

# Ohmic Hetero-Junction of n-Type Silicon and Tungsten Trioxide for Visible-Light Sensitive Photocatalyst

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## Abstract

Visible light-sensitive photocatalyst was developed by combining n-type silicon (n-Si) and tungsten trioxide (WO<sub>3</sub>, n-Si/WO<sub>3</sub>), yielding an ohmic contact in between. In this system, the ohmic contact acted as an electron-and-hole mediator for the transfer of electrons and holes in the conduction band (CB) of WO<sub>3</sub> and in the valence band (VB) of n-Si, respectively. Utilizing thus-constructed n-Si/WO<sub>3</sub>, the decomposition of 2-propanol to CO<sub>2</sub> via acetone was achieved under visible light irradiation, by the contribution of holes in the VB of WO<sub>3</sub> to decompose 2-propanol and the consumption of electrons in the CB of n-Si to reduce O<sub>2</sub>. The combination of p-type Si (p-Si) and WO<sub>3</sub> (p-Si/WO<sub>3</sub>), not the ohmic contact but the rectifying contact, was much less effective, compared to n-Si/WO<sub>3</sub>.

## Keywords

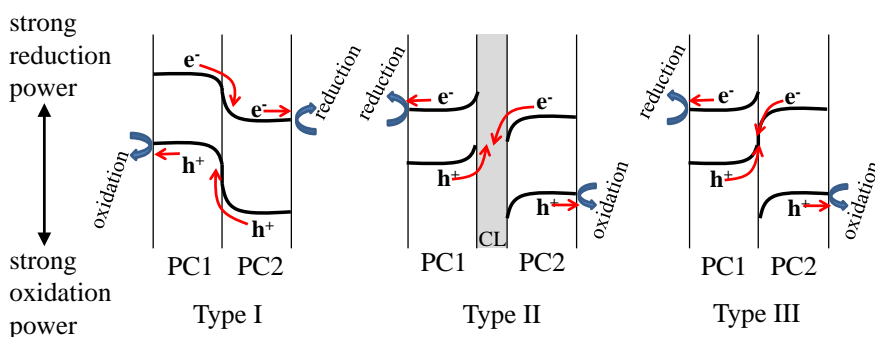
Ohmic Contact, Silicon, Tungsten Trioxide, Visible Light, Oxidative Decomposition, Two-Step Excitation

## 1. Introduction

Various photocatalytic materials have been evaluated for the oxidative decomposition of organic stains and production of hydrogen (H<sub>2</sub>) via water splitting for environmental preservation and generation of clean energy, respectively, by utilizing solar energy [1] [2] [3]. Among examined materials, titanium dioxide (TiO<sub>2</sub>) with which Fujishima and Honda first demonstrated photo induced wa-

ter-splitting [1] is the most promising photocatalysts due to their high performance, abundance, nontoxicity, thermal stability and high resistance against photo-corrosion [2] [3]. Despite these advantageous properties,  $\text{TiO}_2$  is only sensitive to ultraviolet (UV) light and therefore requires modification for the utilization of visible light. To this end, numerous studies have examined the effects of doping foreign elements into  $\text{TiO}_2$  [4] and other UV-light sensitive photocatalysts, such as strontium titanate ( $\text{SrTiO}_3$ ) [5], zinc oxide ( $\text{ZnO}$ ) [2] [3] and so on. Another common method is to produce or find photocatalysts with narrow band-gaps which can absorb visible light [6] [7] [8] [9]. From these studies, combined systems consisting of two such narrow band-gap photocatalysts (PC1/PC2) have been developed, such as tungsten disulfide ( $\text{WS}_2$ )/tungsten trioxide ( $\text{WO}_3$ ), cobalt oxide ( $\text{Co}_3\text{O}_4$ )/bismuth vanadate ( $\text{BiVO}_4$ ), and so on (Type I in scheme 1) [10] [11] after the suggestions made in the literatures as to the more efficient charge separation in the combined system of  $\text{TiO}_2$  and cadmium sulfide ( $\text{CdS}$ ), iron oxide ( $\text{Fe}_2\text{O}_3$ ),  $\text{WO}_3$ ,  $\text{ZnO}$ , copper oxide ( $\text{Cu}_2\text{O}$ ), or bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) etc., resulting in the increase in the lifetime of the charge carriers and the enhancement of the activity [12] [13]. However, all these combined systems are not recommended from the viewpoint of oxidation and reduction potentials of holes and electrons, respectively, after their interparticle transfer because the oxidation power of the holes and reduction powers of the electrons become weak after the transfer (Type I in **Scheme 1**).

