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The stable and uniform characteristics of nitrogen in nitrogen doped titanium dioxide nano photocatalytic particles

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Abstract. N doped TiO_2 nano particles were prepared by heating TiO_2 nano particles in NH_3 + C_3H_8 5vol% atmosphere. The stability and uniformity characteristics of the doped N in the prepared N doped TiO_2 nano particles were studied by X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD). We concluded that the doped N was uniform from the surface to the inside of TiO_2 nano particles and found that the desorption peak of the doped N was more than 900 K in vacuum, showing its high stability and potential of visible light photocatalytic application for N doped TiO_2 nano particles.

1. Introduction

Visible light activated photocatalysts are important due to their ability to efficiently utilize solar irradiation or indoor-light. Recently, studies about doping or modification with non-metals of TiO_2 have attracted much interest. N doped TiO_2 [1-4], C doped TiO_2 [5-7], S doped TiO_2 [8], C and N co-doped TiO_2 [9] show that the photocatalytic activity can be improved through non-metal doping into TiO_2. Our previous studies have also shown that N doped TiO_2 has higher visible light photocatalytic performance than commercial TiO_2 [10, 11]. However, there are few studies focusing on the stable and uniform characteristics of non-metals doped into TiO_2, to the best of our knowledge, though the stable and uniform conditions are very important for their photocatalytic performances not only from the scientific interest but also from the view point of applications. In this study, we prepared N doped TiO_2 nano particles and investigated the stable and uniform characteristics of the doped N by XPS and TPD.

2. Experimental

It was known that N doped TiO_2 nano particles could be prepared by heating TiO_2 primary nano particles in an ammonia atmosphere [1]. Under the consideration of the engineering application of powder heating processes, we built ammonia heating experimental equipment with rotary and pre-desorption processes as shown in Fig. 1. TiO_2 nano particles were set into a furnace tube which was rotated at a rate of 5 rpm during the whole heating process and were heated under air atmosphere to 573K. The particles were then desorbed by vacuum pump to 5 Torr and kept for 0.5h. NH_3 + C_3H_8 5vol%   ammonia gas was then introduced and the furnace heated to 873K and kept for 3h, then switched off and cooled down to room temperature. A quartz tube was used for the furnace tube to

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avoid metal contaminations. The particles of TiO_2 used for the heat-treatment had an average particle diameter of 7 nm and were anatase-type crystalline.

The stable and uniform characteristics of the prepared N doped TiO_2 fine particles were studied by XPS and TPD. The measuring conditions of the XPS analysis were as follows. Apparatus: AXIS-Ultra manufactured by Kratos Co. Excited X-ray source: monochromatic Al Kα line (1486.6 eV). Photoelectron detection angle: 90º (from the surface of the sample). Detection depth: < 10 nm. Charged neutralization gun: used. The measuring conditions of the TPD analysis were as follows. Equipment: temperature programmed desorption gas analyzer (Model: Thermo plus TPD type V). Sample: a powder sample filled in a platinum cell (diameter 6mm, height 2.5mm). Measuring temperature range: from 313 K to 1173 K. Heating rate: 10 K /min. Measuring mode TIC (scanning): m/e = 1 to 100. Vacuum degree at the start of measurement: < or = 2.0×10^{-6} Pa.

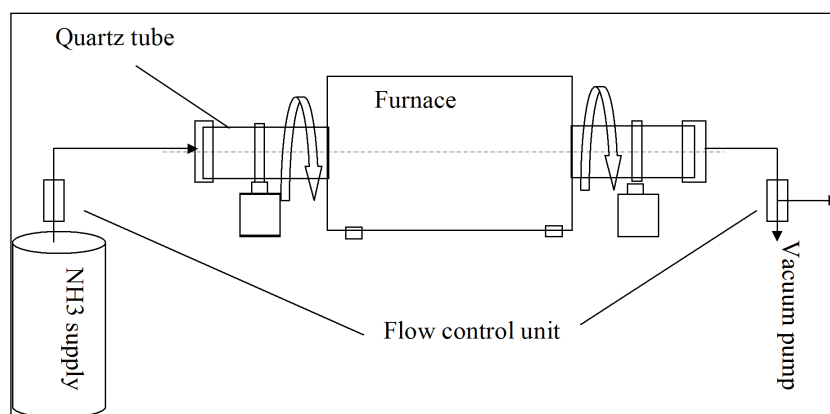Fig. 1. Sketch of experimental equipment for preparing N doped TiO_2 photocatalytic nano particles.

3. Results

The prepared N doped TiO_2 nano particles have the shape of ellipsoidal sphere with a minor axis length of about 20 nm and major axis length of about 40 nm. The crystal structure of the prepared N doped TiO_2 was confirmed by XRD to be anatase. The photocatalytic activity induced by visible light irradiation was evaluated by IPA (isopropanol) photochemical oxidation and found to be higher than commercial TiO_2 [10, 11].

