

## A red anatase TiO<sub>2</sub> photocatalyst for solar energy conversion†

Gang Liu,<sup>‡a</sup> Li-Chang Yin,<sup>‡a</sup> Jianqiang Wang,<sup>b</sup> Ping Niu,<sup>a</sup> Chao Zhen,<sup>a</sup> Yingpeng Xie<sup>a</sup> and Hui-Ming Cheng<sup>\*a</sup>

Received 21st July 2012, Accepted 7th September 2012

DOI: 10.1039/c2ee22930g

Narrowing the bandgap of wide-bandgap semiconductor photocatalysts (for instance, anatase TiO<sub>2</sub>) by introducing suitable heteroatoms has been actively pursued for increasing solar absorption, but usually suffers from a limited thermodynamic/kinetic solubility of substitutional dopants in bulk and/or dopant-induced recombination centres. Here we report a red anatase TiO<sub>2</sub> microsphere with a bandgap gradient varying from 1.94 eV on its surface to 3.22 eV in its core by a conceptually different doping approach for harvesting the full spectrum of visible light. This approach uses a pre-doped interstitial boron gradient to weaken nearby Ti–O bonds for the easy substitution of oxygen by nitrogen, and consequently it substantially improves the nitrogen solubility. Furthermore, no nitrogen-related Ti<sup>3+</sup> was formed in the red TiO<sub>2</sub> due to a charge compensation effect by boron, which inevitably occurs in common nitrogen doped TiO<sub>2</sub>. The red anatase TiO<sub>2</sub> exhibits photoelectrochemical water splitting activity under visible light irradiation. The results obtained may shed light on how to increase high visible light absorbance of wide-bandgap photocatalysts.

### Introduction

Narrowing the bandgap of wide-bandgap photocatalysts for increasing visible light absorption is crucial to advancing their applications in solar energy conversion.<sup>1–18</sup> In the past decade,

anion-doping,<sup>1,2</sup> particularly nitrogen-doping,<sup>1</sup> has been widely used to modify the electronic structures and consequently light absorption ranges of a prototypical photocatalyst TiO<sub>2</sub> (anatase with a bandgap of 3.2 eV and rutile with a bandgap of 3.0 eV). It is recognized that this modification is sensitively affected by both the chemical state and spatial distribution of anion dopants<sup>3,6,19</sup> and that only bulk doping of substitutional dopants for lattice oxygen can result in a desired bandgap narrowing by elevating the valence band edge of the photocatalyst. Unfortunately, dominant cases fall in the class of surface doping of interstitial dopants,<sup>3,6</sup> which causes localized states in the bandgap. Furthermore, new recombination centers associated with dopants are always formed in the doped photocatalyst as a result of the charge balance requirement (for instance, nitrogen-related

<sup>a</sup>Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China. E-mail: cheng@imr.ac.cn; Fax: +86 24 23903126

<sup>b</sup>Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, 239 Zhangheng Road, Shanghai, 201800, China

† Electronic supplementary information (ESI) available: Fig. S1–S7. See DOI: 10.1039/c2ee22930g.

‡ These authors contributed equally to this work.

### Broader context

Photocatalysis is a promising process for solar energy utilization by storing photon energy in chemical bonds. Developing photocatalysts with the ability to strongly absorb visible light is a prerequisite for realizing efficient photocatalysis. Although anatase TiO<sub>2</sub> is the most intensively studied photocatalyst, its application has been restricted because it only responds to the UV region. To overcome this bottleneck, introducing suitable anion dopants has been actively explored. It has been recognized that only bulk doping of substitutional dopants for lattice oxygen can result in a desired bandgap narrowing by elevating the valence band edge. However, the limited solubility of substitutional dopants in bulk and dopant associated recombination centres (*i.e.* Ti<sup>3+</sup>) has impaired the effectiveness of doping. Here, through pre-doping an interstitial boron gradient to weaken nearby Ti–O bonds for the easy substitution of oxygen by nitrogen, we realized a gradient of B–N co-doping with high concentrations in the shell of anatase TiO<sub>2</sub> microspheres to obtain a red TiO<sub>2</sub>. As a consequence, the light absorption edge of the red TiO<sub>2</sub> has been extended up to *ca.* 700 nm covering the full visible light spectrum. Furthermore, no nitrogen-related Ti<sup>3+</sup> was formed in the red TiO<sub>2</sub> due to the charge compensation effect by boron. A photoanode fabricated from the red TiO<sub>2</sub> has the ability to split water under visible light. This different doping approach could be extendable to modify other photocatalysts that demand bulk substitutional doping for increasing visible light absorption.

Ti<sup>3+</sup> in N doped TiO<sub>2</sub>).<sup>7</sup> Although the homogeneous doping of substitutional nitrogen was reported in the layered photocatalysts due to the easy diffusion of dopant from the surface to the bulk through the interlayer galleries,<sup>19,20</sup> introducing substitutional nitrogen into bulk TiO<sub>2</sub> without a layer structure is still hard to realize. The apparent merits of realizing substitutional nitrogen doping in bulk TiO<sub>2</sub> include both the high visible light absorbance and high charge carrier mobility. Therefore, it remains challenging, yet highly desirable, to devise new doping approaches in order to engineer the chemical state and spatial distribution of nitrogen dopant in TiO<sub>2</sub>, especially without introducing additional recombination centers.

The above challenge originally stems from both the high bonding energy ( $D_0$ ) of metal (M)–O (*i.e.*,  $D_0^{\text{Ti-O}} = 346.4 \text{ kJ mol}^{-1}$ )<sup>21</sup> bonds and the charge difference between lattice oxygen and dopant atoms (*i.e.*, O<sup>2-</sup> versus N<sup>3-</sup>) in oxide-based photocatalysts. The key to solving this conundrum should have the dual functions of both weakening M–O bonds and compensating for the charge difference. To solve this problem, we proposed an approach featuring the pre-doped interstitial boron distribution in the bulk as both a bond weakening and charge compensation agent. This approach is based on the following two premises: (1) interstitial B may weaken nearby Ti–O bonds for easy substitution of lattice O<sup>2-</sup> by N<sup>3-</sup> by contributing its extra electrons, which also compensates for the charge difference between N<sup>3-</sup> and O<sup>2-</sup>. (2) The very small ionic radius of the interstitial boron (25 pm for 4-fold coordinated boron) makes it easy to engineer the spatial distribution of boron by diffusion in the cavities (a typical size of *ca.* 100 pm considering the radius of 140 pm for O<sup>2-</sup>) formed by TiO<sub>6</sub> octahedra in TiO<sub>2</sub>, as validated recently,<sup>22</sup> which can correspondingly direct the distribution of substitutional N<sup>3-</sup> by the weakened Ti–O bonds in boron-doped TiO<sub>2</sub>.

