Modification of TiO₂ Nanoparticles with Organodiboron Molecules Inducing Stable Surface Ti³⁺ Complex

Yang Cao, Peng Zhou, Yongguang Tu, ..., Shaojun Guo, Fanyang Mo, Wanhong Ma
fmo@pku.edu.cn

HIGHLIGHTS
Organodiborons are used to reshape the surface electronic state of semiconductor oxides

Diboron adsorption leads to spontaneous charge transfer and reduced surface metal ions

Photodetector based on diboron material affords 10³ fold higher visible light response
Modification of TiO$_2$ Nanoparticles with Organodiboron Molecules Inducing Stable Surface Ti$^{3+}$ Complex

Yang Cao, Peng Zhou, Yongguang Tu, Zheng Liu, Bo-Wei Dong, Aryan Azad, Dongge Ma, Dong Wang, Xu Zhang, Yang Yang, Shang-Da Jiang, Rui Zhu, Shaojun Guo, Fanyang Mo, and Wanhong Ma

SUMMARY

As one of the most promising semiconductor oxide materials, titanium dioxide (TiO$_2$) absorbs UV light but not visible light. To address this limitation, the introduction of Ti$^{3+}$ defects represents a common strategy to render TiO$_2$ visible-light responsive. Unfortunately, current hurdles in Ti$^{3+}$ generation technologies impeded the widespread application of Ti$^{3+}$ modified materials. Herein, we demonstrate a simple and mechanistically distinct approach to generating abundant surface-Ti$^{3+}$ sites without leaving behind oxygen vacancy and sacrificing one-off electron donors. In particular, upon adsorption of organodiboron reagents onto TiO$_2$ nanoparticles, spontaneous electron injection from the diboron-bound O$^–$ site to adjacent Ti$^{4+}$ site leads to an extremely stable blue surface Ti$^{3+}$=O$^–$ complex. Notably, this defect generation protocol is also applicable to other semiconductor oxides including SnO$_2$, Nb$_2$O$_5$, and In$_2$O$_3$. Furthermore, the as-prepared photoelectronic device using this strategy affords 10$^3$-fold higher visible light response and the fabricated perovskite solar cell shows an enhanced performance.

INTRODUCTION

Owing to its abundance, nontoxicity, and stability, semiconductor oxide (TiO$_2$, ZnO, SnO$_2$, etc.) nanoparticles and films have been widely used as wide-band-gap semiconductor photocatalysts for a variety of solar-driven clean energy and environmental technologies, such as photovoltaics and photocatalytic fuel generation (Chen and Mao, 2007; Grätzel, 2001). However, pristine wide band semiconductor oxides is not an appropriate candidate for practical applications since it only adsorbs UV light. The optical response of TiO$_2$ nanocrystal has been tuned to visible region using band gap engineering techniques, including metallic (Dahl et al., 2004; Hoffmann et al., 1993) or nonmetallic (Asahi et al., 2001, 2014; Chen and Burda, 2008; Khan et al., 2002) impurity doping, solid solution formation (Maeda et al., 2006; Wang et al., 2008), and self-structural modification (Liu and Chen, 2014). Among various self-modification techniques, in situ formation of self-doped Ti$^{3+}$ in the bulk phase through the introduction of oxygen vacancy at high temperature is an effective strategy for band gap engineering (Figure 1A) (Zuo et al., 2010). Additionally, hydrogenation of TiO$_2$ nanocrystals can also result in visible-light-responsible materials (Chen et al., 2011). The latest studies show that these low-energy absorption materials arouse utilities in visible light water splitting and microwave and terahertz absorption (Green et al., 2018a, 2018b, 2019a, 2019b; Guan and Chen, 2018; Tian et al., 2017). Unfortunately, harsh reaction conditions and long-time treatment have limited the practicality of these methods, especially in the context of on-site fabrication and reprocessing of light harvesting devices. Alternatively, UV irradiation of TiO$_2$ nanoparticles (Schrauben et al., 2012) or visible light irradiation of dye-sensitized systems can also produce visible-light-responsive blue-surface TiO$_2$ (Figure 1B) (Yan et al., 2017). In both cases, organic sacrificial agents are required, and these agents are irreversibly oxidized by photoinduced holes (e.g., alcohol to aldehyde and I$^–$ to I$_2$). Moreover, such nascent optically active Ti$^{3+}$ center is highly unstable toward O$_2$ owing to instantaneous oxidation to Ti$^{4+}$. To our knowledge, the formation of air-stable surface Ti$^{3+}$ centers using these techniques has not been previously described. We surmise that this is largely due to the difficulty in stabilizing the key Ti$^{3+}$=O$^–$ moiety formed in these processes, as such moiety is highly reactive toward O$_2$ to afford Ti$^{4+}$=O$^–$O$^{2–}$. In light of these constraints, the ability to access air-stable surface Ti$^{3+}$ defects within TiO$_2$ would represent a paradigm shift for the field of TiO$_2$-based oxide semiconductor materials. In this report, we show that this goal can be accomplished through the simultaneous modification of surface O$^{2–}$ and Ti$^{4+}$ sites in TiO$_2$ to afford a persistent, optically active Ti$^{3+}$=O$^–$ species.
Organodiboron compounds constitute a class of stable and highly versatile reagents commonly used in organic synthesis (Neeve et al., 2016). Despite their unique reactivity, to date, the use of these diboron species in the modification of inorganic materials remains surprisingly scarce. Herein, we report a new method for the facile generation of Ti$^{3+}$ defects on TiO$_2$ surface under mild conditions (<80°C enabled by the use of diboron reagents (Figure 1C). In this process, facilitated by the intimate interaction of the diboron reagents with the surface bridging O$_{2e}$ of TiO$_2$, the adsorption of organodiboron agents onto TiO$_2$ nanoparticles leads to spontaneous electron transfer, resulting in a stable, blue surface Ti$^{3+}$-TiO$_2$. Notably, this process does not require complicated synthetic manipulations such as anaerobic photo irradiation or high temperature calcination, which are commonly employed by previously developed techniques.

