



Efficient hydrogen production by photocatalytic water splitting using N-doped TiO₂ film



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ABSTRACT

N-doped TiO₂ film was deposited by RF reactive magnetron sputtering in a mixture gas of N₂, O₂ and Ar. The experimental results show that the crystal structure is anatase phase, and the concentration of substitutional nitrogen is 4.91 at.% which leads to a narrow optical band gap of 2.65 eV. The H₂ production rate of the N-doped TiO₂ film is about 601 μmol g⁻¹ h⁻¹, far higher than that of the undoped TiO₂ film and even about 50 times higher than that of dispersive P25 powder.

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1. Introduction

With the increasing human activities, fossil fuels, which have caused many serious environmental problems, are difficult to maintain the growing energy demand. Therefore, many research groups have already focused on the clean and renewable energy, such as wind, solar, biomass and hydrogen. In particular, hydrogen, generated by photocatalytic water splitting, has attracted considerable attention as an alternative solution for energy crisis and environmental pollution.

The photoelectrochemical hydrogen production was first reported in 1972, in which TiO₂ was used as the photoanode material [1]. Since then, photocatalytic water splitting for hydrogen production using TiO₂ has been extensively studied due to its high photocatalytic activity, stability, non-corrosion and nontoxicity. However, several drawbacks hinder its widespread applications, such as the recombination of photoexcited electron–hole pairs and the large electronic band gap (anatase, 3.2 eV) [2]. One of the effective methods to overcome the drawbacks is doping

nonmetal elements into TiO₂, e.g. N, C, S and F [3–7], among which, nitrogen doping shows obvious advantages [8,9] due to the small ionic radius of nitrogen, unique properties of high thermal stability and low recombination centers. Previous studies [3,10,11] have also indicated that narrow optical band gap and high photocatalytic activity can be obtained by doping N into TiO₂. So far, many techniques have been developed to synthesize N-doped TiO₂, including sol–gel [12,13], hydrothermal method [14], oxidation of titanium nitride [15], pulsed laser deposition [16] and sputtering [17–21], among which TiO₂ films deposited by sputtering exhibit uniform composition [22] and facile control of film thickness [23]. In addition, many methods have been proposed to enhance the water splitting by use of TiO₂-based materials, such as constructing photoelectrochemical cells (PEC, consist of a single-crystal TiO₂ photoanode and a Pt cathode) [1] and p/n-photoelectrolysis cells [24], adjusting pH value [25], adopting particulate photocatalytic system [26], employing NaOH coating [27] and adding cocatalyst (e.g. Pt, Au) [28]. However, there are few reports on using TiO₂ films deposited by sputtering to generate hydrogen without the assistance of metal cathode, bias or loading noble metal. In this work, N-doped TiO₂ films were prepared by RF magnetron sputtering in a mixture of O₂, N₂ and Ar. The intrinsic properties of the films were investigated by XRD, SEM, AFM, XPS and UV–vis spectrophotometer. Hydrogen production was examined by immersing the as-deposited films into 10% aqueous methanol solution. It is found that the photocatalytic activity of N-doped TiO₂ film in water

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splitting was far higher than that of undoped TiO₂ film and even Degussa P25 powders.

2. Experimental

N-doped TiO₂ films were deposited on quartz glass substrates (2 × 4 cm) by RF reactive magnetron sputtering. These substrates were beforehand cleaned, sequentially with acetone, alcohol and de-ionized water, respectively for 20 min in the ultrasonic bath. The working gas was a mixture of N₂ (99.999% pure), O₂ (99.99% pure) and Ar (99.999% pure). The target was a 2-inch-diameter Ti metal plate (99.999% pure). The target-substrate distance was fixed at 70 mm and the base vacuum was 5.8 × 10⁻³ Pa. Before deposition, the substrate temperature was maintained at 400 °C for 2 h to degas and the target was pre-sputtered for 30 min by argon plasma. Afterwards, working gas was introduced into the chamber through three mass flow controllers and flow rate fixed at 5.0sccm (standard cubic centimeter per minute), 3.9sccm, 40sccm for N₂, O₂ and Ar respectively. The total working pressure was set at 0.3 Pa and the RF power was fixed at 130 W. The whole deposition process was conducted at 450 °C for 4 h, during which the substrate rotated around its axis at 8 rotations per minute. Pure TiO₂ film was also deposited under the same condition without N₂ as reference.

