Platinum–Nitrogen-Codoped TiO₂ Photocatalyst: Effect of Acid Catalysts on Visible-Light Activity

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Platinum–nitrogen-codoped TiO₂ (Pt–N–TiO₂) was prepared by a conventional sol–gel process via the addition of different acid catalysts: nitric acid (HNO₃), acetic acid (HAc) and both (HNO₃–HAc). The Pt–N–TiO₂ samples were then characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy and UV–visible diffuse reflectance analysis. The samples successfully exhibited visible-light-induced photocatalysis for the degradation of dichloroacetate (DCA) and 4-chlorophenol (4-CP). The HAc/450 sample (following the notation “added acid catalyst/calcination temperature”) exhibited the highest visible activity for DCA degradation. This finding can be explained by the much stronger visible absorption of the calcined samples than the uncalcined samples and the slightly larger surface area of HAc/450 compared to other calcined TiO₂ samples. However, the performance of 4-CP degradation was proportional to the Pt–N–TiO₂ sample surface area regardless of visible absorption, which could be ascribed to the fact that 4-CP degradation can occur through a surface-complex-mediated pathway under visible irradiation. [doi:10.2320/matertrans.M2012294]

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1. Introduction

TiO₂ photocatalysis has received significant attention as a method for the environmental remediation of recalcitrant pollutants because of its superior photocatalytic activity, chemical stability, low cost and nontoxicity.^{1–6} However, the practical applications of TiO₂ photocatalysis have been limited because TiO₂ is active only under UV irradiation due to its large band gap. Therefore, less than 5% of solar light can be utilized for photoexcitation. Numerous studies have attempted to modify the optical properties of TiO₂ by doping with other elements or sensitization with other colorful inorganic or organic compounds.^{7–10}

The chemical composition of TiO₂ can be altered, substituting a metal for titanium or a nonmetal for oxygen to modify its optical properties without changing its crystal structure.¹⁰ Various dopants have been applied, including transition metal ions such as Cr,⁷ Ru,¹¹ V,¹² and Pt¹³ and nonmetal dopants such as N,^{14,15} C,¹⁶ S^{17,18} and B.¹⁹ These dopants have been successfully introduced into TiO₂ by different doping methods, producing efficient visible-light-induced photocatalysis. More recently, two-element codoped TiO₂ has also been reported to exhibit enhanced photocatalytic activity under visible irradiation.^{20–25} The synergistic effects of such compounds are being actively investigated.

However, the development of visible-light-active doped TiO₂ is mainly limited to research related to the dopant type because of its close relation to the visible-light absorption properties. Although considerable efforts have focused on the development of visible-light-active doped TiO₂ photocatalysts, there is little information on the effects of the synthetic parameters for the doped TiO₂. In contrast, the effects of the synthetic parameters on morphology and photocatalytic activity under UV irradiation have been intensively studied for pure TiO₂. Preparation conditions such as the ratio of alcohol to water, pH, and type of acid catalyst in the sol–gel

preparation of TiO₂ strongly affect the morphology, crystallinity, and UV-light-induced photocatalytic activity.^{26–29} Similarly, the visible-light-induced photocatalytic activities should also vary with the preparation conditions for the same doping ions. However, a detailed understanding of the effects of synthetic parameters on the visible-light-induced photocatalytic activity of doped TiO₂ is still lacking.

In this study, we investigated the effects of the type of acid catalyst used in the sol–gel preparation of Pt–N–TiO₂ on the visible-light-induced photocatalytic activity. We previously investigated the visible-light-active Pt–TiO₂¹³ and nitride Pt–TiO₂.³⁰ The Pt ions in Pt–TiO₂ were present as Pt(IV) and Pt(II) which might be due to partially occupied impurities bands. It has been previously reported that codoping with charge compensated anion donor and cation acceptor pairs not only narrows band gap but also passivates gap states.^{31,32} Therefore, codoping of N and Pt might inhibit the formation of Pt(II) resulting in the photoactivity increase. If this is the case, Pt–N–TiO₂ can be a good example for visible-light-active doped TiO₂ photocatalysts. To codeope Pt and N, precursors of platinum and nitrogen ions were combined in alcohol and mixed with titanium tetraisopropoxide (TTIP). Nitric acid (HNO₃), acetic acid (HAc) or both (HNO₃–HAc) were added during the TTIP hydrolysis. We also compared uncalcined and calcined Pt–N–TiO₂ samples to study the effect of calcination. The characteristic properties of the obtained Pt–N–TiO₂ samples were compared, and their photocatalytic activities for aqueous dichloroacetate (DCA) and 4-chlorophenol (4-CP) degradation were examined.