To overcome the decrease in the oxidation power of the holes and reduction powers of the electrons, the insertion of a conducting layer (CL, metal such as gold (Au), silver (Ag), and tungsten (W) or reduced graphene oxide (RGO)) between two types of photocatalysts was reported [14]-[20] (PC1/CL/PC2, Type II in **Scheme 1**). Regarding the powdered system,  $\text{CdS}/\text{Au}/\text{TiO}_2$ ,  $\text{WO}_3/\text{W}/$  titanium doped-lead bismuth niobium oxide ( $\text{PbBi}_2\text{Nb}_{1.9}\text{Ti}_{0.1}\text{O}_9$ ) were reported for the decomposition of organic substances [14] [15]. For the overall water-splitting under visible light, ruthenium (Ru)-loaded rhodium-doped  $\text{SrTiO}_3$  ( $\text{Ru-STO}:\text{Rh}$ )/RGO/bismuth vanadate ( $\text{BiVO}_4$ ), zinc rhodium oxide ( $\text{ZnRh}_2\text{O}_4$ )/Ag/silver antimonite ( $\text{AgSbO}_3$ ) and  $\text{ZnRh}_2\text{O}_4/\text{Ag}/$ bismuth vanadate ( $\text{Bi}_4\text{V}_2\text{O}_{11}$ ) were reported [16]-[20]. In addition, direct connection of the two or more types of photocatalysts without the conducting layer was also reported based on the



**Scheme 1.** Three types of previously proposed heter-junctioned photocatalysts.

concept of ohmic contact (PC1/PC2, Type III in **Scheme 1**). In most cases, they were a photoelectrochemical (PEC) electrode water-splitting systems, such as n-type silicon (n-Si)/Fe<sub>2</sub>O<sub>3</sub>, gallium indium phosphorus (GaInP<sub>2</sub>)/gallium arsenic (GaAs), three types of amorphous Si, and so on [21] [22] [23]. As for the powdered system, copper bismuth oxide (CuBi<sub>2</sub>O<sub>4</sub>)/WO<sub>3</sub> for the oxidative decomposition of acetaldehyde, and Ru-STO: Rh/BiVO<sub>4</sub> and ZnRh<sub>2</sub>O<sub>4</sub>/defective AgSbO<sub>3</sub> for the overall water-splitting were reported [17] [24] [25]. However, no experimental evidences for the formation of the ohmic contact were demonstrated in all cases but only provided the concept of the ohmic contact. Thus in the present study, we demonstrated that the formation of the ohmic contact could produce a more efficient photocatalyst than that of the rectifying contact by connecting n-Si or p-type silicon (p-Si) with WO<sub>3</sub> (n-Si/WO<sub>3</sub>, p-Si/WO<sub>3</sub>).

