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EFFECT OF HEAT TREATMENT TEMPERATURE ON THE STRUCTURE OF BROOKITE TiO_2 FILM DEPOSITED VIA GREEN SOL-GEL ROUTE FOR PHOTOCATALYTIC ACTIVITY

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ABSTRACT

In this work, the structural and photocatalytic properties of brookite films synthesized by a green solvent-free sol-gel method were investigated with various heat treatment temperatures. According to XRD, the crystallinity of brookite, 31.7° (111) decreased with increasing temperature from 200°C to 500°C. The crystallite size showed an increasing trend with temperature up to a maximum of 58.4 nm at 300°C, followed by a decrease with increasing temperature (up to 500°C) due to dislocation density and oxidation. These brookite thin films were tested for photocatalytic performance in the degradation of methylene blue under visible light. Accordingly, a film treated at 300°C showed a maximum efficiency of 97.8% after 4 hours due to the low band gap energy (3.37 eV) and large crystallite size. Films treated at higher temperatures of 400°C and 500°C showed reduced efficiencies due to reduced crystallinity. The study varied in the influence of heat treatments on structural and photocatalytic performance within brookite films, which presented optimum heat treatment temperature at 300°C.

KEYWORD

Brookite, film, heat treatment temperature, sol-gel, spin coating, photocatalytic

INTRODUCTION

Among all the studied photocatalytic materials, TiO_2 exhibits the best performance, considering its high oxidizing power, chemical stability, low cost, and environmental friendliness. Anatase and rutile are two of the known TiO_2 polymorphs widely used due to their stability, while brookite is considered less because it is more difficult to obtain in pure form and usually appears as a by-product (Manzoli et al., 2022). However, brookite is found to be more vigorous in photocatalytic activity than anatase and rutile and has capabilities in both visible and ultraviolet light (Tran et al., 2017).

In this regard, brookite films can be deposited by different methods, including the sol-gel spin coating method, a simple, efficient, and inexpensive technique. Generally, the sol-gel process involves precursors that, in the presence of catalysts such as HCl promoting crystallite growth, result in TiO_2 polymorphs. Generally, polar solvents such as alcohol delay hydrolysis and condensation, which may affect crystallization and film properties (Verma et al., 2015). However, most toxic solvents pose health and environmental risks upon large-scale application and hence are less "green" (Johari et al., 2019).

Most of the works devoted to brookite synthesis deal with nanoparticles, and there are fewer reports devoted to TiO_2 films and the influence of heat treatment on its properties. No literature is available regarding the investigation of the temperature of heat treatment on the characteristics of brookite thin films prepared using the green sol-gel method without solvent. This work will investigate the role that heat treatment plays in modifying the characteristics of brookite films made by a green sol-gel route.

MATERIAL AND METHODOLOGY

A TiO_2 sol was prepared by mixing 0.2 M titanium (IV) isopropoxide (TTIP) with 64 ml deionized water (DI), adding TTIP dropwise, followed by 0.4 ml HCl, and stirring for 3 hours. The solution aged for 48 hours before 90 micro-litre was deposited onto a glass substrate at 1500 rpm for 30 s, dried at 110°C for 1 hour. The brookite thin films were then heat-treated at 200°C, 300°C, 400°C, and 500°C for 3 hours. For the characterization, the brookite films were with X-ray diffractometer (XRD) PANalytical X'PERT PRO MPD Model PW 3060/60 within the range of 10° - 80°. The optical absorption of brookite thin films was measured by Lambda 35 UV-Vis spectrometer, Perkin Elmer with wavelength ranges of 200 nm – 1100 nm. The band gap of the brookite films was calculated with the Tauc plot method. The thickness of the coating was measured by scanning electron microscope (SEM) with a ZEIS EVO 50. After that, the photocatalytic test was carried out using an OSRAM model with 200 watts of visible radiation serving as a light source 16 cm distant from the dye solution. The temperature in the chamber was maintained at about 25°C using a cooling fan. A brookite film coating was submerged in 25 ml with a concentration of 1×10^{-6} M methylene blue (MB) in a beaker as part of this experiment.

RESULT AND DISCUSSION

XRD analysis of the brookite thin films reveals that the crystallinity varied with heat treatment temperature (Figure 1). At a heat treatment temperature of 200°C, brookite phase is observed at the intense peaks of 31.7° (111) and 66.2° (203), while at 300°C and 400°C, only the 31.7° (111) peak was detected, indicating its crystallinity decreased as the temperature increased. This reduction of the crystallinity is believed to be related to the absence of any solvent in the sol-gel formulation used in the present work, which speeds up hydrolysis and condensation and therefore results in low crystal formation. Other studies also report a decrease in the brookite content and crystallite size at higher temperatures; above 400°C, no crystalline phase is observed as reported by Li et al. (2004). The XRD pattern at 500°C exhibits an amorphous nature, indicating no crystalline TiO_2. In another work, Komaraiah et al. (2016) also observed that the crystallinity of brookite decreases as the temperature of heat treatment increases from 400°C to 500°C. This may be due to thermal instability/metastability of the brookite at elevated temperatures.

