SPECIAL ISSUE: Advanced Materials for Photoelectrochemical Cells

Maximizing the visible light photoelectrochemical activity of B/N-doped anatase TiO₂ microspheres with exposed dominant {001} facets

Xingxing Hong^{1,2}, Yuyang Kang^{1,2}, Chao Zhen¹, Xiangdong Kang¹, Li-Chang Yin¹, John TS Irvine³, Lianzhou Wang⁴, Gang Liu^{1,2*} and Hui-Ming Cheng^{1,5,6}

ABSTRACT Anatase TiO₂ microspheres with exposed dominant {001} facets were doped with interstitial boron to have a concentration gradient with the maximum concentration at the surface. They were then further doped with substitutional nitrogen by heating in an ammonia atmosphere at different temperatures from 440 to 560°C to give surface N concentrations ranging from 7.03 to 15.47 at%. The optical absorption, atomic and electronic structures and visible-light photoelectrochemical water oxidation activity of these materials were investigated. The maximum activity of the doped TiO₂ was achieved at a nitrogen doping temperature of 520°C that gave a high absorbance over the whole visible light region but with no defect-related background absorption.

Keywords: photoelectrochemistry, red TiO₂, water splitting, doping

INTRODUCTION

Solar energy is the most abundant renewable energy source for mankind and plays a very important role in constructing environmental-friendly energy supply systems. Among the various modern technologies for using solar energy, photocatalysis represents an amazing route of simultaneously converting and storing solar energy to chemical energy by inducing targeted redox reactions such as water-splitting to release hydrogen and reducing carbon dioxide to produce high-value chemicals on the photocatalyst surface. Since the pioneering work on

photoelectrochemical water splitting using a rutile TiO₂ single crystal as photoanode [1], intensive studies over 40 years, particularly in the last decade, have achieved substantial developments in photocatalysis [2–9]. Specifically, overall water-splitting on the basis of a solid-state Z-scheme system of La/Rh codoped SrTiO₃/Au/Mo doped BiVO₄ sheets gave a solar-to-hydrogen energy conversion efficiency of over 1% [10]. In addition, photocatalytic water-splitting under irradiation with 600 nm visible light was achieved on a complex metal oxynitride photocatalyst, although its quantum efficiency was still low [11]. The impressive progress strongly demonstrates the great promise of solar-driven photocatalysis in converting solar energy into storable chemical energy.

Compared to the rapid development of complex metal oxide photocatalysts [5,12], making a simple binary photocatalyst TiO₂ active to fully harvest visible light is a challenge [13–22]. TiO₂ is easily available and low-cost, but has no visible light absorption due to its large bandgap of about 3 eV. Introducing suitable heteroatoms to replace Ti and/or O atoms in TiO₂ is feasible for increasing visible light absorption. Among many possible doping strategies, substitutional N-doping (N atom substituting lattice O atom) has been supposed to be able to lift the valence band maximum of TiO₂ due to the higher orbital energy levels of N 2p than those of O 2p. Unfortunately, N-doping is highly limited by low solubility and inhomogeneous distribution in most metal oxides

¹ Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

² School of Materials Science and Engineering, University of Science and Technology of China, Shenyang 110016, China

³ School of Chemistry, University of St. Andrews, Fife KY16 9ST, UK

⁴ Nanomaterials Centre, School of Chemical Engineering and AIBN, the University of Queensland, St Lucia, Brisbane QLD 4072, Australia

⁵ Tsinghua-Berkeley Shenzhen Institute, Tsinghua University, Shenzhen 518055, China

⁶ Center of Excellence in Environmental Studies, King Abdulaziz University, Jeddah 21589, Saudi Arabia