## 2. Experimental Section

### 2.1. Preparations of n-Si/WO<sub>3</sub> and p-Si/WO<sub>3</sub> Electrodes

Single crystal n-Si(100) and p-Si(100) wafers with a thickness of  $525 \pm 25$   $\mu\text{m}$  were purchased from Kyodo International Inc. The n-Si(100) and p-Si(100) wafer surfaces were cleaned by a RCA cleaning method [26]. That is, the successive immersions of the wafers in a boiling mixture of 95% sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) at a volume ratio of 3:1, in a 5% hydrofluoric acid (HF) solution for 5 min, in a boiling mixture of 25% aqueous ammonium (NH<sub>3</sub>), 30% H<sub>2</sub>O<sub>2</sub> and distilled water at a volume ratio of 1:1:3 for 15 min, again in the 5% HF solution for 5 min, and in a 40% ammonium fluoride (NH<sub>4</sub>F) solution for 5 min [26]. On the cleaned n-Si(100) or p-Si(100) surface, a WO<sub>3</sub> film was deposited by sputtering a W metal target under oxygen (O<sub>2</sub>, 40 SCCM)/argon (Ar, 60 SCCM) gas mixture and 1.5 Pa for 16 min at substrate temperature of 400 °C, using a radio frequency (RF) magnetron sputtering apparatus (Tokuda, Model CFS-8EP). The thickness was controlled to be  $\sim 200$  nm.

### 2.2. Preparations of n-Si/WO<sub>3</sub> and p-Si/WO<sub>3</sub> Powders

To obtain n-Si and p-Si powders, the purchased n-Si(100) and p-Si(100) wafers, respectively, were roughly pulverized by a mortar and then finely pulverized using a planetary ball-milling apparatus at 500 rpm for 5 min before use. Then WO<sub>3</sub> was loaded by a liquid phase deposition (LPD) on the surface of either pulverized n-Si or p-Si powder as follows [27]. Briefly, 5.01 g of tungsten acid (H<sub>2</sub>WO<sub>4</sub>, Kanto Chemical) was dissolved in 50 mL of an aqueous solution of 2% HF. 7.45 g of boric acid (H<sub>3</sub>BO<sub>3</sub>) was dissolved in 50 mL of distilled water and was used as the reagent which acts as F<sup>-</sup> scavenger. These two solutions were mixed to use as the reaction solution for WO<sub>3</sub> deposition.  $7.72 \times 10^{-2}$  g of either pulverized n-Si or p-Si powder (Si/WO<sub>3</sub> = 1/60 wt% or 1/7.3 mol%) was stirred with the mixed solution using a magnetic stirrer for 6 h at room temperature. The reaction product was obtained by a filtration, followed by washing with sufficient distilled water and drying at 50 °C. Then the samples were heated at

500 °C for 1 h in air.

### 2.3. Characterizations

The crystal structures of the prepared n-Si/WO<sub>3</sub> and p-Si/WO<sub>3</sub> electrodes and powders were examined by X-ray diffraction (XRD) using a PW-1700 system (Panalytical). A scanning transmission electron microscope (SEM, Hitachi, S-4500) was used to observe the morphology of the prepared samples. UV-visible absorption spectra for the n-Si/WO<sub>3</sub> and p-Si/WO<sub>3</sub> powders were obtained by the diffuse reflection method using a V-650 (JASCO) spectrometer.

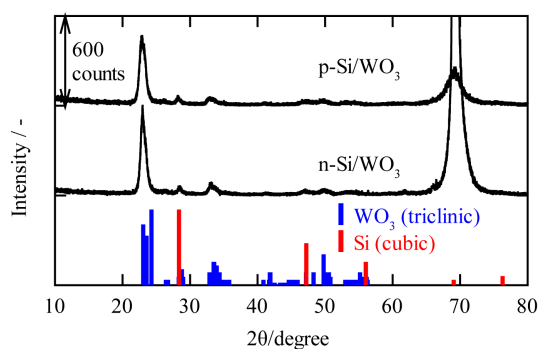
The current-voltage (I-V) analysis in the presence or absence of light from a Xe lamp (LA-251Xe, Hayashi Tokei) for the n-Si/WO<sub>3</sub> and p-Si/WO<sub>3</sub> electrodes were performed in a conventional two electrode system using a potentiostat at (Hokuto Denko, HSV-10). To serve an ohmic electrode, platinum was deposited on WO<sub>3</sub> using a quick coater (Sanyu Electron Co., Ltd., SC-708) and indium (Kanto Chemical) was attached on either n-Si or p-Si.