Previously developed strategies for TiO$_2$ surface modification have mainly focused on the modification of surface Ti sites with organic nucleophiles (e.g., phenol, alcohol, and carboxylic acids). In contrast, surface bridging oxygen (O$_{2e}$) sites have seldom been functionalized with electrophilic organic reagents. We posited that electrophilic organic adsorbates with an appropriate reduction potential might favorably interact with the surface O$_{2e}$ sites. Importantly, this binding event might overcome the barrier of electron transfer from O$_{2e}$ sites to adjacent Ti$^{4+}$ sites and further stabilize the primary charge separation state. We were particularly interested in the use of organic diboron reagents because of their unique Lewis acidity and reducing ability (vide supra). Previous work in the area of synthetic organic chemistry showed that, upon binding to a Lewis basic oxygen atom, these organic diboron species can function as single electron reducing agents, thus allowing for various important transformations (Liu et al., 2019; Mo et al., 2010, 2018; Pietsch et al., 2015; Wang et al., 2016; Zhang and Jiao, 2017). Based on these reasons, we envisioned that, upon the coordination of such diboron compounds with the surface oxygen atom in metal oxide materials, the formation of surface diboron-oxygen Lewis pair may induce single electron transfer from the ipso-O$_{2e}$ site to the adjacent Ti site. Furthermore, the interaction of diboron species with the oxygen atom may stabilize the resulting low-valent Ti–high-valent O pair.

RESULTS AND DISCUSSION
Spectroscopic Characterizations

We use P25 TiO$_2$ to study the surface modification behavior, for P25 TiO$_2$ is typical TiO$_2$ material applied in photochemical applications and shows enhanced performance based on fine nanoparticles and heterointerface between anatase and rutile phases (Xia et al., 2013, 2014). Mechanical mixing of commercial Degussa TiO$_2$ P25 and bis(pinacolato)diboron (B$_2$Pin$_2$, B1) in a nitrogen-filled glove box at room temperature resulted in a rapid color change from white to blue within 1 min (Figure 1E and Video S1). This blue titania, labeled as B1-TiO$_2$-N$_2$, was highly sensitive to O$_2$ and faded immediately upon exposure to air. Unexpectedly, heating B1-TiO$_2$-N$_2$ at 80°C under vacuum for 3 h resulted in a blue sample that is stable under air, which we labeled as B1-TiO$_2$. This sample could be stored outside the glovebox for weeks, and the blue color persisted. Similar transformations were observed with three other diboron compounds as shown in Figures 1 and S1. To fully disperse the diboron compound onto the TiO$_2$ nanoparticles, this heterogeneous reaction was performed in a diboron-soluble solvent, such as methanol or diethyl ether. Same blue samples were obtained after removal of organic solvents under vacuum. On the basis of previous studies (Iorio et al., 2012), the blue color was indicative of the formation of Ti$^{3+}$ defects. To probe whether B1 was oxidized in this process, the newly prepared blue B1-TiO$_2$ sample was extracted with CDCl$_3$, and B1 was found to be the only boron-containing species present in the extract (Figure S2). Additionally, the use of this recovered B1 from the extract for TiO$_2$ modification also gave rise to the same blue titania. Thus, these experiments suggested that diboron compound B1 is not a one-off sacrifice agent. Based on these findings, a new mechanism must be responsible for the formation of this blue TiO$_2$.

To probe the existence of Ti$^{3+}$ species, electron paramagnetic resonance (EPR) spectra (Zuo et al., 2010) of the B1-TiO$_2$ sample were acquired. Low-temperature (2 and 100 K) EPR data feature transitions with $g = 1.97–1.99$, whereas the room temperature EPR is silent (Figure 1F). This behavior is characteristic of Ti$^{3+}$ species as documented by previous studies (Li et al., 2008). The observed $g$ values show the presence of a strong anisotropic paramagnetic Ti$^{3+}$ center, indicating that the local symmetry of Ti$^{3+}$ is vastly broken. Furthermore, this Ti$^{3+}$ EPR signal would be split if B replaces the bridging O or is directly bound to Ti (Gopal et al., 2008). However, in all the cw-EPR measurements, we did not observe the hyperfine coupling originating from the $^{10}$B or $^{11}$B nucleus. This suggests either no or very weak coupling between the B atom.
and the Ti$^{3+}$ center. Moreover, we found that B3-TiO$_2$ shows a g signal at 2.003 at room temperature (Figure S3), which could be characteristic of a Ti$^{3+}$-O$^{2-}$ radical. We also applied the ACTEM method to study the existence and status of diboron molecule on the surface of TiO$_2$. In the high-resolution transmission electron microscopy (HRTEM) image of B3-TiO$_2$ (Figure 1G), we found that the surface of TiO$_2$ nanocrystal is wrapped by an outer layer with ~1-nm thickness. In addition, the EDS mapping of C element under the HADDF model (Figure 1H) shows a carbon-rich surface shell representing adsorbed organic diboron molecule on the TiO$_2$ surface.
Figure 2. Spectroscopic Characterizations
(A) UV-vis spectra of the white TiO₂ P25 and diboron-adsorbed TiO₂ P25. The inset shows the UV-vis spectra of four free diboron compounds.
(B) In situ ATR-FTIR spectrum of B₁ onto TiO₂ over 15 min.
(C) FTIR spectra of free B₁ and B₁-TiO₂.

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Figure 2. Continued

(D) Solid-state $^{11}$B MAS NMR of diboron compounds B and B-TiO$_2$.

(E) XRD pattern of the diboron compounds modified TiO$_2$.

(F) Ti 2p, O 1s, and valence band structure X-ray photoelectron spectroscopy spectra of TiO$_2$ and B$_1$-TiO$_2$.