* Corresponding author (email: gangliu@imr.ac.cn)

with strong metal-oxygen bonds [23–25]. TiO_2 can only introduce some localized states of dopants in the band gap and give rise to a low absorbance of the extended visible light absorption band. Our previous study [25] showed that interstitial boron in anatase TiO_2 can greatly weaken the Ti–O bonds to facilitate the replacement of oxygen with nitrogen. In the subsequent nitrogenation process, the boron concentration gradient in the TiO_2 resulted in a nitrogen concentration gradient in a red B/N doped anatase TiO_2 photocatalyst with a strong absorption band under visible light. Moreover, charge compensation between the boron and nitrogen dopants suppresses the formation of deleterious recombination centers of charge carriers. In contrast to this red TiO_2 with a high concentration of nitrogen dopant, regular nitrogen-doped TiO_2 showed a decreased photocatalytic activity with an increase of nitrogen dopant [26]. Research on the dependence of the photocatalytic activity of red TiO_2 on the concentration of nitrogen dopant and its mechanism at the electronic level probably provide useful guidelines to the development of both red TiO_2 and other binary metal oxide photocatalysts.

In this study, the concentration of nitrogen dopant in red TiO_2 photocatalysts was increased by the nitrogenation temperature from 440 to 560°C and its effect on photoelectrochemical water oxidation activity was studied. Several characterization methods were used to understand the maximum activity at an optimum surface nitrogen concentration.

RESULTS AND DISCUSSION

Interstitial boron-doped TiO_2 microspheres (around 95 wt% anatase and 5 wt% rutile) were prepared by the acid hydrolysis of a TiB_3 precursor according to a reported procedure [27]. The details for nitrogen doping is described in the Supplementary information. The resultant samples with different heating temperatures (440, 480, 520 and 560°C) were denoted TiO_2 -440, TiO_2 -480, TiO_2 -520 and TiO_2 -560. The morphology and the microstructure of representative B/N doped anatase TiO_2 microspheres were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as shown in Fig. 1. The microsphere surface consists of dominant square {001} facets with an edge size of tens of nanometer and minor {101} facets. The angle between {001} and {101} facets measured in Fig. 1c is approximate 111.7°, which matches well with the ideal crystallographic value [28]. Additional N-doping did not change the basic shape of the microspheres. However, compared to the sharp edges of the square {001} facets of the pristine

Figure 1 (a, b) SEM and TEM images of a representative N/B-doped anatase TiO_2 microsphere with the top surface consisting of {001} facets prepared by heating pristine boron-doped anatase microspheres at 520°C in a gaseous ammonia atmosphere. (c, d) High resolution TEM images showing the exposed top {001}/{101} facets, recorded from the region marked by the red rectangle in (b).

Figure 2 Representative XPS spectra of B 1s and N 1s core electrons recorded from the pristine surface of the B/N doped TiO_2 microspheres prepared at different nitrogenation temperatures (440, 480, 520 and 560°C).

boron-doped TiO_2 microspheres [27], the edges of those further doped with N were less defined as a result of the nitrogen diffusion from the surface to the bulk. A high resolution TEM image (Fig. 1d) shows lattice fringes of (001) planes with a spacing of 2.4 Å. Unclear fringes also suggest some disruption of the local atomic structure as a result of the introduction of a high concentration of nitrogen.

The chemical states and the concentrations of nitrogen and boron dopants in different boron/nitrogen doped TiO_2 samples prepared at different nitrogenation temperatures were investigated by X-ray photoelectron spectroscopy (XPS), as given in Fig. 2. The pristine bor-

Figure 3 (a) UV-visible absorption spectra of the B/N-doped TiO_2 microspheres prepared at different nitrogenation temperatures (440, 480, 520 and 560°C) compared to the pristine TiO_2 sample. (b) Corresponding plots of the transformed Kubelka-Munk function against light energy for the different samples.

