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PREPARATION AND CHARACTERIZATION OF PHOTOCATALYTIC PERFORMANCE OF HIERARCHICAL HETEROGENEOUS NANOSTRUCTURED ZnO/TiO_2 FILMS MADE BY DC MAGNETRON SPUTTERING

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Abstract. *With the aim to enhance photocatalytic properties and anti-Ecoli bacteria abilities of TiO_2 thin films; hierarchical heterogeneous nanostructured ZnO/TiO_2 (HNs) films were deposited by DC magnetron sputtering. The obtained results showed that both the photocatalytic performance and anti - Ecoli bacteria ability of HNs films exhibited enhancement in comparison with standard TiO_2 films. This enhancement was explained due to the reduction of the electron - hole recombination and the red shift of absorption edge of the HNs films.*

I. INTRODUCTION

The photoactivity of TiO_2 has been extensively studied and attracted a wide attention for the past two decades and, now it is being extensively applied in the photocatalytic degradation of organic pollutants in water and air, photocatalytic disinfection of bacteria, manufacturing anti-fog and self-cleaning glass etc [1].

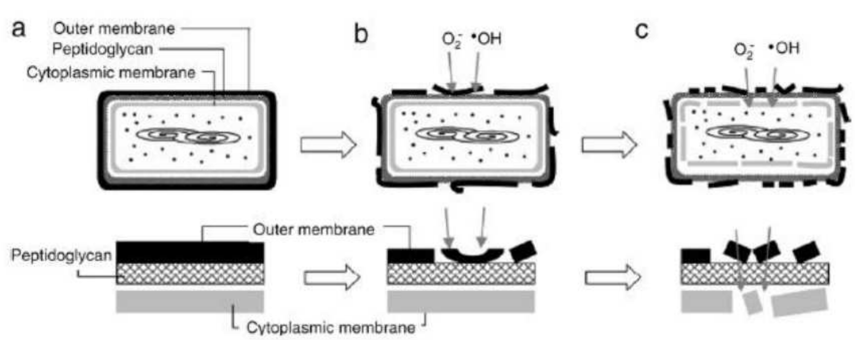

Fig. 1. Schematic illustration of the three stages in the process of E. coli photocatalytic microbial inactivation on the photocatalytic film. In the lower row, part of the cell envelope is magnified [19,20].

Under UVA light irradiation ($\lambda \leq 385$ nm), TiO_2 generate the electron - hole pairs, electrons promoted from the valence band to the conduction band, thus forming an electron–hole pair, that move to the surface. The holes and electrons react with water molecules and oxygen attached to TiO_2 surfaces forming hydroxyl radicals (OH) and superoxide anions (O_2^-). These are highly reactive for both the oxidation of organic substances and the inactivation of bacteria and viruses [19]. Procedures for anti-Ecoli bacteria abilities could be divided into three stages and described in detail by Fig. 1: (1) disordering of the outer membrane of bacteria cells by hydroxyl radicals and superoxide ions (OH, O_2^-); (2) disordering of the inner membrane (the cytoplasmic membrane) and killing of the cell; and (3) decomposition of the dead cell. In the first stage, the outer shell of E. coli cells were decomposed partially by hydroxyl radicals and superoxide ions (OH, O_2^-) in the photocatalytic process. During this stage, cell viability was not lost very efficiently. The partial decomposition of the outer membrane, however, changes the permeability to reactive species. Consequently, reactive species easily reach and attack the inner membrane, leading to the peroxidation of the membrane lipid. The structural and functional disordering of the cytoplasmic membrane due to lipid peroxidation led to the loss of cell viability and cell death. It was also reported that if the illumination continued for a sufficiently long time, the dead cells were found to be decomposed completely.

