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UV Light-assisted Photocatalytic Degradation of Simluated Methylene blue Dye by Multilayered ZnO Films

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다층 ZnO 막에 의한 모의 메틸렌블루 염료의 자외선 광촉매분해

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Abstract : As the use of chemical products increases in daily life, the removal of dye waste has also emerged as an important environmental issue. This dye waste can be decomposed using a photocatalyst, and the photocatalyst can be synthesized very cost-effectively by using the sol-gel technology. The sol-gel technology is not only very useful for nanoscale film formation, but also can simply form multilayer structures. Using a multiple spin coating method, in this study, a ZnO film with a multilayered structure (3 layers, 5 layers) was formed by using zinc oxide (ZnO), which is effective in decomposing various dyes. For performance comparison, a ZnO film having a single layer structure by a single spin coating method was prepared as a control. Structural and elemental analysis of ZnO film was performed using an X-ray diffraction analyzer and an energy dispersive X-ray spectrometer. A nanowire-like surface morphology could be observed through a scanning electron microscope. Additionally, UV-Vis spectrophotometer was used to measure the absorbance of UV light. The ZnO film with a five-layer structure degraded the simulated methylene blue by 49% more than the ZnO film with a single-layer structure. In conclusion, it was found that ZnO having a multilayered structure is useful as a photocatalyst that decomposes methylene blue dye more effectively.

Keywords : photocatalysis, UV absorption, multilayered ZnO, degradation, methylene blue

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요 약 : 일상적인 화학제품들의 사용량이 증가함에 따라 사용되었던 염료 폐기물 처리 또한 중요한 환경적인 문제로 대두되었다. 이러한 염료폐기물은 광촉매를 이용하여 분해시킬 수 있는데, 졸-겔 기술을 활용하면 매우 비용 효율적으로 광촉매를 합성할 수 있다. 졸-겔 기술은 나노스케일의 막 형성에도 상당히 유용하며 간단하게 다층구조를 형성할 수도 있다. 본 연구에서는 다양한 염료 분해에 효과가 있는 산화아연(ZnO) 이용하여 다중 회전도포 방법으로 다층구조(3층, 5층)를 가진 ZnO 막을 형성하였다. 성능비교를 위해 단일 회전도포 방법에 의한 단층구조를 가진 ZnO 막을 대조군으로 준비하였다. X선 회절분석기 및 에너지 분산 X선 분광계를 이용하여 ZnO의 구조 및 원소분석을 수행하였고, 주사전자현미경을 통해 나노선같은 표면형상을 관찰할 수 있었다. 추가적으로 UV-Vis 분광광도계를 활용하여 자외선의 흡수도를 측정하였다. 5층구조를 가진 ZnO 막이 단층 구조를 가진 ZnO 막에 비해 모의 메틸렌 블루를 49% 더 많이 분해하였다. 결론적으로, 다층구조를 가진 ZnO 는 메틸렌블루 염료를 더욱 효과적으로 분해하는 광촉매로써 유용하다는 알 수 있었다.

주제어 : 광촉매, 자외선 흡수, 다층 산화아연, 분해, 메틸렌블루

1. Introduction

In the textile and other sectors, wastewater is produced during the dyeing process. This includes hazardous organic chemicals that have an adverse effect on the environment [1, 2]. Because of these critical problems, it is necessary to remove hazardous organic compounds from wastewater. There are a few techniques for removing harmful organic molecules [3, 4]. Adsorption, microbiological breakdown, enzymatic decomposition, ultrafiltration, osmosis, microfiltration, and photocatalytic dye degradation have all been studied for dye removal from contaminated wastewater. Photocatalyst technology is one of them, and it has gained a lot of attention in recent years[3]. Research focusing on the deposition of thin films and nanocomposites has increased significantly in the last decade, provided that their properties have a strong scientific and technological appeal due to their numerous applications, including photocatalysis, solar cells, pigments, biomedical applications, and humidity sensors others [5–9]. Metal oxides have long been used in photocatalytic applications, including the degradation of hazardous dyestuffs in wastewater. In terms of quantum efficiency and catalytic efficiency, ZnO offers a few benefits.

Zinc oxide (ZnO) is an n-type semiconductor with the same wide-bandgap range as TiO_2, one of the most active semiconductor photocatalysts (3.2~3.3 eV); hence, its photocatalytic capability should be comparable to TiO_2, the most widely used photocatalyst in both water and air decontamination [10–15]. However, other researchers have revealed that ZnO under optimized synthesis conditions can show better performance characteristics then TiO_2 in photocatalytic degradation of certain dyes in an aqueous solution. Aqueous suspensions of powdered ZnO have been used in the majority of photodegradation experiments. However, removing them from water is challenging, thus current research has concentrated on developing highly photoactive immobilized catalysts for water purification. Multilayer structures have gained prominence due to their superior optical and electrical characteristics compared to monolayer thin films. The quality of deposited thin films is better than that of films grown directly on a substrate. However, only a few papers have focused on their photocatalytic activity [6–19].

