Nitrogen Doped TiO$_2$ Photocatalysts Synthesized from Titanium Nitride: Characterizations and Photocatalytic Hydrogen Evolution Performance

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Abstract

A series of nitrogen-doped TiO$_2$ were synthesized by oxidizing titanium nitride (TiN) at different temperatures under ambient condition. The as-prepared samples were systematically characterized by X-ray diffraction, transmission electron microscopy, high-resolution transmission electron microscopy, X-ray photoelectron spectroscopy (XPS), and ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS). The photocatalytic activity for hydrogen evolution of the as-prepared samples was evaluated under UV-Vis light irradiation. XPS investigations confirmed the presence of nitrogen in TiO$_2$ lattice in the chemical environment of O–Ti–N. The UV-Vis DRS results showed that the absorption edge was extended into visible light region. Higher photocatalytic activity than that of commercial titanium dioxide - P25 was observed over the as-prepared nitrogen-doped TiO$_2$ under UV-Vis light illumination.

Keywords: Titanium dioxide · Nitrogen doping · Photocatalysts · Hydrogen evolution
1 Introduction

Hydrogen evolution from photocatalytic water-splitting has drawn tremendous interests for its simplicity, harmlessness and tempting prospect. Since the discovery of the electrochemical photolysis of water over TiO$_2$ electrodes [1], TiO$_2$ has been extensively investigated in photochemical application research [2-7]. The mechanism of water splitting over TiO$_2$ photocatalysts under the action of light is that the semiconductor absorbs photons at wavelengths below its band-gap wavelength, producing electron–hole pairs, and then the photogenerated electrons drive the water-splitting reaction to produce hydrogen [8]. However, the practical application of TiO$_2$ is severely limited by its wide band gap (3.2eV), which facilitates response to only ultraviolet light accounting for less than 5% of the solar spectrum. To date, great efforts have been taken to improve the photocatalytic activity of TiO$_2$ for hydrogen evolution by enlarging its absorption scope [9-13].

Doping TiO$_2$ with non-metallic elements [14-16] is considered to be one of the most efficient approaches to extend the optical absorption edge into visible light region. Recent reports have revealed that elemental nitrogen is an optimal candidate of doping species. N-doped TiO$_2$ can be obtained by various methods [17], such as nitrogen treatment of TiO$_2$ [9-24], direct synthesis [25-31], shock wave action of TiO$_2$ with nitrogen doping source [32] and thermal oxidation of titanium nitride (TiN) [33, 34]. For example, Asahi et al. prepared TiO$_{2-x}$N$_x$ powders by treating anatase TiO$_2$ powders in an NH$_3$ (67%)/Ar atmosphere at 873 K for 3 h [9]. Sathish et al. obtained N-doped TiO$_2$ nanoparticles using TiCl$_4$ and Na$_2$S as precursors and ammonia as the source of nitrogen [35].

Among all these preparation methods, thermal oxidation of TiN is considered as a comparably simple and facile route to prepare N-doped TiO$_2$. Morikawa et al. synthesized N-doped TiO$_2$ by oxidizing TiN powder in oxygen, which showed a significant shift of the absorption edge to the visible light region [33]. Wu et al. reported the photocatalytic activity
for degradation of toluene under visible light irradiation of N-doped TiO$_2$ obtained by annealing TiN at a high temperature ranging from 450°C to 650°C [34]. However, little attempt has been made to investigate their photocatalytic activity for hydrogen evolution under UV-Vis light irradiation. In our previous work [36, 37], we have prepared nitrogen-doped titanium dioxide (TiO$_2$$_x$N$_y$) film with visible light photoresponse by thermal annealing of TiN at 350°C and oxidation of sputtered TiN$_x$ films, respectively. Herein, a series of N-doped TiO$_2$ powders were synthesized by annealing TiN powders under ambient condition at a relatively lower temperature ranging from 350°C to 450°C and their photocatalytic activity for hydrogen evolution from water splitting was investigated under UV-Vis light irradiation compared to that of P25.

2 Experimental Details

TiN powders with an average particle size of 20 nm were purchased from Kaier Company (99%, China). Nitrogen-doped TiO$_2$ powders were prepared by controlled oxidization of TiN powders in a porcelain boat in a muffle furnace. Pristine TiN powders were annealed in air at 350°C, 400°C, and 450°C for 2 h, and the obtained nitrogen-doped TiO$_2$ samples were labeled as N-TiO$_2$-350, N-TiO$_2$-400, and N-TiO$_2$-450, respectively. The weight of the powders after annealing increased about 15 wt% to 19 wt%, less than 25 wt% when the total was replaced by oxygen in theory, suggesting an incomplete oxidation of TiN.

