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Characteristics of Ni 8 wt%-doped titanium dioxide photocatalyst synthesized by mechanical alloying

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Nanocrystalline Ni 8 wt% doped TiO_2 powder was synthesized by mechanical alloying. Microstructural and photo-spectrometiric analysis showed that the Ni added up to 8 wt% was dissolved into the rutile TiO_2 matrix. The absorption threshold of the Ni doped powder shifted from 380 to 500 into the visible light region. (480–500 nm)

KEY WORDS: titanium dioxide; photocatalyst; mechanical alloying.

1. Introduction

TiO_2 is becoming increasingly important due to its potential applications in photocatalysts, photovoltaic solar cells and self-cleaning materials [1–4]. However, TiO_2 has a high energy band gap ($E_g \fallingdotseq 3.2$ eV) that can only be exited by high energy UV irradiation with a wavelength of no longer than 387.5 nm. Therefore, current research has sought to improve the photocatalystic properties of TiO_2 by doping with metals and oxides [5–7]. In contrast to the extensive researches on the anatase phase, very little is known about the rutile phase. And no systematic research on metal-ion doping or clear definition of the nano-size particle effect has yet to be done. In our previous paper [8], nanocrystalline Fe-doped rutile TiO_2 synthesized by mechanical alloying and homogeneous precipitation process at low temperatures (HPPLT) exhibited an absorption threshold in the range 427–496 nm. However, the visible light absorption decreased when the Fe content exceeded 4.57 wt%. In this study, nanocrystalline TiO_2 powders doped with Ni-8 wt% synthesized by mechanical alloying and HPPLT methods. The photocatalytic behaviors of the powders were characterized by measuring the visible light reaction capacity, and the detailed microstructural characteristics of the Ni 8 wt%-doped TiO_2 catalyst system were investigated.

2. Experimental

Nanocrystalline Ni 8 wt%-doped TiO_2 powders were prepared by MA and HPPLT. MA is a very effective process for refining grain size down to a nano-sized range and alloying immiscible elements. In order to get better doping effect, HPPLT rutile powder was selected as the starting powder for mechanical alloying instead of a stable TiO_2 phase. To obtain the meta-stable powder, a $TiO(OH)_2$ precipitate slurry was first prepared from $TiOCl_2$ using the HPPLT process [9] then, the solution was filtered using distilled water. The detailed HPPLT process has been reported elsewhere [9, 10]. The filtered precipitates were dried at 60 °C for 12 h to produce the precipitated TiO_2 powder. The dried powder was mechanically alloyed for 14 h by a planetary ball mill (Fritz mill, P-5) with nickel powders (KOJUNDO Chem. CO., LTD, 99.9%). The Ni contents varied from 4 to 10 wt%. The ball-milling speed was 150 rpm and the ball to powder weight ratio was 15:1. Also, in order to study the phase stability of the HPPLT powder, HPPLT powder was heat treated at 1000 °C for 4 h. The structural evaluation of the alloying process and nanocrystallization process including grain size determination were characterized by high resolution XRD (HRXRD, CuK_{α}, Bruker, DA8 DISCOVER) and by high resolution transmission electron microscopy (HRTEM, 400 KV, JEM 4010). The characteristics of visible light reaction were investigated by UV/VIS-DRS (diffuse reflectance spectroscopy, Perkin-Elmer) and photoluminescence (PC-1 Photon counting Spectroflourmeter). The specific surface area was measured by BET method. Photocatalytic reaction of the powders was estimated by measuring the decomposition of 4-chlorophenol (0.1 mmol) in aqueous solution (500 mL) containing 0.1 g of the TiO_2 photocatalyst. After the photolysis, the remaining carbon concentrations in the aqueous solutions were detected by total organic carbon analyzer (SHIMADZU 4000 autosampler).

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3. Results and discussion

Figure 1 shows the HRXRD patterns of the HPPLT powder, the heat-treated HPPLT powder, commercial P-25 powder (Degussa Co.), and the Ni 8 wt%-doped powder. It can be seen that the Ni 8 wt%-doped powder and the HPPLT powders have a rutile phase whereas the P-25 powder is a mixture of rutile and anatase phase. The position of the rutile's main peak shifted from $2\theta = 27.37°$ of P-25 to 27.33°, 27.26° and 27.15° for heat-treated HPPLT powder, Ni 8 wt%-doped powder and HPPLT powder, respectively. The Ni 8 wt% doped powder and HPPLT powder peaks broadened, but P-25 and heat-treated HPPLT powder peaks were sharp. HPPLT powder exhibited peak broadening characteristic of nanocrystalline material. In the case of Ni 8 wt% doped powder, the peak broadening means a refinement of the average crystallite size and an increase in the internal strain by mechanical deformation during ball milling. So these two powders, Ni 8 wt%-doped and HPPLT, can be thought to be meta stable state phase, compare to stable state phase with P-25 and heat-treated HPPLT. A diffraction peak for elemental Ni was detected when the content of Ni exceeded 8 wt%.