Fig. 2 shows the N1s XPS analytical results of chemical bonding of the doped nitrogen in the prepared sample. It can be seen from the experimental data points that there are a peak at the binding energy of 400 eV and another peak at 396 eV with a shoulder at about 398 eV, which are in the range of 395 - 401 eV observed by several other researches and are typical of N doped TiO_2 [1-4]. After fitting the experimental dots with Gaussian curve, it was obvious that the shoulder at about 398 eV could be fitted by a peak at the same binding energy. According to the studies about N1s XPS spectra of N doped TiO_2 [1-4, 12], the peak at 400 eV belongs to the NHx adsorbed at the surface of the particles, and the peaks at 398 and 396 eV are attributed to the bond of Ti-N, represented by two types of Ti-N bonds, labeled as TiN (1) and TiN (2) in Fig. 2, respectively. The details of the different bonding of TiN (1) and TiN (2) are discussed in the Discussion section. The N concentration was calculated from the peak areas, and found to be 1050 ppm of N for TiN (1) and 2270 ppm of N for TiN (2), respectively.

The N doped into TiO_2 particles is desorbed as N_2 when heating under vacuum. The N_2 TPD spectrum of the prepared N doped sample is shown in Fig. 3. It can be seen that there is a broad N_2 desorption peak from 700 to 1200 K, with a peak at about 1000 K and a shoulder at about 900 K. Considering the XPS results of two types of Ti-N bonds being present, the experimental data was fitted with two Gaussian peaks. The results were peak-1 at 908 K and peak-2 at 1020 K, labeled as TiN (1) and TiN (2) in Fig. 3, respectively. The N concentration was calculated from the peak areas,

and was found to be 759 ppm of N for TiN (1) and 2041 ppm of N for TiN (2). Also, the NH_3 adsorbed on TiO_2 particles is desorbed as NH_3 gas when heating under vacuum. NH_3 desorption of the prepared N doped TiO_2 particles was confirmed by NH_3 TPD spectrum (not shown) below 773 K, and no NH_3 desorption was found around high temperature above 773 K.
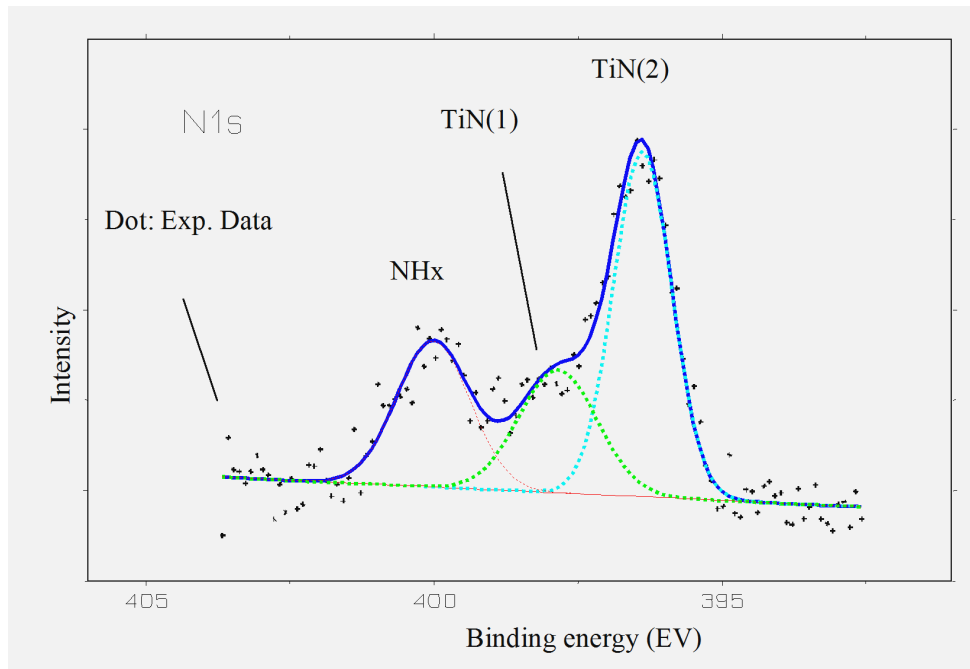