The crystalline structure of the as-deposited N-doped TiO₂ films was identified by X-ray diffraction (XRD, Model D/Max 2550 V, Rigaku, Japan). The thickness and morphology were determined by field emission scanning electron microscopy (FE-SEM, JSM6700F, JEOL, Japan). The surface roughness was estimated by atomic force microscopy (AFM, Nanoscope, NS3A-02, Veeco, USA). The transmittance spectra of the films were measured by a UV-vis spectrophotometer (Lambda 900, PerkinElmer, USA). The chemical compositions and valence-band spectra were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo Scientific, USA).

The hydrogen production was examined by the photocatalytic water splitting testing system (CEL-SPH2N, AULTT, China), irradiated by a 300 W Xe lamp (CEL-HXF300, AULTT, China). The total output of the lamp was 50 W and only 2.6 W of incoming irradiance was obtained below 390 nm. The photocatalytic reaction was carried out in a quartz cell containing 100 mL aqueous methanol solution (CH₃OH: H₂O = 1:10 v/v). Before reaction, the as-deposited film was immersed in the aqueous solution and then oxygen was removed by a mechanical pump. The film-lamp distance was fixed at 12 cm. The amount of H₂ produced was analyzed by a gas chromatograph (SP7800, AULTT, China) using N₂ as carrier gas.

3. Results and discussion

3.1. Crystalline structure and morphology

Fig. 1 shows the XRD patterns of N-doped TiO₂ film. Diffraction peaks observed at 2θ = 25.28°, 36.95°, 37.88°, 38.55°, 48.05°, 54.09°, 54.88°, 62.67°, and 68.76° correspond well with (1 0 1), (1 0 3), (0 0 4), (1 1 2), (2 0 0), (1 0 5), (2 1 1), (2 0 4), and (1 1 6) planes of anatase phase of TiO₂ (JCPDS No. 21-1272), indicating that no other phase (e.g., rutile or brookite) is observed and N-doping has little effect on the crystal structure. Nevertheless, it can be seen that N-doping can greatly influence the growth orientation of anatase TiO₂ particles. As shown in Fig. 1, the intensities of the (0 0 4), (1 1 2), (2 0 0), and especially (2 1 1) peaks become stronger while (1 0 1) peak become weaker for the N-doped TiO₂ film, compared with those of the undoped TiO₂ film. For example, the ratios of I(2 1 1) to I(1 0 1) [I(2 1 1) and I(1 0 1) are the intensities of (2 1 1) and (1 0 1) peaks, respectively] for the N-doped and undoped TiO₂

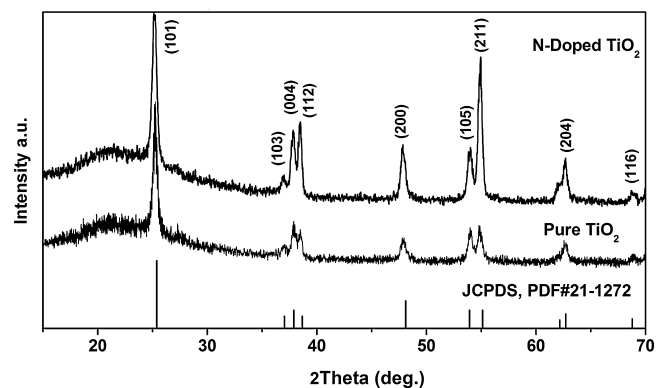


Fig. 1. XRD patterns of pure TiO₂ and N-doped TiO₂ films prepared by RF reactive magnetron sputtering.

films are 100% and 33%. As is well-known, the surface energies of (0 0 1), (1 1 2), (1 0 0), and (2 1 1) planes are all higher than that of (1 0 1) plane [29]. Therefore, high photocatalytic activity of N-doped TiO₂ film is expected, due to its large percentage of exposed (0 0 4), (1 1 2), (2 0 0), and (2 1 1) facets.

