

PHYSICAL CHARACTERIZATION OF Ni(II) DOPED TiO₂ NANOCRYSTAL BY SOL-GEL PROCESS

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ABSTRACT

Ni(II) doped titanium dioxide has been prepared by using sol-gel process. Ni(II) ion was incorporated into titanium dioxide by reacting Ni(II) chloride with titanium tetraisopropoxide (TTiP)-acetyl acetone mixture in isopropanol solvent. The effects of transition metal ion doping on the physical properties have been investigated. UV/Vis spectrophotometer, TGA-DTA, X-ray diffraction (XRD) and DR-UV/Vis were used to investigate the spectra absorption of nanosol, nanoparticle thermal transition, structure of crystal and band edge absorption, respectively. The results at addition of 5% Ni/Ti revealed that absorbance of nanosol increased from 0.811 (λ_{max} : 342 nm) to 2.283 (λ_{max} : 350 nm). The crystallization temperature transition from anatase to rutile decreased from 500 °C to 475 °C. The particle size increased from 18.51 nm to 20.35 nm, while the band gap energy (E_g) decreased from 2.73 eV to 2.51 eV.

Keywords: TiO₂ photocatalyst, Ni(II) doped, sol-gel

INTRODUCTION

Photocatalytic technology has been applied widely in various fields such as environmental purification, anti-bacterial uses and self cleaning. Titanium dioxide (TiO₂) is well known as chemically stable and harmless photocatalyst. Because of these robust photocatalytic properties, application of TiO₂ spreads increasingly [1]. However, ultraviolet-light irradiation is necessary to fulfill its photocatalytic functions, so TiO₂ photocatalyst holds limitation of application range and effective use of light. The effective photoexcitation of TiO₂ semiconductor particles requires application of light with energy equal to or higher than its band gap energy (E_g). For anatase the band gap energy is 3.2 eV and for rutile is 3.02 eV, which correspond to the absorption thresholds of 380 nm and 410 nm for the two polymorphs of titania, respectively. In order to improve the photocatalytic efficiency and to expand the application fields, development of visible-light or natural sunlight responsive photocatalyst is demanded. Currently, visible light photocatalytic materials can be surmounted by modifying the surface of the semiconductor, by using transition metals or non-metallic elements doped into TiO₂, by preparing semiconductors from noble metal oxides with narrow band gap or composite

semiconductors, and by surface sensitization with adsorbed dyes [2].

Transition metal ions are commonly employed as dopants due to their strong absorption of visible light and their similar ionic radius to the parent titanium ion. Nickel is one of transition elements used to modify the titania surface. The effects of Ni²⁺ on the photocatalytic properties of TiO₂ have been investigated by several authors [3,4]. However, as far as we know Ni doped TiO₂ systems is sparsely studied compared to the other areas of transition metal doping, so do the information of their physical properties. In this paper, we want to report the preparation of Ni(II) doped TiO₂ by sol-gel process and their physical properties. Ni(II) was selected as dopant because Ni²⁺ has similar radius as Ti⁴⁺ (the effective ionic radii are 72 pm and 68 pm, respectively). Ni(II) can also form octahedral coordination as Ti⁴⁺. The concentration of the beneficial transition metal should be very small. Large concentrations will be detrimental. It has been argued that although impurity energy level would lead to visible light response for wide band gap semiconductor photocatalyst, it could also act as recombination centers leading to increasing recombination of e⁻/h⁺.

In the present work, metal doping has been done during the sol-gel process. Sol-gel method was chosen since it leads to the greatest possible homogeneous

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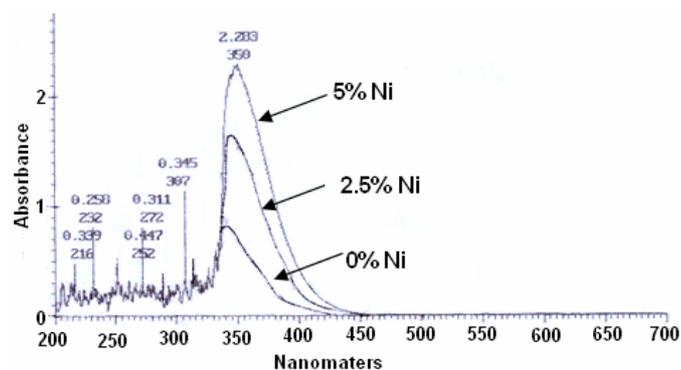


