

Short communication

## Toward enhancement of TiO<sub>2</sub> surface defect sites related to photocatalytic activity via facile nitrogen doping strategy

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## ABSTRACT

This study examined the catalytic activities of three distinct N–Pd@TiO<sub>2</sub> nanoparticles, post-annealed (at 700, 800, and 900 °C) after fabrication on silicon substrates. Systematically, HRPES and SPEM indicated that nitrogen was predominantly doped around PdO nanostructure. Particularly, we prove that photocatalytic activity in effective nitrogen doped surface area is far higher than in undoped area of Pd@TiO<sub>2</sub> nanoparticles by measuring for oxidation reaction of benzenethiol, thioacetic acid, and thiobenzoic acid. Besides to the band gap narrowing, nitrogen doping leads to generate Ti<sup>3+</sup> species or oxygen vacancies site of the surface, which leads to enhance the activity of surface photocatalysis.

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## 1. Introduction

Photocatalysis research has increased in recent years, and a variety of commercial products have been developed to facilitate catalytic reactions. Among the various kinds of materials, the TiO<sub>2</sub> has received significant attention in catalysis research as a catalyst, a catalyst support, and a promoter. In special, due to the strong oxidizing ability of photogenerated holes, the high photostability, and the redox selectivity, TiO<sub>2</sub> becomes one of the most popular and promising catalysts for use in various catalytic applications [1,2].

Although TiO<sub>2</sub> is a promising catalytic material, the widespread use of TiO<sub>2</sub> has been hindered due to its wide band-gap [3–5]. Significant efforts have been applied toward reducing the wide band-gap in order to contribute to the catalytic activity under visible light irradiation with absence of structural change [6–8]. One of the most popular of these approaches involves the insertion of foreign elements as dopants [9–11]. But most previous studies of TiO<sub>2</sub> doping have focused on narrowing band gaps so as to enable catalytic reactions under visible light.

We recently reported the photocatalytic effect of Pd@TiO<sub>2</sub> fabricated using a different annealing temperature (700, 800, and 900 °C) and

confirmed that the cocatalytic effect of PdO formed over 800 °C can enhance the photocatalytic oxidation and narrow the band-gap [12].

In this study, we systematically investigated the effects of nitrogen doping into Pd@TiO<sub>2</sub> (N–Pd@TiO<sub>2</sub>) nanoparticles as cocatalyst-catalyst system. For this purpose, we prepared the N–Pd@TiO<sub>2</sub> nanoparticles formed PdO and Ti<sup>3+</sup> moieties on the nanoparticles' surfaces and observed significantly influence on the optical and enhancement of the catalytic activity by comparing the oxidation reactions of three molecules (benzenethiol; BE, thioacetic acid; TA, and thiobenzoic acid; TBA) using scanning transmission X-ray microscopy (STXM) and high-resolution photoemission spectroscopy (HRPES). For the first time, we found that the nitrogen doping proceeded mainly around PdO moieties and enhanced the catalytic oxidation, as indicated by scanning photoemission microscopy (SPEM). To our knowledge, no systematic study based on microstructural analysis has previously examined nitrogen doping as typical anion-doping with respect to enhancement of surface defect in TiO<sub>2</sub> system.

## 2. Experimental (see supporting information)

## 2.1. Results and discussion

Fig. 1 shows XRD patterns and SEM images of the prepared N–Pd@TiO<sub>2</sub>-700, 800, and 900 samples according to experimental section. The SEM images show the critical annealing dependent morphological changes in the surface and the amounts of PdO covered onto Pd or

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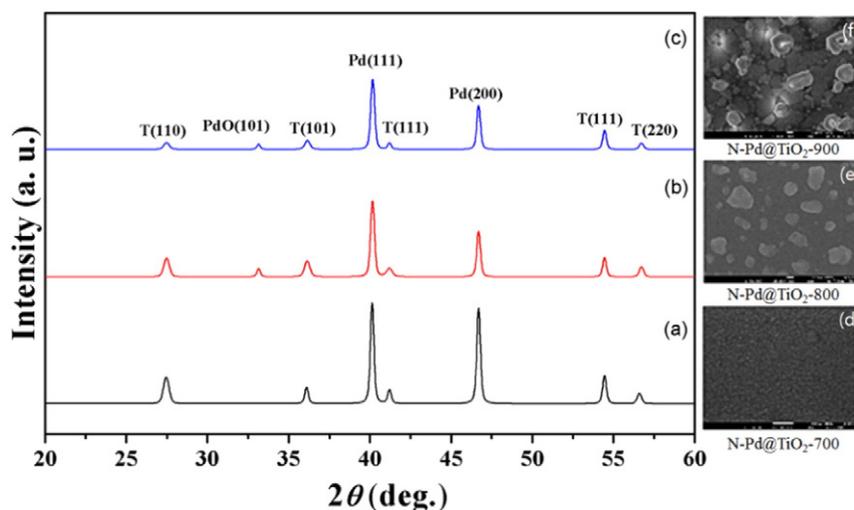


Fig. 1. XRD patterns and SEM images obtained from (a), (d) N-Pd@TiO<sub>2</sub>-700, (b), (e) N-Pd@TiO<sub>2</sub>-800, and (c), (f) N-Pd@TiO<sub>2</sub>-900.

metallic Pd at the surface, as reported previously [12,13]. Moreover, morphology of N-Pd@TiO<sub>2</sub>-700, 800, and 900 samples are very similar to those of Pd@TiO<sub>2</sub>-700, 800, and 900 samples, respectively. So doping process did not accompany the morphological change.