Fig. 2a illustrates the surface morphology of the N-doped TiO₂ film, which exhibits a rough appearance of interconnected TiO₂ nodules. Columnar structure is clearly observed from the cross-sectional image, as shown in Fig. 2b. The width of columnar nanograins is ~40 nm, and the thickness of the film is 900 nm ± 20 nm. The root-mean-square (RMS) roughness of the film is 20.4 nm, measured by AFM (see Fig. 2c).

3.2. Chemical composition and optical band gap

The chemical states and compositions of the undoped and N-doped TiO₂ films were determined by X-ray photoelectron spectroscopy (XPS). Before the surface analysis, Ar sputtering for 20 s was conducted to remove the contamination. Both the films exhibit Ti-2p_{3/2} peaks at 458.5 eV and O-1s peaks at 529.7 eV (data not shown). High-resolution and curve fitting of N-1s XPS spectra of the undoped and N-doped TiO₂ films are plotted in Fig. 3. A pair of N-1s features, located at 396.5 eV and 399.8 eV respectively, are observed in the N-doped TiO₂ sample, while only a broad and weak peak around 399.8 eV is shown in the undoped TiO₂ sample. In general, the peak at 399.8 eV is assigned to either chemisorbed molecular N₂ on the surface or interstitial molecular N₂ [30], while the peak at 396.5 eV is attributed to atomic β-N states (i.e., O–Ti–N bonds) [3,31–33]. As shown in Fig. 3, for the N-doped sample, the peak intensity at 396.5 eV is far stronger than the one at 399.8 eV, indicates the successful incorporation of N into TiO₂ film. The incorporated N is 4.91 at.%, estimated from the integrated intensities of the N-1s peak at 396.5 eV.

It is found that the color of the N-doped TiO₂ film was flavo-green while the undoped TiO₂ film was pale straw yellow. Since the color of a solid is determined by the position of its absorption edge, the UV-vis absorption spectra of these two samples were further studied. As shown in Fig. 4a, the absorption edge of the undoped TiO₂ film ends at about 380 nm, while for the N-doped sample, the absorption edge shifts toward the visible light region where a distinct absorption tail (between 400 and 550 nm) is observed. The absorbance line drops sharply from 400 to 450 nm and then decreases gently from 450 to 550 nm, revealing that the excitation of electrons from localized states in the band gap to unoccupied states in CB may also lead to the absorption of visible light, as well as the transition from VB (valence band) to CB (conduction band). The band gap of the samples was calculated from the absorption spectra by using the Tauc formula [34], as shown in Fig. 4b. The

