EFFECT OF Ni-DOPED ON SURFACE OF TITANIUMDIOXIDE THIN FILM

K. UBOLCHOLLAKHAT [a,*], L. SIKONG[b], W. SANGCHAY[c]

[a]*Department of Physics, Faculty of Science, Thaksin University (TSU), Pattalung, Thailand.*

[b]*Department of Mining and Materials Engineering, Faculty of Engineering, Prince of Songkla University (PSU), Songkhla, Thailand.*

[c]*Faculty of Industrial Technology, SongkhlaRajabhat University, Songkhla, 90000, Thailand.*

TiO_2 thin film was prepared by sol-gel method and dip coating on glass fiber roving. The structure of TiO_2 thin film was determined by XRD. XPS analysis confirmed that Ti and Ni are present on the surface of the catalysts and AFM showed morphologies and roughness of TiO_2 thin film. The result showed anatase phase and $Ni(OH)_2$ structure on Ni doped TiO_2 films. Ni doped effect to porous structures of TiO_2 thin film. The roughness increase with increase the volume of Ni and Ni doping is effect to the roughness and the cracking on TiO_2 surface.

(Received March 20, 2015; Accepted December 28, 2015)

*Keywords:*Photocatalyst, Ni-doped TiO_2, Porous film, Thinfilm

1. Introduction

The air pollution can be found both outdoors and indoors. Pollutants can be trapped inside buildings, causing indoor pollution. And indoor air pollution is emitted from furniture, electrical appliances, gas combustion. The indoor environment is important in human health, because people generally living indoor more than 80% of their time. Therefore, air purification process is required to reduce or remove the hazardous organic matter and microbial from air. Photocatalytic oxidation is a new technique for the reduction of volatile organic compounds of indoor air. This process is performed by activation of photocatalyst using ultraviolet or visible light to produce primarily hydroxyl and superoxide radicals which are the active sites on TiO_2 surfaces for oxidizing volatile organic compounds of indoor air to the final products as water vapour and carbon dioxide [1]. Titanium dioxide (TiO_2) is an excellent photocatalyst. It is widely used as a photocatalyst because it is relatively highly efficient, cheap, non-toxic, chemically and biologically inert and photo stable. TiO_2 in the anatase phase has been used as an excellent photocatalyst and it is well application for purification [2-3]. However, the efficiency of TiO_2 photocatalytic is low for its application. The effective ways to improve the TiO_2 photocatalytic activity such as improving photocatalytic activity [4-5] and increasing surface activation sites [6]. Many researchers have the studied the behaviour of introduced metal ions into TiO_2 such as Ag [7-8] for photocatalytic activity efficiency and added organic compound into TiO_2 such as TEA [9] and PEG [10] for increasing surface. However, organic compounds are effect to hindrance anatase-rutile phase transformation. The doped Ni may improve the photocatalytic activity of TiO_2, which is considered to be a probable electron acceptor in TiO_2 thin film and improving roughness of TiO_2 film so in this study we interested TiO_2 doped with transition metallic Ni was synthesized by sol-gel method for modified surface structure and surface area of TiO_2 film.

[*]Corresponding author: kornkanok.ubon@yahoo.co.th

2. Experimental

2.1 Raw materials

Materials used for synthesis of pure TiO_2 and TiO_2-Ni composite films were titanium (IV) isopropoxide (99%) (Fluka Sigma-Aldrich), Nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, Wako), Absolute ethanol (RCI Labscan) and nitric acid were both AR grade

2.2 Sample preparation

Pure TiO_2 and Ni doped TiO_2 films coated on glass slide were prepared by sol-gel method. Titanium (IV) isopropoxide of 10 ml was added into 100 ml ethanol (95%) and it was mixed with the solution prepared by dropping nickel nitrate in 50 ml ethanol. The pH of mixed solution was adjusted to about 5 and it was vigorously stirred at room temperature for 1h until sol was formed. Glass slide was coated with as prepared sol by dip coating and oven drying at 100 ˚C for 12 h before calcinations at 500 ˚C for 1h with a heating rate of 10 ˚C /min.

2.3 Characterization

Microstructure of TiO_2 composite thin films were determined from X-ray diffraction (XRD, RIGAKU TTRAX III, 18 kW, Japan glancing angle X-ray diffraction = 0.4). The data were taken in the range of 10-70 (2θ). The average crystallite size was determined from the X-ray diffraction pattern using Scherer's equation [13]. Structure of doping was determined by X-ray Photoelectron Spectroscopy (XPS, AXIS Ultra DLD, Kratos analytical Ltd.). The surface morphologies and surface roughness of pure TiO_2 and TiO_2 composites films coated on glass slide were observed by using atomic force microscope (AFM, SPA400, SEIKO).

