Rich surface hydroxyl design for nanostructured TiO$_2$ and its hole-trapping effect

Shi-Tian Xiaoa,1, Si-Ming Wua,b,1, Yu Dongb,1, Jia-Wen Liua, Li-Ying Wangd, Lu Wu*, Yue-Xing Zhange, Ge Tian a,c,*, Christoph Jania,f, Menny Shaloms, Yi-Tian Wanga, Yuan-Zhou Lia, Ruo-Kun Jiah, Detlef W. Bahnemanni,j, Xiao-Yu Yanga,c,k,⁎

1 State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, School of Materials Science & Engineering, Wuhan University of Technology, 122 Luoshi Road, Wuhan 430070, China
2 Southern Marine Science and Engineering Guangdong Laboratory (Zhuhai) & School of Chemical Engineering and Technology, Sun Yat-sen University (SYSU), Zhuhai 519000, China
3 School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA
4 State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, The Chinese Academy of Sciences, Wuhan 430071, China
5 Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, College of Chemistry and Chemical Engineering, Huazhong University, Wuhan 430062, China
6 Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität Düsseldorf, Düsseldorf, Germany
7 Department of Chemistry and Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva 8410501, Israel
8 School of Chemical Engineering Northeast Electric Power University, 169 Changchun Road, Jilin 132012, China
9 Department of Photocatalysis and Nanotechnology, Institut für Technische Chemie, Universität Hannover, Callinstrasse 3, D-30167 Hannover, Germany
10 Laboratory for Noncomposite Materials, Department of Photonics, Faculty of Physics, Saint-Petersburg State University, Ulansovskaja Str. 3, Peterhof, Saint-Petersburg 198504, Russia
11 Qingdao National Laboratory for Marine Science and Technology, Qingdao 266237, China

HIGHLIGHTS

- TiO$_2$ with rich surface hydroxyl species (Ti-OH) has been designed using ionic liquid.
- The directed charge transport mechanism of rich Ti-OH have been investigated.
- The rich Ti-OH greatly enhance performances in photocatalysis and energy storage.

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ABSTRACT

The surface hydroxyl groups in TiO$_2$ are crucial to many of its practical applications, but their controlled synthesis represents still a challenge. Herein, nanostructured TiO$_2$ with rich surface hydroxyl species groups and high crystallinity (TiO$_2$-OH) by high-temperature calcination have been developed by using the ionic liquid. Experimental measurements and theoretical calculations show a strong surface hydroxyl signal of two-dimensional $^1$H TQ-SQ MAS NMR, as well as clear changes of the charge density of TiO$_2$ with the rich surface hydroxyl species. Moreover, the rich surface hydroxyl species groups in TiO$_2$ not only significantly enhance its performances involving photogenerated current, photocatalysis and energy storage but also show a bright future on marine applications because of its high activity and stability in simulation seawater. The characteristics and mechanism have been proposed to clarify the generation of surface hydroxyl species of TiO$_2$ and the corresponding directed hole-trapping at an atomic-/nanoscale.
1. Introduction

Titanium dioxide (TiO2) is one of the most widely used semiconductor for photo-electronic application and enables the efficient generation of photocarriers that diffuse to the surface for the photo-chemical reactions [1–4]. A general generation mechanism of photocarriers for TiO2 uses photoexcited electrons from the valence band to the conduction band. Thus, fast transfer and efficient utilization of photocarriers are critical to the high-performance design of TiO2 semiconductors [5–7], The electronic performance can be improved, for example, by introducing impurities, engineering vacancies, composting nano-unites, or changing nano-architectures [8–12]. The key of the mechanism lies in the fact that the carriers would travel to the surface for the photo/electro reactions. The study on the TiO2 surface is therefore an important field, and great progress has been made on the surface chemistry and photocatalysis mechanism of TiO2 at the atomic-level [2,13,14]. Surface hydroxyl groups (Ti-OH) will not only dictate the surface wettability of TiO2, but also trap the holes and improve the conductivity, which is very important to photo-electro reactions [15–18]. The rich surface Ti-OH groups often occur in amorphous or low-cristalline structure, where their photocatalytic activities are not satisfied due to the easy recombination of carriers. High-temperature calcination is often used to increase the crystallization and enhance the performances of the TiO2 [19], but also leads to a high degree of condensation of Ti-OH to Ti-O-Ti and thus a low level of surface hydroxyl groups [20]. It seems therefore impossible to combine the advantageous features of a high degree of crystallization and rich surface hydroxyl groups. Anions such as $S^{2-}$, $N^{3-}$ and $F^{-}$ enable the strong bonding to Ti, and thus replace O in TiO2 for the Ti3+ doping [21–23]. The removal of anions often leaves the TiO2 surface with active oxygen vacancies, which is the active site for adsorption and dissociation of water, and provide a possibility of the formation of surface hydroxyl species of TiO2 [24,25]. In general, the doped anions are often not very stable during the high-temperature calcination (often below 400 °C) [26–29], ionic liquids containing F, as thermally stable salt, are chosen to impurity doping. The starting decomposition temperatures of imidazolium salts can be over 400 °C [8,30], which perfectly match the phase transformation temperature from amorphous to anatase TiO2. It has to be pointed out that the impurity states of photocatalytic semiconductors have been thoroughly studied in order to enhance the absorption of visible light, and to increase the conduction band minimum of TiO2 for the enhancement of their photo/electro activity. There are very rare reports on the nature of TiO2 caused by removal of the anions [31,32].

