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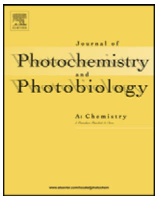

Influence of nitrogen chemical states on photocatalytic activities of nitrogen-doped TiO_2 nanoparticles under visible light

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ABSTRACT

Nitrogen-doped TiO_2 (N-TiO_2) nanoparticles with a homogeneous anatase structure were synthesized using three different chemical methods. X-ray photoelectron spectra (XPS) analysis shows that nitrogen was successfully doped into TiO_2 nanoparticles and the nitrogen atoms are present in both substitutional and interstitial sites. The electron binding energy (BE) of N 1s core level is found to depend on the synthesis methods. Changes in Ti–O bond lengths of the substitutional and interstitial N doped-TiO_2 were calculated by computational geometry optimization, and confirmed by Raman shift analysis. Differences in UV–vis light absorption and visible-light-induced photocatalytic activity of three N-TiO_2 samples were attributed to their different nitrogen states within TiO_2 lattice, which would create different defect levels. The defect levels were confirmed by photoluminescence (PL) analysis and density of states (DOSs) calculation. From one to one correspondence between XP spectrum and photocatalytic activities, it is concluded that nitrogen atoms in substitutional sites enhances the photocatalysis of TiO_2 under visible light more effectively than nitrogen atoms in interstitial sites.

1. Introduction

Photocatalysts that are sensitive to visible light have attracted much attention for their potential use of solar energy [1–4]. In particular, nitrogen-doped TiO_2 is known to be a promising visible-light photocatalyst [2]. Therefore, there have been a number of studies on the synthesis and characterization of various types of N-doped TiO_2, including thin films [2,5–7], single crystals [8–10], and powders [1,4,11–17].

However, the chemical states of doped N and its relation to photocatalytic properties under visible light are still controversial. Saha and Tompkins [18] and Asahi et al. [2] measured the N 1s core levels using XPS analysis and observed three peak structures at binding energies of 402, 400, and 396 eV. They assigned the peaks as atomic β-N (396 eV) and molecularly chemisorbed γ-N_2 (400 and 402 eV) [2,18]. Also, Asahi et al. [2] concluded that the active sites of N for photocatalysis under visible light are the substitutional sites, which correspond to the peak at 396 eV in the XP spectra. Thereafter, Irie et al. [19] observed N 1s peak at 396 eV and explained it to result from a substitutional N in O–Ti–N. Diwald et al. [9] observed the N 1s feature at 396.7 eV and assigned the peak to N_2^- anion replacing oxygen in the TiO_2 lattice. In contrast to these studies, there have been also a great number of reports showing that the signal at around 396 eV is completely absent in N-TiO_2 [4,12,17,20–27]. Burda and co-workers [4,20,24] found that the binding energy of N 1s extended from 397.4 eV to 403.7 eV and was centered at 401.3 eV, and they assigned the peak to partially oxidized N in N–Ti–O linkages. They reported that the synthesized N-TiO_2 nanoparticles had photocatalytic activity in the visible light region [4]. Thereafter, Sathish et al. [17] and Ma et al. [28] found the N 1s core level to be at 398.2 eV and 398.3 eV, respectively. They explained these peaks in terms of nitrogen in N–Ti–O linkages (nitrogen is substituted for oxygen in the initial O–Ti–O structure), and Sathish et al. [17] reported that the N-TiO_2 exhibited photocatalytic activity under the visible light region. A few researchers have reported that the photocatalytic power of N-TiO_2 under visible light is correlated with the N 1s core level peak at around 400 eV [2,9,12,18,23,26,28]. In some of these reports, molecularly adsorbed or interstitially doped N species such as NO and NH_x [1,9,29,30], were proposed to generate the peak at around 400 eV in the XP spectrum and develop the photoactive properties under the visible light.

As stated above, the chemical states of nitrogen and their effects on the photocatalytic activity in the visible light are still controversial. It may be due to the fact that the N doping is very sensitive

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processing conditions. Therefore, previous studies observed only part of chemical states of N allowed in TiO_2. In the present work, N-TiO_2 samples that were synthesized by different methods show that the N 1s binding energy can be 398.3, 401.5, and 400 eV, depending on the processing conditions. This is the first investigation reporting the N 1s binding energy of both 398.3 and 401.5 eV and the effect of N doping states on the photocatalytic properties of N-TiO_2 nanoparticles. The doping states of nitrogen (i.e. substitutional or interstitial) with different binding energy N-TiO_2 were analyzed by combining experimental and theoretical studies. In addition, the effects of the N doping states on the optical properties and photocatalytic activity of N-TiO_2 in the visible region were investigated.

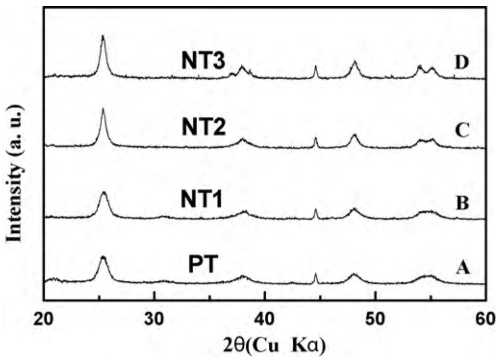

Fig. 1. Powder X-ray diffraction patterns.