3. Results and discussion

3.1 Characterization

The synthesis of pure TiO_2 and TiO_2 doped Ni films were prepared by sol-gel. The result showed that un-doped TiO_2 sol exhibited clear solution while as TiO_2-Ni showed light green solution because the raw material of Ni is $Ni(NO_3)_2 \cdot 6H_2O$ is change to $Ni(OH)_2$ which is yellowish. The XRDpattern of pure TiO_2 and TiO_2-Ni films are coated on glass slide and calcinaed at 500°C showed in Fig.1. The pure TiO_2 exhibit well crystallized anatase phase. XRD peak at $2\theta = 25°$ was anatase main peak of pure TiO_2. Whereas TiO_2 doped Ni exhibited lower crystallized anatase phase. This is interesting to note that the crystallization of anatase phase decrease with an increase Ni content.

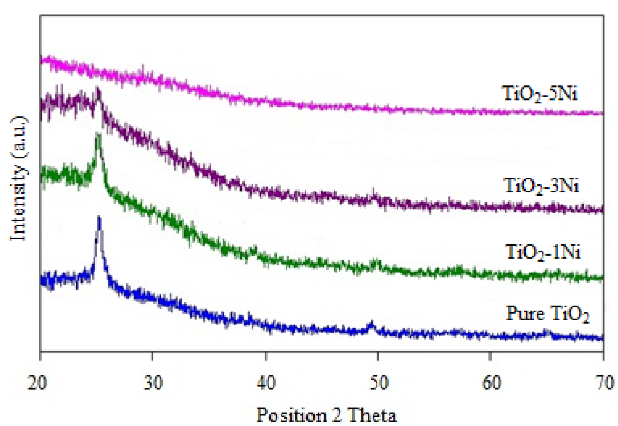

Fig. 1. XRD patterns of pure TiO_2 and Ni doped TiO_2 thin films.

The valance state and the spectra of pure TiO_2 film was examined by XPS analysis as shown in Fig.2.Ti $2p_{1/2}$ and Ti $2p_{3/2}$, peaks are observed at 464.1 eV. and 458.4 eV., respectively. The splitting between the Ti $2p_{1/2}$ and Ti $2p_{3/2}$ is 5.7 eV., demonstrating a normal state of Ti^{4+} ion in the catalyst [11].

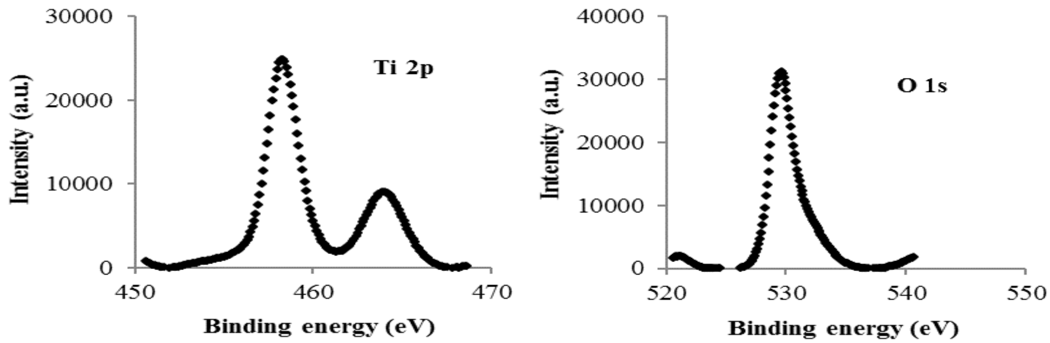

Fig. 2. The XPS spectra of pure TiO_2 film

Fig. 3.shows XPS spectra of Ti 2p, O 1s and Ni 2p spectrum of TiO_2-Ni. Ti 2p, Ti $2p_{3/2}$ and Ti $2p_{1/2}$, peaks are observed at 458.1 and 463.8 eV, respectively. The splitting between the Ti $2p_{1/2}$ and Ti $2p_{3/2}$ is 5.7 eV, demonstrating a normal state of Ti^{4+}ion in the catalyst [12]. The binding energies of O 1s is 529.4 eV is O^{2-} in TiO_2 (-Ti-O-Ti). The XPS spectrum of Ni showed at 855.3 eV for Ni $2p_{3/2}$ peak at 854.5 to 854.9 eV is NiO structure and then peak at 853.0 is $NiTiO_3$ nickel metal [13]. At 855.7 eV could be assigned to $Ni(OH)_2$ [14,15]. This result indicate that the surface of pure TiO_2 was covered with $Ni(OH)_2$ layer with a thickness less than about 3 nm. $Ni(OH)_2$ on the Ni surface formed as a consequence of the reaction between the metallic Ni on surface of TiO_2 and water in the air [16].