on-doped TiO_2 has interstitial boron with a B 1s core electron binding energy of 192.2 eV, indicating the presence of B–O bonds. With the introduction of nitrogen dopant, an additional B 1s signal with a binding energy around 190.3 eV was formed due to the formation of B–N bonds [25]. The ratio of boron in B–N bonds to that in B–O bonds in the sample obtained at 440°C is 0.52 due to the low concentration of the nitrogen dopant and increases to 1.28 for the sample prepared at 560°C (determined from the area ratio of XPS B 1s peaks in B–O and B–N bonds). This is the result of the increased nitrogen content, indicated by the stronger XPS peak of N 1s core. The oxidation state of the dominant nitrogen species (N 1s, binding energy 397.6 eV) in the sample is very close to that in TiN or Ti–N bonds [13], suggesting the substitution of nitrogen for oxygen in the TiO_2 . The unchanged binding energy of the nitrogen species in different samples demonstrates the oxidation state is independent of the nitrogenation temperature. The minor fitted peak centered at 399.3 eV is assigned to the interstitial nitrogen. It seems that, on the basis of the evolution of the two different nitrogen species peaks, high temperature nitrogenation favors the incorporation of substitutional rather than interstitial nitrogen. Moreover, the atomic ratio of nitrogen to titanium increases from 7.03% at 440°C to 15.47% at 560°C (the values for each temperature are given in Table S1). It should be pointed out that the nitrogen concentration given here only reflects the chemical state in several nanometer thick surface layer of the microspheres due to the surface sensitivity of XPS technique itself.

The dependence of the optical absorption band of B/N-doped TiO_2 on the nitrogenation temperature was detected by UV-visible absorption spectroscopy (Fig. 3). Two features are seen in Fig. 3a. 1) A broad absorption

Figure 4 Schematic of the band structures of substitutional nitrogen-doped TiO_2 (containing interstitial boron) with different concentrations of nitrogen dopant: (a) the formation of localized N 2p states at a low concentration of nitrogen dopant in a thin layer; (b) the formation of an isolated narrow N 2p band at a medium concentration of nitrogen dopant in a relatively thick layer; (c) bandgap narrowing at a high enough concentration of nitrogen dopant in a thick layer. CB: conduction band; VB: valence band. The pristine conduction and valence bands are dominated by Ti 3d and O 2p, respectively.

band spanning the whole spectrum of visible light is formed after the incorporation of nitrogen at 440°C. The absorption band gradually increases with the amounts of nitrogen dopant increasing at higher nitrogenation temperatures. 2) No obvious background absorption beyond 700 nm is observed for the three samples obtained at $\leq 520^\circ\text{C}$ while a strong featureless background absorption band beyond 700 nm appears for the TiO_2 -560 sample.

The first feature can be understood as follows. The origin of the visible light absorption band is caused by the newly formed N 2p which has a higher energy level than the pristine O 2p dominated valence band edge of TiO_2 . The dispersion width of N 2p increases with both the concentration and spatial distribution of substitutional nitrogen in TiO_2 as illustrated in Fig. 4. A low concentration of nitrogen located in the thin surface layer only contributes to some localized N 2p states in the bandgap that are responsible for the small shoulder-like absorption band, as in sample TiO_2 -440 (Fig. 4a) [26]. A

medium concentration in the relatively thick surface layer induces the formation of an isolated narrow band of main N 2p states above the pristine valence band that is responsible for a large shoulder-like absorption band seen in e.g., TiO₂-480 (Fig. 4b). A high N concentration in a sufficiently thick layer results in real bandgap narrowing by mixing the N 2p states with the pristine valence band to elevate the band edge for the desired band-to-band redshift of the absorption edge, probably as in sample TiO₂-560 (Fig. 4c) [23,24]. In contrast, the intrinsic bandgap remains basically unchanged in these two conditions (Fig. 4a, b). The plots of the transformed Kubelka–Munk function against the light energy for different samples in Fig. 3b further support the above analysis. The extrapolated edge of the visible light absorption band of sample TiO₂-520 is 1.90 eV. The second feature is actually controlled by the formation of Ti³⁺ defects from the charge imbalance between O²⁻ and N³⁻, which is normally observed in common N-doped TiO₂ [26]. The presence of the interstitial boron with additional donor electrons suppresses the formation of Ti³⁺ by forming B–N bonds (Fig. 2). However, the very high concentration of nitrogen in sample TiO₂-560 exceeds the capability of the boron in maintaining the charge balance, so that some defect states below the TiO₂ conduction band are formed.

