

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: L. Hou, Z. Guan, M. Zhang, C. He, Q. Li and J. Yang, *Catal. Sci. Technol.*, 2018, DOI: 10.1039/C8CY00644J.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/catalysis

View Article Online View Journal

YAL SOCIETY CHEMISTRY

# Journal Name

### ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

# Adjusting the ratio of bulk single-electron-trapped oxygen vacancy/surface oxygen vacancy in TiO<sub>2</sub> for efficient photocatalytic hydrogen evolution

Lili Hou<sup>a</sup>, Zhongjie Guan<sup>a</sup>, Min Zhang<sup>a</sup>, Chunqing He<sup>b</sup>, Qiuye Li<sup>a,\*</sup>, Jianjun Yang<sup>a,\*</sup>

The effect of concentration ratio of bulk single-electron-trapped oxygen vacancies /surface oxygen vacancies on the photocatalytic hydrogen production of TiO<sub>2</sub> was investigated. A series of TiO<sub>2</sub> with the tunable concentration ratio of bulk and surface oxygen vacancies were prepared through NaBH<sub>4</sub> solid-state reduction method. The results of HRTEM, XPS, ESR, PL and UV-Vis DRS verify that surface oxygen vacancies can form on surface of TiO<sub>2</sub> and the concentrations of bulk single-electron-trapped oxygen vacancies and surface oxygen vacancies increase with the increase of the reduction degree. Combined the evaluation of photocatalytic hydrogen production with the analysis of positron annihilation lifetime spectra, it is proved that the concentration ratio of bulk single-electron-trapped oxygen vacancies /surface oxygen vacancies plays the key role on photocatalytic hydrogen production of TiO<sub>2</sub>, and the optimal ratio of bulk single-electronvacancies /surface oxygen leads to the best trapped oxvgen vacancies photoactivity

### Introduction

Expanding the visible light absorption and increasing the separation efficiency of the photo-excited charge carriers are the two key points to improve the photocatalytic yield of TiO<sub>2</sub>. Many approaches have been adopted to resolve these two problems <sup>1-8</sup>, among which self-doping (Ti<sup>3+</sup> ion and oxygen vacancy) is special efficient to promote the photo-response of TiO<sub>2</sub>. Alberto et al reported that a continuous band formed by bulk oxygen vacancies narrowed the band-gap of TiO<sub>2</sub> to improve light absorption <sup>9</sup>. Li et al prepared Ti<sup>3+</sup> self-doped TiO<sub>2</sub> via in situ surface hydrogenation synthesis method that exhibited visible light photocatalytic performance <sup>10</sup>. A great deal of theoretical calculation <sup>11-13</sup> and experimental researches  $^{\rm 14\text{-}16}$  on the defects of  $\rm TiO_2$  have identified that the surface and bulk defects have different and important effects on photocatalytic mechanism and the functions of bulk and surface defects are so complicated. Therefore, to study their synergistic effect on the photocatalytic performance has been a hotspot. Kong et al. reported that decreasing the relative bulk/surface defect concentration ratio of TiO2 could significantly improve the charges separation efficiency and enhance the photocatalytic performance remarkably <sup>17</sup>. But, the type of defect was not identified in this work. Wang et al.

E-mail: qiuyeli@henu.edu.cn, yangjianjun@henu.edu.cn.

declared that the photogenerated charges separation efficiency could be improved obviously by tuning the ratio of bulk Ti<sup>3+</sup>/surface defects <sup>18</sup>. Although some researches have studied the different functions of bulk/surface defects on photoactivity, yet the type of the bulk or surface defects is still ambiguous and their synergistic effect need be further investigated in detail.

Among these defects of TiO<sub>2</sub>, oxygen vacancy, mainly including the surface and bulk oxygen vacancy, is not only important but also easy to be regulated. Surface oxygen vacancy can improve the light absorbance of TiO<sub>2</sub>, and trap electrons to boost the separation of photogenerated charges. Our group has been committed to studying the physical and chemical property of nanotube titanic acid (NTA) systematically  $^{19-22}$  and found that a novel anatase TiO<sub>2</sub> with abundant of bulk oxygen vacancies can be obtained via the dehydration of NTA. Through experiments and theoretical calculation, it was verified that the bulk oxygen vacancies belonged to bulk single-electron-trapped oxygen vacancies (SETOVs) <sup>23</sup>. The SETOVs can form a sub-band under the conduction band of TiO<sub>2</sub>, leading to a visible light absorption, whereas they are also the recombination centres of the photogenerated charges, which is the disadvantage of enhancing the photocatalytic performance. Recently, the surface oxygen vacancy is testified to improve the separation efficiency of the photogenerated charges <sup>24, 25</sup>. Our previous works have also proved that the coexistence of bulk SETOVs and surface oxygen vacancies can remedy the deficiency of bulk SETOVs to improve the photoactivity of  ${\rm TiO_2}^{-26,\ 27}.$ However, excessive surface oxygen vacancies also become the recombination centres of photogenerated charges, resulting in the decrease of photoactivity <sup>25, 28</sup>. Hence, adjusting the ratio

<sup>&</sup>lt;sup>a.</sup> National & Local Joint Engineering Research Centre for Applied Technology of Hybrid Nanomaterials, Collaborative Innovation Centre of Nano Functional Materials and Applications of Henan Province, Henan University, Kaifeng, 475004, China.

<sup>&</sup>lt;sup>b.</sup> Key Laboratory of Nuclear Solid State Physics Hubei Province, School of Physics and Technology, Wuhan University, Wuhan, 430072, China.

of bulk SETOVs and surface oxygen vacancies has the key effect on improving photocatalytic performance of  ${\rm TiO}_2.$ 

Herein, a series of TiO<sub>2</sub> with the different concentration ratios of bulk SETOVs /surface oxygen vacancies were obtained through adjusting the amount of the reductant and the reaction time using the novel TiO<sub>2</sub> as the precursor, and the effect of the ratio of the two oxygen vacancies on the photoactivity was studied accompanied with the positron annihilation experiment in detail.