Amorphous TiO2 is chosen as starting material, because the anions dopants can easily interact with TiO2 during the recrystallization process. Herein, 1-butyl-3-methylimidazolium tetrafluoroborate (designed as [BMIm][BF4]) as F ion dopant is introduced in amorphous TiO2 synthesized by fast hydrolysis-condensation via a hydrothermal treatment process. Anatase TiO2 containing rich surface hydroxyl species (named as TiO2-OH) is then obtained during the removal of the doping BF4- anions and reaction between the oxygen vacancies and water molecules. Multiple techniques such as HRTEM, NMR and XPS, have been applied to investigate the formation of rich surface hydroxyl species of nanostructured TiO2 with significantly improved photo-electro performance.

Fig. 1. (a) SEM image of TiO2-OH, (b), (c) TEM images and (d) HRTEM image of TiO2-OH.
2. Results and discussion

The morphology and structure of TiO\(_2\)-OH was characterized by SEM and TEM (Fig. 1, Figure S1, SI). Fig. 1a and 1b show that TiO\(_2\)-OH consists of aggregates of uniform TiO\(_2\) nanocrystals with uniform sizes ranging from 30 to 40 nm. It is obviously observed in the magnified TEM image (Fig. 1c, Figure S1a) that the single TiO\(_2\) nanocrystals contain inner defect-like pores with a size of about 4 nm, possibly due to the templating effect of ionic liquids. The HRTEM image (Fig. 1d, Figure S1b) show the lattice spacing of the facets in TiO\(_2\) are 0.35 nm and 0.23 nm, referring to the (1 0 1) and (0 0 1) interplanar distance, respectively. An interconnecting amorphous/semi-crystalline interface are clearly seen to bind the TiO\(_2\) nanoparticles and shows a width of around 5 nm (Fig. 1d, blue areas). This crystalline/semi-crystalline/amorphous structure is coherent, and the interface region is always the platform for defect generation. Similar morphology (Figure S4), crystallinity (Figure S2) and pore size distribution (Figure S3) is observed in the TiO\(_2\) samples synthesized with recycled IL, which further indicates the reusability of the IL.

For comparison, the as-prepared amorphous TiO\(_2\) (named as Amorphous TiO\(_2\) or A-TiO\(_2\)), crystalline TiO\(_2\) which contains fluoride from an only hydrothermal-treatment in the presence of the ionic liquid (named as TiO\(_2\)-F) and normal crystalline TiO\(_2\) by hydrothermal treatment in the absence of IL and calcination (named as Normal TiO\(_2\) or N-TiO\(_2\)) are also characterized SEM images show that N-TiO\(_2\) is small nanoparticles with size of around 30–40 nm (Figure S5) and there is no obvious difference between the morphology of N-TiO\(_2\) and TiO\(_2\)-OH. The XRD patterns shown in Figure S2 present that an obvious phase transformation from amorphous phase to anatase phase after hydrothermal treatment and also increased crystallinity after further calcination. TiO\(_2\)-OH shows dual pore size distributions with around 4 nm and 19 nm (Fig. 1, Table S1).