Fig 1. UV/Vis spectra of Ni(II) doped TiO_2 nanosols

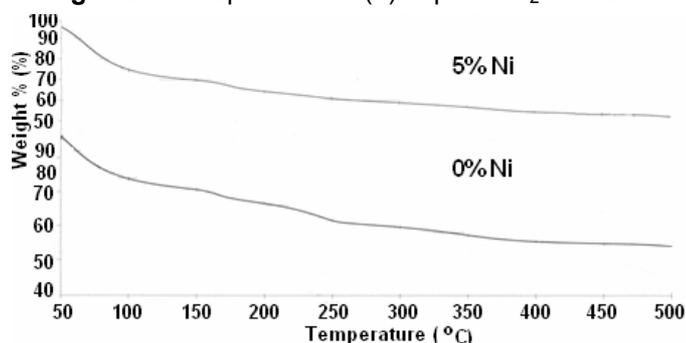


Fig 2. TGA curves of undoped and 5% Ni(II) doped TiO_2

Table 1. The spectra absorption of nanosol Ni doped TiO_2

TiO_2	λ max (nm)	absorbance
undoped	342	0.811
2.5% Ni doped	345	1.563
5% Ni-doped	350	2.283

distribution of the dopant in the host matrix, providing good stoichiometry control and ease of processing [5]. It will be shown that Ni(II) doping into TiO_2 crystal affects the absorption spectra of titania nanosol, anatase to rutile temperature phase transformation, particle size and the band gap energy of the resulted photocatalyst.

EXPERIMENTAL SECTION

Materials

All chemicals were analytical grade and used without further purification. Titanium tetraisopropoxide (TTiP) was purchased from Aldrich, acetylacetone (Acac-H), isopropanol, hydrochloric acid (HCl), nickel (II) dichloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) were obtained from Merck. The solvent used was deionized water.

Instrumentation

UV/Vis spectra of nanosol was monitored using a UV/Vis spectrophotometer (Milton Roy, Spectronic 3000

Array) in the wavelength region of 200–700 nm. Thermal analysis was carried out on a thermal gravimetric analyzer/TGA and differential thermal analyzer/DTA (Shimadzu, TGA/DTA-60) under the flow of N_2 atmosphere (60 mL/min) at a heating rate of $20^\circ\text{C}/\text{min}$ from 50°C to 500°C . The X-ray diffraction pattern of the resulted materials were obtained using an XRD (Rigaku D MAX III VC) of Ni-filtered Cu K α radiation (λ : 1.54056 \AA) at a scan rate of $4^\circ/\text{min}$. Reflectance and absorbance of powder photocatalyst spectra were recorded by an SR UV/Vis spectrophotometer (Pharma Spec. Shimadzu 1700) in the wavelength region of 300–800 nm.

Procedure

Preparation of Ni-doped TiO_2 Powder

Preparation of Ni-doped TiO_2 powder by sol-gel process at room temperature was adopted from Maeda et al. [6] with several change and modification. The molar ratio of each reagent was TTiP: isopropanol: acac-H: HCl: H_2O : Ni = 1: 20: 2: 0.5: 3.2: (0, 0.025, and 0.05). The sol solution was prepared as follows; the mixture of TTiP, acac-H and half volume of isopropanol was stirred for 1 h. Nickel salt was dissolved in the mixture of deionized water, HCl and the other half volume of isopropanol. The nickel salt solution was then stirred for 1 h. Titania sols and nickel salt solutions were mixed and stirred for at least 12 h. Sol solutions were dried at 80°C for 6 h and then calcined at 500°C for 1 h to obtain photocatalyst powder.

RESULT AND DISCUSSION

Nanosol properties

Hydrolysis of TTiP resulted in a polydispersed sol (nanosol) composed of 10–20 nm particles [7]. The UV/Vis spectra of nanosol was monitored to studied the effect of Ni(II) concentration in its nanosol spectra. The spectra were presented in Fig. 1.

