

## PHOTOCATALYTIC DEGRADATION OF FORMIC ACID INAQUEOUS WITH Ni DOPED TiO<sub>2</sub> COATED ON SILICAGEL

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### ABSTRACT

Formic acid (FA) photocatalytic degradation using nickel doped TiO<sub>2</sub> (Ni-TiO<sub>2</sub>) coated on silica grain (Ni-TiO<sub>2</sub>/SiO<sub>2</sub>) by sol-gel method has been studied. Nickel with a different molar ratio as 0.2, 0.4, and 0.8 % mole was used in this study. Samples were characterized by XRD, SEM, and UV-vis spectroscopy. Conditions such as dark, ultraviolet-visible and visible light were performed to assess the photocatalytic ability of Ni-TiO<sub>2</sub>/SiO<sub>2</sub>. The results showed that, catalyst samples had uniform nanosize, anatase crystalline structure and the band-gap energy of Ni-TiO<sub>2</sub>/SiO<sub>2</sub> was lower than that of TiO<sub>2</sub>/SiO<sub>2</sub> sample. The highest photocatalyst activities were obtained at 0.2 % mol of Ni for both irradiations. The FA concentration was not changed in the dark condition. Under ultraviolet-visible irradiation, FA concentration decreased from 10<sup>-4</sup> mM to 2.10<sup>-5</sup>, 7.10<sup>-5</sup> and 9.10<sup>-5</sup> mM with 0.2, 0.4 and 0.8 % mole of Ni, respectively. With visible light condition, FA concentration decreased from 10<sup>-4</sup> mM to 7.10<sup>-5</sup> mM when Ni dopant amount was 0.2 % mole. Change in FA concentration was negligible with 0.4 and 0.8 % mole of Ni dopant amount. It proved that the photocatalytic activity of Ni-TiO<sub>2</sub>/SiO<sub>2</sub> under visible light irradiation was generated by doping a small amount of nickel into TiO<sub>2</sub>. However, under visible light irradiation with 420 nm filter, FA photodegradation of Ni/TiO<sub>2</sub>/SiO<sub>2</sub> increases when Ni dopant content increases from 0 % mole to 0.8 % mole.

*Keywords:* TiO<sub>2</sub>, Ni doping, photocatalyst degradation, formic acid, UV, visible.

### 1. INTRODUCTION

Photodegradation is one of the most effective processes of advanced treatment due to high performance, high selectivity, and simple implementation process. Moreover, photodegradation can destruct organics and create harmless end products such as carbon dioxide, hydrogen oxide and other inorganic ions. In 1972, TiO<sub>2</sub> material has been discovered as exhibiting the photocatalyst characteristic by Fujishima and Honda [1]. TiO<sub>2</sub> semiconductor photocatalyst is

stable, non-corrosive, eco-friendly and of low cost production [2]. However, with a band gap of 3.2 eV, TiO<sub>2</sub> is only active under UV light ( $\lambda < 387$  nm) which only accounts for about 4 % of the solar energy while the visible light contributes about 50 % [2]. In this regard, lot of strategies has been developed to extend the photoresponse of TiO<sub>2</sub> onto the visible region of the spectrum by doping of suitable foreign ions into TiO<sub>2</sub> [3]. The suitable ions are non-metal ions (N, S, P, C) [4 - 6], or metal ions (transition metals, rare earth metals, noble metals). Doping transition metal ions (Fe<sup>3+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> etc) into TiO<sub>2</sub> can decrease electron - hole recombination rate, the band gap of TiO<sub>2</sub> and shift its optical response from UV to the visible light region [7 - 9]. Among the transition metal ions, Ni<sup>2+</sup> has been found to be a more efficient dopant for TiO<sub>2</sub> because it has enhanced the photocatalytic activity of semiconductor photocatalysts [10]. Moreover, nickel is proposed because of its much relative cost-effectiveness [11]. However, metal dopant content is important factor that affects the photocatalytic ability of catalyst. At high metal dopant level, the doping became detrimental to the photocatalytic process, because the excessive oxygen vacancies and metal species can become the recombination centers of electron - hole, hence reducing the photocatalytic efficiency of the catalyst [12]. As Silicagel (SiO<sub>2</sub>) is one of the materials used as the carrier thanks to large surface area and high absorption ability, it is suitable for coating TiO<sub>2</sub> with a size of 20-30 nm by sol-gel method. Several studies for synthesis of photocatalyst material have been presented, including the methods such as impregnation, sol-gel and co-precipitation. The sol-gel process is one of the widely used methods for fabricating nanostructured materials due to its ability to form pure and homogenous products [13, 14]. The present investigation focused on using Ni doped TiO<sub>2</sub>/SiO<sub>2</sub> for photocatalytic degradation of formic acid (FA) in water. Formic acid is a useful model compound for studies of photocatalytic efficiency because (1) it has a simple molecular structure; (2) it is readily susceptible to photodegradation; and (3) it is highly soluble in water [15].

