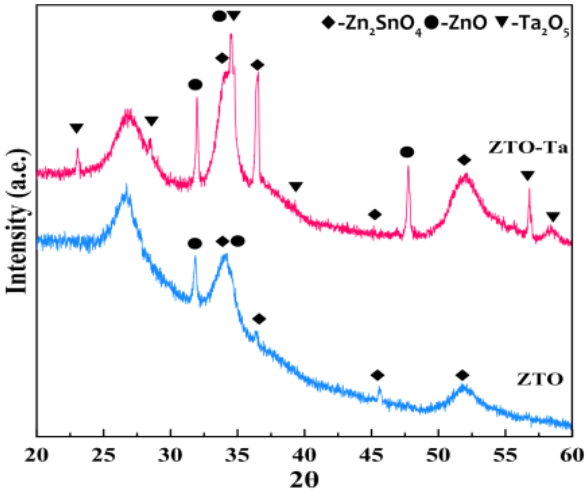

Fig. 2. XRD patterns of synthesized coatings

SEM images (Fig. 3) show that a heterogeneous structure characterizes the surface of the ZTO coating and consists of grains ranging in size from 1 to 5 µm and more.

The coating grows on random points associated with defects on the glass surface (random nucleation), leading to an inhomogeneous structure. The ZTO-Ta coating has a more homogeneous structure represented by agglomerates consisting of finer grains with a size of 1-3 µm. In addition, the surface contains a few long grains not exceeding 4 µm in size. When the ZTO-Ta coating is deposited on a clean quartz glass substrate, coating crystals begin to grow on dispersed Ta_2O_5 particles contained in the precursor solution, which are seed crystals evenly distributed in the sprayed solution and contribute to forming a more homogeneous structure. As seen, ZTO-Ta exhibited higher porosity with a well-distributed irregular shape of tiny pores. Total pores volume of 0.044 m^3g^{-1} was achieved in ZTO-Ta, while ZTO demonstrated 0.023 m^3g^{-1}.

The BET measurement of the specific surface showed a significant increase in this parameter from 35 m^2/g for the ZTO coating to 78 m^2/g for the ZTO-Ta coating.

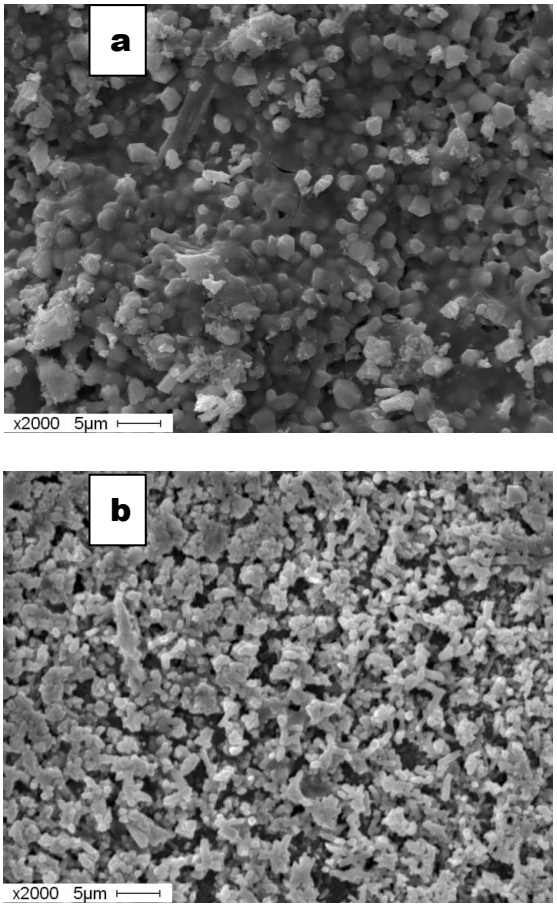

Fig. 3. SEM images of ZTO (a) and ZTO-Ta (b) films

The transmittance spectra of the coatings are shown in Fig. 4. Both are optically transparent. However, introducing Ta2O5 into the coating reduces light transmittance in the visible region of the spectrum. This may result from diffusive light scattering on the surface of the ZTO-Ta coating. The coatings' thickness was observed in the range 550 ± 50 nm.