The photocatalytic activity of the n-Si/WO<sub>3</sub> and p-Si/WO<sub>3</sub> powdered photocatalysts were evaluated by the oxidative decomposition of gaseous 2-propanol irradiated with visible light (>420 nm, 1 mW/cm<sup>2</sup>) from the Xe lamp (the same above) equipped with a glass filter (Y-44, HOYA). For the analysis, 300 mg of the photocatalyst was uniformly spread over a 5.5-cm<sup>2</sup> irradiation area in a 500-ml quartz vessel. Prior to the injection of 6 μmol (~300 ppm) gaseous 2-propanol, the organic pollutants (originating from the air) absorbed on the surface of the photocatalysts were first photo-oxidized into CO<sub>2</sub> and the gas in the quartz vessel was then replaced with pure synthetic air (in the absence of CO<sub>2</sub> and organic pollutants). Following the injection of 2-propanol, the reaction vessel was kept in the dark overnight and was then subjected to visible light irradiation to start the photocatalytic reactions. The concentrations of acetone and CO<sub>2</sub> produced were monitored using a gas chromatograph (model GC-8A, Shimadzu Co., Ltd.).

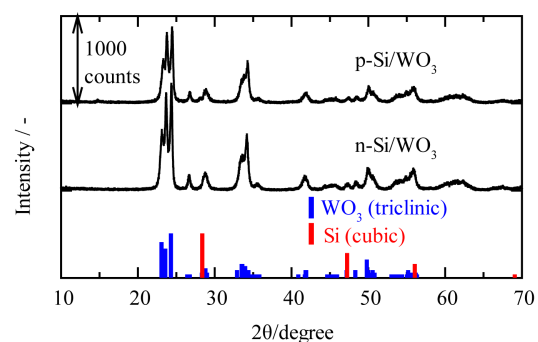
## 3. Results and Discussion

### 3.1. Characterization of the Prepared Electrodes and Powders

**Figure 1** shows XRD patterns of n-Si/WO<sub>3</sub> and p-Si/WO<sub>3</sub> electrodes. The faces of n-Si(100) and p-Si(100) were utilized to deposit WO<sub>3</sub>, so the peak at ~69° corresponding to (400) should be large, and in fact the extremely large (400) peak of n-Si was observed. However, that of p-Si was not so large, which would be attributable to the deviation from the right angle in setting p-Si/WO<sub>3</sub> to the sample holder of the XRD apparatus. The peaks originated from WO<sub>3</sub> on both n-Si and p-Si wafers were quite similar, and WO<sub>3</sub> on both wafers was confirmed to have a single phase, probably the triclinic phase. WO<sub>3</sub> in both n-Si/WO<sub>3</sub> and p-Si/WO<sub>3</sub> powders was confirmed to have a single phase of triclinic WO<sub>3</sub> in the obtained XRD patterns (**Figure 2**). As for Si, being different from **Figure 1**, all the peaks originating from cubic Si were observed although some of the peaks overlapped with those from WO<sub>3</sub>. The peak intensity of Si was not as high as that



**Figure 1.** XRD patterns of the prepared n-Si/WO<sub>3</sub> and p-Si/WO<sub>3</sub> electrodes.



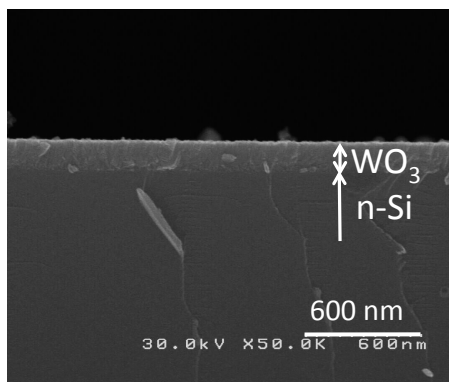
**Figure 2.** XRD patterns of the prepared n-Si/WO<sub>3</sub> and p-Si/WO<sub>3</sub> powders.

of WO<sub>3</sub> because WO<sub>3</sub> powders completely covered the surface of Si as discussed below.

