Research Article

Photocatalytic Degradation of NO_x Using Ni-Containing TiO_2

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The nickel-containing titania was synthesized and employed in the photomineralization of NO_x . A nickel-modified titania photocatalyst was prepared by photodeposition method with using Degussa-P25 TiO_2 particle and nickel chloride as raw materials, respectively. The physical analyses were carried out using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), transmittance electron microscope (TEM), and photoluminescence spectroscopy (PL), to observe changes in particles following nickel modification. The results showed that Ni does not enter into the TiO_2 crystal lattice and is dispersed onto the TiO_2 surface uniformly. Ni improved the intensity of PL spectra with an appropriate Ni content on the TiO_2 surface. The modified titanium dioxide with 0.1 mol% of nickel exhibited two times the NO_x -removal activity of bare TiO_2 under ultraviolet illumination. The nickel content in this photodeposition process plays an important role in affinity to NO_x molecules, recombination rate of electron-hole pair, and content of active site on the TiO_2 surface and therefore affects the optical and photocatalytic properties.

1. Introduction

Since the discovery of the photoelectrochemical splitting of water using titanium dioxide electrodes [1–3], researchers have extensively studied semiconductor-based photocatalysis. Today, titanium dioxide is a representative photocatalyst material, due to its powerful redox properties and wide range of applications, such as air purification, water purification, deodorization, self-cleaning surfaces, antibacterial coating, and so forth [1, 4–7].

The photocatalytic capacity of TiO_2 powder heavily depends on its microstructure and physical properties, which are in turn determined by the preparation conditions [8–10]. Several attempts have been made to increase the photodegradation efficiency of TiO_2 , by either noble metal deposition or ion doping [11–14]. For example, Pt-doped, N-doped, C-doped, and S-doped TiO_2 are applied as visible-light-responsive photocatalysts [1, 12–14], and cocatalysts and co-adsorbents, such as Ag, Au, activated carbon, and carbon nanotubes (CNTs) [10, 15–17], are used for the improvement of photocatalytic activity under UV illumination. However, in developing their widespread use for any practical application, the cost and stability of the material must be considered first. The anion and noble metal dopants do not have much practicability due to their insufficient

stability, complicated preparation process, and expensive raw material. In contrast, transition metal cations have been found to be applied dopants and cocatalysts for the improvement of photocatalytic activity [18–24]. Some researchers report that the Ni^{2+} ion dopant improves the photocatalytic activity of certain semiconductor photocatalyst because the existence of Ni^{2+} suppresses recombination of electron-hole pair on the TiO_2 surface [18–20]. However, the raw material and processes of these previous works, such as organic precursors, sol-gel, and ion-implantation methods [18–22], are not inexpensive enough for mass production. Herein, we present a facile and cost-effective method for the preparation of highly active nickel-containing TiO_2 developed using TiO_2 particle and nickel chloride.

2. Experimental Details

2.1. Preparation of Ni- TiO_2 Particle. The nickel-containing, nanostructured TiO_2 particles were prepared by the photoreduction process by using nickel chloride and Degussa P25 as a nickel precursor and a pristine photocatalyst, respectively. Ni- TiO_2 was prepared by mixing 3 g of nonporous TiO_2 (Degussa P25), 50 mL of ethanol, and certain amount of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 200 mL of double-distilled water. The

FIGURE 1: Schematic continuous flow reaction system for photocatalytic degradation of NO.

solution was well mixed by ultrasonic treatment for 1 h. The initial pH value was adjusted to 8 with 0.1 M of NaOH solution [23]. A nitrogen stream at the rate of 30 mL/min was continuously introduced into the reaction chamber to remove oxygen in the solution. The solution was then irradiated with four UVC lamps (Philips TUV 10 W/G10 T8) with an intensity of 2 mW/cm² for 3 h. Ni ions were reduced to nickel metallic nanoparticles by the photo-generated electrons of TiO₂, then deposited on the surface of TiO₂. The Ni-TiO₂ particles were obtained by centrifugation at 10000 rpm, washing with DI water, and drying at 373 K for 12 h. Sample nomenclature was defined as follows: $x\%$ Ni/TiO₂ photocatalyst prepared by the photodeposition process with nickel content x mol%. The Ni/TiO₂ molar ratios were controlled at 0, 0.05, 0.1, 0.2, 0.5, 1, 2, and 4%.