### Experimental

Published on 02 May 2018. Downloaded by National University of Singapore on 06/05/2018 21:11:35

### Materials preparation

Anatase TiO<sub>2</sub> with bulk SETOVs was prepared via calcining NTA at 400 °C for 2 h. NTA powder was obtained with commercial P25 as precursor via hydrothermal process according to our previous reports <sup>29, 30</sup>. Typically, 3 g P25 were mixed uniformly with 300 mL NaOH (10 M) aqueous solution, and then the white mixture was poured into 100 mL autoclave and heated at 150 °C for 24 h. The resulting white precipitate was washed with distilled water until ca. neutral pH and then immersed in 500 mL 0.1 M HCl solution for 7 h for ion-exchange Na<sup>+</sup>/H<sup>+</sup>, followed by the removal of Cl<sup>-</sup> by washing with distilled water until ca. neutral pH. The as-achieved precipitate was dried at room temperature under vacuum, leading to the desired product was NTA.

The prepared TiO<sub>2</sub> and NaBH<sub>4</sub> were mixed in different proportions and grinded thoroughly for 30 min. The mixed powder was calcined at 300 °C under Ar atmosphere for different time, and then washed with distilled water to remove the residual NaBH<sub>4</sub> completely. Finally, the resultant products were dried at room temperature under vacuum, which were denoted as TiO<sub>2</sub>-Rx(y) (R represented reduction, x was calcination time, y was the mixed mass proportion of TiO<sub>2</sub> and NaBH<sub>4</sub>).

### Characterizations

The X-ray diffraction (XRD) test was carried out on German Bruker D8 - ADVANCE diffractometer with Cu Kα radiation, the scanning range was 5 - 90° with 4 °/min of scanning speed. A high resolution transmission electron microscope (HRTEM, JEM-2100) was taken to observe the morphology of the prepared samples at 200 kV. The Brunauer-Emmett-Teller (BET) was used to measure the specific surface area of the samples by nitrogen adsorption-desorption isotherms at 77 K. The ultraviolet-visible diffuse reflectance spectra (DRS) of the photocatalysts were recorded in 200 - 800 nm region with an UV - 2600 ultraviolet-visible spectrophotometer against BaSO<sub>4</sub>. The photoluminescence (PL) spectra were measured on a fluorescence spectrometer (JY HORIBA FluoroLog - 3) equipped with an excitation wavelength of 300 nm. X-ray photoelectron spectroscopy (XPS, AXISULTRA) was employed to identify the chemical states of the surface compositions in a Kratos-Axis-Ultra system equipped with monochromatic Al Ka X-rays (1486.6 eV). The electron spin resonance (ESR) spectra of the samples were recorded on a Bruker E500 spectrometer in air at room temperature. The photocurrent-time curve was obtained by a three-electrode photoelectrochemical cell and workstation (CHI600E China) with a 300 W xenon lamp with 100 mL 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution as the electrolyte.

Positron annihilation lifetime spectra (PALS) were employed under a ORTEC-583 fast - fast coincident system using the coincidence spectrometer at room temperature, which had a 270 ps prompt time resolution (FWHM) of the  $\gamma$ -ray from a 60Co source under the experimental conditions. The powder samples were pressed into a disk (10.0 mm \* 1.0 mm). A positron source (30 µci 22 Na) was sandwiched between two same sample disks. The positron lifetime spectrum with 106 counts was divided to several lifetime components through the PATFIT program.

### Evaluation of photocatalytic hydrogen production

The photocatalytic hydrogen production evaluation was conducted in a top-irradiation closed online system (CEL-SPH2N, China Education Au-light Company Limited) under UV-Vis or  $\lambda > 420$  nm visible light irradiation. The incident light source was 300 W Xe lamp (CEL-HXF300, Beijing) and the light intensity was 200 mW/cm<sup>2</sup>. Typically, 50 mg sample was dispersed into 100 mL of 20 % methanol/water mixed solution under magnetic stirring. A calculated amount of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O ethanol solution was added into the reaction solution to load 1 wt.% Pt as co-catalyst via a photo-deposition method. After the action system was vacuumed for 30 min, the reaction solution was irradiated under constantly stirring for five hours. During reaction process, 1mL gas product was sampled and analysed every 30 min by the online GC-7920 gas chromatograph (CEAULIGHT, China) with a thermal conductivity detector, and the high-purity Ar was used as carrier gas.

### **Results and discussion**

Phase structure, morphology and BET analysis of catalysts



The X-ray diffraction (XRD) test is performed to obtain the phase structure of the prepared samples, and the results are shown in Fig. 1. All samples present the diffraction peaks at  $2\theta$  values of 25.3, 37.8, 48.1, 54.0, and 55.0, which can be

#### Journal Name

attributed to the (101), (004), (200), (105), and (211) crystal facets of anatase  $TiO_2$  (PDF card 21-1272, JCPDS). That demonstrates that NTA has completely transformed to anatase TiO<sub>2</sub> via calcination. Compared with TiO<sub>2</sub>, the peak intensity of the reduced samples apparently weaken, which proves that their crystallinity lowers and the defect sites increase after reduction <sup>31</sup>. In addition, it is not difficult to find that the peak intensity of TiO<sub>2</sub>-R10(8:1) is similar to that of TiO<sub>2</sub> because the reduction degree of TiO2-R10(8:1) is too low to influence its surface structure obviously. Moreover, the peak intensity of the reduced samples gradually weaken with the augment of the reduction degree. When TiO<sub>2</sub> is reduced via calcination with NaBH<sub>4</sub>, the amount of NaBH<sub>4</sub> and calcination time directly influence the reduction degree of TiO<sub>2</sub>. The results show that the surface of the reduced samples don't remain stoichiometric structure and oxygen vacancies on the surface lead to form the disordered structure and the thickness of the disordered layer is affected by the reduction degree <sup>31, 32</sup>.