(G) Normalized Ti-L edge XANES spectra of TiO$_2$ and B$_1$-TiO$_2$.

(H) Normalized O-K edge XANES spectra of TiO$_2$ and B$_1$-TiO$_2$.

We next investigated the structures and properties of these diboron-TiO$_2$ nanoparticles with powder X-ray diffraction (PXRD), solid-state UV-vis spectroscopy (UV-vis), in situ attenuated total reflectance-Fourier transform infrared spectroscopy (in situ ATR-FTIR) and solid-state $^{11}$B magic angle spinning nuclear magnetic resonance ($^{11}$B MAS NMR). PXRD analysis (Figure S4) shows that the commercial P25 sample is a mixture of anatase-phase and rutile-phase TiO$_2$. The PXRD pattern of TiO$_2$ remained the same upon adsorption of the diboron reagent, indicating that no phase change occurred in this process. Thus, this result suggests that the blue species is likely related to surface engineering rather than bulk phase modification. The solid-state UV-vis spectra in Figure 2A showed that neither the pristine white TiO$_2$ nor the diboron compound absorbs light (>400 nm). First, absorption bands beginning at 400 nm and steadily growing into the near-infrared (NIR) region were observed for all four B-TiO$_2$ samples. These adsorption bands were different from that arising from metal to ligand charge transfer of the surface complex between Ti$^{3+}$ sites and organic ligands commonly observed in previous work (Lang et al., 2012). The UV-vis absorption spectra associated with Ti$^{3+}$ materials can differ between different preparation methods (Howe and Gratzel, 1985). In our case, the diboron-modified TiO$_2$ samples were found to absorb visible light with higher intensity in the NIR region compared to the pristine TiO$_2$. As shown in Figure 2C, this signal is absent in B$_1$ owing to the C$_2$ symmetry of this diboron molecule. In contrast, a new peak at 1010 cm$^{-1}$ corresponding to B-B stretching emerged in the B$_1$-TiO$_2$ sample, thereby demonstrating the formation of the oxygen-diboron Lewis pair.

Solid-state $^{11}$B MAS NMR spectroscopy was next used to elucidate the binding details of the diboron reagent with the TiO$_2$ surface. Upon adsorption, the B(sp$^3$)-B(sp$^3$) adducts should exhibit two distinct boron environments in the solid-state NMR spectra. As shown in Figure 2D, in all four cases, new peaks appear and shift upfield, indicating changes in the chemical environment of the two B atoms. Previous studies revealed that the $^{11}$B signal of sp$^3$ hybridized tetracoordinate boron undergoes an upfield shift relative to the sp$^2$ hybridized tricoordinate one (Nöth and Wrackmeyer, 1978). Thus, we attribute the peaks close to 0 ppm to B atom bound to the surface O atom of TiO$_2$ nanoparticles. X-ray diffraction (XRD) was applied to examine the structure of the TiO$_2$ by diboron compound modification (Figure 2E). According to the XRD results, no change of the lattice was characterized. To further our understanding of the surface interaction between the diboron molecule and TiO$_2$ nanoparticles, we carried out XPS and SXANES studies. The Ti 2p spectra shows that the peaks were shifted for 0.2 eV toward the lower-binding-energy region; this also happened in O 1s spectra (Figure 2F). The valence band spectra show that the band level shifts to lower energy, a shift from 2.5 to 2.16 eV. The Ti 2p, O 1s spectra change more electron location in O 2p orbital and Ti$^{3+}$ edge region and the EXANE region (Figure S6). The reason is that the diboron compound is bonded with surface ipso-O$^2$ atoms. Moreover, the B 1s XPS also provides consistent results indexing of B species with different binding energies (Figure S7). On the basis of these spectroscopic evidences, we propose that the coordination of diboron compound with surface O sites on TiO$_2$ facilitates the electron transfer from the ipso-O$^2$ to the adjacent Ti$^{4+}$ site and this coordination further stabilizes the newly formed Ti$^{3+}$-
species. We note that the activation of inert lattice O\textsuperscript{2-} and the stabilization of surface Ti\textsuperscript{3+} enabled by the formation of \( \text{B} \equiv \text{O} \equiv \text{Ti} \textsuperscript{3+} \) moiety is a novel process that has not been reported in TiO\textsubscript{2} modification.

**DFT Calculation Results**

We next investigated the surface Ti\textsuperscript{3+}–O\textsuperscript{2-} structure in the blue TiO\textsubscript{2} nanoparticles by simulating the adsorption of B1 on the TiO\textsubscript{2} (101) surface. According to the literature, the (101) facet in anatase TiO\textsubscript{2} is the dominant facet, and we set up the adsorption model of anatase TiO\textsubscript{2} (101) facet (Lazzeri et al., 2001). Our calculations showed that the Fermi levels in no adsorption is located in the TiO\textsubscript{2} band gap (Figures 3A and 3C). Importantly, the diboron-adsorbed TiO\textsubscript{2} model shows a clear charge transfer from B1 to the TiO\textsubscript{2} (101) surface (Figure 3B).

Furthermore, the Bader charge calculation showed substantial electron transfer from the B1 atom to the bridging O atom. Furthermore, those electrons (light blue region) are localized between the bridging O atom and the neighbor surface Ti atom according to the calculated charge difference density mapping. The calculated projected density of state (PDOS) plots showed that the Fermi level rises to the bottom of the TiO\textsubscript{2} conduction band, which is mainly derived from Ti 3d states (Figure 3D). Some Ti 3d and O 2p states below the Fermi level appear, which are filled with electrons. The filled Ti 3d states indicate the partial reduction of the surface Ti sites, which explains the existence of the Ti\textsuperscript{3+} species observed in our EPR experiments. Moreover, the adsorption model of B2, B3, and B4 on TiO\textsubscript{2} (101) surface was also calculated (Figures S8A–S8C and S9). These data showed that a new electron-filled band-gap state consisting of Ti 3d appears in all the three models (Figures S8D–S8F and S9). This strongly suggested that the adsorption of organic diboron compounds can lead to the formation of Ti\textsuperscript{3+} species on the TiO\textsubscript{2} surface. The adsorption model based on rutile TiO\textsubscript{2} showed similar results (Figures S10 and S11).