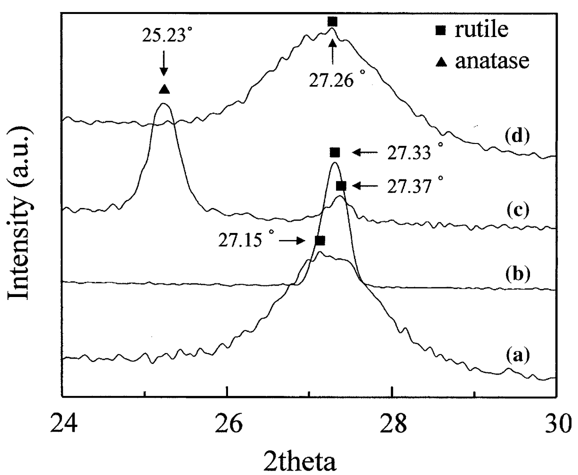

Figure 1. HRXRD patterns of TiO_2 powders. (a) HPPLT powder, (b) heat-treated HPPLT powder, (c) P-25 and (d) Ni-doped TiO_2.

HRTEM analyses were conducted to observe morphologies of the alloyed powders and to locate the position of Ni within the mechanical alloyed powders. Figure 2 shows HRTEM micrographs of the Ni 8 wt%-doped powders and the P-25 powder. Figure 2(a) shows that the 8 wt% Ni-doped powder consisted of spherical particles with an average grain size of less than 4 nm. In the P-25 powders, spherical particles were observed, with an average grain size ranging from 20 to 30 nm as shown in figure 2(c). The electron diffraction pattern of the Ni-doped powder is shown in figure 2(b). Ring patterns for (110), (101), and (200) planes of the rutile phase were observed. However, Ni patterns were not detected. This suggests that doping occurred by the complete dissolution of Ni in the rutile TiO_2 matrix. SEM analyses with energy-dispersive spectrometry were performed to follow the atomic distribution with milling

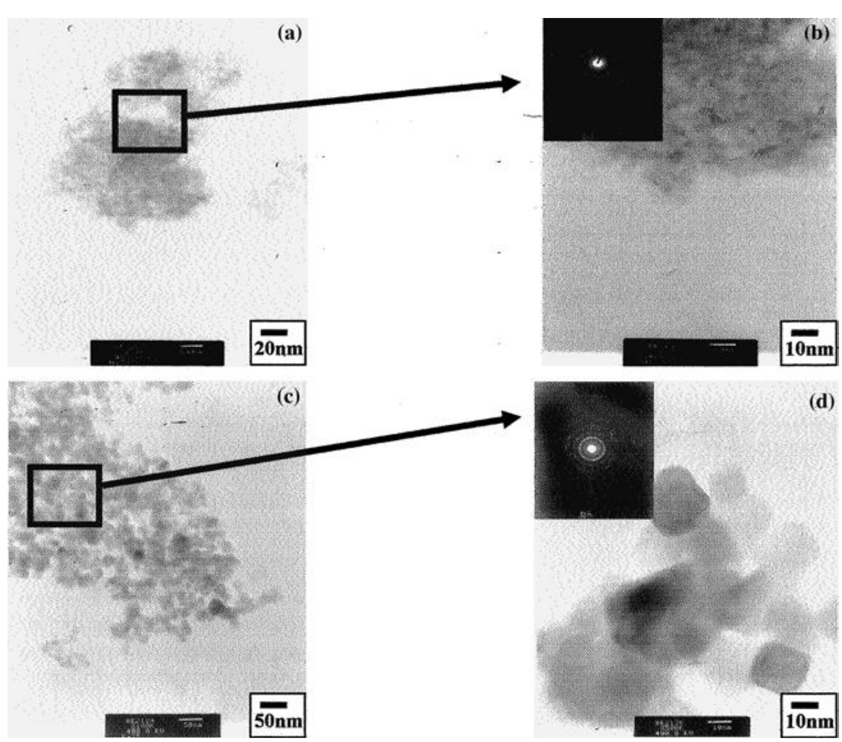

Figure 2. HRTEM micrographs of the mechanical alloyed TiO_2powder and P-25. (a) Ni-doped TiO_2, (b) electron diffraction pattern of mechanical alloyed TiO_2, (c) P-25 (Degussa Co.) and (d) electron diffraction pattern of P-25.