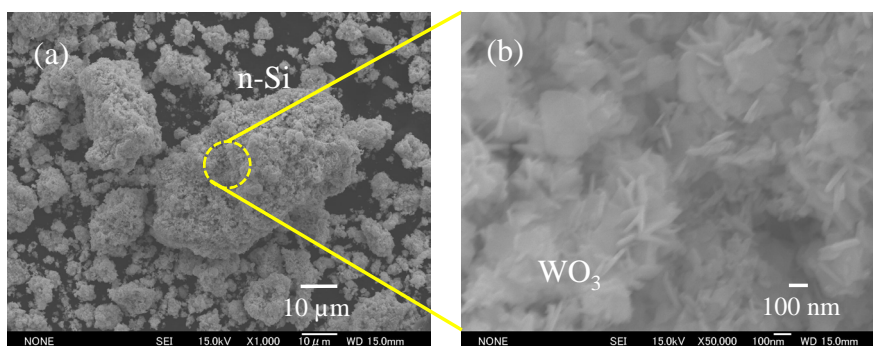
**Figure 3** shows the cross sectional SEM image of the n-Si/WO<sub>3</sub> electrode. The dense WO<sub>3</sub> film with a thickness of ~200 nm was observed, similar to p-Si/WO<sub>3</sub> (not shown here). In **Figure 4**, the SEM image of the n-Si/WO<sub>3</sub> powder is shown. The entire surface of each Si powder was covered (**Figure 4(a)**) by the needle-like WO<sub>3</sub> powders (**Figure 4(b)**), which coincided well with the results of Deki *et al.* [27]. **Figure 5** shows the UV-visible absorption spectra for commercially available WO<sub>3</sub>, prepared n-Si/WO<sub>3</sub> and p-Si/WO<sub>3</sub> powders. The absorption over a wider wavelength region (>500 nm) clearly increased for n-Si/WO<sub>3</sub> and p-Si/WO<sub>3</sub>, indicating the successful connection of WO<sub>3</sub> and n- or p-Si. In addition, the absorptions over 500 nm of n-Si/WO<sub>3</sub> and p-Si/WO<sub>3</sub> were similar within a several percent, so the amounts of WO<sub>3</sub> connected to n-Si and p-Si were presumed to be similar.

### 3.2. I-V Analysis

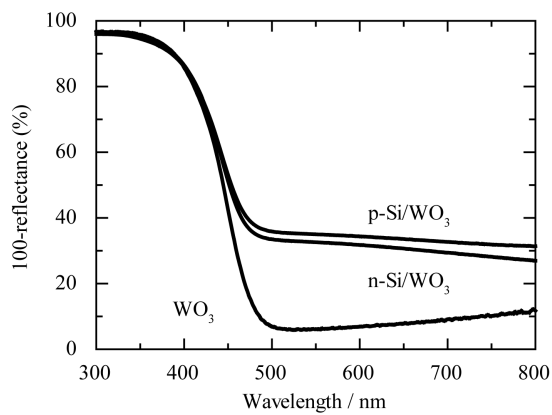
We examined the I-V analysis in the dark and under light irradiation as shown in **Figure 6**. The typical rectifying I-V (typical p-n junction) behavior in p-Si/WO<sub>3</sub> was observed, particularly, under irradiation with light. It is plausible to consider the contact of p-Si and WO<sub>3</sub> (n-type semiconductor). That is, p-Si has the more negative energy of Fermi level ( $E_f$ ) than that of WO<sub>3</sub> when we consider



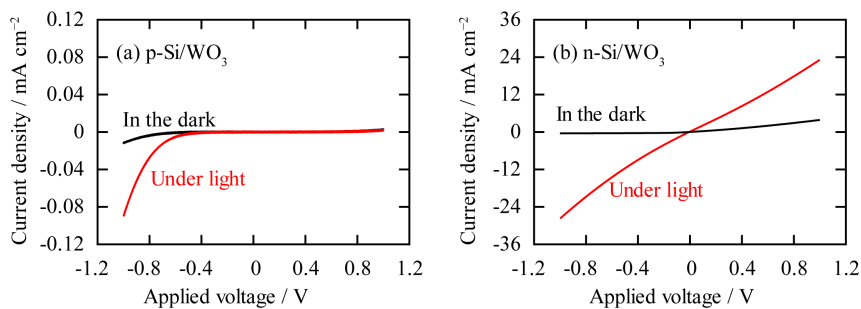
**Figure 3.** A cross sectional SEM image of the n-Si/WO<sub>3</sub> electrode.