The adsorption model of the interface between anatase TiO\textsubscript{2} and rutile TiO\textsubscript{2} was also set up to evaluate the heterojunction in P25 nanoparticles (Figures S12 and S13). To interpret the stability of the surface Ti\textsuperscript{3+} in B-TiO\textsubscript{2} in the air atmosphere, the oxygen adsorption models were set. The calculation result shows that O\textsubscript{2} molecule is
hesitant to adsorb to the adjacent Ti5c site of the molecule (energy rising process), which represents the protection role of the molecule (Figure S14 and Table S1).

Photodetectors and Perovskite Solar Cells Performance

To further explore the optoelectronic properties of this diboron-adsorbed TiO2 material under visible-light excitation, thin films were then fabricated into photodetectors (denoted as FTO/TiO2/diboron/Spiro-OMeTAD/Au, Figure 4A). The time-dependent current curves (I-t) for these diboron-type photodetectors and Perovskite Solar Cells Performance

Figure 4. Photodetectors and Perovskite Solar Cells Performance

(A) Schematic of the FTO/TiO2/diboron/Spiro-OMeTAD/Au photodetector.

(B) Time-dependent current curves for the detectors under light illumination (λ > 400 nm) with 10 s on-off switching intervals.

(C) Time-dependent current curves for these photodetectors under illumination intensities (λ > 400 nm) of 19.5, 26.5, 35.0, and 44.5 mW cm².

(D) Nyquist plots from the photodetectors in the dark.

(E) Schematic of the ITO/SnO2/diboron/Perovskite/Spiro-OMeTAD/Au solar cell.

(F) Current density-voltage curves (J-V) of the diboron-modified perovskite solar cell.

(G) Photovoltaic parameters of the diboron-modified perovskite solar cell. FF, fill factor; PCE, power conversion efficiency.

| Reference | 1.105 | 23.46 | 79.45 | 20.60 |
| B3 treated | 1.143 | 23.35 | 80.32 | 21.44 |

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photodetectors under visible-light illumination (>400 nm) exhibited excellent on-off switching repetitions through five cycles (interval = 10 s) (Figure 4B). The photocurrent for these four diboron-type detectors increased linearly with the light intensity (Figures 4C and S15 and Table S2). In contrast, the observed photocurrent for TiO2 without diboron modification did not change regardless of the on-off state, which was ascribed to the intrinsic band gap of anatase TiO2 (3.2 eV). Furthermore, the charge transport process in diboron-modified devices was investigated using electrochemical impedance spectroscopy measurements in the dark at 0 V (Figure 4D). The larger semicircle radius of Nyquist plot in the low-frequency region for the B3 device compared with the B1, B2, and B4 devices indicated less electron recombination (Kim et al., 2012). This observation agreed well with the highest photocurrent for the B3 device (Figure 4B). The IPCE (incident photon-to-electron conversion efficiency) was also evaluated, and the B3-TiO2 device shows the best performance (Figure S16). The B-TiO2 photodetectors show good response toward long-time on-off tests compared with the TiO2 photodetector (Figures S17 and S18), and the response of the photodetectors does not attenuate after being stored in a dry air atmosphere for at least 7 months (Figure S19). We also fabricated solar cells based on the diboron molecule interface modulation, and the J-V performance of the device was characterized showing an improved solar cell performance (Figures 4E–4G). The data show that the B3-treated device based on the B3-SnO2 interface has a better performance compared with the reference device of SnO2-based perovskite solar cell.

We note that previously developed solar cells such as dye-sensitized solar cells and perovskite solar cells inevitably involve the use of expensive dyes and/or toxic and unstable reagents. Thus, our approach to generating visible-light active center via the adsorption of stable and inexpensive diboron compounds holds great advantages over these traditional techniques. Furthermore, a diverse range of diboron compounds can be conveniently synthesized from B4, potentially allowing for the fine-tuning of semiconductor-based materials. More importantly, the present strategy is not limited to TiO2. In our studies, we have determined that a broad range of other common semiconducting oxides, including ZnO, SnO2, Nb2O5, and In2O3, were also successfully modified by diboron reagents, thus clearly demonstrating the generality of this method for semiconducting metal oxide modification (Figure S20).

**Limitations of the Study**

In the current study, perovskite solar cells assembled from B-TiO2 display relatively poor performance (Figure S21). Many factors such as device fabrication could influence the performance of such device. Additionally, in our present work, mesoporous TiO2 was used in B-TiO2-based devices, whereas planar SnO2 was used in B-SnO2-based devices. We are uncertain if this deviation led to the contrasting device performance based on B-TiO2 and B-SnO2 materials. Nonetheless, the three orders of magnitude improvement observed in the B-TiO2-based photodetector clearly demonstrates the utility of this diboron-based modification strategy. Currently, we are actively pursuing other applications based on diboron-modified semiconductor oxide materials featuring unique surface defects.

**METHODS**

All methods can be found in the accompanying Transparent Methods supplemental file.

**SUPPLEMENTAL INFORMATION**

Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.09.024.