## 2. EXPERIMENTAL

### 2.1. Preparation of nanometer-sized Ni - doped TiO<sub>2</sub>

Ni ion doped TiO<sub>2</sub> were synthesized via sol-gel method. In this method, tetraisopropylorthotitanat Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> (TTIP) (Merck, > 98 %) was dissolved with acetylacetone C<sub>5</sub>H<sub>8</sub>O<sub>2</sub> (ACAC) (Merck, > 99 %) as chelating agent and absolute ethanol C<sub>2</sub>H<sub>6</sub>O (EtOH) (China, > 99.7 %) as solvent, according to the molar ratio 1: 1: 34, respectively to form a light yellowish clear solution, and stirred for 15 minutes at room temperature. Nickel ions were prepared separately by dissolving required content of nickel(II) nitrate Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (Merck, > 98 %) with suitable ethanol amount. Then, the light yellowish solution was added drop wise into nickel ion solution. The mixture was stirred for about 5 hours at room temperature. Silica gel with a diameter of about 1.7 - 4.0 mm provided by Fuji Silysia Chemical Ltd (Japan) was soaked in the sol solution for 60 minutes. A Ni-TiO<sub>2</sub>/SiO<sub>2</sub> sample was synthesized by drying sol at 105 °C and annealing at 500 °C for 3 hours. The molar ratio of Ni ion in the photocatalyst was varied from 0 to 0.8 mole%. Samples were denoted as Ni<sub>x</sub>-TiO<sub>2</sub>/SiO<sub>2</sub>, where x refers to mol% of dopant Ni. The crystallization of Ni-TiO<sub>2</sub>/SiO<sub>2</sub> was investigated using a X-ray diffractometer (Bruker D2 Phaser) with CuK $\alpha$  radiation. Their surface morphology and element analysis were characterized using scanning electron microscopy (SEM JSM 6010LA) with X-ray microanalysis. A spectrophotometer (Shimadzu UV-VIS-NIR Spectrometer UV-3600) was used to investigate the absorption properties of the material.

## 2.2. The formic acid photodegradation activity evaluation of Ni ion doped TiO<sub>2</sub>

Photocatalytic degradation experiments were carried out in a reaction system including two glass tube reactor (200 mm length, 7 mm internal diameter), two UV lamp (20 W BLB, Toshiba,  $\lambda_{\text{max}} = 352 \text{ nm}$ ) or fluorescent lamps (20 W FL, Toshiba FLR20SEX-N/M-H). The prepared 500 mL of  $10^{-4} \text{ M}$  formic acid were taken in a beaker and passed through the photocatalytic system. The flow rate was  $7.5 \text{ L.h}^{-1}$ . Samples were taken from the beaker at preset time intervals. The concentration of formic acid was measured by IC (Tosoh IC-2000), a TSK-gel Super-IC AZ, oven temperature of  $40^\circ\text{C}$ . The eluent was performed with  $3.4 \text{ mmol.L}^{-1} \text{ NaCO}_3$  and  $1.7 \text{ mmol.L}^{-1} \text{ NaHCO}_3$  (1/1), under a flow rate of  $0.8 \text{ mL.min}^{-1}$ .

## 3. RESULTS AND DISCUSSIONS

### 3.1. Structural analysis

The structures of Ni-TiO<sub>2</sub>/SiO<sub>2</sub> with different Ni doping contents (0, 0.2, 0.4, and 0.8 % mole) were characterized via XRD, whose patterns are shown in Figure 1. For all samples, there were typical diffraction peaks of anatase TiO<sub>2</sub> located at  $\theta = 25.28^\circ$ ,  $37.55^\circ$ ,  $48.14^\circ$  and  $54.21^\circ$  corresponding to planes  $\langle 101 \rangle$ ,  $\langle 004 \rangle$ ,  $\langle 200 \rangle$  and  $\langle 211 \rangle$ , respectively.

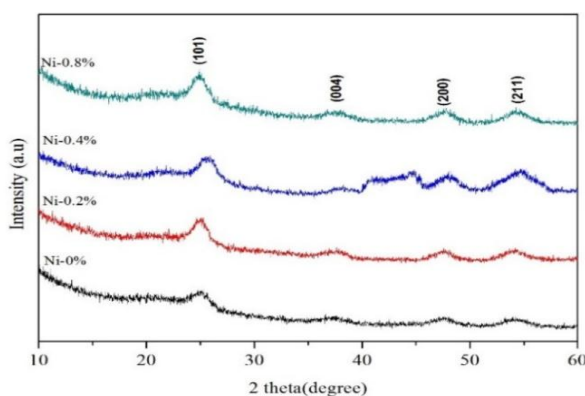


Figure 1. XRD patterns of Ni-TiO<sub>2</sub>/SiO<sub>2</sub> samples (Ni amount = 0, 0.2, 0.4, and 0.8 % mole).