To obtain information about the surface hydroxyl species of TiO\(_2\) groups, various techniques have been used including FT-IR (Figure S6) and \(^{1}H\) NMR (Fig. 2, Figure S7-S8). It is obviously to be seen that the intensity and integral area of the the peak of TiO\(_2\)-OH, which is assigned to hydroxyl group, are higher than the N-TiO\(_2\). Both of TiO\(_2\)-OH and N-TiO\(_2\) show the similar chemical shift at 5.4 ppm and 1.2 ppm due to the large influence on the \(^{1}H\) NMR chemical shift of surface hydroxyl species of TiO\(_2\) by the hydrogen bond network. 2D \(^{1}H\) TQ-SQ MAS NMR methods are therefore applied which can avoid the influence of the water signal [33]. Generally, the signal ranging from 6.5 to 8.9 ppm is assigned to surface hydroxyl species groups from broken Ti-O-Ti bonds in the bulk phase and from 1.2 to 3.5 ppm is assigned to the location of surface hydroxyl species groups at the surface [34,35]. As shown in Fig. 2a, the signal at (1.6, 1.6 + 1.6 + 1.6) demonstrates that in TiO\(_2\)-OH, three surface hydroxyl species of TiO\(_2\) with \(\delta H = 1.6\) ppm are spatially close [34], which indicates the existence of surface hydroxyl species groups. The signal at (6.8, 6.8 + 6.8 + 5.2) indicates that two surface hydroxyl species of TiO\(_2\) from Ti defect sites in the bulk with \(\delta H = 6.8\) ppm are spatially close with the relatively stable surface hydroxyl species groups at \(\delta H = 5.2\) ppm [36]. In N-TiO\(_2\), only disordered noise exists and no signal of surface hydroxyl species groups is observed (Fig. 2b), which means that the surface hydroxyl species of TiO\(_2\) is directly due to the presence of IL during the synthesis process. To further investigate the formation of surface hydroxyl species groups, \(^{19}F\) NMR spectroscopy of TiO\(_2\)-F and TiO\(_2\)-OH has been performed (Fig. 2c). The dominant resonances in the \(^{19}F\) spectrum, representing the BF\(_4\) anion (\(\delta = -150\) ppm) [37], Ti\(_2\)-F (\(\delta = -83\) ppm, bridging F) and Ti\(_3\)-F (\(\delta = 5\) ppm, 3-coordinated F) are clearly observed [38,39], suggesting successful doping. After calcination at 600 °C for 4 h, no obvious signal of F species is observed in NMR, indicating the removal of the F species. From the combination of the \(^{1}H\) and \(^{19}F\) NMR spectra, it could be
concluded that with the removal of bridging F and 3-coordinated F, the surface hydroxyl species of TiO$_2$ forms at Ti defect sites, while the removal of terminal F form the terminal surface hydroxyl species of TiO$_2$. This interesting correspondence of F-removal and OH-formation provides evidence for the high-temperature formation of surface hydroxyl species of TiO$_2$.