The crystal phases of the samples were analyzed by X-ray diffraction (XRD, Bruker D/8 advanced diffractometer) using a diffractometer with Cu K$_\alpha$ radiation. The morphology structure and oxidizing process were examined by transmission electron microscopy (TEM: JEOL JEM-2011, Japan) and energy-dispersive X-ray spectroscopy. The UV-Vis absorption spectra were obtained using a Cary-50 Scan UV–Vis spectrophotometer recorded from 200 to 800 nm. The XPS experiments were carried out on a PHI-5000 C ESCA system (Perkin Elmer)
with Al/Mg Kα radiation. Binding energies were calibrated using the contaminated carbon (C1s = 284.6 eV).

The photocatalytic performance of the as-prepared samples was evaluated by hydrogen evolution from water splitting under UV-Vis light irradiation at room temperature. The light intensity was measured to be 100 mW•cm⁻² by an optical power meter (Thermo Oriel, USA) from a 500 W Xe lamp with a water filter to remove the infrared part of the spectrum. In a typical process, 50 mg of the photocatalyst was added to 100 mL of aqueous solution containing 0.1 M Na₂S and 0.04 M Na₂SO₃. The mixture was dispersed by ultrasonic stirring for 15 min and deaerated with N₂ gas for 30 min prior to the irradiation of UV-Vis light under magnetic stirring. The evolution gas was periodically analyzed with a gas chromatograph (GC7900, TCD, molecular sieve 5 Å, N₂ carrier).

3 Results and Discussion

3.1 Structure and Morphology

The crystal structure of TiN precursor and the as-prepared N-TiO₂ powders were identified by XRD patterns as shown in Fig.1. Calcination of the TiN precursor generates mixed phases of anatase and a small fraction of rutile. Well-defined TiO₂ anatase at 25.3° can be observed for the sample of N-TiO₂-350. With the annealing temperature rising, the intensity of the peaks ascribed to anatase and rutile phases increased for the sample N-TiO₂-400 and N-TiO₂-450, respectively, probably due to heavier oxidation of TiN powders into TiO₂ and the improved degree of crystallization, suggesting incomplete oxidation of TiN for sample N-TiO₂-350 and N-TiO₂-400. However, doping of nitrogen did not change the crystalline structure of TiO₂ [38,39], possibly because of a low doping content [40]. The average crystal sizes for anatase and rutile TiO₂ in N-TiO₂-450 are 17 nm and 22 nm, respectively, calculated
using the Scherrer equation [41] with the proportion of anatase as about 88% estimated from the relative peak intensities [42].

The structure of N-doped TiO$_2$ powders was further investigated by TEM and high-resolution (HRTEM) as shown in Fig. 2. It can be observed that the N-doped TiO$_2$ particles obtained by annealing TiN at 350°C for 1 h were well dispersed with an average size of about 18 nm as shown in Fig. 2(a). Two sets of lattice fringes can be observed in the HRTEM images in Fig. 2(b). The fringes in the center with a d-spacing of 0.24 nm correspond to (111) plane of residual TiN crystal structure, and the other set of fringes around TiN with d-spacing of 0.35 nm can correspond to (101) plane of anatase TiO$_2$, suggesting that TiN precursor was gradually oxidized from outside to inside which is in good consistent with the XRD results. Fig. 2(c) shows the corresponding selected area electron diffraction (SAED) pattern in Fig. 2(b). The diffraction rings can be indexed to anatase TiO$_2$ with one diffraction ring between (004) and (200) rings to (200) plane of residual TiN, further confirming the incomplete oxidation TiN.

3.2 Chemical States of Doped Nitrogen

The chemical states of nitrogen in the as-prepared N-TiO$_2$ samples were investigated with XPS measurements and the results were shown in Fig. 3. For TiN precursor, the characteristic peaks of C1s (284.6 eV), Ti2p (458.5 eV), O1s (530.2 eV) and N1s peak (396.1 eV) can be recognized clearly, while the N1s peak at the same position can not be observed clearly for the as-prepared N-TiO$_2$ samples, suggesting that almost no residual TiN precursor remains on the surface of the as-prepared samples, which is in accordance with the XRD and TEM results. It was observed that a shift for higher binding energy of Ti 2p occurred after TiN annealing, which demonstrated that nitrogen was doped into the lattice of TiO$_2$ [43] during the process of calcination.

Fig. 4 shows the N 1s XPS spectra of the samples. A typical binding energy at 396.1 eV
is observed for TiN precursor, which is ascribed to Ti–N bonds [10, 44]. The N-doped TiO$_2$ nanoparticles exhibit a small and weak peak centered at 399.5 eV, which is assigned to doping N in O–Ti–N linkages [31]. The atomic ratio of N/Ti for TiN, N-TiO$_2$-350, N-TiO$_2$-400, and N-TiO$_2$-450 was calculated to be 65, 3.6, 1.7, and 1.2 %, respectively, indicating that the content of nitrogen doping decreased with the increase of annealing temperature.