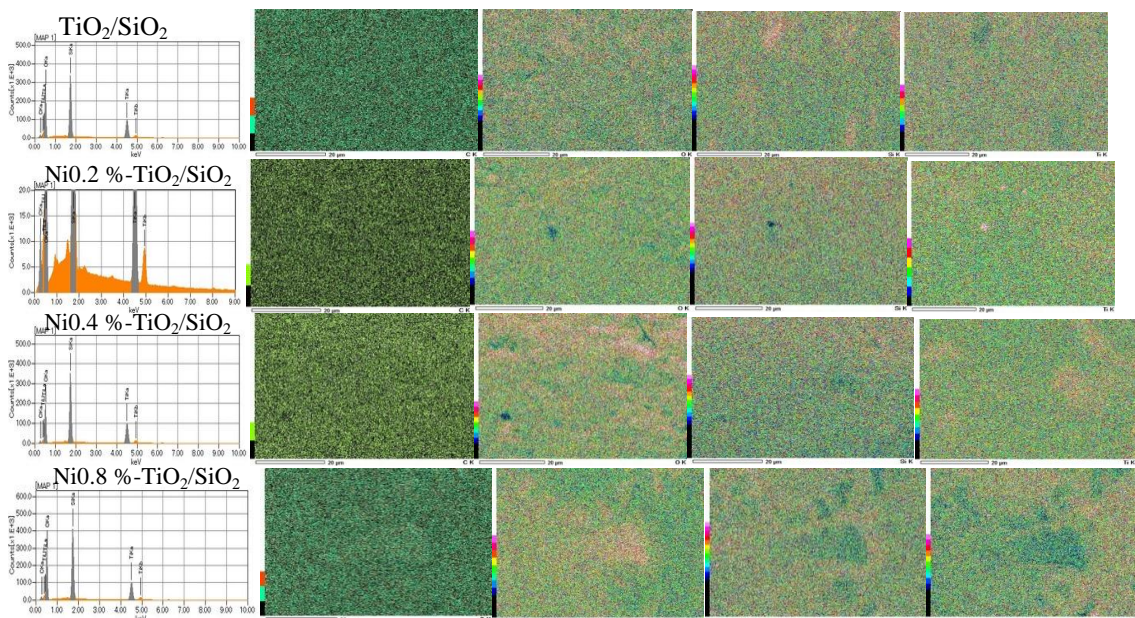


Figure 2. EDX spectra of Ni-TiO<sub>2</sub>/SiO<sub>2</sub> samples (Ni amount = 0, 0.2, 0.4, and 0.8 % mole).

The EDX spectra results of all synthesized materials are illustrated in Fig. 2, the sample surfaces were quite uniform in the 20  $\mu\text{m}$  range. It can be observed that Si, Ti and O were present on the surface of the samples but a Ni peak did not a in all of them. This could be due to the amount of Ni in the samples were too small to be detected when using the EDX method. Figure 3 depicts the absorption spectra of the prepared photocatalysts. It is known that the absorption of light influences photocatalytic activity significantly. The TiO<sub>2</sub>/SiO<sub>2</sub> sample shows an absorption edge at around 400 nm (3.11 eV). Doping with Ni has caused peak shifting at around 400-431 nm (visible region). The band gap energies of various photocatalysts are calculated from the Tauc Plots and the results are shown in Table 1. As can be seen, the absorption spectra of the Ni-doped TiO<sub>2</sub> samples had a red-shift that is larger than that of TiO<sub>2</sub>/SiO<sub>2</sub>, the absorption in the visible light region indicated the prepared samples could be visible-light-driven photocatalysts.

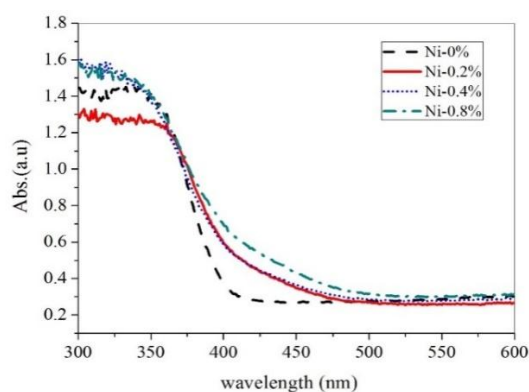


Figure 3. Absorption spectra of Ni-TiO<sub>2</sub>/SiO<sub>2</sub> samples (Ni amount = 0, 0.2, 0.4, and 0.8 % mole).

Table 1. The band gap energy of Ni - TiO<sub>2</sub>/SiO<sub>2</sub> with different concentrations of Ni.