The above hypothesis falls within the scope of B/N codoping. The early studies on B/N codoping in TiO<sub>2</sub> showed that the codoping without B–N bonding leads to a limited visible light absorption band.<sup>23–25</sup> Although the subsequent efforts realized B–N bonding by nitriding surface boron modified TiO<sub>2</sub>,<sup>26,27</sup> the visible light absorbance induced is still low because the nitrogen dopants are predominantly located on the surface. To this end, B/N codoping still fails to cause a high visible light absorption band in TiO<sub>2</sub>. According to the hypothesis, the prerequisite to realize a high visible light absorption band in TiO<sub>2</sub> with the B/N codoping strategy is to use TiO<sub>2</sub> with bulk contained boron for subsequent nitrogen doping. Recently, we have developed anatase TiO<sub>2</sub> microspheres with an interstitial B<sup>σ+</sup> ( $\sigma \leq 3$ ) gradient shell of around 50 nm thickness,<sup>22</sup> which might be an ideal candidate for verifying the above hypothesis and realizing the high visible light absorption band. In this work, we carried out nitrogen-doping by calcining these microspheres in a gaseous ammonia atmosphere. In contrast to the previously reported N doped TiO<sub>2</sub> or N/B codoped TiO<sub>2</sub> that were typically yellow,<sup>1,23–27</sup> the unusual red TiO<sub>2</sub> microspheres were obtained by introducing nitrogen in the interstitial boron gradient shell of TiO<sub>2</sub> microspheres. The origin of forming red TiO<sub>2</sub> was experimentally and theoretically investigated. Significant insight is gained into the role of interstitial boron in weakening nearby Ti–O bonds and thus facilitating the substitution of O by N. Furthermore, this red anatase TiO<sub>2</sub> shows photoelectrochemical water splitting activity under visible light irradiation. To the best of our knowledge, this represents the first case of realizing red anatase TiO<sub>2</sub>.

## Experimental

### Sample preparation

Anatase TiO<sub>2</sub> microspheres with an interstitial B<sup>σ+</sup> ( $\sigma \leq 3$ ) gradient shell were synthesized according to our recently developed procedure.<sup>22</sup> Specifically, the acidic hydrolysis of crystalline TiB<sub>2</sub> in a Teflon-lined autoclave at 180 °C for 24 h led to the formation of anatase TiO<sub>2</sub> microspheres with the substitutional boron (B<sup>δ-</sup>,  $\delta \leq 2$ ) in the core. The subsequent heating at 600 °C in air for 2 h resulted in the diffusion of boron from the core to the shell of microspheres, accompanying the change of substitutional B<sup>δ-</sup> to interstitial B<sup>σ+</sup>. To prepare red anatase TiO<sub>2</sub>, the white anatase TiO<sub>2</sub> microspheres with an interstitial boron shell (for simplicity, these TiO<sub>2</sub> microspheres are defined as white TiO<sub>2</sub> in this work) were further heated between 580 and 620 °C in a gaseous ammonia atmosphere with a flux of 50 mL min<sup>-1</sup> for 60 min. The phase transition temperature of white TiO<sub>2</sub> to TiN in the gaseous ammonia was measured to be 700 °C (Fig. S1†).

### Characterization

X-Ray diffraction (XRD) patterns of the samples were recorded with a Rigaku diffractometer using Cu K $\alpha$  irradiation. Their morphology was observed by scanning electron microscopy (Nova NanoSEM 430). The optical absorption spectra of the samples were recorded with a UV-visible spectrophotometer (JASCO V-550). Raman spectra were collected by using Lab-Ram HR 800. Chemical compositions and states were analyzed using X-ray photoelectron spectroscopy (XPS) (Thermo Escalab 250, a monochromatic Al K $\alpha$  X-ray source). All binding energies were referenced to the C 1s peak (284.6 eV) arising from the adventitious carbon. Electron spin resonance (ESR) spectra were recorded at room temperature using a JEOL JES-FA200 ESR spectrometer. The X-ray absorption spectra at the Ti L-edge were recorded in a total electron yield mode at beamline U18 of the National Synchrotron Radiation Laboratory (NSRL), China. The beamline covered an energy range from 100 to 1000 eV, with an energy resolution at 0.2 eV.

### Theoretical calculations

All calculations presented in this work were carried out using the Vienna ab initio simulation package,<sup>28,29</sup> as described elsewhere.<sup>22</sup> Briefly, the exchange-correlation effects were treated within the generalized gradient approximation by using the Perdew–Burke–Ernzerhof function.<sup>30</sup> The electron-ion interactions were described by using the frozen-core projector augmented wave approach,<sup>31,32</sup> and the Kohn–Sham one-electron valence states were expanded on the basis of plane waves with a cutoff energy of 450 eV. A cubic 2 × 2 × 1 supercell (32 O atoms and 16 Ti atoms) was used to model interstitial B-doped bulk anatase and a 3 × 3 × 3 *k*-point mesh was used for the Brillouin zone sampling. The total and projected electron density of states were calculated using the tetrahedral integration method.<sup>33</sup> The formation enthalpy ( $E_{\text{form}}$ ) and the substitution enthalpy ( $E_{\text{sub}}$ ) for B and N co-doped anatase TiO<sub>2</sub> (Ti<sub>16</sub>O<sub>32</sub>BN<sub>*x*</sub>) were calculated respectively, based on the following definitions,

$$E_{\text{form}} = \frac{E[\text{Ti}_{16}\text{O}_{32-x}\text{BN}_x] - 8 \times E[\text{hcp-Ti}] - \frac{1}{12}E[\alpha\text{-boron}] - \frac{x}{2} \times E[\text{N}_2] + \frac{32-x}{2} \times E[\text{O}_2]}{49}$$

$$E_{\text{sub}} = \frac{E[\text{Ti}_{16}\text{O}_{32-x}\text{BN}_x] - E[\text{Ti}_{16}\text{O}_{32}\text{B}] - x \times E[\text{N}] + x \times E[\text{O}]}{49}$$

here,  $E[\text{Ti}_{16}\text{O}_{32-x}\text{BN}_x]$  and  $E[\text{Ti}_{16}\text{O}_{32}\text{B}]$  are the total energies of interstitial B-doped  $\text{TiO}_2$  with and without N substituted lattice O.  $E[\text{hcp-Ti}]$  is the total energy of bulk Ti (2 Ti atoms within the primitive unit cell) with a hexagonal close packed (hcp) structure, and  $E[\alpha\text{-boron}]$  is the total energy of bulk  $\alpha$ -boron (12 B atoms within the primitive unit cell),  $E[\text{N}_2]$  ( $E[\text{N}]$ ) and  $E[\text{O}_2]$  ( $E[\text{O}]$ ) are the total energies of a gaseous  $\text{N}_2$  molecule (an isolated N atom) and a gaseous  $\text{O}_2$  molecule (an isolated O atom). By using above definition, the formation enthalpy of pure anatase  $\text{TiO}_2$  was calculated to be  $-9.99$  eV, which is very close to the experimental value ( $-9.73$  eV).<sup>34</sup>

### Photoelectrode preparation

According to the procedure reported previously,<sup>35</sup> the red  $\text{TiO}_2$  microspheres were deposited on a fluorine-doped tin oxide (FTO) transparent conductive glass substrate by electrophoretic deposition. In detail, 40 mg of the red  $\text{TiO}_2$  was suspended in 50 mL of acetone solution containing 10 mg of iodine under ultrasonic treatment. The deposition was conducted with a two-electrode process at the applied bias of 10 V for 8 min, where both electrodes were FTO substrates (the surface area coated in the solution is  $1 \times 2$  cm<sup>2</sup>). The deposited electrode was then heated at 400 °C for 30 min in air. To increase the interconnection between the particles, 20  $\mu\text{L}$  of diluted  $\text{TiCl}_4$  with methanol was dropped on the heated electrode. This procedure was repeated 5 times after the electrode was dried each time. Finally, the electrode was heated at 450 °C for 30 min.