Comparison of the absorption spectra of B/N doped TiO₂ with that of layer-structure Cs_{0.68}Ti_{1.83}O₄ homogeneously doped with nitrogen where the N/Ti atomic ratio from 1.09% to 16.94% [29], reveals distinctly different changes in the additional visible light absorption band caused by nitrogen doping. The B/N doping results in a highly similar light absorption onset at around 750 nm but gradually increased absorbance with increased nitrogen content. In contrast, homogeneous N doping in Cs_{0.68}Ti_{1.83}O₄ results in similar absorbance but a gradual band-to-band redshift of the light absorption onset in samples with increasing nitrogen dopant. Moreover, the nature of such a band-to-band redshift is independent of N concentration in the case of homogeneous N doping. The distinct optical absorption modes caused by nitrogen doping lead to the different spatial distributions and concentrations of nitrogen dopant in the TiO₂ and Cs_{0.68}Ti_{1.83}O₄. In principle, narrowing the bandgap of a semiconductor by doping requires the involvement of heteroatoms in the strong uniform interaction field from long-range ordered intrinsic lattice. For the homogeneous doping, the uniform distribution of N dopant throughout the whole particles, which is kinetically controlled by the layered structure of Cs_{0.68}Ti_{1.83}O₄,

can lead to bandgap narrowing. The concentration of N, which is thermodynamically controlled by the nitrogenation temperature, determines the bandgap narrowing and thus the absorption onset by changing the dispersion width of N 2p states. For a doping gradient, the gradual decrease of N dopant concentration from the top surface to zero in the bulk leads to an inhomogeneous atomic interaction along the direction of the concentration gradient. The features of the interstitial boron-assisted substitutional nitrogen doping process in terms of both the concentration and spatial distribution of nitrogen dopant are thermodynamically controlled by the nitrogenation temperature. Low-temperature nitrogenation results in a higher concentration of nitrogen in boron-doped TiO₂ for a maximum absorption onset compared to that in layered Cs_{0.68}Ti_{1.83}O₄ (for example, N/Ti 7.03% in TiO₂ at 440°C vs. 1.09% in Cs_{0.68}Ti_{1.83}O₄ at 500°C). However, the diffusion length in non-layered TiO₂ at low nitrogenation temperatures is so limited that the involvement of nitrogen in the strong long-range interaction of intrinsic lattice atoms is not enough to induce bandgap narrowing. A higher nitrogenation temperature favors both substitutional nitrogen doping and diffusion of nitrogen from surface to bulk for the desired bandgap narrowing.

In addition to the substantial changes in the optical absorption band caused by nitrogen doping in boron-doped TiO₂, the local atomic structure was also modulated as revealed in Raman and Fourier transform infrared (FTIR) spectra. Anatase TiO₂ has six Raman active modes, 3E_g + 2B_{1g} + A_{1g} [30], where one of the two B_{1g} modes is hard to distinguish from the A_{1g} mode at around 515 cm⁻¹ (Fig. 5). Compared to the pristine boron-doped TiO₂, further nitrogen doping conducted at different temperatures shows the unchanged Raman shifts of B_{1g}, E_{g(2)} and E_{g(3)}. However, the E_{g(1)} mode in TiO₂-520 and TiO₂-560 shows an upshift from 144 to 146 cm⁻¹. Moreover, the doublet of the B_{1g} + A_{1g} modes at around 515 cm⁻¹ is split into two separate modes centered at 514 and 494 cm⁻¹, respectively. The splitting of such a doublet can be observed at low temperature [31]. In the current case, the incorporation of a high concentration of nitrogen heteroatom into the framework of TiO₂ changes the force constants of Ti–O bonds to induce the splitting of the doublet. In contrast, most nitrogen doped TiO₂ did not show such splitting probably because of the low concentration of nitrogen dopant and surface distribution of nitrogen dopant. The ~20 cm⁻¹ shift of the fingerprint region of TiO₂ below 1,000 cm⁻¹ towards a low wave-number in the FTIR spectra at the high concentration of

Figure 5 (a, b) Raman spectra of B/N-doped TiO₂ microspheres prepared at different nitrogenation temperatures (440, 480, 520 and 560°C) compared to the pristine boron-doped TiO₂ sample. The wavelength of the excitation light is 633 nm.