Samples	$\lambda$ (nm)	Eg (eV)
TiO <sub>2</sub> /SiO <sub>2</sub>	400	3.11
Ni 0.2 % -TiO <sub>2</sub> /SiO <sub>2</sub>	414	3.00
Ni 0.4 % -TiO <sub>2</sub> /SiO <sub>2</sub>	419	2.96
Ni 0.8 % -TiO <sub>2</sub> /SiO <sub>2</sub>	431	2.88

### 3.2. Photodegradation of formic acid by Ni/TiO<sub>2</sub>/SiO<sub>2</sub>

The results of FA photodegradation by Ni/TiO<sub>2</sub>/SiO<sub>2</sub> are illustrated in Fig. 4 (a). Under dark condition, there was no change of FA concentration. Therefore, the dark adsorption of FA on the catalyst surface is not shown. When the UV lamp was switched on, FA concentration decreased strongly for TiO<sub>2</sub>/SiO<sub>2</sub> and Ni-0.2 %/TiO<sub>2</sub>/SiO<sub>2</sub> samples. When Ni dopant content was 0.4 and 0.8 %, FA concentration decreased slightly. Thus, photocatalytic ability of material decreases when Ni dopant content increases from 0.2 % to 0.8 %. Fig. 4 (b) showed that effect of Ni content to FA photodegradation under visible light condition. It was found that under visible light condition, FA photodegradation activity by Ni-0.4 %/TiO<sub>2</sub>/SiO<sub>2</sub> and Ni-0.8 %/TiO<sub>2</sub>/SiO<sub>2</sub> samples were negligible, photocatalytic efficiency was from 1.2 to 5.5 %. When Ni dopant content of 0.2 %, FA concentration decrease slightly, photocatalytic efficiency was 17 % after 14 hours circulation. For TiO<sub>2</sub>/SiO<sub>2</sub> sample, under visible light FA photodegradation ability of this material is the highest. This result may be explained that fluorescent light emits small levels of UV radiation [16] thus under fluorescent light, TiO<sub>2</sub>/SiO<sub>2</sub> have FA photocatalytic degradation ability. The result of FA photocatalytic degradation by Ni/TiO<sub>2</sub>/SiO<sub>2</sub> under visible light irradiation with 420 nm filter are showed in Fig. 4 (c). FA photodegradation activity of Ni/TiO<sub>2</sub>/SiO<sub>2</sub> samples increased with increasing Ni dopant content from 0 % mole to 0.8 % mole. Thus, doping Ni<sup>2+</sup> ion into TiO<sub>2</sub> to shift its optical response from UV to the visible light region.

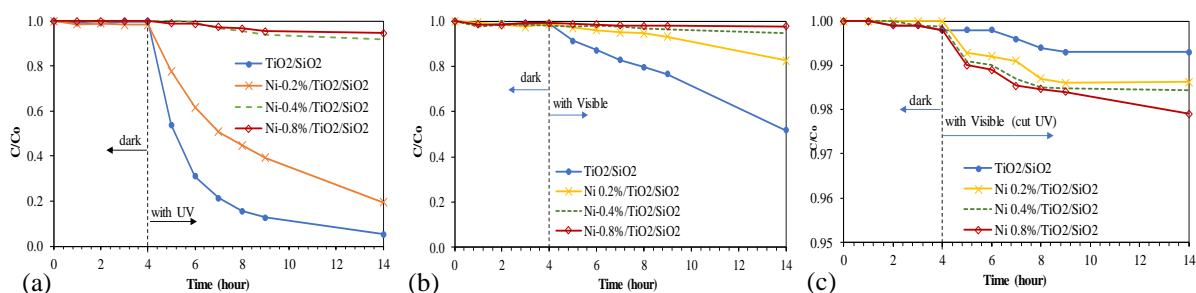


Figure 4. Effects of Ni dopant content on FA photodegradation under UV light (a), visible light (b), visible light (cut UV) (c).

#### 4. CONCLUSION

In the present investigation, a study has been carried out on the photocatalytic degradation of formic acid by Ni doped TiO<sub>2</sub>/SiO<sub>2</sub> nano-composite. The experiment results showed that catalyst samples had uniform nano size, anatase crystalline structure and the band-gap energy of Ni-TiO<sub>2</sub>/SiO<sub>2</sub> (2.88-3.00 eV) was lower than that of TiO<sub>2</sub>/SiO<sub>2</sub> sample (3.11 eV). The photocatalytic activity of Ni-doped TiO<sub>2</sub>/SiO<sub>2</sub> materials under UV or visible light irradiation depends on Ni content in the dopant and decreases with increasing Ni content from 0 % mole to 0.8 % mole. Under visible light irradiation with 420 nm filter, FA photodegradation of Ni/TiO<sub>2</sub>/SiO<sub>2</sub> increases when Ni dopant content increases from 0 % mole to 0.8 % mole.

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