### Photoelectrochemical measurements

Photoelectrochemical measurements were carried out in a quartz cell with a conventional three-electrode process. The red  $\text{TiO}_2$  photoelectrode as the anode, and a Pt foil and Ag/AgCl electrode served as the working electrode, counter electrode and reference electrode, respectively. The electrolyte was a 0.2 M  $\text{Na}_2\text{SO}_4$  aqueous solution. The light source was a 300 W Xe lamp (Beijing Trusttech Co. Ltd, PLS-SXE-300UV). UV light was removed with a 420 nm long-pass glass filter. The photoanode surface area illuminated was 2 cm<sup>2</sup>. The gaseous product from the photoelectrochemical cell under irradiation was analyzed using a gas chromatograph (GC, Agilent 7890A). The incident photon-to-current conversion efficiency (IPCE) was calculated according to the following equation:  $\text{IPCE} (\%) = [1240 \times \text{photocurrent density} (\text{mA cm}^{-2})] / [\text{wavelength} (\text{nm}) \times \text{photon flux} (\text{mW cm}^{-2})] \times 100\%$ .

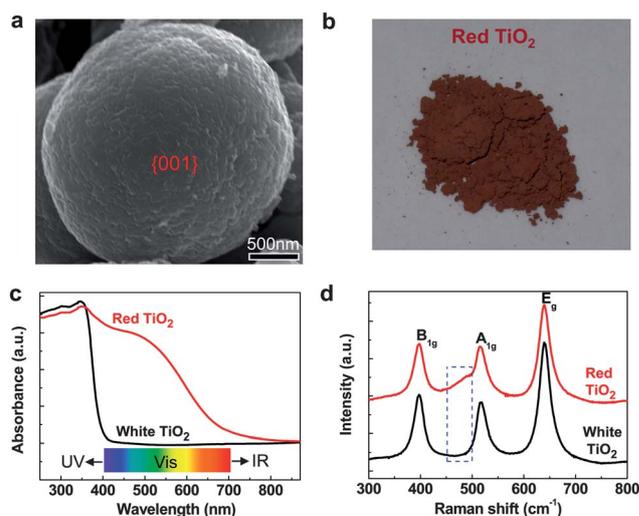
## Results and discussion

Nitrogen doping at 600 °C did not change the morphology or the crystal structure of the  $\text{TiO}_2$  microspheres with exposed {001} facets (Fig. 1a and S2†). As a result of nitrogen-doping, the

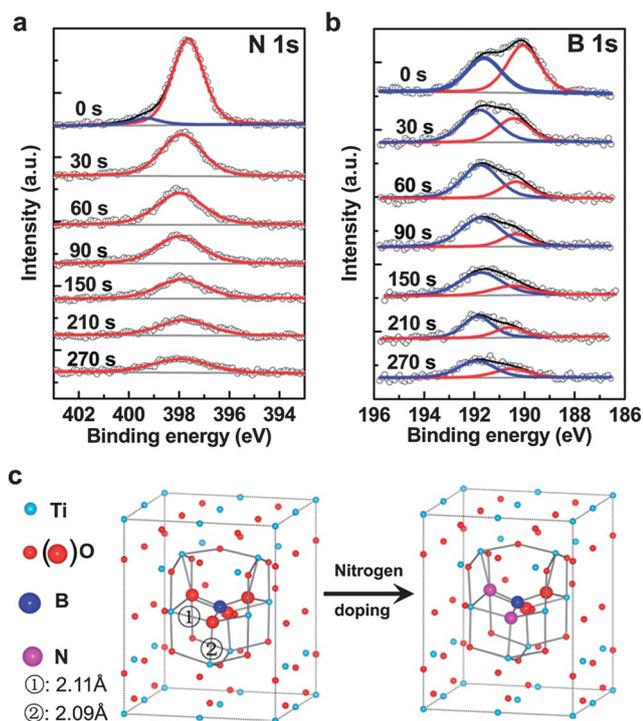
sample's color changes from white to red (Fig. 1b), which is remarkably different from the commonly observed yellowish nitrogen doped  $\text{TiO}_2$ .<sup>1</sup> UV-visible absorption spectra in Fig. 1c show that, compared to the pristine white  $\text{TiO}_2$  with an absorption edge of ca. 400 nm, the red  $\text{TiO}_2$  has an extended absorption edge up to ca. 700 nm covering the full visible light spectrum. The reference nitrogen-doped anatase  $\text{TiO}_2$  prepared under the same conditions has only a very small visible light absorption band ranging from 400 nm to 550 nm (Fig. S3†).

Raman spectroscopy was used to detect the possible influence of nitrogen on the geometric structure of  $\text{TiO}_2$ . Anatase gives six active modes, namely,  $E_{\text{g}(1)}$ ,  $E_{\text{g}(2)}$ ,  $E_{\text{g}(3)}$ ,  $B_{1\text{g}(1)}$ ,  $B_{1\text{g}(2)}$  and  $A_{1\text{g}}$ , with frequencies at 144, 197, 639, 399, 519, and 513 cm<sup>-1</sup>, respectively.<sup>36</sup> Besides these six typical modes (the  $B_{1\text{g}(2)}$  and  $A_{1\text{g}}$  modes usually appear as an overlapped peak) in Fig. S4,† an additional active mode ranging from 450 cm<sup>-1</sup> to 500 cm<sup>-1</sup> is observed in the red  $\text{TiO}_2$  (Fig. 1d). This mode cannot be attributed to other phases (rutile and brookite) of  $\text{TiO}_2$ . Furthermore, no such mode was detected in the common nitrogen-doped anatase  $\text{TiO}_2$ . A possible explanation for this new peak is that substitutional nitrogen doped in the bulk  $\text{TiO}_2$  (Fig. 2) breaks down the Raman selection rules to generate a new active mode by lowering the geometric symmetries of  $\text{TiO}_2$ .<sup>8,37</sup>

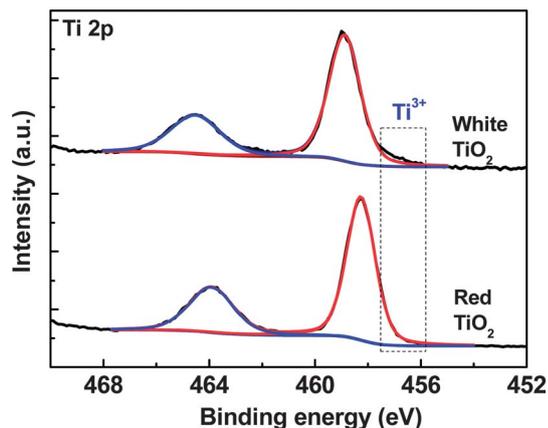
The chemical states and spatial distributions of nitrogen and boron in the red  $\text{TiO}_2$  were investigated by X-ray photoelectron spectroscopy (XPS), as shown in Fig. 2. A strong peak at 397.6 eV and a weak shoulder peak at 399.3 eV appear in the N 1s XPS spectrum recorded from the surface of the red  $\text{TiO}_2$  microspheres (Fig. 2a). The former originates from the substitution of nitrogen for lattice oxygen by forming Ti–N bonds,<sup>1</sup> and the latter is from interstitial nitrogen.<sup>38</sup> Prior to nitrogen-doping, the interstitial boron, dominantly coordinated in the tetragonal unit  $[\text{BO}_4]$  in the white  $\text{TiO}_2$ ,<sup>22</sup> gives a single B1s XPS peak with its center at 192.2



**Fig. 1** (a) SEM image of a red  $\text{TiO}_2$  microsphere; (b) optical photograph of the prepared red  $\text{TiO}_2$  sample; (c) and (d) UV-visible absorption and Raman spectra of the white  $\text{TiO}_2$  and red  $\text{TiO}_2$ .