3.3 UV-Vis Absorption Performance

The powders turn yellowish from pristine deep dark in color after annealing. Fig. 5 shows the typical optical absorbance spectra obtained by the diffuse reflection of the N-doped TiO$_2$ samples and P25. Noticeable shift of the absorption edge into the visible light region was observed for both N-TiO$_2$-400 and N-TiO$_2$-450 compared with that of P25. The extended light absorption was attributed to the substituional doping of nitrogen into the TiO$_2$ lattice [9, 33], which was confirmed by the XPS characterizations.

3.4 Photocatalytic Activity for Hydrogen Evolution

Fig. 6 shows the photocatalytic activity of the as-prepared samples for hydrogen evolution under UV-Vis light irradiation. A significant improvement of overall hydrogen evolution is observed for the N-doped TiO$_2$ samples compared with that of P25. It is found that the total amount of hydrogen evolution increases correspondingly with the increase of annealing temperature of TiN precursor. The improved photocatalytic activity of the as-prepared N-TiO$_2$ with the increase of annealing temperature is ascribed to the decreased content of doped nitrogen, suggesting that nitrogen doping sites with high concentration could also serve as recombination sites [9, 10], which is disadvantageous to hydrogen evolution. The highest photocatalytic activity was observed for N-TiO$_2$-450 among the as-prepared samples under UV-Vis light irradiation with an H$_2$ evolution rate of 18.0 μmol·h$^{-1}$, which is 1.4 times higher
than that of P25.

4 Conclusions

In this work, N-doped TiO$_2$ nanostructured photocatalysts have been successfully synthesized by annealing TiN powders under ambient condition at a relatively low temperature range. The XPS results demonstrate that nitrogen is substitutionally doped into the lattice of TiO$_2$ and the doped nitrogen mainly exists as O–Ti–N. The photoresponse of TiO$_2$ was enlarged into the visible light region by nitrogen doping. The highest photocatalytic activity for hydrogen production was obtained for N-doped TiO$_2$ synthesized by annealing TiN precursor at 450°C among the as-prepared samples compared with that of P25. N-doped TiO$_2$ prepared in such a facile way shows potential application in hydrogen production for its enhanced photocatalytic activity in the UV-Vis light region. More work is underway to further enhance the photocatalytic activity through the modification of the resulted N-doped TiO$_2$.

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**Figure captions**

**Fig. 1** XRD patterns of the samples. (a) Pristine TiN, (b) N-TiO$_2$-350, (c) N-TiO$_2$-400, (d) N-TiO$_2$-450.

**Fig. 2** TEM (a) and HRTEM (b) images of N-TiO$_2$-350 obtained by TiN annealing at 350°C for 1 h in air; (c) the corresponding selected-area electron diffraction (SAED) in (b).

**Fig. 3** XPS spectra of the samples. (a) TiN, (b) N-TiO$_2$-350, (c) N-TiO$_2$-400, (d) N-TiO$_2$-450.

**Fig. 4** The N1s XPS spectra of (a) TiN, (b) N-TiO$_2$-350, (c) N-TiO$_2$-400, and (d) N-TiO$_2$-450.

**Fig. 5** Typical UV-Vis diffuse reflectance spectra of the as-prepared N-TiO$_2$ samples and P25.

**Fig. 6** Reaction time profiles of H$_2$ evolution under UV-Vis light irradiation (100 mW/cm$^2$) over the photocatalysts (50 mg) using 0.1M Na$_2$S-0.04 M Na$_2$SO$_3$ as the sacrificial agent. (a) P25, (b) N-TiO$_2$-350, (c) N-TiO$_2$-400, (d) N-TiO$_2$-450.
References


**Figure 1**

![XRD patterns of the samples](image)

Fig. 1 XRD patterns of the samples. (a) Pristine TiN, (b) N-TiO$_2$-350, (c) N-TiO$_2$-400, (d) N-TiO$_2$-450.
**Fig. 2** TEM (a) and HRTEM (b) images of N-TiO₂-350 obtained by TiN annealing at 350°C for 1 h in air; the inset is the fast Fourier transform (FFT) spectrum of the edge of the black part of (b).
Fig. 2(b) TEM (a) and HRTEM (b) images of N-TiO$_2$-350 obtained by TiN annealing at 350°C for 1 h in air; the inset is the fast Fourier transform (FFT) spectrum of the edge of the black part of (b).
Fig. 3 XPS spectra of the samples. (a) TiN, (b) N-TiO$_2$-350, (c) N-TiO$_2$-400, (d) N-TiO$_2$-450.

Fig. 4 The N1s XPS spectra of (a) TiN, (b) N-TiO$_2$-350, (c) N-TiO$_2$-400, and (d) N-TiO$_2$-450.
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