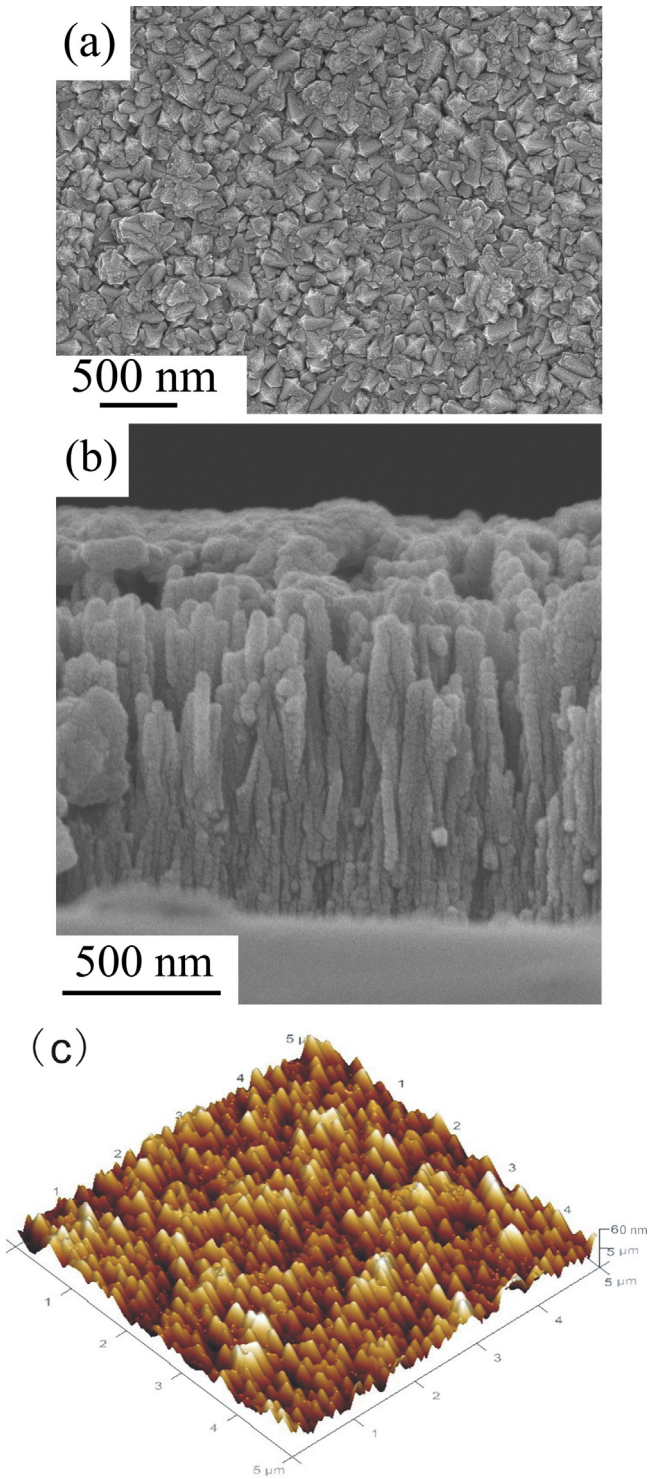


Fig. 2. (a) Surface and (b) cross-sectional SEM images and (c) AFM image of the N-doped TiO₂ film.

optical band gap is 2.65 eV for the N-doped sample and 3.28 eV for the undoped TiO₂ sample, indicating that N-doping can evidently narrow the band gap of TiO₂. This is due to the overlap between nitrogen and oxygen 2p orbital mainly from the N doping according to our XPS data (the specific peak at 395.5 eV of N-doped sample). The band-narrowing and the enhanced absorption in the visible-light region (see Fig. 4a) can lead to higher utilization efficiency of sunlight.

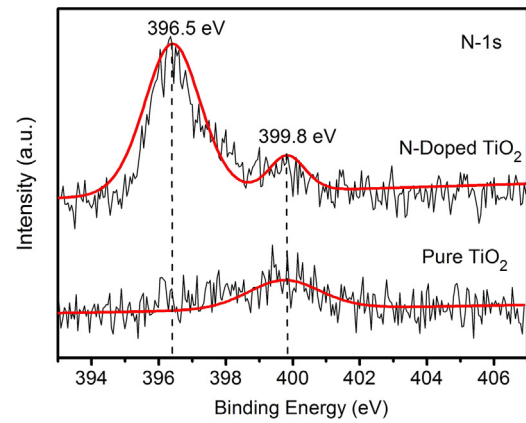


Fig. 3. N-1s XPS spectra collected from N-doped TiO₂ and pure TiO₂ films.