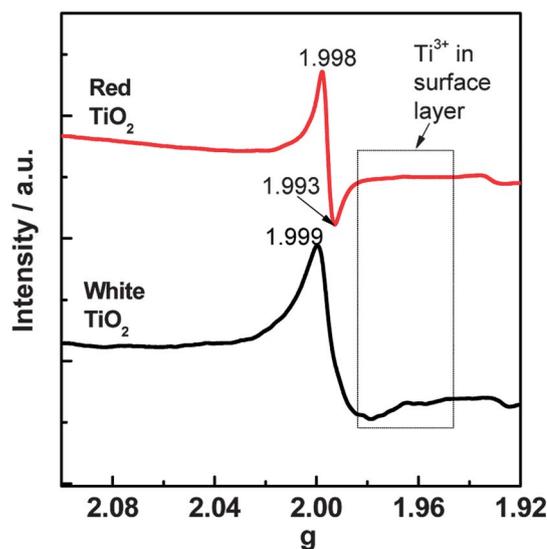


**Fig. 2** Time-dependent high resolution XPS spectra of (a) N 1s and (b) B 1s of the red TiO<sub>2</sub> microspheres upon Ar<sup>+</sup> sputtering from 0 to 270 s. (c) Structure models of a 2 × 2 × 1 supercell for the anatase TiO<sub>2</sub> with a tetragonal unit of [BO<sub>4</sub>] in the white TiO<sub>2</sub> (the left panel) and [BO<sub>4-x</sub>N<sub>x</sub>] (1 ≤ x ≤ 4, as an example x = 2) in the red TiO<sub>2</sub> (the right panel).



**Fig. 3** High resolution Ti 2p XPS spectra recorded from the pristine surface layer of the white and red TiO<sub>2</sub>.

eV.<sup>22</sup> With the incorporation of substitutional nitrogen in the red TiO<sub>2</sub>, we observed an additional B 1s peak with its binding energy at 190.1 eV (Fig. 2b), which is a typical value for BN or B–N bonds.<sup>27,39</sup> Our first-principles calculations suggest that the charge state of boron in [BO<sub>4</sub>] decreases from +2.3 to +2.1 with the incorporation of nitrogen in [BO<sub>4-x</sub>N<sub>x</sub>] (x = 3), which can explain the shift of B 1s XPS peak towards low energy after nitrogen doping. Based on these results, we can conclude that the substitution of nitrogen for lattice oxygen occurs in [BO<sub>4</sub>] units and consequently forms [BO<sub>4-x</sub>N<sub>x</sub>] (1 ≤ x ≤ 4) units in the red TiO<sub>2</sub>, as illustrated in Fig. 2c. This is the reason why both Ti–N and B–N bonds were detected. In addition, the redistribution of charges in

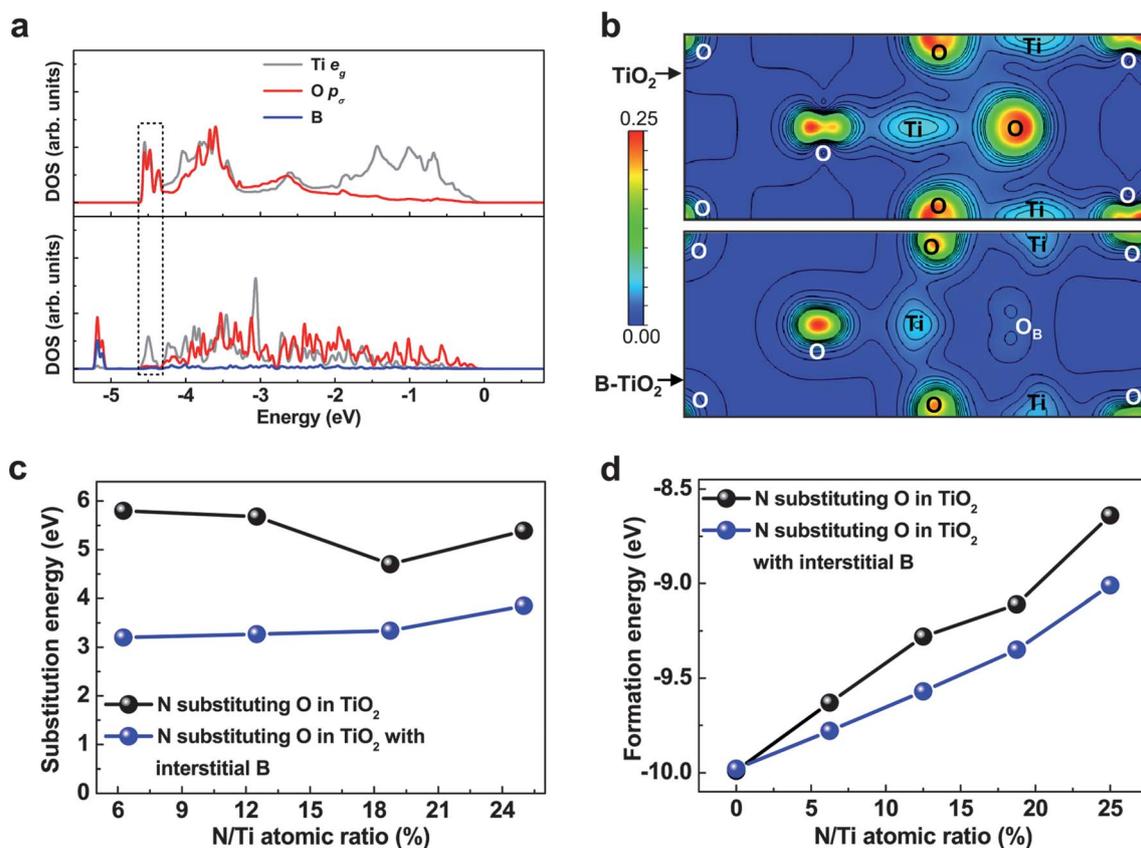


**Fig. 4** ESR spectra of the white TiO<sub>2</sub> and red TiO<sub>2</sub> measured at room temperature.

the red TiO<sub>2</sub> with the incorporated N causes a XPS binding energy shift of Ti 2p and O 1s (Table 1 in the ESI†).