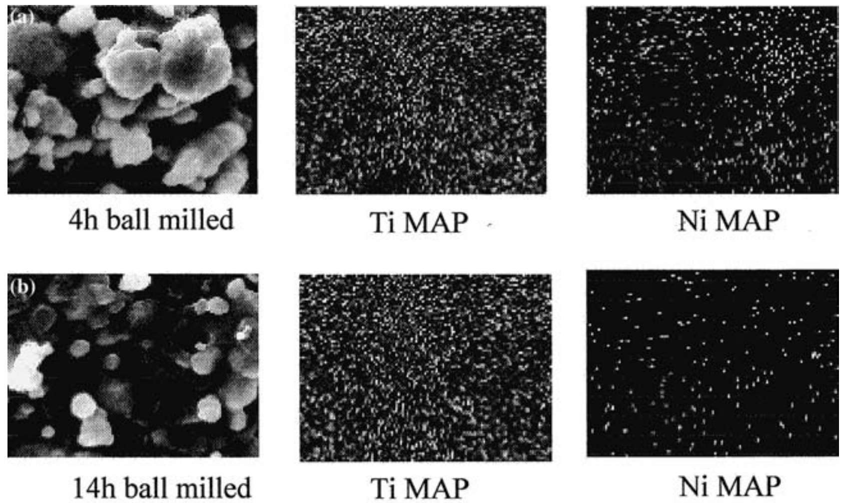

Figure 3. SEM micrographs and EDS images showing cross-section of Ni 8 wt%-doped TiO_2. (a) for 4 h milling and (b) for 14 h milling.

Table 1
Quantitative analysis result for Ni 8 wt%-doped TiO_2

Spectrum	O	Ti	Ni	Total
1	14.51	77.90	7.59	100.00
2	18.41	73.97	7.62	100.00
Max.	18.41	77.90	7.52	
Min.	14.51	73.97	7.69	

time and the results are shown in figure 3 and table 1. It is confirmed that Ni was uniformly distributed in the powder and the Ni composition was in a good agreement with the nominal value.

BET analysis show that the Ni-doped powder has a larger surface area (234 m^2/g) than the P-25 powder and HPPLT powder (about 50 and 150 m^2/g). Therefore, the photocatalytic reaction rate of the Ni-doped powder should be higher than that of the other powders.

Figure 4 show the results of diffuse reflectance spectra of the HPPLT, the Ni 8 wt%-doped powder and the P-25 powder. The onset of diffuse reflectance spectra of the Ni 8 wt%-doped powder shifted to wavelength longer (480–500 nm) than those of the HPPLT and P-25 powders (380–410 nm) [12]. Also, it is interesting to notice that the Ni 8 wt%-doped powder shows photo-absorption in the visible light region (= 480–500 nm). This suggests that the Ni 8 wt%-doped TiO_2 has the ability to respond to the wavelength of visible light region. The results show significant improvement over previous results of Fe-doped TiO_2 [8].

Figure 5 shows the photoluminescence spectra of the HPPLT powder, Ni 8 wt%-doped powder and P-25, respectively. The HPPLT powder and the P-25 had emission peaks at around 408 nm (3.03 eV), while Ni 8 wt%-doped powders had emission peak at around 454 nm (2.72 eV). Addition of Ni caused a shift of the

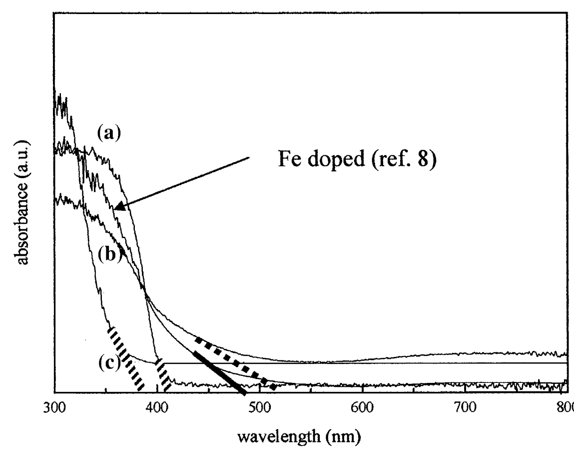

Figure 4. UV/VIS-DRS data. (a) HPPLT powder, (b) Ni-doped TiO_2 and (c) P-25.