However, there are two bottlenecks of photocatalytic TiO_2 that reduce process efficiencies: (1) the narrow light-response range and (2) the low separation probability of photoinduced electron-hole pairs in stable semiconductor photocatalysts. Hence, numerous studies have been conducted worldwide to produce more efficiency in photocatalysts. One of the effective strategies to enhance photocatalytic activity is research and fabrication materials having hierarchical heterostructures. Hierarchical structures including TiO_2/SnO_2 [2, 3], TiO_2/Fe_2O_3 [4], ZnO/SnO_2 [5], TiO_2/ZrO_2 [6], TiO_2/Cu_2O [7], TiO_2/ZnO [8–11], etc have the advantage of optimizing surface area. Furthermore, the coupling of different semiconductor oxides not only creates heterojunctions, possessing different energy levels for their corresponding conduction band and valence band, but also can be used to strengthen photocatalysis. Such an approach possesses significant advantages in promoting the separation of photo-excited electron-hole pairs through various carrier-transfer pathways and in the extension of the light-response range by coupling suitable electronic structures in materials. In terms of the energetics, electrons ow into the semiconductor 1 while holes oppositely diffuse into the semiconductor 2. Consequently, more electrons reach the semiconductor 1 surface to cause reduction of O_2, whereas holes are probably consumed for oxidation reaction at the edge of the ZnO lm. Thus the interfacial electron transfer from semiconductor 2 to semiconductor 1 can explain the higher photocatalytic activity of hierarchical heterogeneous nanostructured films. That is to say, a better charge separation in the coupled lm is enhanced by fast electron-transfer process from the conduction band of semiconductor 2 to that of semiconductor 1. Thus, the charge recombination is suppressed more in the coupled lm than in the single lm [8–11].

In this research, hierarchical heterogeneous nanostructured ZnO/TiO_2 (HNs) films were prepared on glass substrate by Dc magnetron sputtering. The crystalline structures and surface morphology and optical properties were characterized by using, respectively X-ray diffraction (XRD), scanning electron microscope (SEM), atomic force

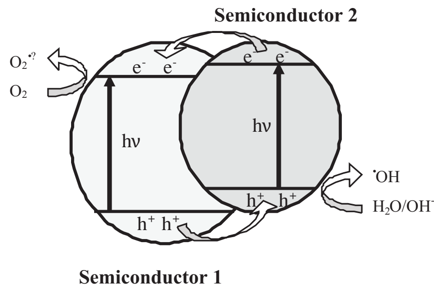

Fig. 2. Schematic diagram illustrating the charge transfer process in the ZnO-TiO$_2$(HNs) films.

microscopy (AFM), and ultraviolet–visible absorption spectroscopy (UV–vis). The photocatalytic activity of the ZnO/TiO2 (HNs) thin films were evaluated by identifying the degraded rates of methylene blue solution and anti - Ecoli bacteria abilities.

II. EXPERIMENTAL

The ZnO/TiO$_2$ (HNs) thin films were deposited on ordinarily optical microscope glass slides (Marienfeld, Germany) by using Dc- magnetron sputtering. The slides were cleaned with acetone, alcohol and treated surface by plasma discharge in 1.33 Pa vacuum before thin film deposition. A plate with 7.6 cm in diameter made from the pure (99.9%) zinc oxide was used for the target. The sputtering chamber was pumped down to about 6.66×10^{-4} Pa. Then, highly purified argon (99.99%) was introduced. Before deposition, the zinc oxide target was pre-sputtered for about 5 minutes with a shutter covering the substrate. The fabricated parameters of ZnO layers consist of the 6 cm substrate-target distance (h), 1.20 Pa sputtering pressure (p) and 56 W sputtering power (P). After ZnO thin films were deposited, the TiO$_2$ thin films were deposited on them by Dc reactive magnetron sputtering from the titanium metal target (purity, 99.9%) and mixtures of Ar, O$_2$ as reactive gases with fabrication parameters consist of the 6 cm substrate-target distance (cm), 13 mtorr sputtering pressure, 120 W sputtering power [12,13].

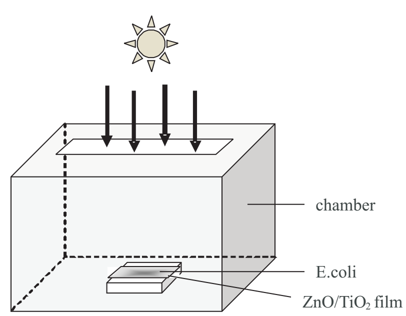

Fig. 3. Pattern of the evaluating system of anti - Ecoli bacteria ability of ZnO/TiO$_2$ (HNs) films.