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AUTHOR CONTRIBUTIONS
F.M. conceived the idea. Y.C., P.Z., Y.T., Z.L., and B.-W.D. performed experiments. Y.C., P.Z., and X.Z. conducted the DFT calculation. All authors analyzed data. Y.C., P.Z., Y.T., X.Z., Y.Y., S.-D.J., F.M., and W.M. wrote the manuscript. F.M. directed the whole project.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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Supplemental Information

Modification of TiO₂ Nanoparticles
with Organodiboron Molecules Inducing
Stable Surface Ti³⁺ Complex

Yang Cao, Peng Zhou, Yongguang Tu, Zheng Liu, Bo-Wei Dong, Aryan Azad, Dongge Ma, Dong Wang, Xu Zhang, Yang Yang, Shang-Da Jiang, Rui Zhu, Shaojun Guo, Fanyang Mo, and Wanhong Ma
Supplementary Materials

This PDF file includes:

  Transparent Methods
  Figures S1 to S21
  Tables S1 to S3
Transparent Methods

EXPERIMENTAL PROCEDURES

Sample preparations
B1-TiO2-N2 sample: In a glovebox, 50 mg B2Pin2 was dissolved in 2 mL dry CH3OH. Then 0.5 g TiO2 (Degussa P25, 20 nm) was added into the solution. The mixture was stirred for overnight at room temperature. After evaporation of the solvent by an oil pump, the titled sample was obtained as a blue powder. This blue titania is sensitive to oxygen and will fade when exposed to air. However, when the sample is again isolated from air, the blue color returns. By the same procedure, the corresponding B2-TiO2-N2, B3-TiO2-N2, B4-TiO2-N2 were prepared from B2 B2(OH)4, B3 B2Cat2, B4 B2(NMe2)4, respectively.

B1-TiO2 sample: This sample was obtained by heating the above sample at 80 °C under high vacuum for 3 h. B2-TiO2, B3-TiO2 and B4-TiO2 were obtained by the same procedure.

Device Fabrication
Photodetector fabrication:
The pre-patterned FTO substrates (NSG) were cleaned by UV-ozone treatment for 15 min, followed by cleaning ultrasonically with deionized water, detergent, acetone, and isopropanol in succession for 20 min. A 30 nm TiO2 compact layer was deposited on the pre-cleaned FTO glass by spray pyrolysis using O2 as the carrying gas at 450 °C from a precursor solution of 0.6 mL titanium diisopropoxide bis(acetylacetonate) and 0.4 mL acetylacetonate in 9 mL anhydrous ethanol. A 150 nm mesoporous TiO2 was coated on the substrate by spin-coating with a speed of 5000 rpm for 10 s with a ramp rate of 2000 rpm s⁻¹, from a diluted 30 nm TiO2 particle paste (Dyesol 30 NR-D) in ethanol with the weight ratio of TiO2 paste/ethanol = 1:6, and then the substrate was sintered at 500 °C for 30 min.

For the adsorption of diboron compounds, the mesoporous TiO2 films were immersed in 5 mg mL⁻¹ B2Pin2, B2Cat2, B2(OH)4 in anhydrous isopropanol at room temperature for 24 h in the nitrogen glove box, respectively. Then the diboron-sensitized TiO2 films were heated
at 100 °C for 5 min. For the sample of B$_2$(NMe$_2$)$_4$-sensitized TiO$_2$ films, B$_2$(NMe$_2$)$_4$ solvent was spin-coated on the TiO$_2$ film with a speed of 2500 rpm for 20 s, then annealed at 40 °C for 2 min to remove extra solvent. The amount of diboron compounds on each film were examined by ICP method (Table S3). After cooling down to room temperature, 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) solution was spin-coated onto the active layer at 4000 rpm for 30 s. A spiro-OMeTAD solution was prepared by dissolving 72.3 mg of spiro-OMeTAD in 1 mL of chlorobenzene, to which 28.8 mL of 4-tert-butyl pyridine and 17.5 mL of lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) solution (520 mg Li-TFSI in 1 mL acetonitrile) were added. All devices were stored in a desiccator (humidity < 15 %) for 12 h. Finally, 80 nm of gold was deposited under vacuum through a shadow mask.

**Solar cell fabrication:**

**SnO$_2$-based perovskite solar cells fabrication.** The ITO substrates were cleaned with ultrapure water, acetone, ethanol and isopropanol subsequently. The cleaned ITO substrates were treated under ozone irradiation for 45 min. Then the subsequent were coated with a SnO$_2$ nanocrystal solution at 4000 rpm/min for 30 second forming a 50 nm thick layer, then annealed at 150 °C for 30 min in air atmosphere. Then 0.1 mM B3 DMF solution were spin coated onto the layer for 5000 rpm for 30 second in N$_2$ atmosphere, then annealed at 70 °C for 5 min. The perovskite film was fabricated by a two-step solution process: the 1.3 M PbI$_2$ in DMF/DMSO (9:1) mixture were spin-coated on the ITO substrate for 2500 rpm/min for 30 second, then annealed for 1 min at 70 °C in N$_2$ glovebox. A mixed organic cation isopropanol solution (MAI 0.12 M; MABr 0.05 M; MACl 0.07 M; FAI 0.23 M) were spin coated for 30 second at 2300 rpm/min and subsequent annealation at 150 °C. Then a spiro-OMeTAD/chlorobenzene solution including 35 μL Li-TFSI/acetonitrile, 30 μL 4-tertbutylpyridine, was coated onto the perovskite layer with 3500 rpm/min for 30 second. After that, 80 nm Au were deposit onto the substrate by thermo evaporation method. The fabricated solar cell was stored in a desiccator (humidity < 15 %) for 12 h before performance measurement.