Equally important, no Ti<sup>3+</sup> was detected in the nitrogen contained surface layer of the red TiO<sub>2</sub> microspheres by XPS and ESR. The shoulder between 455.5 eV and 455.8 eV in the Ti 2p XPS spectrum of the white TiO<sub>2</sub>, which originated from Ti<sup>3+</sup> in the surface layer,<sup>40</sup> is completely quenched after nitrogen doping (Fig. 3). Confirmation that the nitrogen contained surface layer is Ti<sup>3+</sup>-free can be achieved by comparing the ESR spectra in Fig. 4. Compared to the only sharp signal at around g = 1.996 in the red TiO<sub>2</sub>, an additional weak broad signal from g = 1.98 to 1.95 appears in the white TiO<sub>2</sub>. The latter can be clearly assigned to the Ti<sup>3+</sup> species in the surface layer by referring to the surface plasma-treated anatase TiO<sub>2</sub> and H<sub>2</sub>-treated anatase TiO<sub>2</sub>,<sup>41,42</sup> where the surface layer Ti<sup>3+</sup> gives a similar ESR signal. Based on the fact that the signal is nearly unchanged upon incorporation of nitrogen in the surface layer of the red TiO<sub>2</sub>, we infer that some inner defects independent of N doping should be responsible for the sharp signal at around g = 1.996, although it is challenging to identify the origin of the sharp signal in both samples. The removal of Ti<sup>3+</sup> from nitrogen contained surface layer confirmed above can be explained by the extra electrons provided by the pre-doped interstitial boron that can effectively compensate for the charge difference between the substitutional N<sup>3-</sup> and lattice O<sup>2-</sup> (this can be understood according to the following defect equations: B + Ti<sup>4+</sup> → 1/σ B<sup>σ+</sup> + Ti<sup>3+</sup>; Ti<sup>3+</sup> + O<sup>2-</sup> + N → Ti<sup>4+</sup> + N<sup>3-</sup> + O). However, oxygen vacancies and related Ti<sup>3+</sup> are always formed in the nitrogen containing surface of common nitrogen-doped TiO<sub>2</sub> as demonstrated by Batzill *et al.*<sup>7</sup>

It is important to point out that substitutional nitrogen exists not only in the surface but also the deep layer of the boron contained shell of the red TiO<sub>2</sub> microspheres, as demonstrated in the time-dependent depth profile of the N 1s spectrum in Fig. 2a. The atomic ratio of N to O and Ti in the surface is as high as 4.1% (only 0.76% in the reference nitrogen doped TiO<sub>2</sub>) and gradually decreases with increasing depth to around 50 nm from the surface, suggesting much improved solubility of substitutional



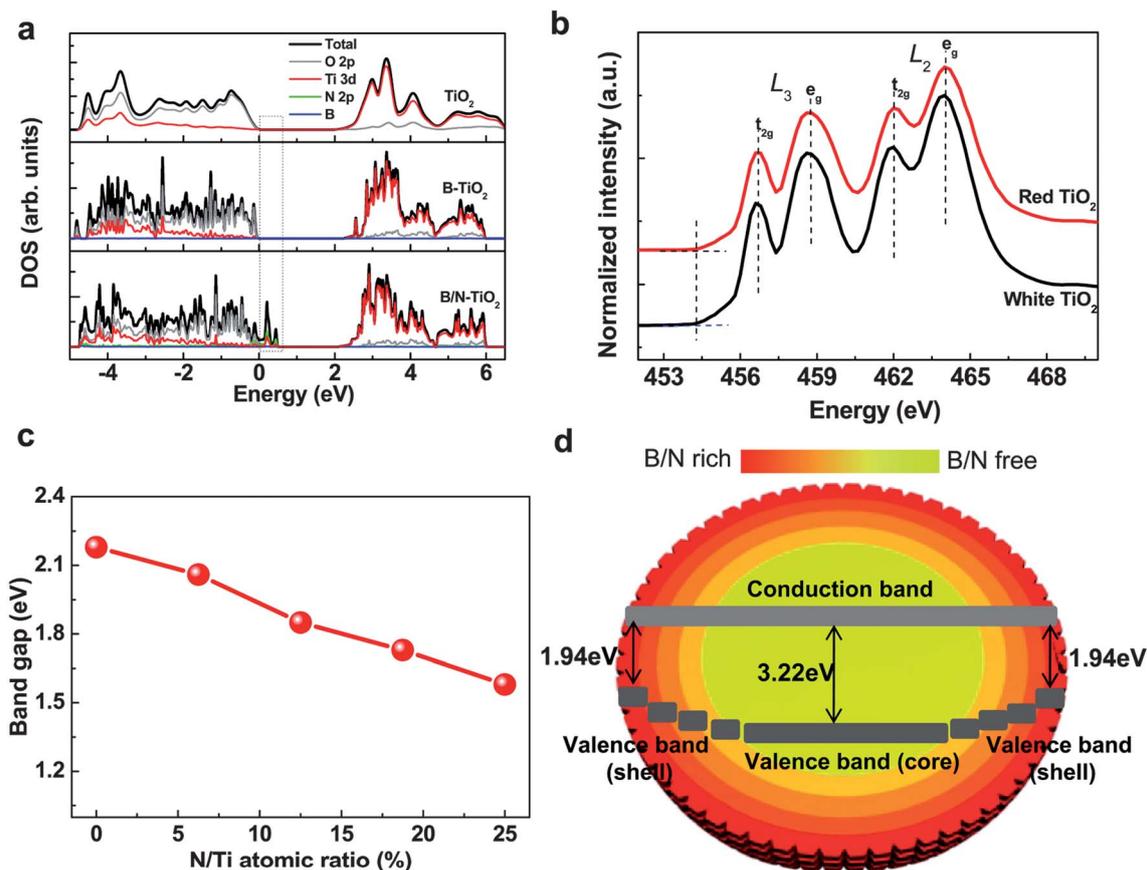
**Fig. 5** (a) Projected DOS of Ti–O bonds in the pristine (upper panel) and boron doped TiO<sub>2</sub> (lower panel); (b) electron densities at the Z point of the pristine and boron doped TiO<sub>2</sub> in the (010) (the Z point is defined in Fig. S6†). The contours start from  $1 \times 10^{-3}$  electron per a.u.<sup>3</sup> and change successively by a step of  $1 \times 10^{-2}$  electron per a.u.<sup>3</sup>. O<sub>B</sub> in the lower panel indicates the lattice oxygen close to interstitial boron; (c) and (d) plots of the formation energy and substitution energy of the nitrogen doped TiO<sub>2</sub> with and without interstitial boron as a function of N/Ti atomic ratios.

nitrogen and its gradient distribution in the outer layer of the red TiO<sub>2</sub> microspheres. Furthermore, the N gradient is basically similar to the gradients of both total boron (Fig. 2a in ref. 22) and boron in B–N bonds (Fig. 2b), strongly indicating the important role of the pre-doped interstitial boron gradient in directing the distribution of substitutional nitrogen, as expected.