2.2. Characterization. The photocatalyst crystal phase was identified using X-ray diffraction with Cu K α ($\lambda = 0.154$ nm) radiation (Shimadzu Rigaku D/Max RCXRD 6000). Average particle size and morphology was obtained by transmission electron microscopy (TEM, Hitachi S600-100 KV). The photoluminescence spectroscopy (PL) data were obtained on a luminescence spectrometer (Jasco FP-6500LE) under excitation with 325 nm irradiation. Material compositions were determined by X-ray photoelectron spectroscopy (Perkin Elmer SSI-M probe XPS system and S4800) and energy dispersion spectroscopy (Horiba, EX-210).

2.3. Photocatalytic Activity. Figure 1 depicted the continuous flow system used for NO_x degradation over TiO₂. A round-shaped Pyrex glass vessel ($\phi \times H$, 10 cm $\times$ 4 cm) was used as the photoreactor to conduct the degradation of NO_x, and a sample dish (ϕ , 7 cm) was located inside the vessel containing the TiO₂ powder. A black lamp provided a UV light source with an intensity of 1 mW/cm² (Sankyo Denki FL 20SBLB, main peak located at 352 nm). The NO_x degradation was carried out at room temperature using an air stream containing 1.0 ppm NO as feedstock. Two mass flow controllers (MFCs) (Brooks 5850E) manipulated relative humidity (RH = 50%) in the feeding stream. The

reaction gas in the feeding stream passed through the vessel containing TiO₂ powder (0.2 g) at a flow rate of 1 L/min. An on-line chemiluminescent NO_x analyzer (Eco Physics, CLD 700 AL) continuously monitored NO and NO₂ concentrations for gas analysis in the outlet.

3. Results and Discussion

3.1. Photocatalytic NO_x Degradation over Ni-TiO₂. Many researchers use NO oxidation to determine photocatalytic reactivity in various TiO₂ photocatalytic applications [11–13, 15, 25]. The electron-hole pair (e^- - h^+) generated upon light excitation is trapped at the TiO₂ surface as spatially separated redox-active sites. The general mechanism of NO_x oxidation by photocatalyst is as follows. Hydrogen ions and hydroxide ions are dissociated from water. The active oxygen species are produced on the TiO₂ surface. The nitric monoxide is oxidized to nitric acid or nitrous acid by active oxygen species. Based on the gas-phase chemistry of NO_x [25, 26], NO is converted to HNO₃ as a consecutive photooxidation via a NO₂ intermediate:

Finally, the nitric acid forms on the catalyst. Photocatalyst activity will lessen as acid accumulates. To illustrate the reaction behavior of NO photocatalytic oxidation, 0.2 g of 0.1% Ni-TiO₂ and 1 mW/cm² of light intensity were used to conduct the experiment. At first, a 1 ppm NO gas stream was introduced into the photoreactor under dark conditions. As shown in the Figure 2, in the beginning, the NO concentration in the gas phase dropped rapidly without

TABLE 1: The apparent quantum yields and selectivities of NO₂ of various catalysts: catalyst loading: 0.2 g, intensity of irradiation: 1 mW/cm², inlet concentration of NO, 1 ppm, inlet flow rate, 1 L/min, relative humidity: 55%, reaction temperature, 26°C.

Catalyst	P25	0.05% Ni	0.1% Ni	0.2% Ni	0.5% Ni	1% Ni	4% Ni
Φ (%)	2.13	2.63	2.85	2.58	2.07	1.80	1.30
Sel. _{NO₂} (%)	62.8	30.7	24.4	29.5	36.9	48.5	56.0

FIGURE 2: Time-course of the changes in concentration of NO, NO₂, and NO_x in the presence of 0.1% Ni-TiO₂ under UV light, reaction conditions as given in Table 1.

generation of NO₂ due to NO adsorption on the TiO₂. A few minutes later (2–4 min), the NO was saturated on the TiO₂ and in the photoreactor, and the NO concentration was thus returned to 1 ppm. The UV lamps were turned on to start this photocatalytic reaction. The steady state of this photocatalytic reaction was achieved as soon as the photocatalyst was illuminated. The NO concentration decreased from 1 to 0.57 ppm, and the NO₂ concentration increased to 0.1 ppm. The NO_x concentration, which represents the accumulated mixture of NO and NO₂, was maintained at 0.67 ppm under UV illumination. The activities of these TiO₂ samples do not obviously decrease during 30 mins of operation, due to the short reaction time.