**TiO$_2$-based perovskite solar cells fabrication.** The pre-patterned FTO substrates (NSG) were cleaned by UV-ozone treatment for 15 min, followed by cleaning ultrasonically with deionized water, detergent, acetone, and isopropanol in succession for 20 min. A 30
nm TiO$_2$ compact layer was deposited on the pre-cleaned FTO glass by spray pyrolysis using O$_2$ as the carrying gas at 450 °C from a precursor solution of 0.6 mL titanium diisopropoxide bis(acetylacetonate) and 0.4 mL acetylacetone in 9 mL anhydrous ethanol. A 150 nm mesoporous TiO$_2$ was coated on the substrate by spin-coating with a speed of 5000 rpm for 10 s with a ramp rate of 2000 rpm s$^{-1}$, from a diluted 30 nm TiO$_2$ particle paste (Dyesol 30 NR-D) in ethanol with the weight ratio of TiO$_2$ paste/ethanol = 6:1, and then the substrate was sintered at 500 °C for 30 min. After cooling down to room temperature, 5 mg mL$^{-1}$ B$_2$Pin$_2$ in anhydrous isopropanol was spin-coated onto the TiO$_2$ film with a speed of 2000 rpm for 20 s in N$_2$ atmosphere, then annealed 100 °C for 5 min. The cesium-containing triple cation perovskite precursor solution was prepared by mixing PbI$_2$ (1.15 M), FAI (1.09 M), PbBr$_2$ (0.20 M), MABr (0.14 M) and CsI (0.06 M) in a mixed solvent of DMF/DMSO/NMP (DMF/DMSO, 4/1, v/v) and stirred at 70 °C for 10 min before use. The perovskite solution was deposited on TiO$_2$ substrate with two-step program: 2000 rpm for 10 s with a ramping up speed of 2000 rpm/s, and 6000 rpm for 30 s with a ramping up speed of 2000 rpm/s, respectively. 100 μL of chlorobenzene was poured on the center of the spinning substrate during the spin-coating step at 15 s before the end of the procedure. The substrate was then immediately transferred on a hot plate and heated at 100 °C for 1 h. After cooling down to room temperature, 20 μL of 60 mM Spiro-OMeTAD solution was spin-coated on the perovskite layer at 4000 rpm for 30 s. A Spiro-OMeTAD solution was prepared by dissolving 72.3 mg of Spiro-OMeTAD in 1 mL of chlorobenzene, to which 28.8 μL of 4-tert-butyl pyridine and 17.5 μL of lithium bis(tri-uoromethanesulfonyl)imide (Li-TFSI) solution (520 mg LI-TFSI in 1 mL acetonitrile) were added. All devices were stored in a desiccator (humidity < 15%) in the dark for 12 h. Finally, 80 nm of gold was deposited under vacuum through a shadow mask to ensure the same active layer area (0.0863 cm$^2$).

**Materials and Methods**

*The characterization details:*

Electron paramagnetic resonance was collected on a Bruker EMX plus under continuous wave model of X wave at room temperature or low temperature hold by liquid Helium.
FT-IR spectroscopy were collected on a Thermal Nicolet iS 50 spectrometer equipped with a MCT detector with high resolution, which is cooled to 77 K by liquid N\textsubscript{2} during the detecting period. For each sample, the data were collected for 128 scans at 4 cm\textsuperscript{-1} resolutions. Solid-state $^{11}$B NMR spectra were performed on a JEOL JNM-ECZ600R NMR spectrometer (14.1 T) equipped with a 3.2 mm probe at room temperature. The corresponding $^{11}$B Larmor frequency is 192.4 MHz. A standard solid single pulse sequence was employed, and the $\tau$/2 pulse widths was 4 $\mu$s. The $^{11}$B NMR experiments were carried out with an effective sample volume of 50 $\mu$L and a sample spinning rate of about 20 kHz. Chemical shifts are referenced to 0.1 M B(OH)$_3$ in D$_2$O at 19.6 ppm, solid NaBH$_4$ at -42.1 ppm. All spectra were acquired using 1024 scans with a recycle delay time of 5s. The collected NMR data were processed using Delta software. X-ray diffraction spectra were collected on a Rigaku RINT 2000 spectrometer. Photo detection measurement were performed on a CHI 670E electrochemical workstation from Shanghai Chen Hua Company. The light source was irradiated from a 300 W solar simulator from Newport Company with a 400 nm cut off. Impedance spectroscopy measurements were carried out by CHI670E electrochemical workstation. Solid state UV-VIS-NIR spectrograph were collected on a UV-3600 plus Shimadzu UV-VIS-NIR spectroscopy. XPS spectra were collected on a Thermo Scientific Escalab 250Xi spectrometer. The XAS measurements of the TiO$_2$ and diboron modified TiO$_2$ sample were operated in transmittance mode at the XAS beamline of BL14W of Shanghai Synchrotron Source (3.5 GeV). The energy range of the beamline were 4 to 15 keV. The collect data were fitted using the ATHENA software package. The test sample were prepared by mixing of 50 mg LiF and 7 mg TiO$_2$ or B-TiO$_2$ and then press to a tablet. A Si (311) monochromator were used to collect the data and the energy were calibrated by using a Ti metal foil. We collect the Ti K line data around 4966 eV. The Ti L line and O K line were collected on the BL08U1 of Shanghai Synchrotron Source. Boron K-edges, oxygen K-edges, Titanium L-edges sXANES spectra were collected in total electron yield (TEY) mode at beamline 08U1A of Shanghai Synchrotron Radiation Center. The spectra were calibrated with a clean gold mesh which give a simultaneous photocurrent based on the photon flux.
ATR-FTIR measurements:
The ATR-FTIR measurements were performed on a Nicolet 6700 FTIR instrument with a mercury cadmium telluride (MCT) detector. IR spectra ranging from 4000 to 1000 cm\(^{-1}\) were recorded by averaging 32 scans with a resolution of 4 cm\(^{-1}\). The TiO\(_2\) film was coated on a ZnSe crystal. 2 mL of methanol was dripped onto the film surface and then purged with Ar for 5 min at a flow rate of 20 mL min\(^{-1}\). After adsorption equilibrium was achieved, the background spectrum was collected. Then a B\(_2\)Pin\(_2\)-containing methanol solution was added and the corresponding IR spectrum was recorded.