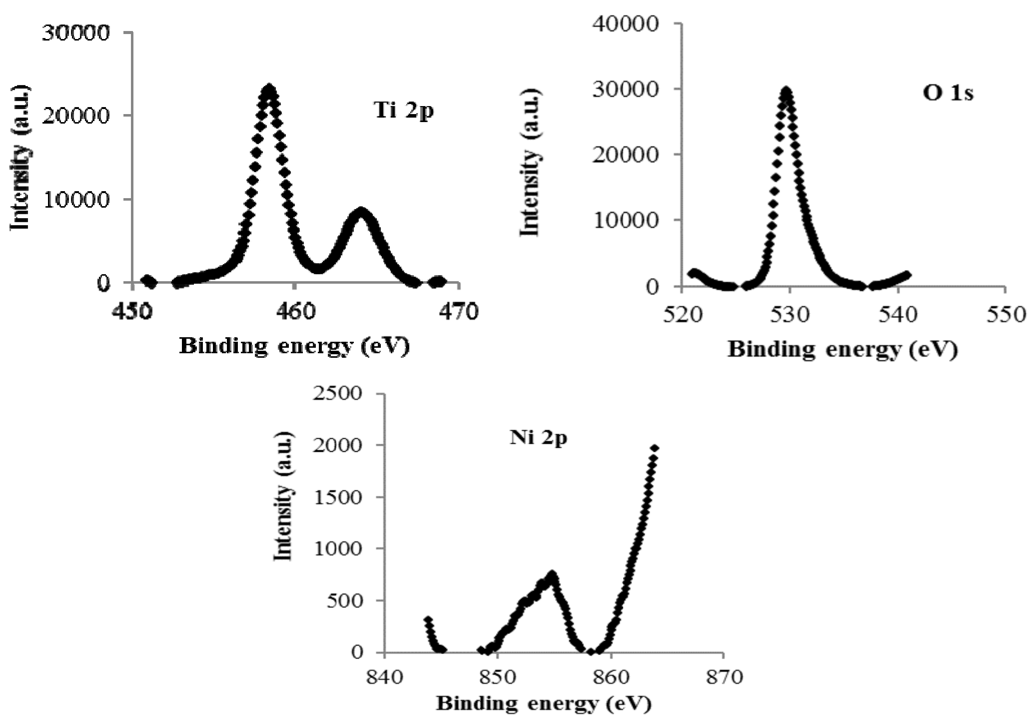

Fig. 3.The XPS spectra of Ni doped TiO_2 films.

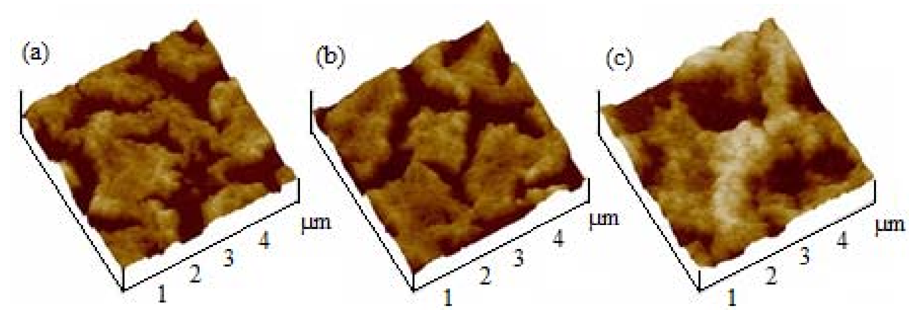

Fig. 4. AFM images of (a) TiO_2–1Ni (b) TiO_2–3Ni and (c) TiO_2–5Ni.