Figure 2 HRTEM images of TiO\_2-R50(2:1) (a) and TiO\_2-R10(4:1) (b), the inset figure was TEM image of TiO\_2-R10(4:1).

Next, TEM is conducted to visually verify the surface structure of the reduced samples. It can be seen from the insert figure of Fig. 2b that the morphologies of TiO<sub>2</sub>-R10(4:1) are coexistence of nanoparticles and nanotubes, which indicates that the part of nanotubes broke after NTA were calcined. Furthermore, The specific surface areas of TiO<sub>2</sub>, TiO<sub>2</sub>-R10(8:1), TiO<sub>2</sub>-R10(4:1), TiO<sub>2</sub>-R10(2:1) and TiO<sub>2</sub>-R50(2:1) are 246.5, 235.3, 227.3, 219.5 and 213.2 m<sup>2</sup>/g, respectively. The fact that the samples have the similar specific surface areas indicates that morphologies of the samples are not apparently influenced after the NaBH<sub>4</sub> reduction. The HRTEM images of TiO<sub>2</sub>-R50(2:1) and TiO<sub>2</sub>-R10(4:1) clearly show that the distance of lattice fringe is about 0.35 nm, which is corresponding to (101) facet of anatase TiO<sub>2</sub>  $^{27}$ . Fig. 2a shows that a ca. 1 nm disordered layer covers on the surface of TiO<sub>2</sub>-R50(2:1), and Fig. 2b shows that the surface of TiO<sub>2</sub>-R10(4:1) presents a discontinuous disordered layer, which is ca. 0.4 nm. A great deal of studies have demonstrated that abundant of surface oxygen vacancies lead to appear the disordered form of surface structure <sup>33, 34</sup>. A large amount of oxygen vacancies make the surface structure of  $TiO_2$  nonstoichiometric, so that DOI: 10.1039/C8CY00644J ARTICLE

the ordered lattice is destroyed, resulting in the appearance of the disordered layer. The thickness of the disordered layer is related to the concentration of surface oxygen vacancies, therefore the surface of  $TiO_2$ -R50(2:1) is coated by a thick disordered layer because of the deep reduction degree, meanwhile the surface of  $TiO_2$ -R10(4:1) only appear a discontinuous and thin disordered layer due to the slight reduction degree. The HRTEM results coincide with the XRD analysis, which show that the surface oxygen vacancies have formed on the surface of the prepared samples by the NaBH<sub>4</sub> reduction and the concentrations of surface oxygen vacancies can vary with the reduction degree.

### **XPS and ESR analysis**

XPS and ESR spectra are also employed to further verify the existence of Ti<sup>3+</sup> and oxygen vacancy. XPS can provide the useful information for the chemical states of Ti atoms and the bonding environment of O atoms. Fig. 3a shows that the Ti 2p peak of TiO<sub>2</sub>-R50(2:1) is unsymmetrical, which can be fitted into four peaks at 458.3, 458.7, 463.8 and 464.5 eV. The peaks at 458.3 eV and 463.8 eV are assigned to  ${\rm Ti}^{3+}\ 2p_{3/2}$  and  ${\rm Ti}^{3+}$ 2p<sub>1/2</sub>, and the peaks at 458.7 eV and 464.5 eV are assigned to  $Ti^{4+} 2p_{3/2}$  and  $Ti^{4+} 2p_{1/2}$ , respectively <sup>18, 35, 36</sup>. This indicates that some Ti<sup>3+</sup> ions have been formed on the surface of TiO<sub>2</sub>-R50(2:1). NaBH<sub>4</sub> decomposes and produces active hydrogen, which has the stronger reduction capability than H<sub>2</sub>. Active hydrogen combines rapidly with O atom on the surface of TiO<sub>2</sub> to form OH-species and further become H<sub>2</sub>O molecule, resulting in the generation of oxygen vacancy, and then electron transfers from oxygen vacancy to Ti<sup>4+</sup> to form Ti<sup>3+</sup> ion <sup>37</sup>. As shown in Fig. 3a, the Ti 2p XPS of TiO<sub>2</sub>-R10(4:1) does not have the peak of  ${\rm Ti}^{3+}$  and only has two individual peak at 458.7 eV and 464.5 eV, which are assigned to the binding energies of  ${\rm Ti}^{4+}\ 2p_{3/2}$  and  ${\rm Ti}^{4+}\ 2p_{1/2},$  respectively. Meanwhile, the Ti 2ppeaks of TiO<sub>2</sub> are located at 459.0 eV and 464.7 eV , which are in good accordance with the typical characteristics of the Ti-O–Ti bonds in TiO<sub>2</sub>  $^{27}$ . Compared with TiO<sub>2</sub>, the Ti 2p peaks of TiO<sub>2</sub>-R10(4:1) tend to shift 0.3 eV towards lower binding energy due to the change of chemical environment for Ti<sup>4+</sup>. It is possibly because the amount of Ti<sup>3+</sup> ions on the surface of  $TiO_2$ -R10(4:1) is too few to be detected by XPS, but the existence of Ti<sup>3+</sup> can increase electron density to weaken the bind energy  $^{38, 39}$ . Compared with the O1s XPS spectra of TiO<sub>2</sub>, TiO<sub>2</sub>-R10(4:1) and TiO<sub>2</sub>-R50(2:1) (Fig. 3b), O1s binding energy of the two reduced samples shift to lower binding energy direction in sequence than TiO<sub>2</sub>. The O1s peak of TiO<sub>2</sub>-R10(4:1) and TiO<sub>2</sub>-R50(2:1) shifts towards lower binding energy of 0.2 and 0.5 eV than TiO<sub>2</sub>. The formation of Ti<sup>3+</sup> ions would indeed impact the bond energy of Ti-O band. The reduction degree of TiO<sub>2</sub>-R50(2:1) is larger than that of TiO<sub>2</sub>-R10(4:1), so the concentration of its oxygen vacancies is higher, which influences the chemical environment of O1s more obviously.