Computational details:
The electronic properties of the no adsorption and adsorption models of B\(_1\) on the TiO\(_2\) \{101\} surface were investigated using the Vienna Ab-initio Simulation Package (VASP). The Perdew-Burke-Ernzerhof (PBE) of the generalized gradient approximation (GGA) was used as the exchange-correlation function (Perdew et al., 1996; Perdew and Wang, 1992). The interaction between the valence electrons and the ionic core was described by the PAW pseudo-potential. The anatase TiO\(_2\) \{101\} facet is a typical model used to simulate the TiO\(_2\) crystal surface. The interactions between the two adjacent B\(_1\) molecules on the periodic TiO\(_2\) surface were modeled using one 2 × 4 \{101\} supercell with four O–Ti–O layers (Figure 3a and 3b). Two models were optimized with adsorption and without adsorption. Considering the balance between the supercell size and the calculational cost, the geometry was only optimized at the gamma point. The energy cutoff of the plane-wave basis was set to 350 eV and the energy convergence was set to 1.0 × 10\(^{-4}\) eV. The interactions between the two adjacent B\(_1\) molecules on the periodic rutile \{110\} TiO\(_2\) surface were modeled using one 2 × 4 \{110\} supercell with four O–Ti–O layers. The heterojunction adsorption model by joining anatase \{112\} and rutile \{101\} of 8A/3R (phase ratio of anatase/rutile phase: 8/3) were also modeled to simulate the adsorption on the heterojunction region.(Zhao et al., 2015) The adsorption energy (\(E_{\text{ads}}\)) of the B\(_1\) molecules adsorbed on the TiO\(_2\) \{101\} surface was calculated using Equation (1) where \(E_{\text{total}}\) is the total energy of the B\(_1\)-adsorbed TiO\(_2\) \{101\} surface, \(E(\text{TiO}_2)\) is the free energy of the TiO\(_2\) \{101\} surface, and \(E(B1)\) is the free energy of one B\(_1\) molecule in vacuum.

\[
E_{\text{ads}} = E_{\text{total}} - E(\text{TiO}_2) - E(B1) \quad (1)
\]
After the geometry optimization, the Monkhorst-Pack $2 \times 2 \times 1$ k-point mesh was used for the partial density of state (PDOS) calculations for the optimized adsorption models. The charge difference density mapping and the bader charge were also calculated to investigate the charge transfer between the B1 and the TiO$_2$ surface.
Figure S1. EPR signal of (A) B2-TiO2-N2 (B) B3-TiO2-N2 (C) B4-TiO2-N2 at room temperature or 100 K (The sample were protected under N2 atmosphere during measurement). Related to Figure 1.
Figure S2. $^1$H NMR spectra indicate that B1 is unchanged upon extraction from the adsorbed sample. Related to Figure 1.
Figure S3. EPR signal of B3-TiO₂. Related to Figure 1.
Figure S4. XRD pattern of boron compound adsorbed on TiO$_2$ by heat treatment at 80 °C and pristine TiO$_2$ (Degussa P25, A: anatase, R: rutile). Related to Figure 2.
**Figure S5.** Calculated vibrational spectra of B1 (B2Pin₂, blue line) based on G09 package and experimental FT-IR transmission spectra (red line) (The frequency were corrected by a factor of 0.9614, at 6-31G* level). Related to Figure 2.
Figure S6. (A) Ti K edge line of B3-TiO2 and pristine TiO2. (B) Extend XAFS spectra of B3-TiO2 and pristine TiO2. Related to Figure 2.
Figure S7. B 1s XPS spectra of B1-TiO2 and simulate multiple peak fitting curve. Related to Figure 2.
Figure S8. The optimized geometry structures of (A) B2 B2(OH)₄, (B) B3 B2Cat₂ and (C) B4 B2(NMe₂)₄ adsorbed TiO₂ {101} surface. Projected density of state (PDOS) plots of (D) B2 B2(OH)₄, (E) B3 B2cat₂ and (F) B4 B2(NMe₂)₄-adsorbed TiO₂ {101} surface. The dashed line stands for the Fermi level. Related to Figure 3.
Figure S9. The optimized geometric structures and charge density difference plots of (A) B$_1$ B$_2$Pin$_2$ (B) B$_2$(OH)$_4$, (C) B$_3$Cat$_2$ and (D) B$_4$ B$_2$(NMe$_2$)$_4$ adsorbed TiO$_2$ {101} surface. The isosurface levels are set at 0.001 e Å$^{-3}$. The yellow and skyblue surfaces represent electron depletion and accumulation, respectively. Related to Figure 3.
Figure S10. The optimized geometric structures and charge density difference plots of (A) B1 B2Pin2 (B) B2 B2(OH)4, (C) B3 B2Cat2 and (D) B4 B2(NMe2)4 adsorbed on rutile TiO2 {110} surface. The isosurface levels are set at 0.001 e Å⁻³. Related to Figure 3.
Figure S11. Projected density of state (PDOS) plots of (A) pristine TiO₂, (B) B1 B₂Pin₂, (C) B2 B₂(OH)₄, (D) B3 B₂cat₂ and (E) B4 B₂(NMe₂)₄-adsorbed rutile TiO₂ {110} surface. The dashed line stands for the Fermi level. Related to Figure 3.
Figure S12. The isosurfaces of the electron density difference plots of B3 molecule adsorption on (A) the interface of anatase \{112\} (right) and rutile \{101\} (left) TiO$_2$ (phase ratio of anatase/rutile=8/3), (B) the surface of anatase \{101\}, (C) the surface of rutile \{110\}. The isosurfaces of the electron density difference plots are 0.001 e Å$^{-3}$. The yellow and light blue surfaces represent electron depletion and accumulation. The blue, red, yellow, green and pink spheres stand for the Ti, O, C, B and H atoms. Related to Figure 3.
Figure S13. Projected density of states (PDOS) plots of (A) pristine B3 adsorption on the anatase{112}-rutile{101} interface, (B) B3 B$_{2}$cat$_{2}$-adsorbed anatase{112}-rutile{101} interface, (C) pristine anatase {101} surface, (D) B3 B$_{2}$cat$_{2}$-adsorbed anatase {101} surface, (E) pristine rutile {110} surface, (F) B3 B$_{2}$cat$_{2}$-adsorbed rutile {110} surface. The dashed lines stand for the Fermi level. Related to Figure 3.
Figure S14. Optimized geometry structures of O₂ adsorption on the TiO₂ {101} plane of (A) B1-TiO₂, (B) B2-TiO₂, (C) B3-TiO₂, (D) B4-TiO₂ (adsorb to the Ti₅c site adjacent to the O₂c site with diboron compound adsorption). Related to Figure 3.
Figure S15. The simulated linear dynamic response SNR curve (signal to noise response). Related to Figure 4.
Figure S16. IPCE spectra of the photodetectors and the integration of the IPCE spectra for the photodetectors. Related to Figure 4.
**Figure S17.** The transient photocurrent curve of the diboron compound devices and TiO₂ device alone with on off light switches (λ > 400 nm). Related to Figure 4.
Figure S18. The comparation time dependent current curves for the B3-TiO₂ and TiO₂ detectors under light illumination with 10 s on/off switching intervals. (no cut off filter). Related to Figure 4.
Figure S19. The transient photocurrent curve of the diboron compound device alone with on off light switches stored in the air atmosphere for 6 months (light source: 300 W Xe lamp with a 400 nm cut filter). Related to Figure 4.
Figure S20. (A-D) EPR spectra of B1-metal oxides at various temperatures. (E-H) UV-Vis spectra of B-metal oxides. In these preliminary studies, by adopting a same adsorption operation to other common semiconductor oxides, such as ZnO, In₂O₃, SnO₂ and Nb₂O₅, similar phenomena were observed. EPR spectra demonstrated the appearance of reduced metal species, such as Zn⁺, In²⁺, Sn³⁺ and Nb⁴⁺. Additionally, the UV-Vis of these modified materials were also collected. These diboron-modified metal oxides samples were found to absorb visible light with higher intensity in the NIR region. Related to Figure 4.
Figure S21. (A) Schematic of the FTO/TiO2/Perovskite/Spiro-OMeTAD/Au solar cell (B) Current density-voltage curves (J-V) of the diboron modified perovskite solar cell. Related to Figure 4.