The experimental XPS data have been further used to study the differences of binding energy, the chemical environments and phase varieties of the surface’s properties of the samples (Fig. 3a, Figure S9, S10). The binding energy of Ti 2p$_{3/2}$ of TiO$_2$-F is 0.4 eV higher than that of TiO$_2$-OH and A-TiO$_2$ (Fig. 3a, Figure S10a), which is traced to its high F···Ti interaction energy. After calcination at 600 °C for 4 h, most of the coordinated F species are removed, which lowers the Ti 2p$_{3/2}$ binding energy in TiO$_2$-OH. The removal of F species is further proven by the F 1 s spectrum (Figure S10d). The peak of TiO$_2$-F at 684.8 eV assigned to physically adsorbed F species and Ti-F of TiO$_2$ and after calcination there is no obvious peak.[40,41]. The two peaks at 457.5 eV and 463.3 eV (Figure S9a) indicate the presence of Ti$_3^+$ in addition to the Ti$_4^+$ oxidation state [42], which may be attributed to oxygen vacancies. The peak at 531.5 eV in O 1 s XPS spectra (Figure S9, b) is assigned to the surface hydroxyl groups [43–45]. The evidence of oxygen vacancies and Ti$_3^+$ are provided in the EPR spectrum (Fig. 3b), in which the sharp peaks with $g_1 = 2.002$ is assigned to oxygen vacancies [46] and $g_2 = 1.933$ is assigned to Ti$_3^+$ in N-TiO$_2$ and TiO$_2$-OH [47], suggesting n-type semiconducting properties of calcined TiO$_2$x which are associated with oxygen vacancies and titanium interstitials. Fig. 3c shows the periodic on/off photocurrent response of TiO$_2$-OH, A-TiO$_2$, N-TiO$_2$, and TiO$_2$-F under UV–Vis light irradiation. After 600 s’ light irradiation for stability, the photocurrent density measured at a bias voltage of 0.5 V (vs. SCE) for TiO$_2$-OH (13.6 μA) is found to be almost 22.6 times that of A-TiO$_2$ (0.6 μA), 7.5 times that of TiO$_2$-F (1.8 μA) and 3.3 times that of N-TiO$_2$ (4.1 μA). In addition, the electro-chemical impedance spectroscopy (EIS) of TiO$_2$-OH and other samples is studied (Figure S11). The order of the arc radius of EIS Nyquist plots of TiO$_2$-OH is smaller than that of A-TiO$_2$, TiO$_2$-F and N-TiO$_2$ after UV–vis irradiation, which indicates the lowest charge transfer resistance of TiO$_2$-OH. We further calculate the charge density of the simulated structure of different TiO$_2$ to further investigate the influence of surface hydroxyl species groups. Fig. 3d displays the model of TiO$_2$ with Ti-OH groups from broken Ti-O-Ti bonds, Ti-OH groups at the surface and O defect. The neighboring atoms of surface hydroxyl species groups get more electrons, in comparison with TiO$_2$ with only O defect (Fig. 3e) and normal TiO$_2$ (Fig. 3f).

The hydroxy groups are able to trap the holes because of high electron density, and thus contributing to efficient carriers’ transmission from inside to surface and high conduction of TiO$_2$, which are very important to widely practical applications, such as photocatalysis and storage of lithium/sodium cations [48–50]. Therefore, the photocatalytic activity (Figure S12) and photocatalytic activity in liquid/gas degradation and storages of lithium/sodium ions (Fig. 4, Figure S13-S16) are tested for further investigation. The photocatalytic activity test in photodegradation of MB (Fig. 4a, Figure S13) shows that the TiO$_2$-OH exhibits the highest degradation rate constant (1.27 × 10$^{-1}$ min$^{-1}$) and photocatalytic activity, for example, 42.3 times that of A-TiO$_2$, 3.6 times that of TiO$_2$-F, 3.0 times that of N-TiO$_2$ and 1.7 times that of commercial TiO$_2$ nanoparticles (name as Nano-TiO$_2$). Similarly, TiO$_2$-OH also shows the highest photocatalytic activity in photodegradation
of acetone, with a rate constant of $1.31 \times 10^{-2}$ min$^{-1}$; almost 130 times of A-TiO$_2$, 3.5 times that of TiO$_2$-F, 3.0 times that of N-TiO$_2$ and 1.7 times that of Nano-TiO$_2$.

Fig. 4b displays the photocatalytic activity for the H$_2$ production in water and seawater of N-TiO$_2$, TiO$_2$-OH, TiO$_2$-F and A-TiO$_2$ under UV–vis light irradiation. In water, TiO$_2$-OH exhibits the highest photocatalytic activity with a rate constant of 1158 μmol/h, which is about 8.7 times that of A-TiO$_2$, 4.5 times that of N-TiO$_2$ and 8.1 times that of TiO$_2$-F. Very interestingly, in seawater, TiO$_2$-OH also exhibits the highest photocatalytic activity with a rate constant of 932 μmol/h, which is about 9.8 times that of A-TiO$_2$, 4.7 times that of N-TiO$_2$ and 8.6 times that of TiO$_2$-F. In comparison with the photocatalytic activity for H$_2$ production of other TiO$_2$-based materials from up-to-date literature (Table S2), our sample TiO$_2$-OH shows the significant performance in photocatalytic activity for H$_2$ production. The only possibility is the strong bonding between the Pt and TiO$_2$-OH, attributed to high water affinity of hydroxyl group [51]. Further investigation of the photocatalytic stability of TiO$_2$-OH shows 90% of photocatalytic activity (MB degradation) and more than 85% of photocatalytic activity (H$_2$ production under simulation seawater) is retained after five cycles of photocatalysis (Figure S14). Similarly, the photoanode of TiO$_2$-OH has also been proven its higher ability to prevent 304SS from corrosion effectively (Figure S15) according to photo-induced cathodic protection theory [52]. It is therefore noteworthy that the TiO$_2$-OH show a bright future on marine applications because of its high activity and stability in simulation seawater. Note that the big difference of photocatalytic activities of TiO$_2$-OH with oxygen vacancies and rich hydroxyl groups and N-TiO$_2$ with oxygen vacancies and poor hydroxyl groups indicates that the hydroxyl groups would be the main factor to influence their activities. Besides, TiO$_2$-OH also shows better performance on lithium and sodium storage than TiO$_2$-N and A-TiO$_2$ for example, 1.4-fold and 1.3-fold of N-TiO$_2$ in Li$^+$/Na$^+$ capacity (Fig. 4b,4c and Figure S16). The higher capacity may be attributed to the defect mesopores and nanoscale defects in TiO$_2$-OH, which decrease the diffusion distance of M$^+$ (Li$^+$ or Na$^+$) and promote M$^+$ (Li$^+$ or Na$^+$) insertion /desertion. (see all detailed description of energy storage in supporting information).