**Figure 4.** SEM images of the n-Si/WO<sub>3</sub> powder. (b) is the enlargement of (a).



**Figure 5.** UV-visible absorption spectra of WO<sub>3</sub>, n-Si/WO<sub>3</sub> and p-Si/WO<sub>3</sub> powders.

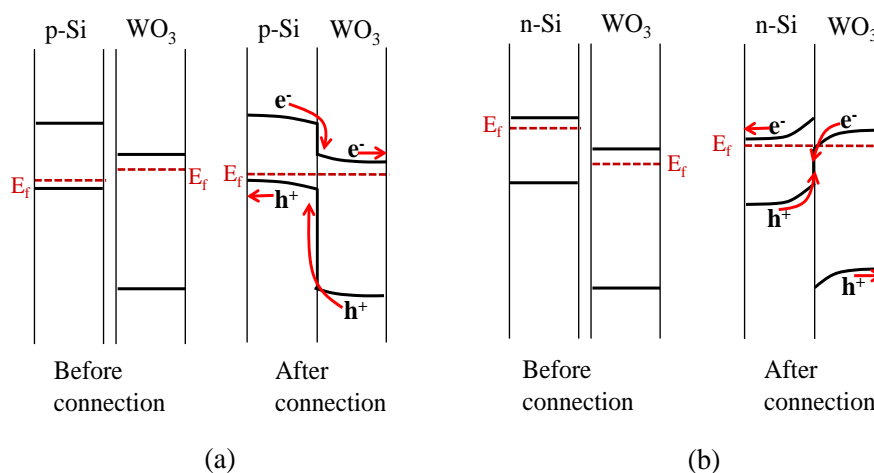


**Figure 6.** I-V characteristics of (a) p-Si/WO<sub>3</sub> and (b) n-Si/WO<sub>3</sub> heterojunctions.

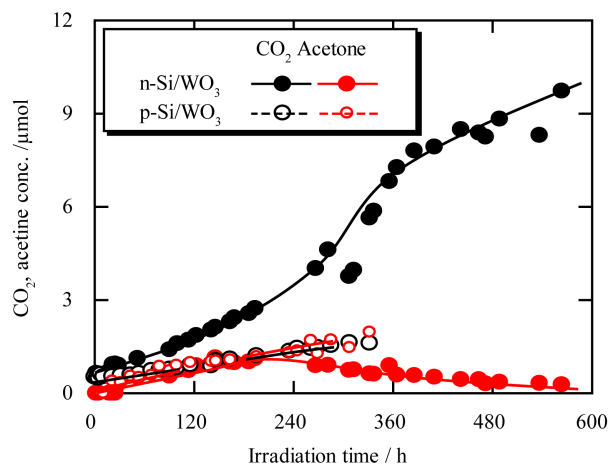
the vacuum level as zero energy (**Scheme 2(a)**). In contrast, the ohmic I-V characteristic in n-Si/WO<sub>3</sub> was observed. As shown in **Scheme 2(b)**, WO<sub>3</sub> has the more negative energy of  $E_f$  than that of n-Si, so it is probable to form the ohmic contact between n-Si and WO<sub>3</sub>. In addition, irradiated with light, the current density of n-Si/WO<sub>3</sub> was demonstrated to be much larger than that of p-Si/WO<sub>3</sub>. This means that the interparticle charge transfer, that is, charge transfer between photo generated holes in the valence band (VB) of n-Si and photoexcited electrons in the conduction band (CB) of WO<sub>3</sub> proceeded (**Scheme 2(b)**). Such an ohmic I-V characteristic was also observed in In<sub>2</sub>O<sub>3</sub>-Cu<sub>2</sub>O system with poor-photovoltaic properties [28]. However, we can anticipate that the ohmic contact will function positively in terms of photocatalytic activity as discussed below.