DOI: 10.1039/C8CY00644J Journal Name



Figure 3 XPS spectra of Ti 2p peaks (a) and O1s peaks (b) for TiO<sub>2</sub>-R50(2:1), TiO<sub>2</sub>-R10(4:1) and TiO<sub>2</sub>.

ARTICLE

Published on 02 May 2018. Downloaded by National University of Singapore on 06/05/2018 21:11:35.



Fig. 4a shows that  $TiO_2$  has only a ESR signal peak at g=2.002, and TiO<sub>2</sub>-R50(2:1) has two ESR signal peaks locating at g=1.982 and g=2.002 respectively. The ESR peak intensity at g=2.002 of the two samples are strong, which can be attributed to bulk single-electron-trapped oxygen vacancy (SETOV) <sup>23, 40</sup>. It is confirmed in our previous work that NTA could transform to a kind of novel anatase  $TiO_2$  with abundant SETOVs via dehydration. According to the literatures, the ESR signal peak of surface  $Ti^{3+}$  is located at g=1.980, and the ESR signal peak of lattice  $Ti^{3+}$  is located at g=1.990  $^{41-43}$ . So the signal peak at g=1.982 should be attributed to the surface paramagnetic  $Ti^{3+}$ . The surface oxygen vacancy possessing two electrons or no electron can't present ESR signal peak directly, however Ti4+ can trap the electron of oxygen vacancy to be reduced to Ti<sup>3+</sup>, so the existence of Ti<sup>3+</sup> signal can demonstrate the formation of surface oxygen vacancies indirectly by ESR technology. This results illustrate that TiO<sub>2</sub>-R50(2:1) has not only bulk SETOVs but also surface oxygen vacancies, which also verify surface oxygen vacancies can be formed successfully on the surface of TiO<sub>2</sub> by means of NaBH<sub>4</sub> reduction. Notably, the ESR signal peaks at g=2.002 of  $TiO_2$ -R50(2:1) is higher than that of  $TiO_2$ , indicating that the concentration of bulk SETOVs of TiO2-R50(2:1) is higher than TiO<sub>2</sub>. Based on the literatures  $^{25, 44}$ active hydrogen released from the decomposition of NaBH<sub>4</sub> is

easy to diffuse from the surface to the subsurface because the adsorption energy of active hydrogen on the subsurface  $O_{2c}$  of TiO<sub>2</sub> is smaller than that on surface, so the concentration of bulk oxygen vacancies is also influenced in the reduction process. As shown in Fig. 4b, the samples of TiO<sub>2</sub>-R10(4:1) and TiO<sub>2</sub>-R10(8:1) only exhibit the signal peaks at g=2.002 because the concentration of the surface oxygen vacancies is too low to be detected, which agrees with the analysis of XPS. In addition, the concentration of bulk SETOVs of TiO<sub>2</sub>, TiO<sub>2</sub>-R10(8:1) and TiO<sub>2</sub>-R10(4:1) gradually increase with the increase of the reduction degree. The relationship between the concentration of SETOVs and the intensity of ESR signal peak is proportional <sup>45</sup>. This proves also that the concentration of bulk oxygen vacancies can be weakly influenced by active hydrogen released from NaBH<sub>4</sub> decomposition.

The results of TEM, XPS and ESR demonstrate that the surface oxygen vacancies are indeed formed via NaBH<sub>4</sub> reduction, and then the concentration of bulk and surface oxygen vacancies of the samples gradually increase with the increase of the reduction degree. That is to say, the concentration of bulk and surface oxygen vacancies can be adjusted through tuning the amount of NaBH<sub>4</sub> and the reaction time.

Journal Name

#### PL and Optical absorption properties



Fig. 5 shows the PL spectra of the prepared samples with the excitation light wavelength of 300 nm. Normally, three main factors of intrinsic absorption, oxygen vacancy and surface state would cause the PL response of TiO<sub>2</sub> nanoparticles <sup>46, 47</sup>, so PL technique is often used to study the defect site of TiO<sub>2</sub> nanoparticles. As shown in Fig.5, all the samples exhibit a strong PL signal peak at 394 nm, which are attributed to the intrinsic property of TiO<sub>2</sub>. TiO<sub>2</sub>-R50(2:1) has the strongest PL signal peak and the PL peak intensity gradually weaken with the different reduction degree of TiO<sub>2</sub>. The stronger PL signal means that the more defects existed <sup>48, 49</sup>. Hence, PL results also prove that TiO<sub>2</sub> with different concentration of bulk and surface oxygen defects can be obtained via tuning the amount of NaBH<sub>4</sub> and the reaction time.