The proposed formation of TiO$_2$-OH is shown in Fig. 5A. The amorphous TiO$_2$ is firstly mixed with [BMIm][BF$_4$] (Fig. 5A, a). During the hydrothermal process, with the phase transformation from amorphous TiO$_2$ to crystalline TiO$_2$, the TiO$_2$-BF$_4$ [BMIm] oligomers are formed owing to the strong F···Ti interaction and the template effect of the ionic liquid. With the increasing hydrothermal time, the nanocrystals continue to grow, resulting in a larger particle size and nanofusion domains (Fig. 5A, b). The ionic liquid acts as a template to form mesostructured defects and the nanoparticles self-organize to form secondary mesoporosity (Fig. 5A, b). The surface hydroxyl would be obtained when the F···Ti breaks when the [Bmim][BF$_4$] and organic impurities are removed by high-temperature calcination, the nanosstructured anatase TiO$_2$ with rich surface hydroxyl can be finally obtained (Fig. 5A, c), the anatase TiO$_2$ with rich surface hydroxyl can be described as:

$$\text{TiO}_2 + x\text{H}_2\text{O} \rightarrow \text{TiO}_{2-x}\cdot2x\text{OH}$$

These hydroxyl groups may come from dehydration of organic impurities and the formation of TiO$_2$ could be the escape of the O species from the lattice under the unstable thermodynamic state. (See detailed description of the formation of hydroxyl groups and oxygen vacancies in Supporting Information).

Fig. 5B shows the proposed mechanism of photocatalysis and Li$^+$/Na$^+$ storage. The left of Fig. 5B shows the performance of TiO$_2$-OH on photodegradation and photogeneration of H$_2$. Upon UV–Vis light irradiation, the surface OH groups would trap the photogenerated holes. These holes would further convert H$_2$O and OH$^-$ to highly reactive OH, which enable to degrade dye molecules. For the photocatalytic
hydrogen generation process, the surface OH groups act as electron donors and it is benefit for the charge transfer to Pt which improves the photogeneration of hydrogen. The Li⁺/Na⁺ storage mechanism of TiO₂-OH is illustrated in the right area of Fig. 5B, the mesoporous structure can promote the insertion of ions and shorten the diffusion distance of the electrolyte. Moreover, the gathered electrons on the surface attributed to surface hydroxyl species groups can enhance the electrical conductivity and electron transfer, which consequently boost the insertion and desertion of Li⁺ and Na⁺.

3. Conclusion

In summary, a facile approach to design nanostructured TiO₂ with rich surface hydroxyl species groups and high crystallinity is presented.
The results show that TiO₂·OH has enhanced catalytic activity on photo-electro performances. Experimental research and theoretical calculations have been carried out to study the rich Ti-OH in TiO₂ and its specific features, such as: (i) directed and fast carries pathway caused by holes-trapping effect of surface hydroxyl species of TiO₂, (ii) coherent amorphous-nanocrystal homo-structures, and (iii) mesoporous structure for fast mass-diffusion. The formation of rich surface hydroxyl species of TiO₂ at high-temperature our proposed are a possible explanation, although it will still need further characterizations. This work provides an effective method for the controlled synthesis of OH groups and new insights for the design of high-performance TiO₂.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References