Table S1. The adsorption energy of oxygen molecule to the diboron molecule pre-absorption TiO2 \{101\} plane. Related to Figure 3.

|         | $E_{(TiO2-B)}$ (eV) | $E_{(O2)}$ (eV) | $E_{(TiO2-B-O2)}$ (eV) | $E_{ad}$ (eV) |
|---------|---------------------|-----------------|------------------------|--------------|
| B1-TiO2 | -2063.56119598      | -9.44011081     | -2071.61712553         | 0.18418126   |
| B2-TiO2 | -1883.20183442      | -9.44011081     | -1891.54740527         | 0.90453996   |
| B3-TiO2 | -2002.25704951      | -9.44011081     | -2011.19765769         | 0.59950263   |
| B4-TiO2 | -2028.25727155      | -9.44011081     | -2036.34654405         | 1.35083831   |

The adsorption energy of oxygen molecule to the diboron molecule pre-absorption TiO2 \{101\} plane was calculated:

\[ E_{ad} = E_{(TiO2-B-O2)} - E_{(TiO2-B)} - E_{(O2)} \]
Table S2. The parameter of the photodetector devices. Related to Figure 4.

| Photodetector | R (μA/W) | D (10^{12} Jones) | I_{light}/I_{dark} | SNR  |
|---------------|----------|--------------------|--------------------|------|
| TiO₂          | 0.18     | 27.7               | 3.06               | 2.05 |
| B₄-TiO₂       | 35.4     | 3.2                | 5.39               | 4.39 |
| B₂-TiO₂       | 151      | 9.3                | 214                | 213  |
| B₁-TiO₂       | 406      | 10.0               | 726                | 725  |
| B₃-TiO₂       | 814      | 8.9                | 778                | 777  |

The illumination power was calculated as $P_{ill} = 44.5 \text{ mW/cm}^2 \times 0.0863 \text{ cm}^2 = 3.84 \text{ mW}$.

The detail of the origin of the photocurrent

1. The responsivity R is calculated according to the equation:
   
   $$R = \frac{(I_{light} - I_{dark})}{P_{ill}}$$

   $P_{ill}$ is definite as the illumination power on the photo harvest area of the device.

2. The light-detection ability of the photodetector can be evaluated by D:
   
   $$D = R \times \left(\frac{S}{2qI_{dark}}\right)^{1/2}$$

3. The signal-to-noise ratio (SNR) can be defined as:
   
   $$SNR = \frac{(I_{light} - I_{dark})}{I_{dark}}$$

We get the amount of the diboron compounds by detection of B element concentration using ICP method (ICP-MS, iCAP Q, Thermo, Waltham, USA). We modified the mesoporous TiO₂ layer with diboron molecules as depicted in the experimental part. The mesoporous TiO₂ layer were then removed from the FTO glass and this sample was subject to ICP measurement. The results are given below.

Table S3. Amount of the diboron compounds on FTO glass. Related to Figure 4.

| Diboron compound | c (B) μg/L (original data, amount of 4 FTO) | Diboron compound molecule weight | Diboron compound mass per FTO (μg) | Diboron compound molar per FTO (μmol) |
|------------------|------------------------------------------|---------------------------------|-----------------------------------|--------------------------------------|
| B₁-TiO₂          | 794.8                                    | 253.94                          | 22.9354                           | 0.090318                             |
| B₂-TiO₂          | 1027                                     | 89.65                           | 10.46256                          | 0.116705                             |
| B₃-TiO₂          | 1037.6                                   | 237.81                          | 28.03996                          | 0.117909                             |
| B₄-TiO₂          | 775                                      | 197.92                          | 17.43045                          | 0.088068                             |
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