### 3.3. Decomposition of Gaseous 2-Propanol

We next examined the 2-propanol decomposition in the presence of the p-Si/WO<sub>3</sub> and n-Si/WO<sub>3</sub> photocatalysts under visible-light irradiation (**Figure 7**). In the presence of n-Si/WO<sub>3</sub>, the evolved acetone initially increased and then decreased. This decrease was accompanied by the increase in the CO<sub>2</sub> production. This behavior is plausible as it is known that 2-propanol decomposes into CO<sub>2</sub>, which is the final product, via acetone, the intermediate product [29]. In contrast, in the presence of p-Si/WO<sub>3</sub>, both acetone and CO<sub>2</sub> increased monotonically up to irradiation time of ~330 h. We cannot exclude the possibility that the acetone concentration would decrease after further irradiation of visible light, accompanied by the increase in the CO<sub>2</sub> evolution in the presence of p-Si/WO<sub>3</sub>. Even in such a case, it is readily apparent that the CO<sub>2</sub> generation rate was smaller compared to that of n-Si/WO<sub>3</sub> during the acetone-increasing period. In addition, the longer acetone-increasing period indicates that acetone is reluctantly decomposed to CO<sub>2</sub> in the presence of p-Si/WO<sub>3</sub>. It is generally accepted that 2-propanol is easily decomposed to acetone; however acetone is hardly decom



**Scheme 2.** Band alignments of (a) before and after connection of p-Si and WO<sub>3</sub>, and (b) that of n-Si and WO<sub>3</sub>. The charge transfer processes are also shown in the alignments after connection.



**Figure 7.** Changes in acetone and CO<sub>2</sub> concentrations as functions of time in the presence of n-Si/WO<sub>3</sub> and p-Si/WO<sub>3</sub> under visible light irradiation.

posed to CO<sub>2</sub>. Thus, in any case, we can confidently conclude that the photocatalytic oxidative activity of n-Si/WO<sub>3</sub> is much higher than that of p-Si/WO<sub>3</sub>.

It is well-known that the photo-produced holes play an important role in the generation of photocatalytic oxidative activity. In this sense, WO<sub>3</sub> is a candidate for having holes with strong oxidative power because the VB top potential of WO<sub>3</sub> is 3.1 - 3.2 V (vs. SHE, pH = 0 [30]). The potential is even more positive than that of anatase TiO<sub>2</sub> (3.04 V vs. SHE, pH = 0 [31]), which has already been widely utilized as practical applications. The photo-generated electrons also play a crucial role in the generation of the photocatalytic oxidative activity. That is, to generate the photocatalytic oxidative activity, the photo-generated electrons need to be consumed in the O<sub>2</sub> reduction because photocatalysts are usually utilized in air. If the photo-generated electrons are not consumed, the photo-produced holes will be recombined with them and eliminated. The CB bottom of TiO<sub>2</sub> lies at -0.16 V (vs. SHE, pH = 0 [31]), which is slightly more negative than that of one-electron O<sub>2</sub> reduction (O<sub>2</sub> + H<sup>+</sup> + e<sup>-</sup> → HO<sub>2</sub>, -0.046 V vs. SHE, pH = 0 [31]). Thus, O<sub>2</sub> reduction is expected to proceed in the TiO<sub>2</sub> photocatalyst. In contrast, the CB bottom of WO<sub>3</sub> lies at 0.3 - 0.5 V vs. SHE [30], so the photo-generated electrons cannot react with O<sub>2</sub> through one-electron reaction. This is the reason why WO<sub>3</sub> exhibits very low photocatalytic oxidative activity although the photo-produced holes in its VB have the strong oxidative power. To realize WO<sub>3</sub> for the highly active photocatalyst, either Pt or Cu(II) is loaded on WO<sub>3</sub> (Pt/WO<sub>3</sub>, Cu(II)/WO<sub>3</sub>) [32] [33]. Again, WO<sub>3</sub> exhibits very low photocatalytic oxidative activity because the photogenerated electrons cannot reduce O<sub>2</sub> through the one-electron reaction reduction. Pt or electron injected Cu(II) (*i.e.*, Cu(I)) acts as a catalyst for multi-electron oxygen reduction (two electron reduction: O<sub>2</sub> + 2H<sup>+</sup> + 2e<sup>-</sup> → H<sub>2</sub>O<sub>2</sub>, 0.68 V; or four-electron reduction: O<sub>2</sub> + 2H<sub>2</sub>O + 4H<sup>+</sup> + 4e<sup>-</sup> → 4H<sub>2</sub>O, 1.23 V [32]). Thus the photogenerated electrons in either Pt/WO<sub>3</sub> or Cu(II)/WO<sub>3</sub> are consumed in the multi-electron reduction