The UV-Vis diffuse reflection spectroscopy is employed to study the effect of bulk and surface oxygen vacancy on the optical absorption of the samples. Fig. 6 shows that all the samples have the strong absorption intensity in the UV region. TiO<sub>2</sub> presents a weak absorption in the visible light region because that abundant single electron oxygen vacancies (SETOVs) in the bulk can form a sub-band under conduction band of TiO<sub>2</sub>, which extends its light absorption range to the visible light region <sup>23</sup>. It is also found that the reduced samples have stronger light absorption than TiO<sub>2</sub> in visible light region, and that the absorption intensity gradually heighten with the

increase of the reduction degree. The higher the reduction degree, the heavier the concentration of surface and bulk oxygen vacancies. Both surface and bulk oxygen vacancies could improve visible light absorption  $^{50}$ . Notably, TiO<sub>2</sub>-R50(2:1) and TiO<sub>2</sub>-R10(2:1) present a broader absorption than those of TiO<sub>2</sub>-R10(4:1) and TiO<sub>2</sub>-R10(8:1), especially in the visible light region of 500-800 nm, which are caused by the high concentration of surface oxygen vacancies, coinciding with the above analysis of TEM, XPS and PL <sup>51, 52</sup>. The color of TiO<sub>2</sub> is white and the color of the reduced samples gradually deepen with the increase of the reduction degree, and the color of  $TiO_2$ -R50(2:1) turns to grey in the end. Herein, the results that the visible light absorption of the reduced samples are successively enhanced and the color of the samples can gradually deepen illustrate that lots of surface oxygen vacancies can be formed on the surface of the reduced samples via NaBH<sub>4</sub> reduction and the concentration of bulk and surface oxygen vacancies is related to the amount of NaBH<sub>4</sub> and reaction time.

# Photocatalytic hydrogen production of the samples and photocurrent analysis

The photocatalytic hydrogen production rates of the samples are shown in Fig. 7. As seen from Fig.7a, all the samples have high photocatalytic hydrogen production rates under UV-Vis light irradiation. The photocatalytic hydrogen production rates of all the reduced samples are higher than that of TiO<sub>2</sub>, which is 14.9 mmol·g<sup>-1</sup>·h<sup>-1</sup>. Both the bulk SETOVs and surface oxygen vacancies can contribute to the extension of the light absorption region, leading to the improvement of photoactivity. The above UV-Vis spectra also illustrated that the absorbance of the reduced samples improved gradually as the increase of the reduction degree. Interestingly, the photocatalytic hydrogen production rates of the reduced samples increase firstly and then decrease with the increase of the reduction degree, and TiO<sub>2</sub>-R10(4:1) presents the highest photocatalytic hydrogen production rate. From the above analysis, we know that the BET surface areas of these samples are similar, and that the light absorption intensity of TiO<sub>2</sub>-R10(4:1) isn't strongest. So the photoelectric separation efficiency should be the main reason for the large difference of their photocativity. Surface oxygen vacancies can trap electron and rapidly transfer towards cocatalyst to accelerate the separation of photo-generate charges <sup>17, 53</sup>. However, the results further identify that the surface oxygen vacancy is not the more the better, and the optimum ratio of bulk SETOVs and surface oxygen vacancies can lead to the best photoactivity. Fig. 7b shows the photocatalytic hydrogen production rates of all samples under visible light irradiation ( $\lambda$ > 420 nm). Surface oxygen vacancies can greatly enhance the visible light absorption, so the photoactivity of the reduced samples are much higher than TiO<sub>2</sub>. TiO<sub>2</sub>-R10(4:1) still exhibit the best photoactivity, and that its photocatalytic hydrogen production rate is about 3 times higher than that of TiO<sub>2</sub> under visible light irradiation. That further verifies that the suitable concentration ratio of bulk SETOVs and surface oxygen

## Journal Name

ARTICLE





Figure 7 Photocatalytic activity of H<sub>2</sub> production rate on the samples (a: under UV-Vis light irradiation, b: under visible light irradiation).



Figure 8 Stability test of  $TiO_2$ -R10(4:1) for photocatalytic H<sub>2</sub> production under UV-Vis irradiation.



Figure 9 Photocurrent-time curves of the samples under UV-Vis light irradiation.

vacancies is more beneficial to the improvement of photoactivity.

The stability of photocatalyst is important for photocatalytic reaction, so the stability of  $TiO_2$ -R10(4:1) is evaluated by long-time cycle experiments. As seen from Fig. 8, the photocatalytic hydrogen production rate in the first-cycle test is slightly higher than the later, and the photoactivity of  $TiO_2$ -R10(4:1) tends to be stable after the first cycle.

The photocurrent response of the samples was also conducted under UV-Vis light irradiation, and the results are illustrated in Fig. 9. The photocurrent intensity of all the reduced samples are higher than that of  $TiO_2$ , and that the photocurrent intensity of  $TiO_2$ -R10(4:1) is the highest one, which is consistent with the above the results of their photoactivity. This confirms that surface oxygen vacancies can

extend light absorption and improve the separation of photogenerated charges, but excessive surface oxygen vacancies also become the recombination centres of photogenerated electrons and holes. Therefore, the optimum ratio of bulk and surface oxygen vacancies can result in the best efficient separation of photogenerated charges, which is the essential condition for obtaining the high photocatalytic performance.

# Effect of bulk/surface oxygen vacancies ratio on photocatalytic activity

Positron annihilation lifetime spectra (PALS) is a powerful and sensitive technique to study qualitatively the oxygen vacancies

## Journal Name

# ARTICLE

Table 1 Positron Lifetime, Relative Intensities and Production H<sub>2</sub> Rate of the prepared samples