Figure 3 shows the NO_x removal and NO₂ generation rates obtained using various Ni-containing TiO₂ particles under UV irradiation. The NO_x removal activity for these samples with different Ni content decreased in the order: 0.1% Ni-TiO₂ > 0.2% Ni-TiO₂ > 0.05% Ni-TiO₂ > 0.5% Ni-TiO₂ > 1% Ni-TiO₂ > P25 > 4% Ni-TiO₂, indicating the optimal Ni content is 0.1 mol%. The 0.1% Ni-TiO₂ has two times the NO_x-removal activity of P25 particle. Under UV illumination, these Ni-containing photocatalysts exhibit better activities in NO_x mineralization than pristine TiO₂, except for 4% Ni-TiO₂. The apparent quantum efficiency (Φ) and selectivity of NO₂ (Sel._{NO₂}) further computed based on the following equations [12, 13, 27] are listed in Table 1:

$$\varphi = \frac{\text{mole of (NO + NO}_2\text{) degraded}}{\text{Einstein of incident photons}} \quad (7)$$

$$\text{Sel.}_{\text{NO}_2} = \frac{[\text{NO}_2]_{\text{generated}}}{[\text{NO}]_{\text{converted}}}. \quad (8)$$

The order of apparent quantum efficiency (0.1% Ni-TiO₂ > 0.05% Ni-TiO₂ > 0.2% Ni-TiO₂ > P25 > 0.5% Ni-TiO₂ > 1% Ni-TiO₂ > 4% Ni-TiO₂) is not consistent with the NO_x removal activity. It indicates that the nickel content over 0.5% is excess to reduce the active area of TiO₂, resulting in the small quantum efficiency. When comparing the reaction behaviours over P25 and 0.05–0.2% Ni-TiO₂ samples, no significant difference in the NO conversion was observed, and the NO₂ generation rates over these Ni-TiO₂ samples were much less than that over P25, resulting in the better photocatalytic activity of the Ni-TiO₂. The selectivity of NO₂ of the photocatalyst has a great effect on the NO_x-removal activity, as shown in Table 1 and Figure 3. For example, the NO_x removal activity of 1% Ni-TiO₂ is better than P25 even if the quantum efficiency of P25 is larger than 1% Ni-TiO₂. It might be the Ni particle has a good affinity to NO₂. The platinum-modified TiO₂ also has this property [16], and Ni is much cheaper than Pt. It is a worthy property for NO removal photocatalysis because NO₂ is an undesired intermediate in the consecutive oxidation of NO, where the threshold concentrations of NO₂ and NO are 3 and 25 ppm, respectively, [12].

According to the reaction scheme of the photooxidation of NO, the photocatalyst would be deactivated after long-term operation due to the coverage of active sites by adsorbed NO₃[−] ions at the catalyst surface. However, the adsorbed NO₃[−] ions could be easily rinsed out with DI water, enabling regeneration of the catalyst. Figure 3 also indicates the removal rates of NO_x over 1st-, 3rd-, and 5th-regenerated 0.1% Ni-TiO₂ samples. The experimental results indicate the photocatalytic activity will be gradually decreased with the increase in operation and regeneration times. The photocatalytic activity of 0.1% Ni-TiO₂ sample becomes stable after four reaction and regeneration cycles. It showed that over 93% of the photocatalytic activity could be recovered after multi-reaction-regeneration cycles. The reason for the slight decrease of photocatalytic activity is that the unstable nickel particles peel off from the TiO₂ surface in the regeneration procedure. It can be confirmed by checking the nickel contents with using energy dispersive X-ray analysis after the regeneration procedure. It indicates most nickel particles on the TiO₂ surface are quite stable. This means that the prepared Ni-TiO₂ could provide very good stability for NO_x degradation. As a result, good stability, easy regeneration, and high reactivity will provide a great opportunity for the application in air purification with using nickel-modified photocatalysts.