2. Experimental Procedure

2.1 Sample preparation and characterization

Pt–N–TiO₂ samples were prepared using a sol–gel method. TTIP (90 mL) was mixed with 20 mL of ethanol solution containing H₂PtCl₆ and NH₄Cl ((Pt or N)/Ti molar ratio = 0.005). The mixture was added dropwise to 500 mL of aqueous solution containing 2 mL of acid catalyst (HNO₃,

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HAc, or HNO₃ and HAc). The result colloidal suspension was stirred at 80°C for 4 h and evaporated at 40°C using a rotavapor. The obtained powder was used as prepared or calcined at 450°C for 3 h under an air atmosphere. The calcined powder was washed to remove impurities such as chlorides and nitrates and then dried. Using these procedures, we obtained six types of Pt–N–TiO₂ photocatalysts, denoted as HNO₃/450, HAc/450, HNO₃–HAc/450, HNO₃, HAc and HNO₃–HAc according to the acid catalyst and calcination temperature (when applicable).

The phase identification of the Pt–N–TiO₂ samples was performed using powder X-ray diffraction (XRD) with Cu K α radiation (Rigaku D/Max-2500, 18 kW). The BET surface area was determined from nitrogen adsorption–desorption isotherms at 77 K (ASAP2020, Micrometrics). The effective surface areas were estimated at relative pressures (P/P_0) ranging from 0.01 to 0.1. Diffuse reflectance UV–visible absorption spectra (DRS) of the powder samples were obtained using a UV–vis spectrophotometer (Varian Cary 100) equipped with a diffuse reflectance accessory. The morphology was examined using field-emission scanning electron microscopy (FE-SEM, S-4200, Hitachi) and Cs-corrected scanning transmission electron microscopy (STEM, JEM-ARM200F, JEOL). The atomic composition of Pt–N–TiO₂ powders was determined by X-ray photoelectron spectroscopy (XPS, XSAM 800 dpi, Kratos) using the Mg K α line (1253.6 eV) as the excitation source. The elemental contents of the powder samples were determined by elemental analysis (EA1112, ThermoFinnigan) and ICP-OES (OPTIMA 7300V, PerkinElmer).

2.2 Photocatalytic activity testing

The photocatalytic activities of the Pt–N–TiO₂ samples for dichloroacetate (DCA) and 4-chlorophenol (4-CP) were measured in aqueous suspensions. Pt–N–TiO₂ powder was dispersed in distilled water at 0.5 g/L and sonicated for 30 s. The desired amount of DCA or 4-CP stock solution was added to the suspension, and the solution pH was adjusted with HCl or NaOH standard solution. The resultant solution was stirred for 30 min in the dark to allow the equilibrium adsorption of the substrate on the photocatalyst surface. A 300 W Xe arc lamp (Oriol) was used as a light source, and the light beam was passed through a 10 cm IR water filter and a cutoff filter ($\lambda > 420$ nm) and focused onto a 90 mL cylindrical quartz reactor with a window (40 mm diameter). The sample aliquots were intermittently withdrawn using a 1 mL syringe during visible irradiation and filtered through a 0.45 μ m PTFE filter (Millipore). The degradation of DCA and 4-CP was monitored using an ion chromatograph (IC, Dionex ICS-3000 series) and a high-performance liquid chromatograph (HPLC, Agilent 1100 series), respectively. The concentration of chloride ions produced from the degradation of DCA and 4-CP was also monitored by IC.

3. Results and Discussion

3.1 Crystal structures and morphological features of Pt–N–TiO₂

Crystallinity is critical in determining the photocatalytic activities of TiO₂ photocatalysts. Figure 1 shows the XRD

Fig. 1 XRD patterns of the Pt–N–TiO₂ powders synthesized under different conditions.

patterns of synthesized Pt–N–TiO₂ powders for the various acid catalysts studied here and with or without calcination. All synthesized Pt–N–TiO₂ powders without calcination only exhibited the anatase phase. The rutile phase did not appear, even for the samples calcined at 450°C, which was in accordance with the fact that TiO₂ powders obtained through a sol–gel process primarily exhibit the anatase phase. Diffraction peaks other than that of anatase were not found, indicating that new impurity phases were not created as a result of the substitution of Pt and N ions into the TiO₂ lattice. The different acid catalysts added in the sol–gel process did not affect the crystallinity of the TiO₂ powders, and the degree of crystallinity increased with the heat treatment at 450°C as expected.