Samples	$\tau_1[ps]$	$\tau_2[ps]$	<i>I</i> <sub>1</sub> [%]	<i>I</i> <sub>2</sub> [%]	I1/I2	rate/H₂ (mmol/g/h)
TiO <sub>2</sub> -R10(8:1)	189	322	46.33	53.67	0.86	16.4
TiO <sub>2</sub> -R10(4:1)	206	336	56.58	43.42	1.30	22.5
TiO <sub>2</sub> -R10(2:1)	208	341	60.03	39.97	1.50	20.6
TiO <sub>2</sub> -R50(2:1)	211	345	61.74	38.26	1.61	16.5

of TiO<sub>2</sub> in the very low concentration range. When the positrons are injected into the TiO<sub>2</sub>, they preferentially diffuse into the low electron density regions (e.g. microvoids, mono vacancies and vacancy clusters ), then are thermalized and annihilated by electrons, finally leading to emitting the y rays, which will provide the lifetime of positrons and the information of various defects  $^{54}$ . In the work, the anatase TiO<sub>2</sub> prepared via the dehydration of NTA possess abundant bulk SETOVs, the surface oxygen vacancies are formed on the surface of the anatase TiO<sub>2</sub> through the NaBH<sub>4</sub> reduction, meanwhile the concentration of the bulk SETOVs is also influenced. The concentrations of bulk and surface oxygen vacancies could be adjusted through tuning the amount of NaBH<sub>4</sub> and the reaction time. PALS technique is used to characterize the bulk and surface oxygen vacancies of the TiO<sub>2</sub> samples and study the correlation between the concentration ratio of bulk/surface oxygen vacancies and the photocatalytic performance. As shown from table 1, the two lifetime components  $\tau_1$  and  $\tau_2$  with the relative intensities  $I_1$  and  $I_2$  are obtained for the reduced samples with the different reduction degree  $^{55}$ . The shorter lifetime component ( $\tau_1$ ) should be due to the free annihilation of positrons in the defect-free crystal. In the disordered system, the small monovacancies or oxygen vacancies can lower the electron density and decrease the annihilation rate <sup>56</sup>. The bulk SETOV in the samples can trap the positron because it possesses one electron, which has been reported in our previous work  $^{22, 23}$ . For the anatase TiO<sub>2</sub> with fine crystal, the positron diffusion length is about 45nm and the  $\tau_1$  is approximately 178 ps <sup>57</sup>. Based on the literatures <sup>17, 51</sup> the shorter lifetime  $(\tau_1)$  component attributes to the bulk annihilation rate, the bulk SETOVs annihilation rate and the positron diffusion from bulk to surface, as well as  $\tau_1$  is the reciprocal of the sum of them. The morphology and phase structure of the samples are similar, so the different concentrations of bulk SETOVs directly influence the value of  $\tau_1$ . The  $\tau_1$  of the reduced samples are not only all higher than that of the anatase TiO<sub>2</sub> with fine crystal (~178 ps) but also increase gradually as the increase of the reduction degree. These results indicate that bulk SETOVs exist in the samples

and the concentration of SETOVs increases as the increase of the reduction degree. The longer lifetime component ( $\tau_2$ ) generally arises from the larger size defects e.g.  $Ti^{3+}$  or oxygen vacancy clusters, because the average electron density of the larger size defects is lower than that of the small size defect, so the positron lifetime is longer <sup>57</sup>. The above characterizations have proved that the surface oxygen vacancies can be formed on the surface of the reduced samples. Surface oxygen vacancies can gather to form dimers, trimers, or clusters. Therefore, the lifetime component ( $\tau_2$ ) quantificationally reveals the surface oxygen vacancies. Due to the increasing concentration of surface oxygen vacancies, the  $\tau_2$  of the reduced samples gradually increase with the enhancement of the reduction degree.

Except for the positron lifetime, its intensity (1) embodies the relative concentration of the bulk or surface oxygen vacancies. The ratios of  $I_1$  to  $I_2$  ( $I_1/I_2$ ) for TiO<sub>2</sub>-R10(8:1), TiO<sub>2</sub>-R10(4:1), TiO<sub>2</sub>-R10(2:1) and TiO2-R50(2:1) are 0.86, 1.30, 1.50 and 1.61, respectively. Apparently, the  $I_1$  of these samples increases and their  $I_2$  decreases with the increase of reduction degree, indicating the increased concentration of bulk SETOVs is more than that of surface oxygen vacancies. The result implies that the influence of the active hydrogen on the bulk SETOVs is larger than that on the surface oxygen vacancies. The reason should be deduce from two aspects. Firstly, active hydrogen released from NaBH<sub>4</sub> decomposition is easy to diffuse from the surface to the subsurface. Secondly, the morphologies of the samples are all coexistence of nanoparticles and nanotubes, the size of nanoparticle is about 20 nm and the wall thickness of titanic acid nanotube is only about 2 nm. So, the effect of active hydrogen atoms on bulk SETOVs is greater than surface oxygen vacancies due to the small size of samples, which is consistent with the above characterization.

The effect of the concentration ratio of bulk SETOVs / surface oxygen vacancies  $(I_1/I_2)$  on photocatalytic hydrogen productive rate is shown in Table 1. The photocatalytic hydrogen production rates of the four samples increase firstly

DOI: 10.1039/C8CY00644J

Journal Name

### ARTICLE

and then decrease with the increase of  $I_1/I_2$ . TiO<sub>2</sub>-R10(4:1) presents the highest photocatalytic hydrogen productive rate. The bulk SETOVs contribute to extending the light absorption range, but they are also detrimental to the photocatalytic activity of TiO<sub>2</sub> as the recombination centre of the photogenerated charges. Surface oxygen vacancies can facilitate the separation of photogenerated charges as the trap sites of photogenerated electrons. However, the results indicate that the excessive bulk SETOVs and surface oxygen vacancies are unfavorable for the improvement of the photocatalytic hydrogen production, the concentration ratio of bulk SETOVs /surface oxygen vacancies plays the direct and important effect on photocatalytic hydrogen production performance of TiO<sub>2</sub>, and the suitable ratio of bulk SETOVs / surface oxygen vacancies can lead to the best photoactivity.