Figure 6 (a) The applied bias dependent photoelectrochemical water oxidation current curve for photoanodes of B/N-doped TiO₂ microspheres prepared at different nitrogenation temperatures (440, 480, 520 and 560°C) compared with that of the pristine TiO₂ sample under visible light irradiation ($\lambda > 420$ nm). (b) The enlarged I - V curve in the bias range from -0.18 to -0.05 V showing one light-on and light-off cycle in (a). The scanning direction is from negative to positive bias.

nitrogen doping in Fig. S2 supports the local structure modulation caused by nitrogen doping. Note that the peak at $3,446\text{ cm}^{-1}$ assigned to surface hydroxyl groups and adsorbed water molecules [32,33] shows a negligible intensity change, suggesting good retention of the surface hydrophilicity of TiO₂ upon nitrogen doping.

The dependence of the photocatalytic activity of the B/N-doped TiO₂ obtained above on the concentration of nitrogen dopant was studied by recording the photoelectrochemical water oxidation behavior of the TiO₂ based photoanodes under visible light irradiation (>420 nm). Nitrogen doping greatly increases the photocurrent of the doped TiO₂ photoanodes. The photocurrent density increases monotonically with increased nitrogenation temperature up to 520°C but decreases at a nitrogenation temperature of 560°C (Fig. 6a). This trend can be understood from the balance between the enhanced visible light absorption and an increased number of recombination centers of photogenerated charge carriers with a larger amount of nitrogen dopant. The Ti³⁺

defects generated by a high concentration of nitrogen dopant achieved at 560°C, as illustrated in Fig. 3, act as recombination centers to impair the photoelectrochemical activity.

The photocurrent density (J_{photo}) generated by the illuminated photoanode can be depicted as follows:

$$J_{\text{photo}} = qg \frac{k_{\text{tr}}}{k_{\text{tr}} + k_{\text{rec}}}, \quad (1)$$

where, q is the unit charge, g is the flux of holes into the surface, k_{tr} is the rate constant for hole transfer and k_{rec} is the rate constant for electron/hole recombination at the surface. k_{tr} is considered to be independent of the potential applied. k_{rec} is proportional to the electron concentration at the surface (n_{surf}) that decreases with the increase of band bending as follows.

$$n_{\text{surf}} = n_b \exp\left(\frac{-q\phi_{\text{sc}}}{k_B T}\right), \quad (2)$$

where n_b is the electron (majority carrier) concentration in bulk, ϕ_{sc} is the band bending potential at the surface

and increases with the increase of applied potential. Therefore, the photocurrent density increases with the increase of potential applied for each sample due to the reduction of k_{rec} . The increased photocurrent density at the fixed potential with the increase of nitrogenation temperature below 520°C is mainly attributed to the improved absorption in visible light region that correspondingly increases g . Although further increasing nitrogenation temperature beyond 520°C can increase visible light absorption for a larger g value, the k_{rec} is also greatly improved as a result of the generation of the Ti^{3+} defects as deleterious recombination centers.

On the other hand, the photoanodes of B/N-doped TiO_2 with different nitrogen contents show distinct photocurrent generation behaviors between the switching on and off of light as highlighted in Fig. 6b. Compared to the flat step-like photocurrent response to the switching on and off of light in the photoanode of the pristine boron-doped TiO_2 , the high nitrogen doping causes a striking jump of the photocurrent as a result of the charging process when the light is switched on [34,35]. This striking jump is similar in all the nitrogen-doped TiO_2 photoanodes. The stored charges in the TiO_2 -440 and TiO_2 -480 photoanodes are discharged by releasing cathodic current after the light irradiation is blocked, while no cathodic current was observed in the TiO_2 -520, TiO_2 -560 and TiO_2 photoanodes. This difference could be caused by the different electronic structures of doped TiO_2 . Different from the samples with delocalized N 2p states, the localized nature of the N 2p states in the TiO_2 -440 and TiO_2 -480 samples limits the mobility of photo-generated holes in the material under visible light irradiation so that the slow release of the stored charges can contribute to the dark current.