Data from Fig. 1 indicates that all TiO_2 samples behave similarly. The addition of 5% Ni/Ti resulted in larger red shifting of the maximum of the absorption wavelength (λ_{max}) and its absorbance. This phenomena is possibly because of induced photoactive transitions of Ni^{2+} in the nanosols. Table 1 shows the electronic absorption data of the Ni(II) doped and undoped TiO_2 nanosols.

Thermal properties

The thermogravimetric analysis (TGA) was done to study the weight loss of the pure TiO_2 compare to Ni-doped TiO_2 powder. Fig. 2 shows thermogram of

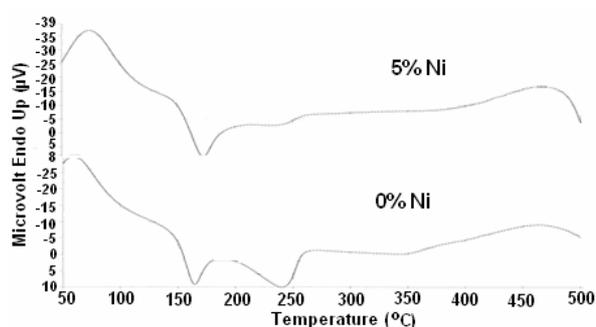
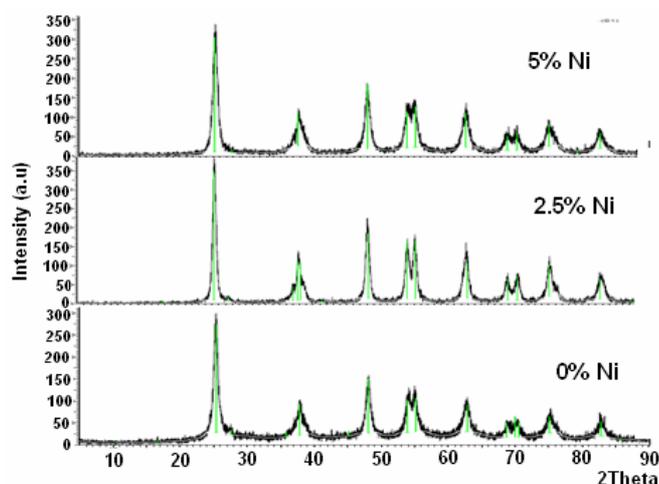
Table 2. The lattice parameters of undoped and Ni-doped TiO₂

TiO ₂	2θ	hkl	d (Å)	a (Å) ^{a)}	c (Å) ^{a)}	Particle size (nm) ^{b)}	Crystal phase ^{c)}
un doped	25.401	[101]	3.503	3.769	9.448	18.510	93.98% Anatase 6.02% Rutile
	37.899	[004]	2.372				
	48.137	[200]	1.888				
2.5% Ni doped	25.267	[101]	3.521	3.789	9.528	18.505	95.28% Anatase 4.72% Rutile
	37.725	[004]	2.328				
	48.264	[200]	1.884				
5% Ni-doped	25.258	[101]	3.523	3.791	9.528	20.355	96.35% Anatase 3.65% Rutile
	37.723	[004]	2.382				
	47.990	[200]	1.894				

^{a)} calculated with Bragg's equation with tetragonal system [14]

^{b)} calculated with Scherrer equation [14]

^{c)} calculated with Spur-Myers equation [14]

**Fig 3.** DTA curves of undoped and 5% Ni(II) doped TiO₂**Fig 4.** XRD patterns of Ni(II)-doped and undoped TiO₂ after calcination at 500 °C

undoped and 5% Ni/Ti doped TiO₂. The total weight loss in the whole temperature range was 40% for undoped and 45% for 5% Ni/Ti doped. Both thermogram showed that significant decrease of weight occurred at temperature ranging from 50 to 200 °C due to the desorption of physisorbed water (T_{bp} :100 °C), Acac-H (T_{bp} :138 °C) and isopropanol (T_{bp} :82 °C). Relatively small decrease of weight after 200–350 °C was possibly resulted from desorption of unhydrolyzed precursor remained in TiO₂ [8]. From temperature 350 to 500 °C, there is much slower of about 5 and 8% weight loss of

the undoped and Ni doped TiO₂, respectively due to crystallization of these nanoparticles.