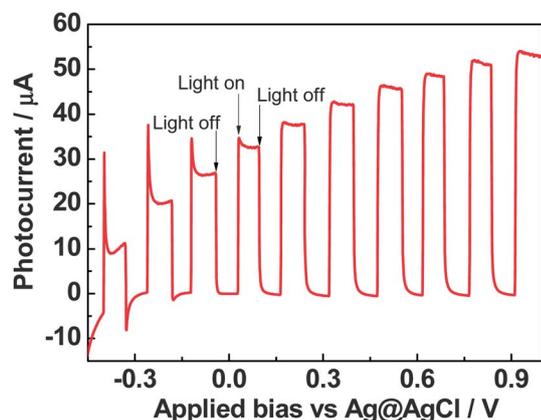
As mentioned above, improved solubility of substitutional nitrogen and substantially increased visible light absorption were obtained in the red TiO<sub>2</sub>. In order to understand how the interstitial boron improves the solubility of substitutional nitrogen in anatase TiO<sub>2</sub>, we first studied the effect of the interstitial boron on modifying the local atomic structures of TiO<sub>2</sub>. Compared to the pristine TiO<sub>2</sub>, the inward relaxation of oxygen atoms to “screen” the positively charged interstitial boron atoms is clearly visible in Fig. 2c, resulting in twelve elongated Ti–O bonds with two different bond lengths (2.11 Å and 2.09 Å, labeled in Fig. 2c) surrounding a boron atom in a tetragonal [BO<sub>4</sub>] unit, compared with those in the pristine TiO<sub>2</sub> (1.95 Å and 2.00 Å, labeled in Fig. S5†).

The elongation of Ti–O bonds surrounding the interstitial boron atoms, in principle, indicates weakening of these Ti–O bonds. To confirm this expectation, we decomposed the density of states (DOS) of a Ti–O bond, which is located in the lowest part of the upper valence band (highlighted by a black short-dotted rectangle), into Ti e<sub>g</sub> and O p<sub>σ</sub> (in the Ti<sub>3</sub>O cluster plane)

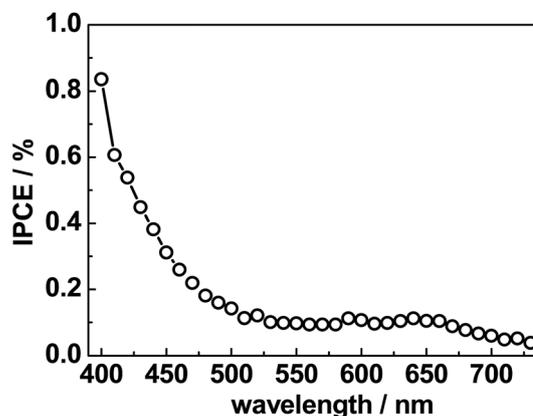
contributions, as shown in Fig. 5a. As expected, the Ti–O bonds surrounding an interstitial boron in B-doped TiO<sub>2</sub> are largely weakened (O p<sub>σ</sub> contribution is highly suppressed in the lower panel in Fig. 5a) compared with those in the pristine TiO<sub>2</sub> (the O p<sub>σ</sub> contribution overlaps with the Ti e<sub>g</sub> contribution in the upper panel in Fig. 5a). This Ti–O bond weakening is further proved by comparing electron density plots at the Z point for the pristine TiO<sub>2</sub> and the interstitial boron-doped TiO<sub>2</sub>, as shown in Fig. 5b. This should lead to the easier substitution of O for N. As suggested in Fig. 5c, the theoretical substitution energy of substituting lattice oxygen by nitrogen in TiO<sub>2</sub> at different N/Ti ratios is apparently lowered by the interstitial boron. In particular, the energy cost markedly decreases from 5.80 to 3.20 eV per atom at a N/Ti ratio of 6.25 at.%, which is close to our experimental N/Ti ratio. These results also indicate that nitrogen dopants will prefer to substitute for lattice oxygen atoms in the weakened Ti–O bonds surrounding boron atoms, which consequently results in the formation of both B–N and Ti–N bonds as experimentally observed in Fig. 2. The calculated formation energy ( $E_{\text{form}}$ ) of various TiO<sub>2</sub> configurations (Fig. 5d) shows that the  $E_{\text{form}}$  of nitrogen-doped TiO<sub>2</sub> with interstitial boron is 0.15–0.41 eV per TiO<sub>2</sub> lower than that without interstitial boron, which unambiguously shows a chemical stability improvement in the nitrogen-doped TiO<sub>2</sub> with interstitial boron. Therefore, the high solubility of substitutional nitrogen obtained in the red TiO<sub>2</sub>



**Fig. 6** (a) The density of states (DOS) of anatase TiO<sub>2</sub>, anatase TiO<sub>2</sub> doped with an interstitial boron in a [BO<sub>4</sub>] unit (denoted as B-TiO<sub>2</sub>) and anatase TiO<sub>2</sub> doped with a [BO<sub>4-x</sub>N<sub>x</sub>] ( $x = 4$ ) (denoted as B/N-TiO<sub>2</sub>); (b) comparison of X-ray absorption spectra of Ti L<sub>2</sub> and L<sub>3</sub> edges of the white and red TiO<sub>2</sub>; (c) the N/Ti atomic ratio dependent bandgap of anatase TiO<sub>2</sub> with interstitial boron; (d) schematic of band structures of the red TiO<sub>2</sub> with a bandgap gradient.



**Fig. 7** Applied potential bias-dependent photocurrent generated by the photoanode of the red TiO<sub>2</sub> microspheres under visible light ( $\lambda > 420$  nm).

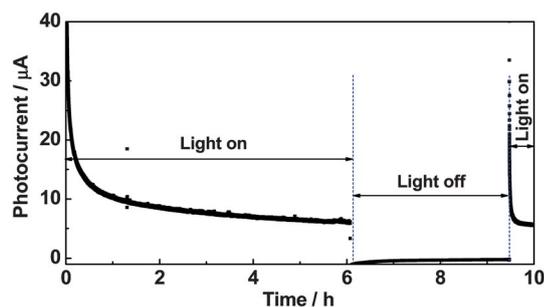


**Fig. 8** The IPCE of the red TiO<sub>2</sub> microsphere photoanode measured at an applied potential of 0.3 V versus Ag/AgCl.

can be ascribed to the synergistic effect of substitution energy reduction and chemical stability improvement due to the existence of pre-doped interstitial boron in bulk TiO<sub>2</sub>.

We also investigated how the improved solubility of substitutional nitrogen by interstitial boron changes the band structure for the optical absorption properties of the red TiO<sub>2</sub> shown in Fig. 1c. First-principles calculations were conducted to explore

the electronic structures of the pristine TiO<sub>2</sub>, TiO<sub>2</sub> with an interstitial boron in a [BO<sub>4</sub>] unit, and TiO<sub>2</sub> with an interstitial boron in a [BO<sub>4-x</sub>N<sub>x</sub>] ( $x = 4$ ) unit. The DOS for these systems are plotted as a function of electron energy in Fig. 6a. The valence and conduction bands of TiO<sub>2</sub> mainly consist of O 2p and Ti 3d orbitals as reported,<sup>40</sup> showing a bandgap of 2.12 eV



**Fig. 9** The long-time photocurrent stability of the red  $\text{TiO}_2$  microsphere photoanode. The light intensity used in this test was one-fifth of the intensity used in Fig. 7 in order to reduce thermal effects on electrolyte during the long-time irradiation.