It is useful to compare the dependence of the photoelectrochemical activity of the B/N-doped TiO_2 on the nitrogen concentration with that of the homogeneous nitrogen-doped $\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_4$ and also nitrogen-doped TiO_2 . Both the B/N-doped TiO_2 and homogeneous nitrogen-doped $\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_4$ [29] show similar trends in that the activity increases as the nitrogen concentration increases. In contrast, the activity of nitrogen-doped TiO_2 with a shoulder-like absorption band decreases with increased nitrogen concentration [26] because the number of oxygen vacancies, which promote the recombination of electrons and holes, increase with the increase of nitrogen dopant. In the cases of homogeneous nitrogen-doped $\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_4$ and B/N-doped TiO_2 , the interstitial boron and cesium ions can compensate for the charge imbalance between O^{2-} and N^{3-} to suppress the formation of re-

combination centers.

The photoelectrochemical water oxidation activity in Fig. 6 achieved with bare B/N-doped TiO_2 photoanodes is low, though the photocurrent density of the photoanode of doped TiO_2 with an optimized amount of boron and nitrogen is about two times higher than that of the photoanode of the red TiO_2 with hydrogen filled oxygen vacancies [36]. It is anticipated that loading suitable co-catalysts for oxygen evolution reaction on B/N-doped TiO_2 can further improve activity and is to be conducted in future studies.

CONCLUSION

A series of B/N-doped TiO_2 materials with different nitrogen concentrations were prepared by annealing interstitial boron-doped TiO_2 microspheres with exposed {001} facets in gaseous ammonia at different temperatures (440, 480, 520 and 560°C). The ratio of nitrogen dopant to titanium in TiO_2 gradually increased from 7.03 at% at 440°C to 15.47 at% at 560°C. An additional absorption band was formed in the whole spectrum of visible light, and its absorbance increased with an increased nitrogen concentration. Particularly, as a consequence of bandgap narrowing, the sample obtained at 520°C has the highest absorbance in visible light and no background absorption associated with the defects. The photoelectrochemical water oxidation activity under visible light irradiation increases with an increase in the amount of nitrogen dopant before the formation of oxygen vacancies. The sample obtained at 520°C gives the highest activity among the series of B/N doped anatase TiO_2 photocatalysts.

Received 27 January 2018; accepted 16 February 2018;
published online 15 March 2018

- 1 Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 1972, 238: 37–38
- 2 Zou Z, Ye J, Sayama K, *et al.* Direct splitting of water under visible light irradiation with an oxide semiconductor photocatalyst. *Nature*, 2001, 414: 625–627
- 3 Wang X, Maeda K, Thomas A, *et al.* A metal-free polymeric photocatalyst for hydrogen production from water under visible light. *Nat Mater*, 2009, 8: 76–80
- 4 Tada H, Mitsui T, Kiyonaga T, *et al.* All-solid-state Z-scheme in CdS-Au-TiO_2 three-component nanojunction system. *Nat Mater*, 2006, 5: 782–786
- 5 Kudo A, Miseki Y. Heterogeneous photocatalyst materials for water splitting. *Chem Soc Rev*, 2009, 38: 253–278
- 6 Yan H, Yang J, Ma G, *et al.* Visible-light-driven hydrogen production with extremely high quantum efficiency on Pt-PdS/CdS photocatalyst. *J Catal*, 2009, 266: 165–168
- 7 Hu S, Shaner MR, Beardslee JA, *et al.* Amorphous TiO_2 coatings stabilize Si, GaAs, and GaP photoanodes for efficient water oxidation. *Science*, 2014, 344: 1005–1009