3.3. Hydrogen production

The photocatalytic activity of the N-doped TiO₂ film and pure TiO₂ film was tested in an aqueous methanol solution under the Xe lamp irradiation for 10 h. Two forms of Degussa P25 were tested on the same condition as reference: powder (0.1 g of mass, and a magnetic stirrer was employed during the reaction) and film (deposited on a 2 × 4 cm quartz glass substrate by spin-coating; the thickness is about 1 μm). Methanol, worked as sacrificial reagent, may also undergo photocatalytic reforming to produce hydrogen, thus a blank experiment was also carried out during which no hydrogen can be detected (data not shown here). As shown in Fig. 5, the amount of hydrogen produced by N-doped TiO₂ film and P25 powder increases almost linearly with the irradiation time, while, in stark contrast, H₂ generated is hardly detected by using either

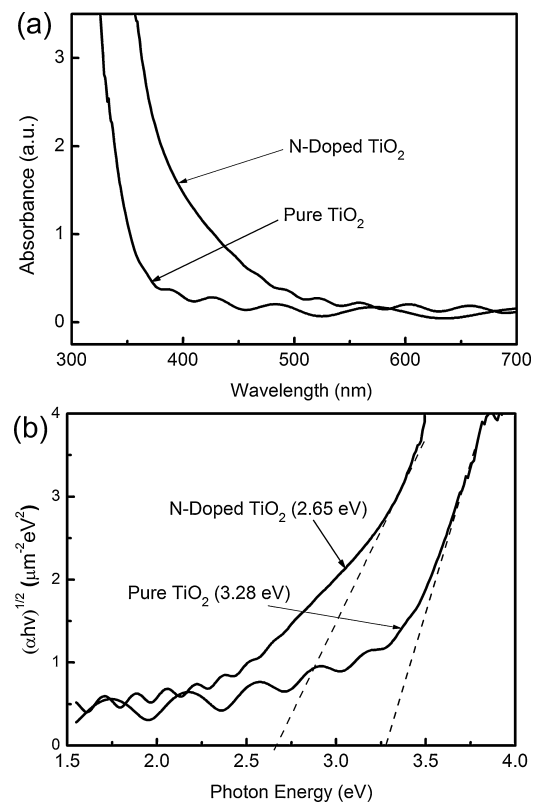


Fig. 4. (a) Absorption spectra and (b) the plots of $(\alpha h\nu)^{1/2}$ as a function of photo energy ($h\nu$) for the undoped and N-doped TiO₂ films.

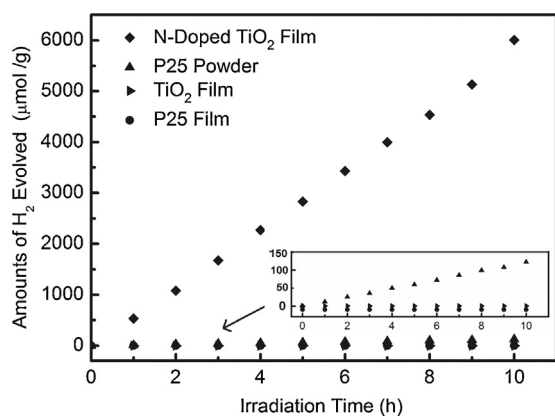


Fig. 5. Hydrogen evolution profiles of N-doped TiO₂ film, P25 powder, TiO₂ film and P25 film.