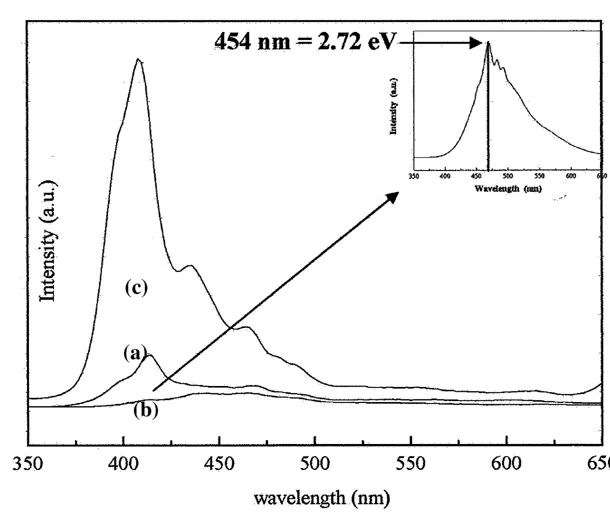

Figure 5. Photoluminescence data. (a) HPPLT powder (b) Ni-doped TiO_2 and (c) P-25.

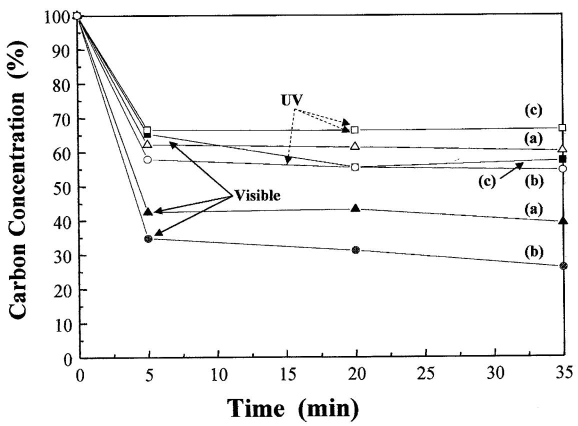

Figure 6. Photocatalytic decomposition of 4-Chrolophenol using various TiO_2 powders. (a) HPPLT powder, (b) Ni-doped TiO_2 and (c) P-25.

luminescence spectrum towards longer wavelength region in agreement with DRS spectra. An intense green photoluminescence was observed in the visible region with wide spectral width for the Ni 8 wt%-doped TiO_2, but the intensity decreased by doping. The decrease of luminescence intensity, upon doping, may be due to the new absorption was induced by localization of the trapping level near the valance band or conduction band.

Photocatalytic reaction of the Ni 8 wt%-doped TiO_2 powder under UV and visible light irradiation were evaluated by measuring the decomposition of 4-chlorophenol, and the results are shown in Figure 6. Under UV and visible light irradiation, the reaction ability of Ni 8 wt%-doped TiO_2 was much higher than that of P-25 and HPPLT powders. And no degradation of 4-chlrolophenol was observed in the absence of TiO_2 powder or without irradiation. It is very important that we synthesized a new TiO_2 powder which shows photocatalytic reaction under visible light range.

4. Conclusion

Nanocrystalline Ni-8 wt% doped TiO_2 powders could be synthesized by mechanical alloying and HPPLT. HRTEM and EDS investigation verified that the added Ni atoms were dissolved in the metastable rutile TiO_2 lattice with an average grain size of 2–4 nm. The UV/VIS-DRS absorption showed that the nano-sized Ni doped powder had a higher wavelength range (480–500 nm) than the commercial P-25 powder and the HPPLT powder (380–400 nm). PL spectrum of Ni 8 wt%-doped TiO_2 showed a shift in emission peak towards the longer wavelength region, suggesting a decrease in the band gap (2.72 eV). And Ni 8 wt%-doped TiO_2 had high reaction ability for decomposition of 4-chlorophenol in aqueous solution under UV and visible light.

Acknowledgments

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