- 8 Yang J, Wang D, Han H, *et al.* Roles of cocatalysts in photocatalysis and photoelectrocatalysis. *Acc Chem Res*, 2013, 46: 1900–1909
- 9 Maeda K, Teramura K, Lu D, *et al.* Photocatalyst releasing hydrogen from water. *Nature*, 2006, 440: 295–295
- 10 Wang Q, Hisatomi T, Jia Q, *et al.* Scalable water splitting on particulate photocatalyst sheets with a solar-to-hydrogen energy conversion efficiency exceeding 1%. *Nat Mater*, 2016, 15: 611–615
- 11 Pan C, Takata T, Nakabayashi M, *et al.* A complex perovskite-type oxynitride: the first photocatalyst for water splitting operable at up to 600 nm. *Angew Chem Int Ed*, 2015, 54: 2955–2959
- 12 Zhang G, Liu G, Wang L, *et al.* Inorganic perovskite photocatalysts for solar energy utilization. *Chem Soc Rev*, 2016, 45: 5951–5984
- 13 Asahi R, Morikawa T, Ohwaki T, *et al.* Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science*, 2001, 293: 269–271
- 14 Chen X, Liu L, Yu PY, *et al.* Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals. *Science*, 2011, 331: 746–750
- 15 Asahi R, Morikawa T, Irie H, *et al.* Nitrogen-doped titanium dioxide as visible-light-sensitive photocatalyst: designs, developments, and prospects. *Chem Rev*, 2014, 114: 9824–9852
- 16 Kapilashrami M, Zhang Y, Liu YS, *et al.* Probing the optical property and electronic structure of TiO₂ nanomaterials for renewable energy applications. *Chem Rev*, 2014, 114: 9662–9707
- 17 Zong X, Xing Z, Yu H, *et al.* Photocatalytic water oxidation on F, N co-doped TiO₂ with dominant exposed {001} facets under visible light. *Chem Commun*, 2011, 47: 11742
- 18 Zhao W, Ma W, Chen C, *et al.* Efficient degradation of toxic organic pollutants with Ni₂O₃/TiO_{2-x}B_x under visible irradiation. *J Am Chem Soc*, 2004, 126: 4782–4783
- 19 Sun Q, Cortie D, Zhang S, *et al.* The formation of defect-pairs for highly efficient visible-light catalysts. *Adv Mater*, 2017, 29: 1605123
- 20 Parks Cheney C, Vilmercati P, Martin EW, *et al.* Origins of electronic band gap reduction in Cr/N codoped TiO₂. *Phys Rev Lett*, 2014, 112: 036404
- 21 Gai Y, Li J, Li SS, *et al.* Design of narrow-gap TiO₂: A passivated codoping approach for enhanced photoelectrochemical activity. *Phys Rev Lett*, 2009, 102: 036402
- 22 Zhu W, Qiu X, Iancu V, *et al.* Band gap narrowing of titanium oxide semiconductors by noncompensated anion-cation codoping for enhanced visible-light photoactivity. *Phys Rev Lett*, 2009, 103: 226401
- 23 Liu G, Wang L, Sun C, *et al.* Band-to-band visible-light photon excitation and photoactivity induced by homogeneous nitrogen doping in layered titanates. *Chem Mater*, 2009, 21: 1266–1274
- 24 Liu G, Wang L, Yang HG, *et al.* Titania-based photocatalysts—crystal growth, doping and heterostructuring. *J Mater Chem*, 2010, 20: 831–843
- 25 Liu G, Yin LC, Wang J, *et al.* A red anatase TiO₂ photocatalyst for solar energy conversion. *Energy Environ Sci*, 2012, 5: 9603
- 26 Irie H, Watanabe Y, Hashimoto K. Nitrogen-concentration dependence on photocatalytic activity of TiO_{2-x}N_x powders. *J Phys Chem B*, 2003, 107: 5483–5486
- 27 Liu G, Pan J, Yin L, *et al.* Heteroatom-modulated switching of photocatalytic hydrogen and oxygen evolution preferences of anatase TiO₂ microspheres. *Adv Funct Mater*, 2012, 22: 3233–3238
- 28 Yang HG, Sun CH, Qiao SZ, *et al.* Anatase TiO₂ single crystals with a large percentage of reactive facets. *Nature*, 2008, 453: 638–641
- 29 Liu G, Niu P, Wang L, *et al.* Achieving maximum photo-oxidation reactivity of Cs_{0.68}Ti_{1.83}O_{4-x}N_x photocatalysts through valence band fine-tuning. *Catal Sci Technol*, 2011, 1: 222
- 30 Ohsaka T, Izumi F, Fujiki Y. Raman spectrum of anatase, TiO₂. *J Raman Spectrosc*, 1978, 7: 321–324
- 31 Balachandran U, Eror NG. Raman spectra of titanium dioxide. *J Solid State Chem*, 1982, 42: 276–282
- 32 Tanaka K, White JM. Characterization of species adsorbed on oxidized and reduced anatase. *J Phys Chem*, 1982, 86: 4708–4714
- 33 Sánchez E, López T, Gómez R, *et al.* Synthesis and characterization of sol-gel Pt/TiO₂ catalyst. *J Solid State Chem*, 1996, 122: 309–314
- 34 Liu G, Shi J, Zhang F, *et al.* A tantalum nitride photoanode modified with a hole-storage layer for highly stable solar water splitting. *Angew Chem Int Ed*, 2014, 53: 7295–7299
- 35 Yang Y, Liu G, Irvine JTS, *et al.* Enhanced photocatalytic H₂ production in core-shell engineered rutile TiO₂. *Adv Mater*, 2016, 28: 5850–5856
- 36 Yang Y, Yin LC, Gong Y, *et al.* An unusual strong visible-light absorption band in red anatase TiO₂ photocatalyst induced by atomic hydrogen-occupied oxygen vacancies. *Adv Mater*, 2018, 30: 1704479