### Conclusions

Published on 02 May 2018. Downloaded by National University of Singapore on 06/05/2018 21:11:35

In the work, TiO<sub>2</sub> with the different concentration ratios of bulk SETOVs /surface oxygen vacancies are prepared via adjusting the amount of NaBH<sub>4</sub> and the reaction time. It is confirmed by TEM, XPS and ESR that the active hydrogen produced by NaBH<sub>4</sub> decomposition can prompt the formation of surface oxygen vacancies and increase the concentration of bulk and surface oxygen vacancies. The existence of surface oxygen vacancies enhance the photocatalytic hydrogen productive efficiency of TiO<sub>2</sub>. Especially, the photocatalytic hydrogen production rate of TiO<sub>2</sub>-R10(4:1) is about 3 times higher than that of TiO<sub>2</sub> under visible light irradiation. TiO<sub>2</sub>-R10(4:1) has the best photocatalytic hydrogen production activity due to the suitable concentration ratio of bulk SETOVs /surface oxygen vacancies. Our conclusion is that the concentration ratio of bulk SETOVs /surface oxygen vacancies have the direct and important effect on photocatalytic performance of TiO<sub>2</sub>, and the appropriate ratio of bulk SETOVs /surface oxygen vacancies leads to the best photocatalytic hydrogen production rate. This work provides a deeply insight into the correlation of bulk/surface oxygen vacancies and photoactivity, and the strategy also contributes to improving the photoactivity of other photocatalysts with oxygen vacancies.

### **Conflicts of interest**

There are no conflicts to declare.

### Acknowledgements

This work was supported by the National Natural Science Foundation of China (21673066, 51702087 and 21703054), Program for Science & Technology Innovation Talents (15HASTIT043) and Innovative Research Team (16IRTSTHN015) from the University of Henan Province.

### Notes and references

- 1 T. T. Isimjan, M. Trifkovic, I. Abdullahi, S. Rohani and A. K. Ray, *Topics in Catalysis*, 2014, 58, 114-122.
- 2 L. K. Preethi, R. P. Antony, T. Mathews, L. Walczak and C. S. Gopinath, *Scientific reports*, 2017, 7, 14314.
- 3 R. Abe, K. Shinmei, N. Koumura, K. Hara and B. Ohtani, Journal of the American Chemical Society, 2013, 135, 16872-16884.
- 4 Q. Li and G. Lu, Journal of Molecular Catalysis A: Chemical, 2007, 266, 75-79.
- 5 J. Cai, J. Huang, M. Ge, J. locozzia, Z. Lin, K. Q. Zhang and Y. Lai, *Small*, 2017, 13.
- 6 M. V. Dozzi, G. L. Chiarello, M. Pedroni, S. Livraghi, E. Giamello and E. Selli, *Applied Catalysis B: Environmental*, 2017, 209, 417-428.
- 7 J. Cai, Y. Zhu, D. Liu, M. Meng, Z. Hu and Z. Jiang, ACS Catalysis, 2015, 5, 1708-1716.
- 8 Y. Sasaki, H. Nemoto, K. Saito and A. Kudo, *J Phys Chem C*, 2009, 113, 17536-17542.
- 9 A. Naldoni, M. Allieta, S. Santangelo, M. Marelli, F. Fabbri, S. Cappelli, C. L. Bianchi, R. Psaro and V. Dal Santo, *Journal of the American Chemical Society*, 2012, 134, 7600-7603.
- 10 J. Huo, Y. Hu, H. Jiang and C. Li, *Nanoscale*, 2014, 6, 9078-9084.
- 11 G. Mattioli, F. Filippone, P. Alippi and A. Amore Bonapasta, *Physical Review B*, 2008, 78, 241201(4).
- 12 H. X. Zhang, M. Zhao and Q. Jiang, *Applied Physics Letters*, 2013, 103, 023111.
- 13 H. Cheng and A. Selloni, *Physical Review B*, 2009, 79, 092101(4).
- 14 J. Lee, D. C. Sorescu and X. Deng, *Journal of the American Chemical Society*, 2011, 133, 10066-10069.
- 15 J. M. Coronado, A. J. Maira, J. C. Conesa, K. L. Yeung, V. Augugliaro and J. Soria, *Langmuir*, 2001, 17, 5368-5374.
- 16 U. Diebold, Surface Science Reports, 2003, 48, 53-229.
- 17 M. Kong, Y. Li, X. Chen, T. Tian, P. Fang, F. Zheng and X. Zhao, Journal of the American Chemical Society, 2011, 133, 16414-16417.
- 18 F. Wang, W. Ge, T. Shen, B. Ye, Z. Fu and Y. Lu, Applied Surface Science, 2017, 410, 513-518.
- 19 J. J. Yang, Z. S. Jin, X. D. Wang, W. Li, J. W. Zhang, S. L. Zhang, X. Y. Guo and Z. J. Zhang, *Dalton Trans.*, 2003, 3898-3901.
- 20 J. W. Zhang, X. Y. Guo, Z. S. Jin, S. L. Zhang, J. F. Zhou and Z. J. Zhang, *Chinese Chemical Letters*, 2003, 14, 419-422.
- 21 Q. Li, X. Wang, Z. Jin, D. Yang, S. Zhang, X. Guo, J. Yang and Z. Zhang, *Journal of Nanoparticle Research*, 2006, 9, 951-957.
- 22 L. Qian, Z. S. Jin, J. W. Zhang, Y. B. Huang, Z. J. Zhang and Z. L. Du, *Applied Physics A*, 2004, 80, 1801-1805.
- 23 H. Li, F. Ren, J. Liu, Q. Wang, Q. Li, J. Yang and Y. Wang, Applied Catalysis B: Environmental, 2015, 172, 37-45.
- 24 J. Cai, M. Wu, Y. Wang, H. Zhang, M. Meng, Y. Tian, X. Li, J. Zhang, L. Zheng and J. Gong, *Chem*, 2017, 2, 877-892.
- 25 H. Tan, Z. Zhao, M. Niu, C. Mao, D. Cao, D. Cheng, P. Feng and Z. Sun, *Nanoscale*, 2014, 6, 10216-10223.
- 26 L. Hou, M. Zhang, Z. Guan, Q. Li and J. Yang, *Applied Surface Science*, 2018, 428, 640-647.
- 27 J. Li, M. Zhang, Z. Guan, Q. Li, C. He and J. Yang, Applied Catalysis B: Environmental, 2017, 206, 300-307.
- 28 M. Liu, H. Li and W. Wang, *Catalysis Today*, 2016, 264, 236-242.
- 29 F. Ren, H. Li, Y. Wang and J. Yang, Applied Catalysis B: Environmental, 2015, 176, 160-172.
- 30 Y. Wang, M. Jing, M. Zhang and J. Yang, *Catalysis Communications*, 2012, 20, 46-50.
- 31 Y. Cao, Z. Xing, Y. Shen, Z. Li, X. Wu, X. Yan, J. Zou, S. Yang and W. Zhou, *Chemical Engineering Journal*, 2017, 325, 199-207.
- 32 H. Zhang, Z. Xing, Y. Zhang, Z. Li, X. Wu, C. Liu, Q. Zhu and W. Zhou, *RSC Advances*, 2015, 5, 107150-107157.