The synthesis of multilayered ZnO films and their usage for photocatalytic degradation of simulated methyl blue (MB) dye under UV light was demonstrated in this work. The

formation of catalytic multilayer thin films and the factors that lead to degradation are thoroughly examined. A field emission scanning electron microscope (FESEM), energy-dispersive spectroscopy (EDS), and an X-ray diffractometer (XRD) were used to examine multilayer ZnO films.

2. Experiment

2.1. Chemicals and Materials

Zinc-acetate-dihydrate (ZAD), monoethanolamine (MEA), ethanol isopropyl-alcohol (IPA), acetone, and deionized water were acquired from Sigma-Aldrich, Seoul, Korea, for the preparation of ZnO Solution. All materials were used without modification while the glass substrate for the film deposition was purchased from MTI Korea.

2.2. Catalyst Preparation

Sol-gel spin-coating (SGSC) technology was used to deposit multi-layer, ZnO triple-layer, and ZnO single-layer thin films on a glass substrate from 0.25-M solutions of ZAD and EA in ethanol. Zinc acetate dihydrate was used as the main precursor, at first, ZnO solution was made by dissolving ZAD in ethanol at 65 ℃ and adding mono ethylene amine as a stabilizer drop by drop until the pH reached 9. The solution was then agitated constantly for 2 hours to obtain a transparent solution. After that, the solution was aged for 10 hours at room temperate (25 ℃). The resulting solution was stirred for 20 hours at 75 ℃, yielding a clear, stable, and homogenous solution. Before coating, Standard microscope slides (MTI) substrates were sonicated in IPA and then acetone for 30 minutes and subsequently with deionized water and dried in air. These solutions were spin-coated onto the clean glass substrates and annealed at 200 ℃ for 1 h. Four layers of Zinc oxide coatings were created by repeating the previous technique three times.

2.3. Photocatalyst characterization

A field emission scanning electron microscope (FESEM) was used to explore the morphology of ZnO thin films (TESCAN, Brno, Czech Republic, MIRA3). The elemental analysis of the produced films was performed using energy-dispersive spectroscopy (EDS, Brno, Czech Republic). An X-ray diffractometer (Empyrean) was used to analyze the phase of a ZnO thin film using a Cu target at a wavelength of 1.5406, a step size of 0.02°, and a scanning range of 5° to 80°. A UV/Vis spectrophotometer Lambda 25 was also used to make the optical measurements. UV-vis spectrophotometer with a resolution of 2.0 nm operated in the range of 0-1200 nm.

2.4. Photocatalytic experiments

The films were then put in a 50 ppm methylene blue (MB) dye solution and exposed to UV source (4 UV lamps of each 30W) with a UV wavelength of 365 nm. The concentration of MB dye was measured at different UV light exposure times at their corresponding λmax (absorbance) was measured using a UV absorption spectrophotometer to estimate dye removal in water, and the findings are provided in the following sections. As a result, the degradation rate for MB dye compounds may be determined based on the change in absorbance.

3. Results and discussion

3.1. Morphology and structure

The morphology of ZnO thin films was studied using a FESEM. Multiple spin coatings were required for the uniform thin film of ZnO deposited by the SGSC. As a result, a proper investigation was carried out to determine the effect of various spin coatings of ZnO thin films, and samples with 1, 3, and 5 spin-coating cycles were studied using FESEM and EDS analysis, the findings of which are presented in Figure 1 and Figure 2. The results