SEM and TEM image analysis revealed that the morphology was identical to the typical TiO₂ nanoparticles and independent of the acid catalysts added during the Pt–N–TiO₂ synthesis. Figure 2 shows the SEM and TEM images of a representative Pt–N–TiO₂ (HAc/450) sample. Spherical nanoparticles agglomerated, and the primary particle size was approximately 10 nm. The SAED pattern displayed obvious rings, indicative of a polycrystalline structure. In addition, the lattice parameter obtained by the calculation of the d -spacing using the radius rings and lattice spacing was 0.35 nm, which was in accordance with the lattice spacing of the (101) plane of anatase TiO₂.

3.2 Evidence of platinum and nitrogen dopants in TiO₂

Table 1 displays the Pt and N contents in the synthesized Pt–N–TiO₂ powders. The Pt content was estimated by ICP analysis as consistently in the range of ca. 0.8 and 1 atom%. However, the N content obtained by elemental analysis varied from ca. 0.1 to 1.4 atom% and that for the samples calcined at 450°C was dramatically lower, which might be due to the ignition loss of nitrogen compounds at high temperature.

Figure 3 compares the XPS spectra of the synthesized Pt–N–TiO₂ powders for the Pt 4f and N 1s bands to evaluate the Pt and N oxidation states. Although the peaks were unclear because of the small amount of Pt and N precursor added, the presence of Pt and N atoms on the sample surface was confirmed. The binding energy at which the N 1s band appeared was 400 eV, as shown in Fig. 3, which suggests that doped N ions exist in an interstitial form. Asahi *et al.*

Fig. 2 (a) SEM image, (b) TEM image and (c) diffractogram of Pt–N–TiO₂ (HAc/450). A diffraction pattern of rings was obtained by fast Fourier transformation.

Table 1 Platinum (Pt) and nitrogen (N) contents of the prepared Pt–N–TiO₂ samples determined by ICP and elemental analysis measurements, respectively.

	Pt content (%)	N content (%)
HNO ₃ /450	1.046	0.092
HAc/450	0.985	0.153
HNO ₃ –HAc/450	0.893	0.111
HNO ₃	0.987	1.359
HAc	0.871	0.251
HNO ₃ –HAc	0.775	0.933

reported that the substitutional form of N atoms that appears at 396 eV is closely related to the photoreactivity of the N–TiO₂.¹⁴⁾ Diwald *et al.* also reported that the interstitial form of N atoms appears at 400 eV and that these dopants are mainly responsible for the visible activity of N–TiO₂.³³⁾ On the other hand, XPS peaks for the Pt 4f band were observed with subtle changes but were not fully distinguishable, preventing the determination of the Pt oxidation state for the samples. XPS analysis was insufficient for evaluating the dependence of acid catalysts on the chemical environment of Pt ions.

It is natural that the photocatalytic reaction under visible irradiation is initiated by the photon absorption of the photocatalysts. Figure 4 shows the diffuse reflectance UV–visible spectra of the prepared Pt–N–TiO₂ samples. The visible-light absorption of the heat-treated samples was much

Fig. 3 XPS spectra of the Pt 4f and N 1s band region for the Pt–N–TiO₂ powders synthesized under different conditions.

stronger than that of the uncalcined samples, and the degree of visible-light absorption was strongly influenced by the identity of the acid catalyst added during the sample preparation. The visible-light absorption of HNO₃/450 was

Fig. 4 Diffuse reflectance UV–visible spectra of the Pt–N–TiO₂ powders synthesized under different conditions.

weaker than that of HAc/450, as shown in Fig. 4. This might be attributed to the increase of defect sites and the incomplete decomposition of carbon species of HAc. The pK_a values of HNO₃ and HAc are -1.3 and 4.8 , respectively. This means that the HNO₃ is stronger acid than HAc. The strength of acids could be proportional to the rate of crystallization in sol–gel process. Accordingly, the defect sites might be easily formed in the presence of HAc. Furthermore, it is possible that the carbon species which were originated from the acetic acid were not completely decomposed and some of them remain on the surface of Pt–N–TiO₂. The reflectance spectrum of HNO₃–HAc/450 displayed significant background absorption in the visible region up to 800 nm, which

might originate from the partially reduced form of Pt or Ti ions rather than the presence of dopant ions.