Furthermore, the photocatalytic activity of the prepared ZnO/TiO_2 (HNs) films were evaluated by the degraded rates of methylene blue (MB) solution over irradiation time (Zeman method [14–16] with SP-300 spectrophotometer) and anti - Ecoli bacteria abilities by using the colony counting method. In this research, the UV light source (Philips, 12 V- 9 W) having wavelength range from 365 nm to 400nm was used to irradiate on the films and evaluate their photocatalytic activity (Fig. 3). The mechanism investigated anti - Ecoli bacteria abilities of the photocatalytic ZnO/TiO_2 (HNs) films relies on the growth of a bacterial cell in an agar plate to form a visible colony, only living or viable bacterial cells will be counted, films was evaluated as follows as follow: First, the thin films are illuminated by UV light over time and they are put into dilutions (the dilution are about 10^{-3}, the permitted range determined by colony counting method is from 25 to 250). Then, the dilutions mix into agar plates, they are incubated in 24 hours, colonies were formed on all agar plates, counting the resulting bacterial colonies forming unit [17, 19].

III. RESULTS AND DISCUSSION

Fig. 4 showes that the largest transmittance of the ZnO/TiO_2 HNs films was of about 85% that can be comparable to the transmittance of TiO_2 films. The specific features of all the ZnO/TiO_2 HNs films have red-shifted absorbed edge region of visible light more than TiO_2 film (Fig. 4) [11]. In addition, when the ZnO and TiO_2 molecules in contact with each other, they will affect the structure of each bank as bending energy of the two materials in contact positions. The bottom of the conduction band of TiO_2 peaks will curl down and bent over the conduction of ZnO (Fig. 2). The bend led to the band gap at both junctions are significantly reduced thus can extend the catalytic region of the visible band [5].

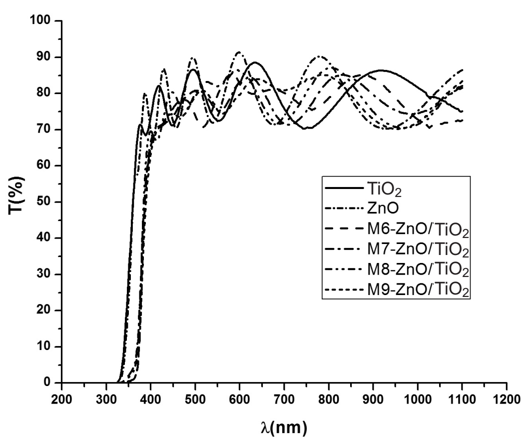

Fig. 4. The transmission spectra of the ZnO/TiO_2, TiO_2 and ZnO (HNs) films.

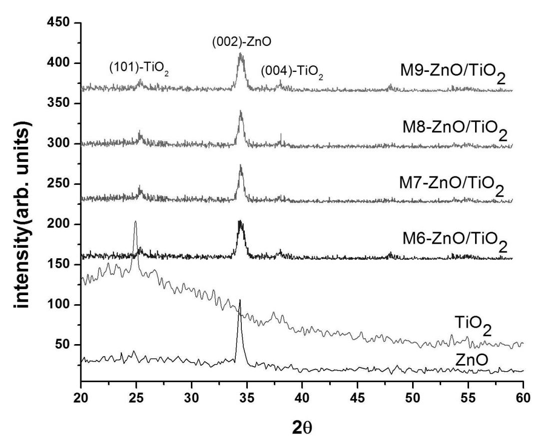

Fig. 5. XRD of TiO_2 film and ZnO/TiO_2, TiO_2 and ZnO (HNs) films.

The XRD diagrams (Fig. 5) show that the presence of ZnO component was defined by the preferred orientation (002) and composition of TiO_2 anatase phase was characterized by preferred orientation on A (101) and A (004). Obviously, those results demonstrate that ZnO/TiO_2HNs film fabricated with parameters as in Table 1 has good crystallinity and stability. The change of thickness of the ZnO/TiO_2 HNs film does not have significantly affect on their crystal structures.

Table 1. The fabricating parameters of ZnO/TiO_2(HNS) films

Code	The samples	ZnO layer (nm)	TiO_2 layer (nm)
M2	TiO_2	-	460
M6	ZnO/TiO_2	180	460
M7	ZnO/TiO_2	250	460
M8	ZnO/TiO_2	300	460
M9	ZnO/TiO_2	360	460

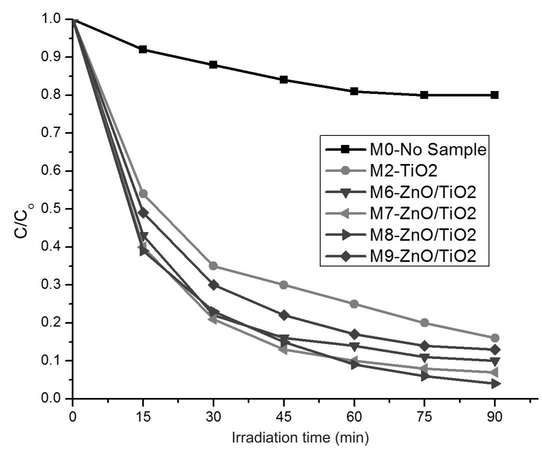

Fig. 6. Photocatalytic degradation of MB solution of the various samples under UAV.