3.2. Characterization of Ni-TiO₂. Figure 4 illustrates the X-ray diffraction patterns of the samples before and after

FIGURE 3: Effect of Ni content and regeneration time on the removal rate of NO_x.

photodeposition treatment. The XRD pattern of the prepared TiO₂ powder in Figure 4 reveals the peaks of anatase (101) and rutile (110) at $2\theta = 25.4^\circ$ and 27.5° , respectively, indicating that the bulk P25 TiO₂ composition is a mixture of rutile and anatase. Since all samples were dried at the relatively low temperature of 373 K and only a small amount of Ni salt was added, there were no significant differences between the samples. No peaks corresponding to crystalline phase of Ni metal and NiO were found due to small crystallite size and low nickel content. According to Scherrer's equation, by using the full width at half maximum height of the main peaks at $2\theta = 25.4^\circ$ and 27.5° , respectively, for anatase and rutile phases, the TiO₂ anatase and rutile grain sizes of all prepared samples were around 21 and 15 nm. The results indicate that the addition of Ni salt produced insignificant changes in the primary TiO₂ particle size.

Figure 5 shows the morphology of the Ni-deposited titanium oxide as captured by TEM. The deposited Ni particles measuring approximately 1–3 nm were dispersed on the surface of the P25. The pH value of the slurry influences the morphology of deposited metal particles on the TiO₂ surface [28]. This study finds that the reduction rate increases as the pH value increases. However, Ni particles cannot adhere well on TiO₂ when the pH value is higher than 10. The optimal pH value for the photodeposition of Ni in our study was found to be 8 [23]. The stability of Ni-TiO₂ was confirmed by checking their TEM images after the photocatalytic reaction and regeneration procedure.

Element composition and chemical states on the surface of prepared samples were determined by XPS high-resolution scans over the Ti 2p and Ni 2p spectra regions. Figure 6(a) shows the Ni 2p spectra of Ni-TiO₂ samples. For 0.1–1% Ni-TiO₂ samples, their spectra exhibit broad peaks due to the small amount of Ni, and indicate the existence of Ni(II) and Ni(III) in these TiO₂ particles. However, the plenty amount of Ni(0) is found on the surface of 4% Ni-TiO₂ particle. In the preparation of Ni-TiO₂ via the

FIGURE 4: XRD patterns of prepared TiO₂ samples.

photodeposition process, the valence state of nickel on the TiO₂ surface should be zero because nickel ions are reduced by the photo-produced electrons from the TiO₂. The Ni 2p_{3/2} peaks of the samples assigned for Ni(0), Ni(II), and Ni(III) of binding energy are 852.9, 854.3, and 855.9 eV, respectively, [18–20, 23]. The compounds regarding Ni(II) and Ni(III) are major in the forms of NiO and Ni₂O₃ because the existence of Cl on the TiO₂ surface is not observed. The metal oxides could be resulted from the oxidation of small nickel particles by heating in air [23, 29]. The Ni content of 4% Ni-TiO₂ should be much more than those of other samples, and therefore partial nickel on the 4% Ni-TiO₂ are not oxidized. The relatively atomic ratios of Ni(0), Ni(II), and Ni(III) species on the 4% Ni-TiO₂ are 55:26:19, as estimated from XPS results. In Figure 6(b), Ti (2p_{3/2,1/2}) core level spectra confirm that the Ti(IV) is indeed present in the pristine TiO₂ sample. However, the Ti 2p_{3/2} peak becomes broad and asymmetric with increasing Ni content. We interpreted the Ti 2p_{3/2} peak for the Ni-TiO₂ sample as a combination of the Ti(IV) (peak at 458.7 eV) and a Ti(III) (peak at 457.2 eV). The appearance of Ti(III) is probably due to the loss of oxygen atoms from TiO₂ during the oxidation of metallic nickel particles. Moreover, following the Ar⁺ ion etching process of 4% Ni-TiO₂, the peak intensities associated with the Ti(III) species decreased; after 90 s of etching (etching depth = 5 nm), the Ti(III) species could not be observed on the TiO₂. This shows that the Ti(III) species exists predominantly on the surface, as shown in Figure 6(b). It indicates the partial Ti(IV) species on the surface is reduced to Ti(III) as the metallic nickel is oxidized to nickel oxide.