3.3 Visible-light activities of Pt–N–TiO₂

The photocatalytic activities of the prepared Pt–N–TiO₂ samples were examined in terms of the degradation of organic compounds under visible irradiation ($\lambda > 420$ nm). In previous study,¹³⁾ it was confirmed that the visible-light-induced degradation of DCA and 4-CP for pristine TiO₂ was negligible. Figure 5(a) compares time-dependent DCA degradation for various samples, showing the remarkable difference in the degradation profile according to the heat-treatment of the samples. Although DCA degradation was negligible for the uncalcined samples, DCA was rapidly decomposed for the calcined samples, with the HAc/450 sample having the highest activity. Furthermore, the chloride production with the calcined samples was quantitatively balanced with the removal of DCA, as shown in Fig. 5(b), which provides strong evidence of DCA degradation by visible-induced photocatalysis. The chloride generation with the uncalcined samples seems to be due to a residue from the sample preparation. In contrast, the 4-CP degradation for the calcined samples was slower than that for the uncalcined samples, with HAc/450 having the highest visible activity among the calcined samples and comparable activity to the uncalcined samples (Fig. 5(c)). This finding can be attributed to the degradation of 4-CP under visible irradiation occurring via an additional pathway to that of DCA. Aromatic compounds, including benzene rings, can form surface complexes on TiO₂ to produce phenoxy groups, and visible absorption by these phenoxy groups can initiate the

Fig. 5 Time-dependent profiles of the photocatalytic degradation of (a) DCA and (c) 4-CP for various Pt–N–TiO₂ samples under visible irradiation. (b) and (d) represent Cl[−] production from DCA and 4-CP degradation, respectively.

Fig. 6 Comparison of the photocatalytic degradation rate of test substrates for various Pt-N-TiO₂ samples.

degradation reaction.³⁴⁾ Accordingly, if this mechanism is dominant, the performance of 4-CP degradation strongly depends on the surface area of TiO₂. The 4-CP degradation of the uncalcined samples with large surface areas was faster than that of the calcined samples, which is consistent with the effect of the surface area on the reaction rate mentioned above. As for DCA, it is plausible that the calcined samples with strong visible absorption showed higher activity because the degradation occurs by the radicals intrinsically generated by band-gap excitation under visible irradiation rather than surface-complex-mediated sensitization. Figure 6 compares the degradation rate of test substrates for various Pt-N-TiO₂ samples and correlates it with the surface area of the samples, clearly showing the positive correlation between the rate of 4-CP degradation and the surface area. HAC/450 exhibited the highest visible-induced photoactivity among the calcined samples, which could be ascribed to its stronger visible absorption and slightly larger surface area relative to the other samples.

4. Conclusion

TiO₂ photocatalysts codoped with platinum and nitrogen were prepared by a conventional sol-gel method with the addition of different acid catalysts: nitric acid, acetic acid and both. Doping TiO₂ nanoparticles with Pt and N for the various acid catalysts did not alter the crystal phase or morphology of the intrinsic TiO₂ particles. The elemental contents of Pt and N were estimated to be approximately 0.8–1 atom% and 0.1–1.4 atom%, respectively. The diffuse reflectance spectra of the prepared samples showed that the visible-light absorption of the heat-treated samples was much stronger than that of the samples without heat treatment.

The photocatalytic activities of the Pt-N-TiO₂ samples were compared in terms of DCA and 4-CP degradation under visible irradiation. The HAC/450 sample exhibited the highest visible activity for DCA degradation, which could be ascribed to the much stronger visible-light absorption of calcined samples than the uncalcined samples and its slightly larger surface area compared to other calcined samples. However, the performance for 4-CP degradation was different from that for DCA. Because 4-CP degradation can occur through a surface-complex-mediated pathway under visible irradiation, it is plausible that the performance of 4-CP

degradation was proportional to the surface area of the samples regardless of their intrinsic visible absorption.

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