(the smaller theoretical bandgap than the experimental one is caused by the well known DFT gap underestimation). Introducing an interstitial boron atom causes no remarkable change in the bandgap of  $\text{TiO}_2$ , which is consistent with the previous theoretical results.<sup>43</sup> Further introducing nitrogen to substitute for the four oxygen atoms surrounding the boron leads to an apparent bandgap narrowing to 1.58 eV by forming additional electronic states above the original valence band maximum (VBM). Partial DOS shows that the increased electronic states mainly consists of N 2p orbitals, which are fully mixed with Ti 3d and O 2p orbitals. Importantly, these states show a dispersed characteristic and merge well with the original VBM as demonstrated in the corresponding energy bands (Fig. S6†). The conduction band of  $\text{TiO}_2$  remains unchanged after the nitrogen substitution, which is further confirmed by comparing the measured X-ray absorption spectra of Ti  $L_2$  and  $L_3$  edges of the white and red  $\text{TiO}_2$  (Fig. 6b).

It is theoretically predicted that the bandgap of nitrogen-doped anatase  $\text{TiO}_2$  with interstitial boron linearly decreases with increasing nitrogen-doping level (Fig. 6c). Experimentally, a nitrogen gradient with the highest level on the surface exists in the shell of the red  $\text{TiO}_2$  microspheres with a thickness of *ca.* 50 nm (Fig. 2a). Based on these results, we can infer that a bandgap gradient varying from 1.94 eV on the surface to 3.22 eV in the core is formed, as illustrated in Fig. 6d (The bandgap values were determined according to Fig. S7†), which is the origin of harvesting the full visible light spectrum for the red  $\text{TiO}_2$ . It is noted that the maximum narrowing of the bandgap ( $2.12 - 1.58 = 0.54$  eV) from the first-principles calculations is lower than that from the experimental measurements ( $3.22 - 1.94 = 1.28$  eV). This can be explained by the well known fact of the bandgap underestimation by using the DFT calculation. However, the narrowing trend of the bandgap due to B–N codoping by the theoretical prediction is well consistent with the experimental observation in qualitative.

As demonstrated above, the remarkable absorption increase in the visible light range (Fig. 1c) is closely related to the B/N gradient formed in the  $\sim 50$  nm-thick shell of the  $\text{TiO}_2$  microspheres (Fig. 2a and b). This result can be further discussed from the view point of the long-range interaction among dopants in different spatial levels. Our previous results showed that homogeneous nitrogen doping in layered  $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_{4-x}\text{N}_x$  particles can realize the band-to-band visible light absorption as a result of

mixing the N 2p states with O 2p states;<sup>19</sup> while sub-nanometer  $\text{Ti}_{0.91}\text{O}_{2-x}\text{N}_x$  nanosheets exfoliated from  $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_{4-x}\text{N}_x$  particles only have a small shoulder-like visible light absorption band due to the localized N 2p states formed in the gap.<sup>44</sup> The amount of nitrogen doped in the  $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_{4-x}\text{N}_x$  particles and  $\text{Ti}_{0.91}\text{O}_{2-x}\text{N}_x$  nanosheets is very close (3% vs. 2.8%), suggesting that the change in the absorption spectrum is independent of the N amount. This result, therefore, strongly indicates the crucial role of the long-range interaction among nitrogen dopants in different  $\text{Ti}_{0.91}\text{O}_{2-x}\text{N}_x$  nanosheets of layered  $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_{4-x}\text{N}_x$  in delocalizing N 2p states for a high visible light absorption band. For the red  $\text{TiO}_2$ , the long-range interaction among B/N dopants located on different spatial levels of the shell certainly exerts its effectiveness in delocalizing dopant states. It should be pointed out that the long-range interaction among the dopants in the shell of  $\text{TiO}_2$  is not as symmetric as that in layered  $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_{4-x}\text{N}_x$  due to the B/N gradient distribution instead of homogeneous distribution. On the other hand, the long-range interaction among B/N dopants in the shell of  $\text{TiO}_2$  is expected to be much stronger than that in layered  $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_{4-x}\text{N}_x$  because of the presence of interlayer galleries in the latter.

The photocatalytic activity of the red  $\text{TiO}_2$  microspheres as a photoanode for photoelectrochemical (PEC) water splitting was investigated. The red  $\text{TiO}_2$  photoanode in a PEC cell with  $\text{Na}_2\text{SO}_4$  solution as electrolyte gives an apparent response to light on/off at the bias applied (Fig. 7) under visible light ( $\lambda > 420$  nm). Under the same condition, the photocurrent generated from the white  $\text{TiO}_2$  photoanode is negligible. The photoresponse of the red  $\text{TiO}_2$  was further investigated by measuring the IPCE of the photoanode. As shown in Fig. 8, the photoanode gives a photocurrent under the irradiation up to around 700 nm, which is consistent with the maximum light absorption range of the red  $\text{TiO}_2$ . It demonstrates that the red  $\text{TiO}_2$  is photocatalytically active for water splitting. In order to doubly confirm water splitting induced by the red  $\text{TiO}_2$  photoanode under irradiation, we analyzed the gaseous product from the PEC cell by GC after different irradiation times. As shown in Fig. S8,† an obvious signal of  $\text{H}_2$  was detected after 1 h irradiation and increased with the irradiation time ( $\text{O}_2$  generation was also confirmed in the gaseous product), clearly suggesting the continuous proceeding of water splitting. Furthermore, the time-dependent photocurrent curve of the photoanode for 10 h irradiation (Fig. 9) demonstrates acceptable stability of the photoanode (the partial photocurrent decrease was probably caused by loss of some particles from the electrode). All these results suggest that the red  $\text{TiO}_2$  has the ability to split water driven by visible light. In addition, it is expected that reducing the particle size (around 2  $\mu\text{m}$ ) of the red  $\text{TiO}_2$  microspheres to the nanoscale should lead to a substantial activity improvement.

## Conclusions

We report a doping approach by using a pre-doped interstitial boron gradient to improve the solubility of substitutional nitrogen in the bulk of anatase  $\text{TiO}_2$  without introducing nitrogen-related  $\text{Ti}^{3+}$ . The origin of the improved solubility of nitrogen is that the interstitial boron effectively weakens the surrounding Ti–O bonds for easier nitrogen substitution and increases the chemical stability of the doped  $\text{TiO}_2$ . Meanwhile, the extra electrons from

boron can compensate for the charge difference between lattice  $O^{2-}$  and substitutional  $N^{3-}$ . The red  $TiO_2$  obtained can absorb a full visible light spectrum due to the bandgap gradient produced, varying from 1.94 eV on the surface to 3.22 eV in the core by gradually elevating VBM. The red  $TiO_2$  based photoanode has the ability to split water under visible light irradiation.

## Acknowledgements

The authors thank the Major Basic Research Program, Ministry of Science and Technology of China (no. 2009CB220001), NSFC (no. 50921004, 51002160, 21090343, 51172243, 51202255), the Solar Energy Initiative of the Chinese Academy of Sciences (CAS) and the Hydrogen Energy Program (KJCX2-YW-H21-01) of CAS for financial support. GL thanks the IMR SYNLT-S. Kê Research Fellowship. LCY acknowledges the grants from Informatization Construction Project of CAS (no. INFO-115-B01), and the GPU Project of MOF (no. ZDYZ2008-2-A12), and the Supercomputing Center, CAS, China.