The XRD patterns collected over the range 20°–60° shows that three synthesized catalysts exhibited characteristic diffraction peaks at  $2\theta = 40^\circ$ , which corresponded to the (111) crystalline plane of the *fcc* Pd nanoparticles [14]. Interestingly, in the N-Pd@TiO<sub>2</sub>-700, there was no peak corresponding to PdO(101). Above 800 °C, however, the PdO(101) peak was detected at a  $2\theta$  value of 33.8° and the intensity of Pd(111) decreased slightly. We also checked the structural changes displayed by these samples before and after nitrogen doping. As expected, three samples show the rutile structure and do not appear any new peak. We then analysed the catalytic oxidation effect by using STXM, HRPES, and SPeM.

Fig. 2 shows the TEM images (insets) and the corresponding XAS spectra by using STXM for N-Pd@TiO<sub>2</sub>-700, 800, and 900 which compare the electronic structures and surface structures. As shown in Fig. 2(a), the Pd pre-edge is existed in all three spectra. Fig. 2(b) shows the Ti *L*-edge (*2p*) in the three samples. On the other hand, the Ti *L*-edge spectra indicate the presence of typical rutile TiO<sub>2</sub> structures [15–17]. The intensities of the two pre-edge peaks of N-Pd@TiO<sub>2</sub>-800 (marked A) located at 456.7 and 457.4 eV exceeded those of

the others samples due to the effective nitrogen doping, which indicates that these peaks corresponded to surface defect structures (the Ti<sup>3+</sup> state) [18,19].

The O *K*-edge spectra differed in a critical manner of the two pre-peaks at 530–540 eV, as shown in Fig. 2(c). The low-energy region of the spectrum (530–540 eV) corresponds to transitions from the O 1s core-level orbital to the O 2*p* orbital [20–22]. Therefore, the differences correspond to defect structures that influence the interactions between the O 2*p* and Ti 3*d* orbitals.

In the N *K*-edge also shows difference between samples. The spectrum of N-Pd@TiO<sub>2</sub>-800 contains very sharp N *K*-edge peak, so we suggest that the presence of nitrogen doping is well occurred. Interestingly, no peak is observed in N-Pd@TiO<sub>2</sub>-900, and the nitrogen doping is not occurred. As mentioned above, these results were obtained due to the dominant presence of PdO and Pd on the N-Pd@TiO<sub>2</sub>-900 surface. Therefore, we could clearly confirm that the Pd@TiO<sub>2</sub>-800 sample is readily doped with nitrogen to yield a distinct electronic structure as a result of the differences between the surface defect structures.

The core level spectra (Pd 3*d*, Ti 2*p*, O 1s, and N 1s) of the N-Pd@TiO<sub>2</sub> nanostructured nanoparticles were obtained using HRPES (see Fig. 3) to determine the changes in the electronic properties. The concentration of Pd was 3.0% on average, as determined from the Pd 3*d* to Ti 2*p* peak ratio

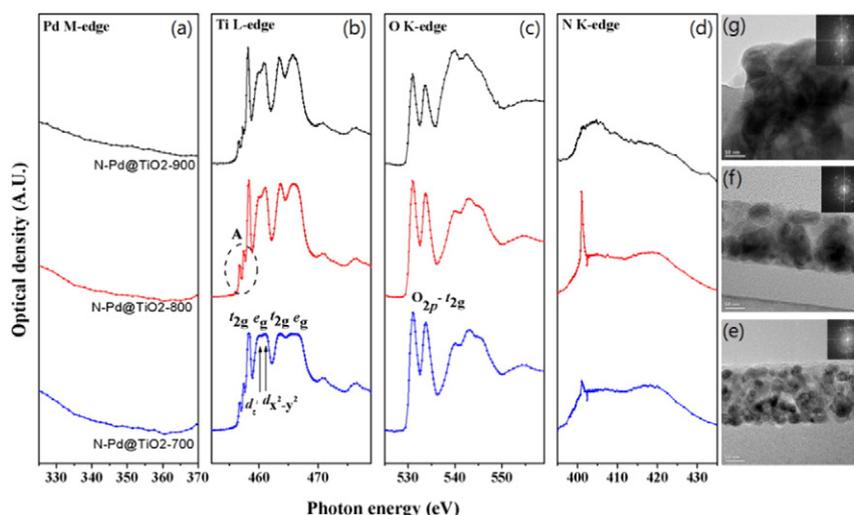


Fig. 2. XAS spectra of (a) Pd *M*-edge, (b) Ti *L*-edge, (c) O *K*-edge, and (d) N *K*-edge for N-Pd@TiO<sub>2</sub>-700 (blue line), 800 (red line), and 900 (black line), TEM images obtained from (e) N-Pd@TiO<sub>2</sub>-700, (f) 800, (g) 900.

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