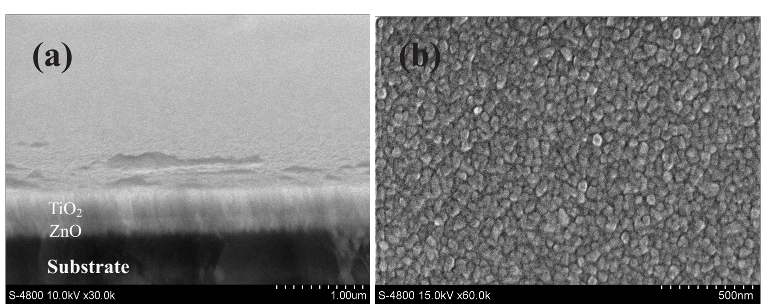

Fig. 7. SEM images of (a) cross-sectional and (b) surface for M8 of ZnO/TiO_2 HNs film.

For comparison, the photocatalytic degradation of MB was also performed using no film on glass (no sample), TiO_2 single layer and ZnO/TiO_2 HNs films (with changing thickness of ZnO layer). Fig. 6 shows that ZnO/TiO_2 HNs films had high photocatalytic activity and its photocatalytic efficiency was higher than those of the TiO_2 single layer. In particular, the M8 film having 300 nm ZnO film thickness and 460 nm TiO_2 film thickness had the highest photocatalytic activity. Referring to previous literature [10,11], the enhanced photocatalytic activity of ZnO/TiO_2 may be mainly attributed to the presence of ZnO/TiO_2 surface hetero-structure, which promotes the separation of the photogenerated electrons and holes and thus decreases the electron–hole pair recombination rate. These results demonstrated that ZnO thickness suitable for this structure about 300 nm. In addition, the increase of photocatalytic performance of them based on the rough surface of one is uniform (Fig. 7) and the shift of the absorption edge towards the visible light region expanding the absorption region of the thin film. With using UVA lamp has a wavelength range of 365 nm – 400 nm thus catalytic features of the ZnO/TiO_2 (HNs) film is higher than TiO_2 thin film. Fig. 7 also shows that ZnO/TiO_2 (HNs) film fabricated by DC sputtering magnetron obviously has two-layer structure, TiO_2 film above has uniform surface and particles in film have small size.

Table 2 and Fig. 8 show that the anti - Ecoli bacteria ability of ZnO/TiO_2 HNs film is better than TiO_2 single film after 60 min min illumination UVA. In particular, the M8 film had the highest anti - Ecoli bacteria ability. After 60 min illumination UVA, the number of colonies counted on agar plates of M8 film is zero while the others show the survival of Ecoli bacteria. This result shows similar photocatalytic degradation of MB solution above which the M8 film is the best.

Table 2. The number of colonies of E. coli bacteria counted on the agar plate of the samples (under UAV, irradiated for 60 min)

Agar plates:	No sample	M2 (TiO_2)	M6 (ZnO/TiO_2)	M7 (ZnO/TiO_2)	M8 (ZnO/TiO_2)	M9 (ZnO/TiO_2)
The number of colonies counted on agar plates	236	53	40	26	0	17

IV. CONCLUSIONS

The heterogeneous nanostructured ZnO/TiO_2(HNs) films were successfully deposited by Dc-sputtering. The films exhibited enhanced photocatalytic performance and anti - Ecoli bacteria ability. The ZnO/TiO_2 film were made at the following conditions: for ZnO: h = 6 cm, p = 1.20 Pa, P =56 W, d = 300 nm; for TiO_2: h= 5 cm, p = 1.73 Pa), P = 120 W, d = 460 nm).

The enhancement in photocatalytic performance and anti - Ecoli bacteria ability of the ZnO/TiO_2 films was explained due to the reduction of the electron - hole recombination and the red shift of absorption edge of the HNs films.