the undoped TiO₂ film or P25 film. P25 is widely accepted as an excellent photocatalyst with large specific surface area, and there is no doubt that its specific surface area is far larger than that of the N-doping TiO₂ film. However, the N-doped TiO₂ film exhibits much higher activity (about 601 μmol H₂ g⁻¹ h⁻¹; Herein, the density of bulk anatase TiO₂ was used to estimate the mass of the film; the film thickness is about 900 nm) than dispersive P25 powder (about 12 μmol H₂ g⁻¹ h⁻¹ when a high-dose of 0.1 g was adopted). As aforementioned, the presence of nitrogen leads to a red-shift of the absorbance edge and enhanced absorption in the visible-light region. Consequently, the N-doped film can be excited by the visible region of irradiation while P25 (as well as the undoped TiO₂ film) can only absorb the UV light. N-doping also leads to the increase of exposed high surface energy facets (See XRD pattern), which means high photocatalytic activity for N-doped TiO₂ film. Additionally, N-doped TiO₂ can promote the formation energy of oxygen vacancies to decrease dramatically from 4.2 eV to 0.6 eV [35,36], resulting in the growing of oxygen vacancies in the film. The oxygen vacancies can work as color centers to enhance the photocatalytic activity. Although there exists disagreement that N in the TiO₂ lattice can suppress the recombination of the electron–hole pairs, the N-doped TiO₂ film shows high photocatalytic activity, about 50 times higher than P25 powder. Furthermore, it should be noticed that cathode, bias and/or noble metal were not employed in this work. Yet the hydrogen production of the film achieves the same level of the powder-form (which owns large specific surface area) N-doped TiO₂, or even higher. For instance, the hydrogen production of N-doped TiO₂ is about 14 times higher than pure TiO₂ in Babu et al.'s work [37], and according to Lin and Shih's research [38], the photocatalytic activity of N-doped TiO₂ is just 15 times higher than Degussa P25 powder.

4. Conclusions

The N-doped TiO₂ film was successfully synthesized by RF reactive magnetron sputtering, with anatase phase and a large percentage of exposed (004), (112), (200), and especially (211) facets. The film, about 900 nm in thickness, is composed of columnar structures. The optical band gap decreases from 3.28 eV (for undoped anatase TiO₂ sample) to 2.65 eV when 4.91 at.% nitrogen is incorporated into the anatase structure. H₂ is photocatalytically produced and the amount of H₂ increases linearly with the exposure time when immersing this sample into 10% aqueous methanol solution and irradiating under the Xe lamp. The H₂ production rate of the N-doped TiO₂ film is about 601 μmol g⁻¹ h⁻¹, far higher than that of the undoped TiO₂ film (H₂ evolution was hardly detected) and even dispersive P25 powder (about 12 μmol H₂ g⁻¹ h⁻¹), which

is attributed to the red shift of the absorbance edge and the large percentage of exposed high surface energy facets.