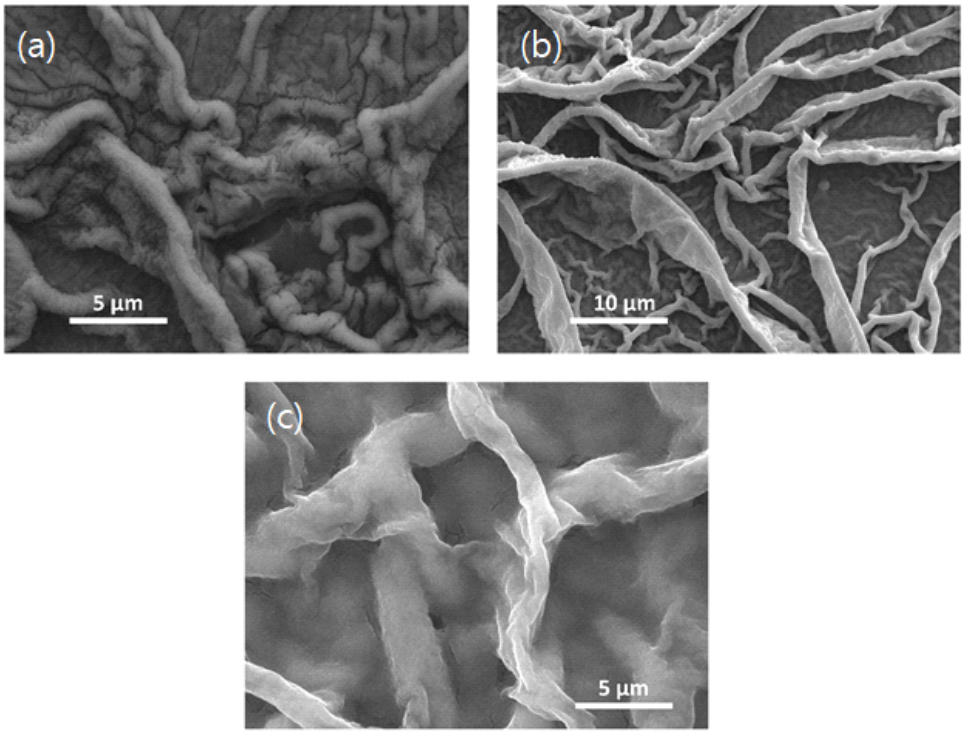

Fig. 1. SEM images of (a) ZnO single layer, (b) ZnO triple layer, (c) ZnO fifth layer.

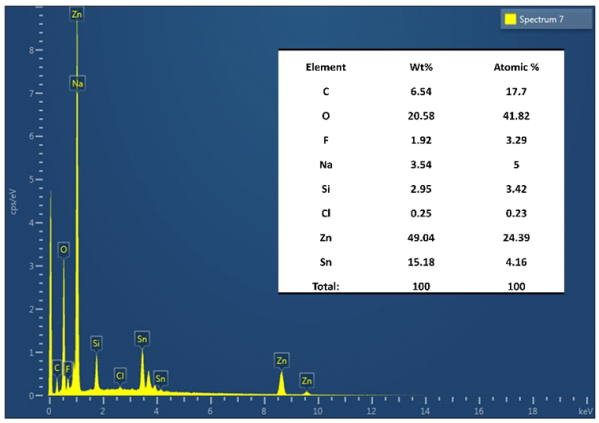

Fig. 2. EDS spectrum of multilayered ZnO.

showed that the thin film obtained after five spin-coating cycles produced the best results and was uniform, but the thin film of ZnO obtained after fewer than seven spin-coating cycles was non-uniform, with varied thicknesses at the center and edges. EDS analysis is commonly used to confirm the elemental composition of provided materials; as a result, EDS analysis was utilized to confirm the successful synthesis of ZnO films. The EDS

spectra of ZnO thin film formed on glass by the SGSC process are shown in Figure 2; it demonstrates that ZnO thin film was successfully produced since zinc (Zn) was present in the spectrum with at. wt.% of around 49.04%.

The crystal structure of produced ZnO thin films was investigated using an X-ray diffractometer (Empyrean) with a step size of 0.02° from 5° to 80° . The result is shown in Figure 3. According to the joint committee of powder diffraction standards (JCPDS) card no. 36-1451 and the literature, XRD analysis of ZnO thin film revealed peaks at 31.7° , 34.4° , and 36.4° , corresponding to lattice planes (100), (002), and (101), respectively, which confirm the hexagonal wurtzite structure of ZnO thin film. The diffraction peaks' positions are independent of film thickness; nonetheless, preferential orientation improves with film thickness. The considerable thickness may give enough space for the thermal motion of particles, resulting in improved crystallite alignment. As the thickness of the film increases, the crystallinity improves. Others have reported similar results [20,21]. This wurtzite crystal lattice structure is responsible for better photocatalytic performance and band gap of 3.3 eV [22].