The photoluminescence emission spectra were detected for various photocatalysts, as presented in Figure 7, to elucidate the fate of e⁻/h⁺ pairs in the semiconductor particles (TiO₂). As anticipated, the pristine TiO₂ photocatalyst (P25) shows a broad PL emission band, which is similar to the results of the literature [30]. The P25 and Ni-TiO₂ samples exhibit similar excitonic PL emission band, demonstrating that the nickel species does not cause the new PL phenomena.

FIGURE 5: TEM morphology of (a) P25 and (b) 1% Ni-TiO₂.

(a)

(b)

FIGURE 6: (a) XPS spectra over Ni 2p (b) Ti 2p of prepared samples.

The spectrum exhibits a broad emission region from 350 to 450 nm wavelengths with an excitation wavelength of 325 nm. The PL intensities of Ni-TiO₂ particles lessen with

FIGURE 7: Photoluminescence spectra of prepared TiO₂ samples.

the increase in the Ni content. A small amount of Ni gives a higher PL intensity of the Ni-TiO₂ particle than P25, but the PL intensity of the Ni-TiO₂ is smaller than that of pristine TiO₂ as the Ni content is more than 1%. It indicates that Ni species in the higher concentration condition do not act as a trapping site to capture photogenerated electron from TiO₂ conduction band, but it becomes the recombination centre of electron-hole as its concentration is less than 0.5%. The excitonic PL intensity of TiO₂ decreases as the increase in particle size, which is ascribed to the decrease in the content of surface oxygen vacancy and defect with increasing particle size [11, 30]. In this work, the TiO₂ size effect on PL intensity should be not significant here due to the small difference in crystallite size between these samples (see Figure 4). Therefore, the loss in PL intensities of 4% and 1% Ni-TiO₂ results from the active sites on the TiO₂ surface are covered by the Ni species. The metal particles on the TiO₂ surface, such as Ag, Au, Pt, act as trapping sites to capture photogenerated electron from TiO₂ conduction band, separating the photogenerated electron-hole pairs [14, 16]. The Ni species on the as-synthesized Ni-TiO₂ particles seems to be the recombination sites of the photogenerated

electron-hole pairs. It is probably as the metallic Ni and Ni ions could capture photogenerated holes and electrons, respectively. Thus, the recombination rate of photogenerated electrons and holes increased, leading to an increase in the PL signal. Some literatures report that the Ni dopant suppresses recombination of electron-hole pair on the TiO₂ surface [18–20]. The different phenomena observed in the former reports and this work are reasonably due to the different preparation process and Ni content. The Ni content used in the former works is 2–10 mol%, so the PL intensity of TiO₂ decreased obviously in the existence of large Ni content [18, 19]. For the above reasons, the results indicate the 0.1% Ni-TiO₂ should exhibit the smallest photocatalytic activity. However, the 0.1% Ni-TiO₂ exhibits the highest removal rate of NO under UV illumination than other samples. It reveals there should be another factors influencing its activity. The light absorbance is not the reason for good photoactivity of Ni-TiO₂ because the UV-vis diffuse reflectance spectra of P25 and 0.1% Ni-TiO₂ are the same (not shown here). Thus, the nickel species exhibits a good affinity to NO and NO₂ molecules, so the photogenerated active oxygen species on TiO₂ particles could contact NO_x molecules rapidly, resulting in the enhancement of PL intensity and NO_x removal rate on the 0.1% Ni-TiO₂.

4. Conclusions

In this study, the Ni-containing TiO₂ particle was successfully prepared via a photodeposition process. Characterization results revealed that the particle size, crystal structure, and light absorption were unchanged after modification with Ni salt. PL spectra identified that the small amount of Ni on TiO₂ enhances the recombination of photogenerated electrons and holes. The nickel species exhibits a good affinity to NO_x molecules, resulting in the increase in NO_x removal rate and the decrease in selectivity of NO₂ over the TiO₂. The excess Ni content on TiO₂ hinders reaction rate, due to coverage effect of nickel species on the active site on TiO₂ surface. Thus, 0.1 mol% Ni content is the proper content to prepare the highly photocatalytic material for removal of NO_x. In conclusion, this simple and energy-saving process for the production of Ni-containing photocatalysts can be applied practically for removal of NO_x.

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