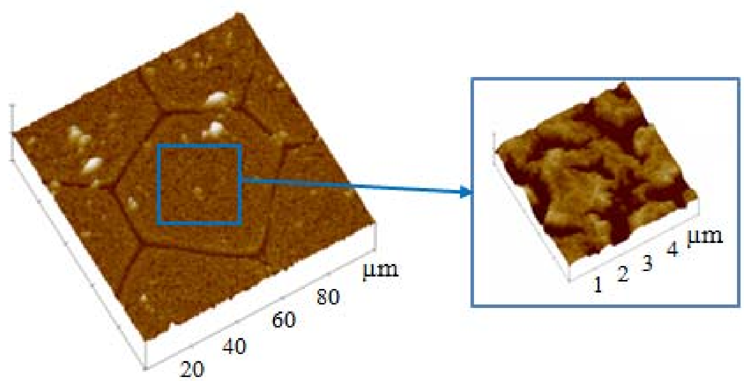

Fig. 5. AFM images of cracking of TiO_2-1Ni

AFM is used to characterize the change of surface morphology of Ni-doped TiO_2 films taken from three samples. The studied surfaces are equal to 5 × 5 µm in area. These porous film structures were clearly observed by AFM images as shown inFigure 4. It was found that TiO_2 doped Ni has high surface roughness and the roughness increase with increase nickel from 1-5 mol% showed as table1. Moreover Ni doped TiO_2 were prepared by sol-gel method and calcined at the temperature 500 ˚C. It observed that Ni substitution of the Ti sites forming nickel titanate ($NiTiO_3$) structure with initial cracking on TiO_2 surface showed as in Figure5.

4. Conclusion

The preparation of pure TiO_2 and Ni doped TiO_2 films were prepared by sol-gel method. The result showed that the structure of Ni doped TiO_2 exhibit lower crystallized anatase phase than pure TiO_2 because Ni hinder anatase phase transformation. The valance state is Ti^{4+} and the spectrum showed of pure TiO_2 are observed at 464.1eV (Ti $2p_{1/2}$) and 458.4 eV (Ti $2p_{3/2}$), respectively. The spectrum Ti $2p_{3/2}$ and Ti $2p_{1/2}$ of Ni doped TiO_2 is shift to lower energy than pure TiO_2 cause of Ni doping in TiO_2 structure. And the XPS spectrum of Ni showed at 855.3 eV for Ni $2p_{3/2}$ this result indicate that the $Ni(OH)_2$ structure. Moreover, It was found that TiO_2 doped Ni has high surface roughness and the roughness increase with increase nickel from1-5 mol%.

Acknowledgements

The authors thank The Department of Mining and Materials Engineering, Faculty of Engineering, Prince of Songkla University (PSU) and Department of Physics, Faculty of Science, Thaksin University (TSU)

References

[1] M. R Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemannt, Chem. Rev. **95**, 69 (1995).
[2] F. Shiraishi, Sh. Yamaguchi and Y. Ohbuchi, Chem. Eng. Sci.**58**, 929 (2003).
[3]Y.Ohko, Y. Nakamura, N. Negishi, S. Matsuzawa and K. Takeuchi, J. Photochem. Photobiol. A: Chem. **205**, 2 (2009).
[4] N. Riaza, F.K. Chong, B. K. Duttac, Z. B. Man, M. S. Khan and E. Nurlael, Chem. Eng. **185**, 108 (2012).
[5] A. Z.Jureka, E.Kowalska, J. W.Sobczakc, W.Lisowski, B.Ohtani,A.Zaleskaa, Appl. Catal. B: Env. **101**, 504 (2011).
[6] Y. A. Kim, J.H. Choi, J. Scott, K. Chiang and R. Amal, Powder. Tech. **180**, 79 (2008).
[7] A.A. Cavalheiro, J.C. Bruno, M.J. Saeki, J.P.S. Valente and A.O. Florentino, Thin Solid Films, **516**, 6240 (2008).
[8] K. Ubolchonlakat, L. Sikong, T. Tontai and F. Saito, Adv. Mater. Res. **150**, 1726 (2011).
[9] K. Ubolchonlakat, L. Sikong, and T. Tontai, J. Nanosci. Nanotechno.**10**, 7522 (2010).
[10] K. Ubolchonlakat, L. Sikong, T. Tontai and F. Saito, Pro. Eng.**32**, 656 (2012).
[11] H. M. Yadava, S.V. Otaria, R. A. Boharaa, S. S. Malic, S. H. Pawara and S. D. Delekara, J. Photochem. Photobiol. A: Chem.**294**, 130 (2014).
[12] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder and G.E. Muilenberg, Physical Electronics Division, USA,(1979).
[13] G.H. Yu, F.W. Zhu and C.L. Chai, Apply Physics A,**76**, 45 (2003).
[14] J.F. Moulder, W.F. Stickel, P.E. Sobol, K.D. Bomben, Physical Electronics, Inc., Minnesota (1995).
[15] M.T. Greiner, M.G. Helander, Z.-B. Wang, W.-M. Tang and Z.-H. Lu, J. Phys. Chem. **114**, 19777, (2010).
[16] H. O. Seo, J. K. Sima, K.-D. Kim, Y. D. Kima, D. C. Lim and S. H. Kim, Appl. Catal. A: Gen.**451**, 43 (2013).