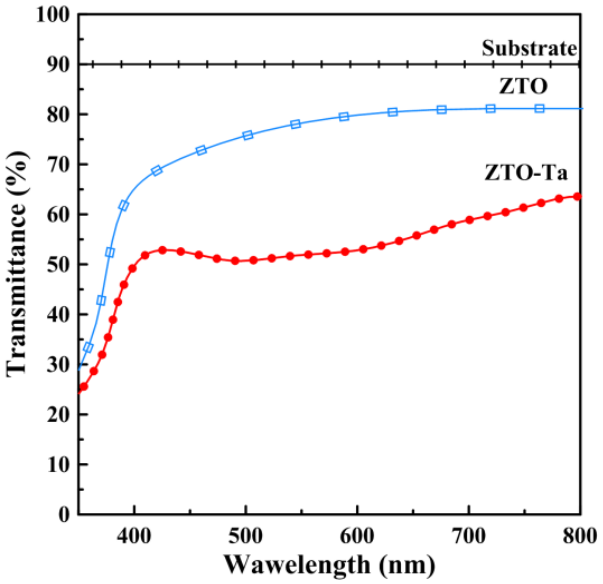

Fig. 4. Transmittance spectra of ZTO and ZTO-Ta coatings

The decomposition kinetics of the methylene blue is presented in Fig. 5. The dye decomposition rate in the presence of the ZTO-Ta coating is slightly higher than that with the ZTO coating. For the ZTO-ZnO coating, 80% water purification from the dye under UV irradiation occurs within three hours. The same depth of water purification occurs only after four hours of UV irradiation for the ZTO coating. This change in the photochemical reaction rate can be directly attributed to the increase in the specific surface of ZTO-Ta. Moreover, this may be due to the influence of the semiconductor Ta_2O_5 with a narrower band gap, which can lead to charge separation and work as a sensitizer.

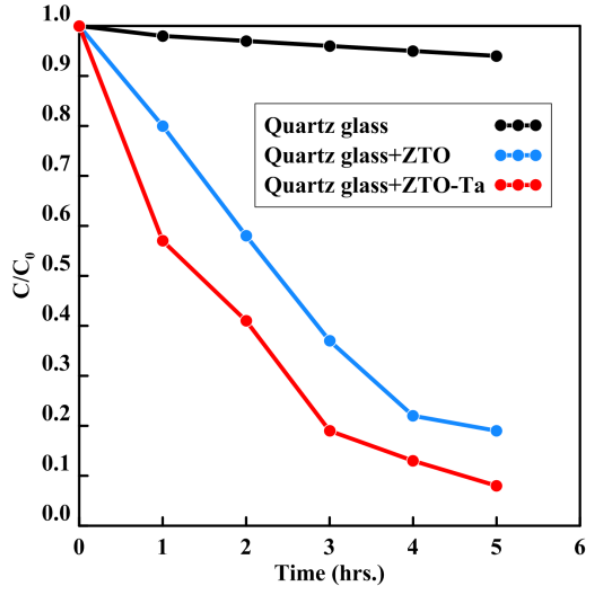

Fig. 5. Photocatalytic degradation of MB under UV-light

The principle behind this effect is that when a nanocomposite of Ta_2O_5 and another semiconductor material (such as ZnO or SnO_2) absorbs light, electron-hole pairs are generated in both semiconductor components. The excited electrons and holes can move between the two materials at the heterojunction interface, resulting in more effective charge separation. This, in turn, suppresses the recombination of the photo-generated electron-hole pairs and extends their lifetime, resulting in enhanced photocatalytic activity.

4. CONCLUSION

ZTO and ZTO-Ta coatings were synthesized on quartz substrates by spray pyrolysis. According to XRD analysis, the coatings are multiphase material consisting mainly of zinc stannate Zn_2SnO_4. Both coatings showed photocatalytic activity in the decomposition of organic dye dissolved in water under UV radiation. However, for the Ta_2O_5-modified coating, methylene blue's decomposition reaction was faster than the ZTO coating. The ZTO-Ta coating was found to have more than twice the specific surface compared to the ZTO coating, but there is a significant decrease in light transmittance in the visible spectrum region.

A nanocomposite thin film prepared by the spray pyrolysis method can effectively produce photocatalytic materials for water pollution treatment. This process allows the controlled incorporation of multiple components and reasonable control over film thickness, nanostructure and morphology.

The effective photocatalyst, with its stability and simple preparation, holds promise for investigating the composites-based ZTO to decompose pollutants and develop effective photoactive materials. Efforts are also being made to study the thin films' electrical properties and photocatalytic reactors for water purification fabrication.

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