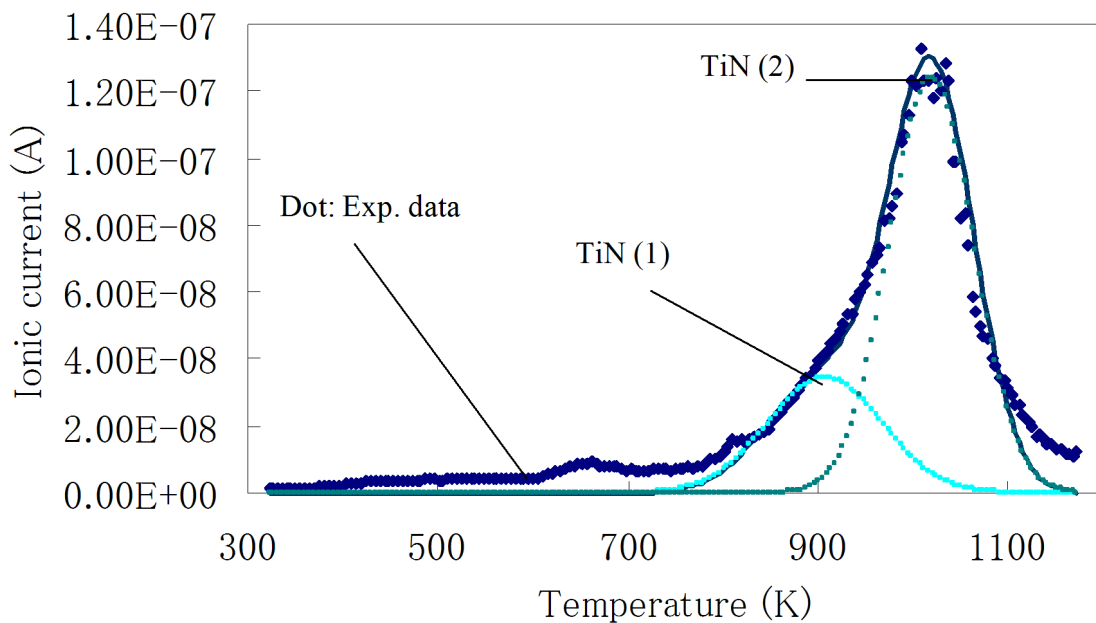Fig. 2. N1s XPS spectra of the prepared N doped TiO_2 nano particles.

Fig. 3. N_2 TPD spectra of the prepared N doped TiO_2 nano particles.

4. Discussion

For the two types of bonding of the N doped into TiO_2 observed in the N1s XPS spectra as shown in Fig. 2, the main peak observed at binding energy 396 eV was consistent with the results of Asahi et al. [1], who found that the visible light photocatalytic activity increased with the increase of the 396 eV peak in N1s XPS spectra, and concluded that the 396 eV peak was attributed to the substitutional site of N. Furthermore, Saha at el. [12] investigated the N1s XPS spectra during the oxidation process of TiN nitride, found that the main peak of N1s XPS was at 397 eV for TiN nitride and shifted to lower binding energy with oxidation time, and assigned the peak at binding energy 396 eV as chemisorbed atomic N. Therefore, we could derive that the peak of 396 eV labelled as TiN (2) in Fig. 2 was attributed to the bonding of Ti-N-Ti. The Ti-N-Ti bond means that the doped N substitutes the oxygen site in the TiO_2 crystal. For the small peak at 398 eV labelled as TiN (1) in Fig. 2, it was hard to assign it to molecularly chemisorbed N_2 which was observed at above 400 eV by Asahi et al.[1] and Saha et al.[12]. The peak could be due to the N invading in crystal lattice interstices of TiO_2, expressed as the Ti-N-O bond, which was supported by our TPD results discussed following.

For TPD detection of N doped TiO_2, the degree of the peak temperature of N desorption represents the degree of strength of N bonded to Ti. The higher the peak temperature of N_2 desorption is, the stronger the N is bonded to Ti. In general, the doped N is more stable in substitution site than in lattice interstice site. Therefore, it was reasonably derived that the N_2 TPD peak at 908 K in Fig. 3 was due to the Ti-N-O bond and the peak at 1020 K was due to the Ti-N-Ti bond. The labels of TiN (1) and TiN (2) in Fig. 3 were consistent with those in Fig. 2. The desorption peak of the doped N was more than 900 K in vacuum, showing its stability and high potential of visible light photocatalytic application for N doped TiO_2 nano particles.

Whether the concentration of the doped N is uniform from the surface to the inside of the particles or not is an important factor to discuss. XPS detection provides structure information about the surface, while TPD detection gives total information including the surface and bulk. Therefore, by comparing the results of XPS with those of TPD, we can get information about the uniform characteristics of the doped N. First, we compared the total concentrations of the doped N calculated from the sum of TiN (1) and TiN (2), 3320 ppm for XPS detection and 2800 ppm for TPD detection. Considering the error of about 10% ~ 20% for the XPS experiment, the results of XPS were derived to be consistent with those of TPD, so we came to the conclusion that the doped N in TiO_2 nano particles was uniform from the surface to the inside of the particles. Next, we compared the Ti-N-O bond and the Ti-N-Ti bond from XPS results with those from TPD results. The concentration of the doped N in Ti-N-O bonds was 1050 ppm from XPS, which was consistent with 759 ppm from TPD, considering the error stated above. Meanwhile, the doped N in Ti-N-Ti bonds was 2270 ppm from XPS, which was also consistent with 2041 ppm from TPD. Therefore, the doped N in the Ti-N-O bonds and in the Ti-N-Ti bonds was uniform from the surface to the inside of the prepared N doped TiO_2 nano particles.

5. Conclusion

N doped TiO_2 nano particles were prepared by heating TiO_2 nano particles in $NH_3 + C_3H_8$ 5vol% atmosphere. We concluded that the doped N was uniform from the surface to the inside of TiO_2 nano particles and found that the desorption peak of the doped N was more than 900 K in vacuum by XPS and TPD detection.

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