Journal Name

- 33 K. Zhang and J. H. Park, The journal of physical chemistry letters, 2017, 8, 199-207.
- 34 W. Zhou, W. Li, J. Q. Wang, Y. Qu, Y. Yang, Y. Xie, K. Zhang, L. Wang, H. Fu and D. Zhao, *Journal of the American Chemical Society*, 2014, 136, 9280-9283.
- 35 L. B. Xiong, J. L. Li, B. Yang and Y. Yu, Journal of Nanomaterials, 2012, 2012, 1-13.
- 36 X. Lu, G. Wang, T. Zhai, M. Yu, J. Gan, Y. Tong and Y. Li, *Nano letters*, 2012, 12, 1690-1696.
- 37 P. Raghunath, W. F. Huang and M. C. Lin, J Chem Phys, 2013, 138, 154705(9).
- 38 H. Chen, Z. Wei, K. Yan, Y. Bai and S. Yang, The journal of physical chemistry letters, 2014, 5, 2890-2896.
- 39 J. Wang, P. Yang and B. Huang, *Applied Surface Science*, 2015, 356, 391-398.
- 40 S. Zhang, W. Li, Z. Jin, J. Yang, J. Zhang, Z. Du and Z. Zhang, Journal of Solid State Chemistry, 2004, 177, 1365-1371.
- 41 Z. Lian, W. Wang, G. Li, F. Tian, K. S. Schanze and H. Li, ACS Appl Mater Interfaces, 2017, 9, 16959-16966.
- 42 Y. Ide, N. Inami, H. Hattori, K. Saito, M. Sohmiya, N. Tsunoji, K. Komaguchi, T. Sano, Y. Bando, D. Golberg and Y. Sugahara, *Angewandte Chemie*, 2016, 55, 3600-3605.
- 43 T. Rajh, A. E. Ostafin, O. I. Micic, D. M. Tiede and M. C. Thurnauer, *J. Phys. Chem.*, 1996, 100, 4538-4545.
- 44. U. Aschauer and A. Selloni, *Phys Chem Chem Phys*, 2012, 14, 16595-16602.
- 45 Q. Li, J. Zhang, Z. Jin, D. Yang, X. Wang, J. Yang and Z. Zhang, Electrochemistry Communications, 2006, 8, 741-746.
- 46 X. Li, Y. Hou, Q. Zhao and G. Chen, *Langmuir*, 2011, 27, 3113-3120.
- 47 J. Hong, J. Cao, J. Sun, H. Li, H. Chen and M. Wang, *Chemical Physics Letters*, 2003, 380, 366-371.
- 48 Y. Zhu, Q. Ling, Y. Liu, H. Wang and Y. Zhu, Applied Catalysis B: Environmental, 2016, 187, 204-211.
- 49 L. Q. Jing, B. F. Xin, F. L. Yuan, L. P. Xue, B. Q. Wang and H. G. Fu, *J Phys Chem B*, 2006, 110, 17860-17865.
- 50 X. Chen, L. Liu and F. Huang, *Chem Soc Rev*, 2015, 44, 1861-1885.
- 51 L. Li, K. Shi, R. Tu, Q. Qian, D. Li, Z. Yang and X. Lu, *Chinese Journal of Catalysis*, 2015, 36, 1943-1948.
- 52 J. Liu, S. Yu, W. Zhu and X. Yan, *Applied Catalysis A: General*, 2015, 500, 30-39.
- 53 F. Li, Q. Gu, Y. Niu, R. Wang, Y. Tong, S. Zhu, H. Zhang, Z. Zhang and X. Wang, *Applied Surface Science*, 2017, 391, 251-258.
- 54 C. He, T. Yoshiie, Q. Xu, K. Sato, S. Peneva and T. D. Troev, *Philosophical Magazine*, 2009, 89, 1183-1195.
- 55 Y. Zhou, W. Xu, J. Li, C. Yin, Y. Liu, B. Zhao, Z. Chen, C. He, W. Mao and K. Ito, *Journal of Applied Physics*, 2018, 123, 025706(8).
- 56 J. Yan, G. Wu, N. Guan, L. Li, Z. Li and X. Cao, *Phys Chem Chem Phys*, 2013, 15, 10978-10988.
- 57 X. Jiang, Y. Zhang, J. Jiang, Y. Rong, Y. Wang, Y. Wu and C. Pan, The Journal of Physical Chemistry C, 2012, 116, 22619-22624.

Page 10 of 10



Co-existence of bulk single-electrontrapped and surface oxygen vacancies do favor to improve the photocatalytic hydrogen evolution.