The DTA curve in Fig. 3, showed endothermic peaks up to 150 °C due to the desorption of the physisorbed water and solvent. The relatively small endothermic peak at 250 °C is possibly resulted from desorption of unhydrolyzed TTIp. This curve also shows a small exothermic peak at about 350 °C, which is possibly because of the phase transformation from amorphous to anatase. The DTA curve also shows a significant exothermic peak start at about 500 °C, which is possibly due to the phase transformation from anatase to rutile crystalline phase of TiO₂ and this result is consistent with the XRD data. The temperature transformation crystallization from anatase to rutile of Ni(II) doped TiO₂ was ~475 °C slightly lower than that of undoped TiO₂ (~500 °C). Crisan et al. [9] reported that the exothermic effect without mass loss, at about 675 °C was assigned for transformation of crystal phase from anatase to rutile.

Lattice parameter characterization

The crystalline phase and composition of Ni-doped TiO₂ were studied by X-ray powder diffraction (XRD). Fig. 4 showed XRD patterns for Ni-doped TiO₂ after calcination at 500 °C. The particle size of the prepared samples and crystal phase were determined from XRD data using Scherrer's formula and Spur-Myers equation respectively, as shown in Table 2. The XRD pattern of 2.5% Ni doped TiO₂ shows that the peak intensity of anatase increases and the width of the [101] diffraction peak of anatase phase ($2\theta = 25^\circ\text{--}26^\circ$) becomes narrower. This suggests that the particle size of Ni-doped TiO₂ nanoparticles increases by doping Ni(II) at certain concentration.

The lattice parameters of doped and undoped TiO₂ are listed in Table 2. It is shown that Ni(II)-doped TiO₂ resulted in the increased average particle size crystallite and crystal lattices. Hwang et al. [3] and Jing et al. [10] reported that the incorporation of Ni induced the expansion distortion of titania lattice and consequently

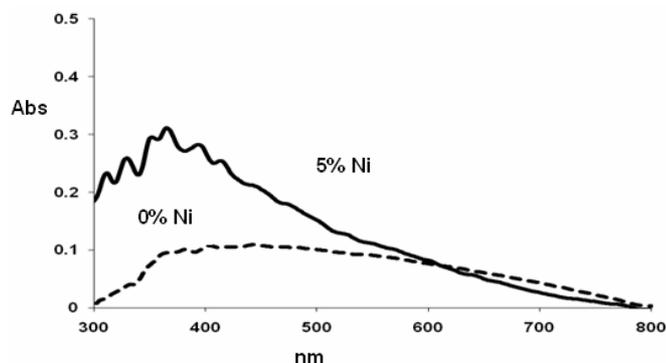


Fig 5. UV-Vis absorption spectra of Ni doped and undoped TiO₂

resulted in an enlargement of the average particle size since the radius of Ni²⁺ (72pm) is higher than Ti⁴⁺ (68 pm).

Ni²⁺ would increase the number of oxygen vacancies in the TiO₂ crystal structure. These oxygen vacancies are responsible for the enhancement of the transformation from anatase to rutile. Therefore Ni doped TiO₂ should have increased ratio of rutile to anatase, however our results are contrary. This is possibly due to the calcination temperature at 500 °C. Crisan et al. [9] reported that transformation from anatase to rutile assigned at temperature about 675 °C.

Band Edge Characterization

The UV-Vis absorption spectra in Fig. 5 showed that both the undoped and 5% Ni doped TiO₂ are photoactive under visible light irradiation. Usually, band gap energy (E_g) values reported in the literature for anatase are around 3.2 eV, whilst 3.0 eV for pure rutile phase [2]. In this work, the addition of 5% mol Ni(II) in TiO₂ resulted slightly lower band gap and higher absorption than the undoped TiO₂. The band gap of the samples was determined by the equation of $E_g = 1239.8 / \lambda$ [11]; where E_g is the band gap (eV) and λ (nm) is the wavelength of the absorption edge in the spectrum. The absorption edge of the undoped TiO₂ occurs at 453 nm, and its band gap energy is estimated about 2.73 eV. While the absorption edge of the 5% Ni(II) doped TiO₂ is 495 nm, and its corresponding band gap energy is estimated of 2.51 eV.