REFERENCES

[1] M. R. Hoffmann, S.T. Martin, W.Y. Choi, and D.W. Bahnemann. *Chem. Rev.* **95** (1995) 69–96
[2] J. Yang, D. Li, X. Wang, X. J. Yang, and L. D. Lu, *J. Solid State Chem.***165** (2002) 193–198.

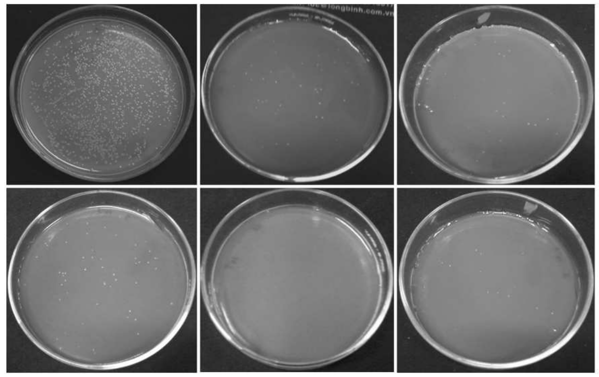

Fig. 8. Images of agar plates show colonies formed on them after the films illuminated UV light in 60 minutes

[3] L. Y. Shi, C. Z. Li, H. C. Gu, and D. Y. Fang, *Mater. Chem. Phys.* **62** (2000) 62–67.
[4] X. W. Zhang, and L. C. Lei, *Appl Surf Sci.* **254** (2008) 2406–2412.
[5] C. Wang, J. , Zhao, X. Wang, B. Mai, G. Sheng, P. Peng, and J. Fu. *Appl. Catal., B: Environ.* **39** (2002) 269–279.
[6] J. L. Li, L. Li, Y. Yu, Y. W. Tang, H. L. Li, and F. P. Du. *Electrochem. Comm.* **6** (2004) 940–943.
[7] M. Long, W. Cai, J. Cai, B. Zhou, X. Chai, and Y. Wu. *J Phys. Chem.* **B110**(41) (2006) 20211–20216.
[8] Liao, Huang, Yu, Su, and Yuan. *J. Photochem Photobiol, A: Chem.* **168** (2004) 7-13.
[9] Liao, D. L. Badour, and B.Q. Liao. *J. Photochem. Photobio., A: Chem.* **194** (2008) 11–19.
[10] Yamaguchi, Y. , Yamazaki, M. , Yoshihara, S. , and Shirakashi, J. *Electroanal. Chem.* **442** (1997) 1–3.
[11] Maolin Zhang, Taicheng An, Xiaolu Liu, Xiaohong Hu, Guoying Sheng, and Jiamo Fu. *Materials Letters* **64** (2010) 1883–1886.
[12] Vu Thi Hanh Thu, Nguyen Huu Chi, Le Van Hieu, Huynh Thanh Dat, Nguyen Quynh Giao, and Pham Kim Ngoc. *Journal of Scientific and Technological Development of VNU-HCM*, **11** (2008) 43 – 50.
[13] Vu Thi Hanh Thu, Nguyen Huu Chi, Le Van Hieu, Huynh Thanh Dat, and Pham Kim Ngoc. *Journal of Scientific and Technological Development of VNU-HCMC* **12**(3) (2009) 16 – 21.
[14] Arturo I Martınez, Dwight R Acosta1 and Alcides A Lopez. *Instituto de Fısica, Mexico DF, Mexico, J. Phys. Condens. Matter.* **16** (2004), S2335 – S2344
[15] K. Madhusudan Reddy, Sunkara V. Manorama, and A. Ramachandra Reddy, *Materials Chemistry and Physics* **78** (2002) 239–245
[16] Vu Thi Hanh Thu, Nguyen Huu Chi, Le Van Hieu, Dinh Cong Truong, and Pham Kim Ngoc. *Comm. Phys.* **18** (4) (2008) 206 - 212.
[17] Jackie Reynolds, and Mark Farinha, *Richland College*, (2005) pp 1-10.
[18] L. Caballero, K. A. Whitehead, N. S. Allen, and J. Verran. *Journal of Photochemistry and Photobiology A: Chemistry* **202** (2009) 92–98
[19] Kayano Sunada, Toshiya Watanabe, and Kazuhito Hashimoto. *Journal of Photochemistry and Photobiology A: Chemistry* **156** (2003) 227–233

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