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References

- [1] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, *Nature* 238 (1972) 37–38.
- [2] A. Fujishima, K. Hashimoto, T. Watanabe, *TiO₂ Photocatalysis: Fundamentals and Applications*, 1st ed., BKC, Tokyo, 1999.
- [3] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Visible-light photocatalysis in nitrogen-doped titanium oxides, *Science* 293 (2001) 269–272.
- [4] S.U.M. Khan, M.A.L-Shahry, W.B. Ingler Jr., Efficient photochemical water splitting by a chemically modified n-TiO₂, *Science* 27 (2002) 2243–2245.
- [5] G. Yang, Z. Yan, T. Xiao, Low-temperature solvothermal synthesis of visible-light-responsive S-doped TiO₂ nanocrystal, *Appl. Surf. Sci.* 258 (2012) 4016–4022.
- [6] J. Xu, Y. Ao, D. Fu, C. Yuan, Low-temperature preparation of F-doped TiO₂ film and its photocatalytic activity under solar light, *Appl. Surf. Sci.* 254 (2008) 3033–3038.
- [7] X. Cheng, X. Yu, Z. Xing, One-step synthesis of visible active C–N–S tridoped TiO₂ photocatalyst from biomolecule cystine, *Appl. Surf. Sci.* 258 (2012) 7644–7650.
- [8] S. Rodrigues, K.T. Ranjit, S. Uma, I.N. Martyanov, K.J. Klambunde, Single-step synthesis of a highly active visible-light photocatalyst for oxidation of a common indoor air pollutant: acetaldehyde, *Adv. Mater.* 17 (2005) 2467–2471.
- [9] W.Y. Choi, A. Termin, M.R. Hoffmann, The role of metal ion dopants in quantum-sized TiO₂: correlation between photoreactivity and charge carrier recombination dynamics, *J. Phys. Chem.* 98 (1994) 13669–13679.
- [10] T. Lindgren, J.M. Mwabora, E. Avendano, J. Jansson, A. Hoel, C.G. Granqvist, S.E. Lindquist, Photoelectrochemical and optical properties of nitrogen doped titanium dioxide films prepared by reactive DC magnetron sputtering, *J. Phys. Chem. B* 107 (2003) 5709–5716.
- [11] O. Diwald, T.L. Thomson, T. Zubkov, E.G. Goralski, S.D. Walck, J.T. Yates, Photochemical activity of nitrogen-doped rutile TiO₂(110) in visible light, *J. Phys. Chem. B* 108 (2004) 6004–6008.
- [12] Y. Cong, J. Zhang, F. Chen, M. Anpo, Synthesis and characterization of nitrogen-doped TiO₂ nanophotocatalyst with high visible light activity, *J. Phys. Chem. C* 111 (2007) 6976–6982.
- [13] J. Wang, W. Zhu, Y. Zhang, S. Liu, An efficient two-step technique for nitrogen-doped titanium dioxide synthesizing: visible-light-induced photodecomposition of methylene blue, *J. Phys. Chem. C* 111 (2006) 1010–1014.
- [14] F. Peng, L.F. Cai, L. Huang, H. Yu, H.J. Wang, Preparation of nitrogen-doped titanium dioxide with visible-light photocatalytic activity using a facile hydrothermal method, *J. Phys. Chem. Solids* 69 (2008) 1657–1664.
- [15] Z.Y. Yu, W. Zhang, M. Ma, X.L. Cui, Visible light photoelectrochemical response of nitrogen-doped TiO₂ thin films prepared by anodic oxidation of titanium nitride films, *Acta. Phys. Chim. Sin.* 25 (2009) 35–40.
- [16] Y. Suda, H. Kawasaki, T. Ueda, T. Ohshima, Preparation of high quality nitrogen doped TiO₂ thin film as a photocatalyst using a pulsed laser deposition method, *Thin Solid Films* 453–454 (2004) 162–166.
- [17] J.M. Mwabora, T. Lindgren, E. Avendaño, T.F. Jaramillo, J. Lu, S.-E.C.-G. Lindquist, Granqvist, structure, composition, and morphology of photoelectrochemically active TiO_{2-x}N_x thin films deposited by reactive DC magnetron sputtering, *J. Phys. Chem. B* 108 (2004) 20193–20198.
- [18] M.S. Wong, H.P. Chou, T.S. Yang, Reactively sputtered N-doped titanium oxide films as visible-light photocatalyst, *Thin Solid Films* 494 (2006) 244–249.
- [19] M.H. Chan, F.H. Lu, X-ray photoelectron spectroscopy analyses of titanium oxynitride films prepared by magnetron sputtering using air/Ar mixtures, *Thin Solid Films* 517 (2006) 5006–5009.
- [20] K.G. Grigorov, I.C. Oliveira, H.S. Maciel, M. Massi, M.S. Oliveir, Jr., Amorim, C.A. Cunha, Optical and morphological properties of N-doped TiO₂ thin films, *Surf. Sci.* 605 (2011) 775–782.
- [21] D. Heřman, J. Šícha, J. Musil, Magnetron sputtering of TiO_xN_y films, *Vacuum* 81 (2006) 285–290.
- [22] S. Yasushi, U. Akira, I. Norihiro, K. Toshihisa, S. Yuzo, High rate deposition of photocatalytic TiO₂ films by DC magnetron sputtering using a TiO_{2-x} target, *J. Vac. Sci. Technol. A* 28 (2008) 903–907.
- [23] R. Dholam, N. Patel, A. Santini, A. Miotello, Efficient indium tin oxide/Cr-doped-TiO₂ multilayer thin films for H₂ production by photocatalytic water-splitting, *Int. J. Hydrogen Energy* 35 (2010) 9581–9590.
- [24] A.J. Nozik, P–N photoelectrolysis cells, *Appl. Phys. Lett.* 29 (1976) 150–153.
- [25] E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca, M. Gratzel, Sustained water cleavage by visible light, *J. Am. Chem. Soc.* 103 (1981) 6324–6329.
- [26] G.N. Schrauzer, T.D. Guth, Photocatalytic reactions. 1. Photolysis of water and photoreduction of nitrogen on titanium dioxide, *J. Am. Chem. Soc.* 99 (1977) 7189–7193.
- [27] K. Yamaguti, S.J. Sato, Photolysis of water over metallized powdered titanium dioxide, *Chem. Soc. Faraday Trans. 1* (81) (1985) 1237–1246.