## Notes and references

- 1 R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science*, 2001, **293**, 269.
- 2 S. U. M. Khan, M. Al-Shahry and W. B. Ingler, *Science*, 2002, **297**, 2243.
- 3 N. I. Serpone, *J. Phys. Chem. B*, 2006, **110**, 24287.
- 4 T. L. Thompson and J. T. Yates, Jr, *Chem. Rev.*, 2006, **106**, 4428.
- 5 X. X. Xu, C. Randorn, P. Efstathiou and T. S. J. Irvine, *Nat. Mater.*, 2012, **11**, 595.
- 6 G. Liu, L. Z. Wang, H. G. Yang, H. M. Cheng and G. Q. Lu, *J. Mater. Chem.*, 2010, **20**, 831.
- 7 M. Batzill, E. H. Morales and U. Diebold, *Phys. Rev. Lett.*, 2006, **96**, 026103.
- 8 X. B. Chen, L. Liu, P. Y. Yu and S. S. Mao, *Science*, 2011, **331**, 746.
- 9 J. G. Tao, T. Luttrell and M. Batzill, *Nat. Chem.*, 2011, **3**, 296.
- 10 W. Choi, A. Termin and M. R. Hoffmann, *J. Phys. Chem.*, 1994, **98**, 13669.
- 11 M. Anpo and M. Takeuchi, *J. Catal.*, 2003, **216**, 505.
- 12 H. Tada, M. Fujishima and H. Kobayashi, *Chem. Soc. Rev.*, 2011, **40**, 4232.
- 13 A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 2009, **38**, 253.
- 14 X. B. Chen, Y. B. Lou, A. C. S. Samia, C. Burda and J. L. Gole, *Adv. Funct. Mater.*, 2005, **15**, 41; E. Martinez-Ferrero, Y. Sakatani, C. Boissiere, D. Grosso, A. Fuertes, J. Fraxedas and C. Sanchez, *Adv. Funct. Mater.*, 2007, **17**, 3348; X. C. Wang, J. C. Yu, Y. L. Chen, L. Wu and X. Z. Fu, *Environ. Sci. Technol.*, 2006, **40**, 2369; Z. G. Xiong and X. S. Zhao, *J. Am. Chem. Soc.*, 2012, **134**, 5754.
- 15 Z. G. Zou, J. H. Ye, K. Sayama and H. Arakawa, *Nature*, 2001, **414**, 625.
- 16 K. Maeda, K. Teramura, D. L. Lu, T. Takata, N. Saito, Y. Inoue and K. Domen, *Nature*, 2006, **440**, 295.
- 17 M. Batzill, *Energy Environ. Sci.*, 2011, **4**, 3275.
- 18 W. Zhao, W. H. Ma, C. C. Chen, J. C. Zhao and Z. G. Shuai, *J. Am. Chem. Soc.*, 2004, **126**, 4782.
- 19 G. Liu, L. Z. Wang, C. H. Sun, X. X. Yan, X. W. Wang, Z. G. Chen, S. C. Smith, H. M. Cheng and G. Q. Lu, *Chem. Mater.*, 2009, **21**, 1266.
- 20 A. Mukherji, R. Marschall, A. Tanksale, C. H. Sun, S. C. Smith, G. Q. Lu and L. Z. Wang, *Adv. Funct. Mater.*, 2011, **21**, 126.
- 21 M. Lazzeri, A. Vittadini and A. Selloni, *Phys. Rev. B: Condens. Matter*, 2001, **63**, 155409.
- 22 G. Liu, J. Pan, L. C. Yin, J. T. S. Irvine, F. Li, J. Tan, P. Wormald and H. M. Cheng, *Adv. Funct. Mater.*, 2012, **22**, 3233.
- 23 V. Gombac, L. Rogatis, A. Gasparotto, G. Vicario, T. Montini, D. Barreca, G. Balducci, P. Fornasiero, E. Tondello and M. Graziani, *Chem. Phys.*, 2007, **339**, 111.
- 24 S. In, A. Orlov, R. Berg, F. Garcia, S. Pedrosa-Jimenez, M. S. Tikhov, D. S. Wright and R. M. Lambert, *J. Am. Chem. Soc.*, 2007, **129**, 13790.
- 25 Q. C. Ling, J. Z. Sun and Q. Y. Zhou, *Appl. Surf. Sci.*, 2008, **254**, 3236.
- 26 G. Liu, Y. N. Zhao, C. H. Sun, F. Li, G. Q. Lu and H. M. Cheng, *Angew. Chem., Int. Ed.*, 2008, **47**, 4516.
- 27 G. Liu, C. H. Sun, L. N. Cheng, Y. G. Jin, H. F. Lu, L. Z. Wang, S. C. Smith, G. Q. Lu and H. M. Cheng, *J. Phys. Chem. C*, 2009, **113**, 12317.
- 28 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter*, 1996, **54**, 11169.
- 29 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15.
- 30 P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 31 P. E. Blöchl, *Phys. Rev. B: Condens. Matter*, 1994, **50**, 17953.
- 32 G. Kresse and D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758.
- 33 P. E. Blöchl, O. Jepsen and O. K. Andersen, *Phys. Rev. B: Condens. Matter*, 1994, **49**, 16223.
- 34 M. W. Chase, Jr, NIST-JANAF thermochemical tables, *J. Phys. Chem. Ref. Data*, 1998, **9**, 1.
- 35 K. Maeda, M. Higashi, B. Siritanaratkul, R. Abe and K. Domen, *J. Am. Chem. Soc.*, 2011, **133**, 12334.
- 36 T. Ohsaka, F. Izumi and Y. Fujiki, *J. Raman Spectrosc.*, 1978, **7**, 321.
- 37 P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors: Physics and Materials Properties*, Springer, Heidelberg, 2010, vol. 4.
- 38 J. Wang, D. N. Tafen, J. P. Lewis, Z. L. Hong, A. Manivannan, M. J. Zhi, M. Li and N. Q. Wu, *J. Am. Chem. Soc.*, 2009, **131**, 12290.
- 39 J. Moulder, W. Stickle and P. Sobol, *Handbook of X-ray Photoelectron Spectroscopy*, (P/N 624755), Perkin-Elmer, Physical Electronics Division, Eden Prairie, MN, 1992.
- 40 U. Diebold, *Surf. Sci. Rep.*, 2003, **48**, 53.
- 41 I. Nakamura, N. Negishi, S. Kutsuna, T. Ihara, S. Sugihara and K. Takeuchi, *J. Mol. Catal. A: Chem.*, 2000, **161**, 205.
- 42 H. Liu, H. T. Ma, X. Z. Li, W. Z. Li, M. Wu and X. H. Bao, *Chemosphere*, 2003, **50**, 39.
- 43 E. Finazzi, C. Di Valentin and G. Pacchioni, *J. Phys. Chem. C*, 2009, **113**, 220.
- 44 G. Liu, L. Z. Wang, C. H. Sun, Z. G. Chen, X. X. Yan, L. N. Cheng, H. M. Cheng and G. Q. Lu, *Chem. Commun.*, 2009, 1383.