Mu et al. [12] reported that a comparison of optical energy gap between undoped TiO₂ and Ni-doped TiO₂ thin films by using chemical solution deposition shows an obvious red shift in Ni doped TiO₂ (band gap of undoped is 3.67 eV and 15% Ni doped is 3.36 eV). Kim et al. [13] with computer simulation reported that when Ni²⁺ atom was substituted for Ti⁴⁺ site of TiO₂ lattice, two additional unoccupied 3d states appeared as defect states in band gap, and occupied 3d states were

hybridized with oxygen 2p states. From the calculation of band decomposed charge density and density of states, it was found that the lower defect state (D1), a Ni 3d-orbital, was hybridized with unoccupied oxygen 2p states and the higher one (D2), localized 3d-orbital of Ni, was located at the middle of band gap. Carp et al. [5] reported that substitution of Ti⁴⁺ by dⁿ metallic ions in the TiO₂ lattice creates allowed energy states in the band gap of TiO₂, which may induce photoactive transitions in the visible light, due to an excitation of an electron from this energy level into TiO₂ conduction band.

CONCLUSION

Ni(II) doped TiO₂ nanoparticles exhibiting photoactive absorption under visible light irradiation were successfully prepared by sol-gel technique followed by calcination at 500 °C. Clearly, concentration of Ni(II) plays a significant role in the spectra absorption of nanosol, formation of the crystal structure, particle size and band edge absorption. Addition of 5% Ni/Ti revealed that absorbance of the corresponding nanosol spectra increased from 0.811 (λ_{max}: 342 nm) to 2.283 (λ_{max}: 350 nm). Crystallization temperature from anatase to rutile decreased from 500 °C to 475 °C. The particle size increased from 18.51 nm to 20.35 nm, while the band gap energy decreased from 2.73 eV to 2.51 eV.

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REFERENCES

1. Fujishima, A., Hashimoto, K. and Watanabe, T., 1996, *TiO₂ Photocatalysis Fundamentals and Applications*, BKC inc., Tokyo.
2. Linsebigler, A.L., Lu, G., and Yates, J.T., 1995, *Chem. Rev.*, 95, 735–758.
3. Hwang, K.S., Jeong, J.H., Ahn, J.H., and Kim, B.H., 2006, *Ceram. Int.*, 32, 935–937.
4. Wilke, K., and Breuer, H.D., 1999, *J. Photochem. Photobiol. A*, 121, 5, 49–53.
5. Carp, O., Huisman, C.L., and Reller, A., 2004, *Prog. Solid State Chem.*, 32, 1-2, 33–177.
6. Maeda, M., and Yamada, T., 2007, *J. Phys. Conf. Ser.*, 61, 755–759.
7. Brinker, C.J., and Scherer, G.W., 1990, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, United Kingdom Edition.

8. Huang, Y.U., Xuxu, Z., Zhongyi, Y., Feng, T., Beibei, F., and Keshan, H., 2007, *Chin. J. Chem. Eng.*, 15, 6, 802–807.
9. Crisan, M., Jitianu, A., Crisan, D., Balasoiu, M., Dragan, N., and Zaharescu, M., 2000, *J. Optoelectron Adv. Mater.*, 2, 4, 339–344.
10. Jing, D., Zhang, Y., and Guo, L., 2005, *Chem. Phys. Lett.*, 415, 1-3, 74–78.
11. Skoog, D.A., and West, D.M., 1980, *Principles of Instrumental Analysis*, 2nd ed., Saunders College.
12. Lim, Y-M., Jeong, J-H., An, K-H., Jeon, Y-S., Jeon, K-O., Hwang, K-S., and Kim, B-H., 2005, *J. Ceram. Process. Res.*, 6, 4, 302–304.
13. Kim, Y.S., Chung, Y.C., and Lee, K.S., 2006, *J Electroceram.*, 17, 2-4, 951–953.
14. Cullity, B.D., and Stock, S.R., 2001, *Elements of X-Ray Diffraction*, 3rd ed., Prentice Hall Inc.