Acknowledgements This work was supported by the Major Basic Research Program, Ministry of Science and Technology of China (2014CB239401), the National Natural Science Foundation of China (51422210, 21633009, 51629201 and 51521091), the Key Research Program of Frontier Sciences CAS (QYZDB-SSW-JSC039). Liu G thanks Newton Advanced Fellowship.

Author contributions Liu G conceived the project and Cheng HM guided the project. Hong X conducted experimental section together with Kang Y and Kang X. Zhen C, Irvine JTS and Wang L analyzed PEC results. Yin LC contributed to electronic structure analysis. Liu G and Hong X wrote the manuscript and all the authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

Xingxing Hong received his BSc degree in Wuhan University in 2015. Now he is a PhD candidate in the Institute of Metal Research (IMR), Chinese Academy of Sciences (CAS) & the University of Science and Technology of China. His current research is focused on homogeneous doping of photocatalysts for visible light water splitting under the supervision of Prof. Gang Liu and Prof. Hui-Ming Cheng.

Gang Liu received his BSc degree in materials physics from Jilin University in 2003. He obtained his PhD degree in materials science at IMR, CAS in 2009. Now he is a professor of IMR, CAS. His main research interest is to develop photocatalytic materials for solar fuels.

B/N掺杂富含{001}晶面锐钛矿TiO₂的最佳可见光光电催化水氧化活性研究

洪星星^{1,2}, 康宇阳^{1,2}, 甄超¹, 康向东¹, 尹利长¹, John TS Irvine³, 王连洲⁴, 刘岗^{1,2*}, 成会明^{1,5,6}

摘要 本文以锐钛矿TiO₂微米球光催化材料为研究对象,其表面主要由{001}晶面组成,间隙掺杂硼原子在微米球中呈浓度梯度分布,浓度最高点位于表面.通过对其在氮气气氛、不同温度下(440–560°C)进行热处理,可实现氮替代晶格氧的掺杂,氮原子掺杂的浓度随着热处理温度的增加,由7.03增加到15.47 at%.随着掺杂氮浓度的增加,所得掺杂TiO₂微米球的可见光吸收强度相应提高.进一步研究所得掺杂TiO₂微米球的可见光吸收、原子和电子结构与可见光光电催化水氧化活性的关联特性,发现在520°C下所得氮掺杂TiO₂的可见光光电催化水氧化活性最大,该样品吸收光谱的显著特征是在可见光区吸光率高,且没有与缺陷相关联的背底吸收.