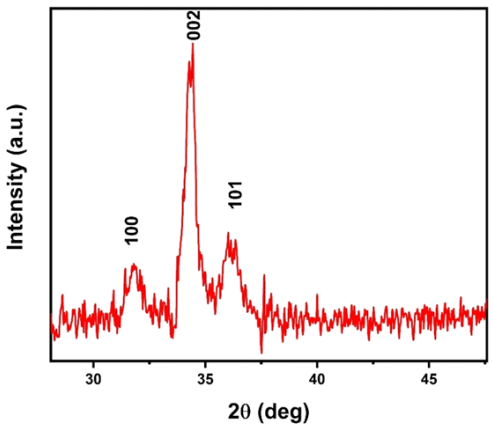

Fig. 3. XRD result of ZnO film.

3.2. Optical Property and Mechanism

The ZnO films transmittance spectra show a high transmittance ([80%]) in the 400-700 nm range. The degradation of samples under UV light irradiation was used to access the morphology-dependent photocatalytic activity of the produced ZnO film nanostructures. The photocatalytic activity of a five-layered ZnO film is about four times that of a single-layer ZnO film. Differences in photocatalytic activity are linked not only to ZnO band-gap energies, charge separation efficiency, various crystal growth habits, pore structure, and crystalline quality, but also to the concentration of oxygen vacancies on the surface, according to the literature [13-24]. In general, oxygen vacancies in ZnO crystallinity defects can operate as an active site to capture photoinduced electrons, and recombination of photoinduced electrons and holes can be successfully suppressed, resulting in considerably increased photocatalytic activity. As demonstrated in Table 1, the intensity of visible emission is significantly increased for five-layered ZnO thin films and the differences in the absorption spectra of 50 ppm MB dye before and after UV irradiation, suggesting a rise in the number of oxygen vacancies VO and improved photocatalytic activity.

As shown in this table, when no UV irradiation was used, the intensity of MB dye absorption remained roughly constant after 20 minutes of stirring, depicting that MB is stable under the above conditions. UV-light, on the other hand, has a noticeable impact on the destruction of MB dye, and decomposition of MB solution after varying exposure time (0-140 mins) of UV irradiation was approximately. The strongest catalytic activity was observed in a multilayer ZnO film, likely owing to the creation of nanoparticles with the highest relative intensity of the peak corresponding to the (002), which had greater energy and hence superior activity. Crystallite

size is critical in heterogeneous catalysis since it is directly connected to a catalyst's efficiency via crystalline quality. The crystallinity of multilayered ZnO films increased when sublayers were utilized, as evidenced by XRD and SEM measurements.

The tentative mechanism of ZnO photocatalyst is described as a process involving methylene blue decomposition, which is mainly mediated by highly reactive oxygen species such as $OH^{\cdot}$ (Eq.(1)). During photodegradation, reactive $OH^{\cdot}$ species were created with the aid of hole (h^{+}) in the valence band (VB) of ZnO during aqueous medium reaction (Eq. (2)). Here, h^{+} was generated in ZnO by UV light exposure. During electrocatalytic degradation, reactive $OH^{\cdot}$ was directly formed by the processes described in Eqs. (3) and (4)[25].

$$C_{16}H_{18}ClN_3S + 51OH^{\cdot} \rightarrow 16CO_2 + 6H_2O + H_2SO_4 + HNO_3 + HCl \quad \text{(Eq. 1)}$$

$$h^{+}_{VB} + H_2O \rightarrow H^{+} + OH^{\cdot} \quad \text{(Eq. 2)}$$

$$ZnO + e^{-} + 2H^{+} \rightarrow Zn^{+} + H_2O \quad \text{(Eq. 3)}$$

$$2H_2O \rightarrow 2H^{+} + 2OH^{\cdot} + 2e^{-} \quad \text{(Eq. 4)}$$

4. Conclusion

In conclusion, multilayered ZnO films were effectively produced using a simple sol-gel process. The crystallinity of the ZnO thin film was enhanced in the presence of the sublayers, according to XRD and SEM measurements. Furthermore, the EDS confirmed the presence of Zn and O in the multilayered deposited films. The addition of layers improves visible light absorption, creates more charge carriers, and increases electron and hole segregation and migration all at the same time. Because of its increased absorption in the visible region and lower band gap energy, the multi-layered ZnO film has better photocatalytic activity on the breakdown of MB than the single ZnO film. The mechanism of photocatalysis is investigated, and the stability determined by the ability to recycle photocatalytic materials.

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Table 1. Photocatalytic degradation of the MB dye at different UV light illumination times

Time (min.)	Absorbance (a.u.)		
	1 spin-coating	3 spin-coating	5 spin-coating
0	2.56	2.56	2.56
20	2.23	2.11	2.05
40	2.01	1.96	1.89
60	1.98	1.77	1.63
80	1.74	1.54	1.32
100	1.66	1.21	1.05
120	1.53	1.11	0.89
140	1.39	0.9	0.71

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