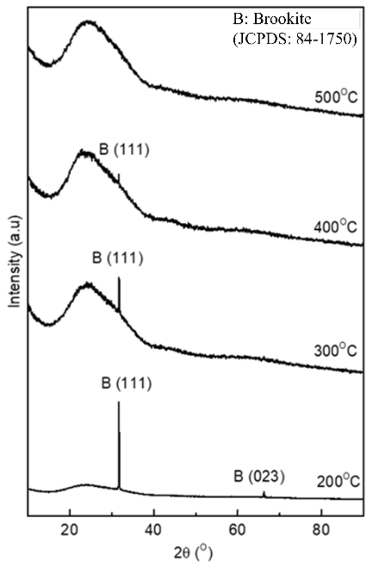

Figure 1: X-ray diffraction (XRD) pattern of brookite thin films heated at different heat treatment temperatures.

The structural properties of brookite thin films, analyzed by XRD, show that the rise in the temperature of heat treatment has a different effect on both crystallite size and band gap energy. In the increased temperature range from 200°C to 300°C, the crystallite size of brookite increases from 47.9 nm to 58.4 nm due to thermally enhanced crystallization. Whereas at 400°C, the crystallite size has decreased to 7.8 nm, which may be due to the rise of dislocation density, strain, or even oxidation at high temperatures. While, for the band gap, the band gap energy decreases from 300°C (3.40 eV) to 200°C (3.37 eV). This is due to the increased thickness of the films. When film thickness is increased from 512.9 nm at 200°C to 619.7 nm at 300°C, probably some defects will be created in films that reduce the band gap energy. Contrarily, at 400°C and 500°C, the band gap energy increases up to 3.55 eV and 3.90 eV, correspondingly, probably due to structural changes and lower film thickness. At higher thicknesses defect-related states, emerging in thicker films of TiO_2, change the band structure and result in a band gap energy reduction. Therefore, film thickness is one of the most important parameters that can alter the optical properties of brookite thin films.

Table 1: The details of structural properties of brookite thin films.

Temperature (°C)	Crystallite size (nm)	Coating thickness (nm)	Band gap (eV)
200	47.9	512.9	3.40
300	58.4	618.7	3.37
400	7.8	436.6	3.55
500		350.6	3.90

The degradation efficiencies of MB under the visible light irradiation by the brookite thin films calcinated at various temperatures were compared. The highest degradation efficiency of the brookite thin film calcinated at 300°C was 58.1% after 1 hour and 97.8% after 4 hours of light exposure. Efficiency is associated with the lowest band gap energy of this film, 3.37 eV, close to visible light and thus increasing the electron transfer processes important in photocatalysis. Illumination, therefore, triggers the excitation of electrons from the valence band to the conduction band of brookite thin films, minimizing the recombination of charges and further encouraging pollutant degradation through reactive species, mainly superoxide radicals (O_2^-) and hydroxyl radicals (OH•). A high degradation of the thin film at 200°C is seen at 95.4% after 4 hours. At even higher temperatures of 400°C and 500°C, the efficiency goes down to 53.1% and 51.8%, respectively. Also, the increased crystallite size at 300°C (58.4 nm) makes a suitable contribution to the photocatalytic degradation efficiency. Large particle size enhances electron transport and allows more dye and photons to be absorbed. Higher temperatures are not favored for this process since smaller crystallite sizes result in lesser efficiency. The influential factors, therefore, of the photocatalytic activity in brookite thin films under visible light irradiation are band gap energy and crystallite size.

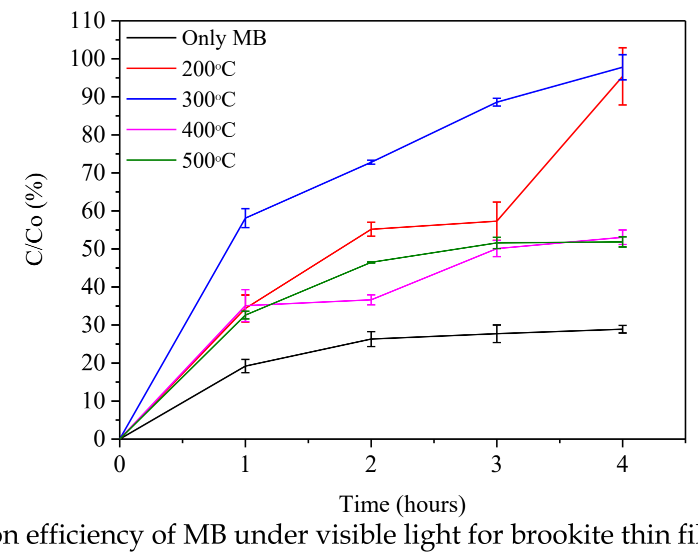

Figure 2: Degradation efficiency of MB under visible light for brookite thin film at different heat treatment temperatures.

CONCLUSION

The brookite films were successfully synthesized by a solvent-free sol-gel method. It was deduced that thin films calcined at 300°C exhibited superior crystallite size and optimum band gap energy, thus leading to high photocatalytic degradation of methylene blue. The increased temperature of the heat treatment reduced the crystallinity and photocatalytic efficiency of the brookite films. Conclusively, 300°C was found to be the optimal temperature of heat treatment to appropriately realize the photocatalysis of brookite.

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