- [28] O. Rosseler, M.V. Shankar, M.K. Le Du, L. Schmidlin, N. Keller, V. Keller, Solar light photocatalytic hydrogen production from water over Pt and Au/TiO₂ (anatase/rutile) photocatalysts: influence of noble metal and porogen promotion, *J. Catal.* 269 (2010) 179–190.
- [29] M. Lazzeri, A. Vittadini, A. Selloni, Structure and energetics of stoichiometric TiO₂ anatase surfaces, *Phys. Rev. B* 63 (2001) 155409–155417.
- [30] M.V. Kuznetsov, J.F. Ahuravlev, V.A. Zhilyaev, V.A. Gubanov, XPS study of the nitrides, oxides and oxynitrides of titanium, *J. Electron Spectrosc. Relat. Phenom.* 58 (1992) 1–9.
- [31] N.C. Saha, H.G. Tompkins, Titanium nitride oxidation chemistry: an X-ray photoelectron spectroscopy study, *J. Appl. Phys.* 72 (1992) 3072–3079.
- [32] I.C. Kang, Q.W. Zhang, S. Yin, T. Sato, F. Saito, Environ. Improvement in photocatalytic activity of TiO₂ under visible irradiation through addition of N-TiO₂, *Sci. Technol.* 42 (2008) 3622–3626.
- [33] H.Q. Sun, Y. Bai, W.Q. Jin, N.P. Xu, Sol, Visible-light-driven TiO₂ catalysts doped with low-concentration nitrogen species, *Energy Mater. Sol. Cells* 92 (2008) 76–83.
- [34] J. Tauc, R. Grigorovici, A. Vancu, Optical properties and electronic structure of amorphous germanium, *Phys. Status Solid.* 15 (1966) 627–637.
- [35] C. Di Valentin, G. Pacchioni, A. Selloni, S. Livraghi, E. Giamello, Characterization of paramagnetic species in N-doped TiO₂ powders by EPR spectroscopy and DFT calculations, *J. Phys. Chem. B* 109 (2005) 11414–11419.
- [36] L. Zhao, Q. Jiang, J. Lian, Visible-light photocatalytic activity of nitrogen-doped TiO₂ thin film prepared by pulsed laser deposition, *Appl. Surf. Sci.* 254 (2008) 4620–4625.
- [37] V.J. Babu, M.K. Kumar, A.S. Nair, T.L. Kheng, S.I. Allakhverdiev, S. Ramakrishna, Visible light photocatalytic water splitting for hydrogen production from N-TiO₂ rice grain shaped electrospun nanostructures, *Int. J. Hydrogen Energy* 37 (2012) 8897–8904.
- [38] H.Y. Lin, C.Y. Shih, Efficient one-pot microwave-assisted hydrothermal synthesis of nitrogen-doped TiO₂ for hydrogen production by photocatalytic water splitting, *Catal. Surv. Asia* 16 (2012) 231–239.