2. Experiment

2.1. Preparation of nanoparticles, films, and photoelectrochemical (PEC) cells

Bare-TiO_2 nanoparticles were synthesized via the hydrolysis of titanium tetraisopropoxide (TTIP, $Ti(OC_3H_7)_4$, 97%, Aldrich Chemicals Co.) with excess water ($[H_2O]:[Ti] = 50:1$) at 80 °C. The sol was stirred at 80 °C for 24 h and dried at 90 °C in an oven. The dried powder was annealed at 450 °C for 1 h in air, and the resultant white powder was denoted as "PT". The three different types of N-TiO_2 nanoparticles called "NT1", "NT2", and "NT3" were prepared by the following methods. NT1 nanoparticles were prepared by annealing the PT powder at 400 °C for 2 h in flowing NH_3 gas. NT2 nanoparticles were synthesized by the hydrolysis of TTIP with NH_4OH solution ($[NH_4OH]:[H_2O]:[Ti] = 5:45:1$) at 80 °C. The sol was stirred for 24 h, centrifuged, and then washed with distilled water five times; the subsequent drying and annealing process was identical to that used for PT. NT3 nanoparticles were synthesized by hydrolysis of titanium chloride (100 mL, 2 M $TiCl_4$ in H_2O) with ammonium hydroxide (900 mL, 5 M NH_4OH in H_2O) at room temperature. The suspension was stirred for 2 h, centrifuged, and then washed with distilled water five times; the subsequent drying and annealing process was identical to that used for PT. The resultant NT1, NT2, and NT3 powders were pale yellow. TiO_2 films were prepared using the synthesized nanoparticles. Dried nanoparticles were dispersed in a mixture of water, ethanol, and acetyl acetone, and then spin-coated on fused silica substrates. The spin-coated films were annealed using the several methods (PT, NT1, NT2, and NT3) described above. The thicknesses of the films were measured using a field-emission scanning electron microscope (FESEM, model JSM-6330F, JEOL, Japan) and all of films were about 1 μm thick.

2.2. Characterization

The crystal structures of the prepared samples were characterized using a powder X-ray diffractometer (XRD, model M18XHF-SRA, MAC-Science Instruments, Japan). The morphologies of the prepared TiO_2 nanoparticles were observed using a high-resolution transmission electron microscope (HRTEM, model JEM 3000F, JEOL, Japan). The chemical states of N in TiO_2 were analyzed using X-ray photoelectron spectroscopy (XPS, model SIGMA PROBE, ThermoVG, UK). The XP spectra were acquired using monochromatic Al–K radiation (100 W), and the core levels of N 1s were calibrated with respect to the C 1s level at 284.5 eV. The diffuse reflectance spectra were obtained using a UV–vis-NIR spectrophotometer (model U-3501, Hitachi, Japan) and were converted to the absorbance spectra by the Kubelka–Munk method. The photoluminescence (PL) spectra of the samples were obtained using a photoluminescence spectrometer (SPEX 1403, SPEX). The specific surface areas of the TiO_2 nanoparticles were measured using a Brunauer–Emmett–Teller (BET) analyzer (BELSORP-mini II, BEL, Japan). The Raman spectra were recorded using a Raman spectrometer (T64000, HORIABA Jobin Yvon, France).

2.3. Evaluation of photocatalytic activity and computational geometry optimization

The photocatalytic activities of the prepared powders were evaluated by measuring the decomposition of phenol (10 ppm) in an aqueous system. The catalyst (0.1 g) was added to 100 mL of phenol solution in a Pyrex reactor. Prior to irradiation, the suspension was stirred in the dark until the concentration of solution was stabilized. A 200 W halogen lamp was used as a light source and a 420-nm cut-off filter was employed to filter UV light and excite samples only by visible light. The concentration of the phenol solution was measured using the UV–vis spectrophotometer. Moreover, the amount of total oraganic carbon (TOC) in the aqueous solution was measured by Total Organic Carbon analyzer (5310C, Sievers, U.S.A.). In addition to the powders, we also examined the photocatalytic activities of the prepared films by measuring the decomposition of stearic acid (10 mM in ethanol) that was spin-coated on the films. A 50 W halogen lamp was used as a visible-light source and a 420-nm cut-off filter was used for selecting only visible light. The amount of stearic acid remaining on the film was quantitatively characterized using a Fourier-transform infrared (FT-IR) spectrophotometer (model DA8-12, Bomen, Canada). Optimized geometry of atoms, electronic band structures, and density of states (DOSs) were calculated by density functional theory (DFT) using the well-tested CASTEP code which is based on the plane-wave pseudopotential method [31]. The generalized gradient approximation (GGA) with gradient corrected functional Perdew–Burke–Ernzerhof (PBE) has been used throughout the calculation. The $2 \times 2 \times 1$ supercell of TiO_2 anatase structure was used for this theoretical study.

Table 1
Nitrogen sources and structural characteristics of undoped- and N-doped TiO_2 nanoparticles.

Sample	N source	Crystallite size (nm)	*d* spacing for (1 0 1) plane (Å)	BET surface area (m^2/g)
PT	–	11.2	3.51	105.76
NT1	NH_3 (gas)	11.5	3.50	106.82
NT2	NH_4OH (aq.)	16.4	3.51	94.38
NT3	NH_4OH (aq.)	17.0	3.51	89.76