of O<sub>2</sub>.

In the n-Si/WO<sub>3</sub> system (**Scheme 2(b)**), we consider that the 2-propanol decomposition performance was derived from the photo-produced holes with the strong oxidative power that were generated in the VB of WO<sub>3</sub> contributing to 2-propanol oxidation, and the photo-excited electrons that were generated in the CB of n-Si contributing to O<sub>2</sub> reduction through one-electron reaction. Importantly, the ohmic contact between n-Si and WO<sub>3</sub> acts as electron-and-hole mediator for the transfer of electrons and holes in the CB of WO<sub>3</sub> and in the VB of n-Si, respectively. Note that, to the best of our knowledge, Si (both n-Si and p-Si) does not function as the multi-electron O<sub>2</sub> reduction catalyst. In the p-Si/WO<sub>3</sub> system (**Scheme 2(a)**), the photo-produced holes in p-Si do not have the potential to oxidize 2-propanol, considering its VB top potential. Contrastly, a portion of the photo-produced holes in WO<sub>3</sub> that exist on its surface across the Si particle can react with 2-propanol, and the photo-excited electrons reduce WO<sub>3</sub> itself to produce protonated WO<sub>3</sub> (H<sub>x</sub>WO<sub>3-y</sub>) and are eliminated. Thus, p-Si/WO<sub>3</sub> exhibited the activity for the 2-propanol decomposition, however the activity was low.

#### 4. Conclusion

We demonstrated the ohmic-contact n-Si/WO<sub>3</sub> system that could decompose 2-propanol into CO<sub>2</sub> via acetone under irradiation with visible light in comparison with the rectifying-contact p-Si/WO<sub>3</sub> system. These results point out a promising direction for producing an efficient photocatalyst by using the ohmic direct-connection with small band-gap materials to utilize the solar spectrum more efficiently.

#### References

- [1] Fujishima, A. and Honda, K. (1972) Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature*, **238**, 37-38. <https://doi.org/10.1038/238037a0>
- [2] Hoffmann, M.R., Martin, S.T., Choi, W. and Bahnemann, D.W. (1995) Environmental Applications of Semiconductor Photocatalysis. *Chemical Reviews*, **95**, 69-96. <https://doi.org/10.1021/cr00033a004>
- [3] Linsebigler, A.L., Lu, G. and Yates, Jr., T. (1995) Photocatalysis on TiO<sub>2</sub> Surfaces: Principles, Mechanisms, and Selected Results. *Chemical Reviews*, **95**, 735-758. <https://doi.org/10.1021/cr00035a013>
- [4] Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K. and Taga, Y. (2001) Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides. *Science*, **293**, 269-271. <https://doi.org/10.1126/science.1061051>
- [5] Yoneyama, H., Koizumi, M. and Tamura, H. (1979) Photolysis of Water on Illuminated Strontium Titanium Trioxide. *Bulletin of the Chemical Society of Japan*, **52**, 3449-3450. <https://doi.org/10.1246/bcsj.52.3449>
- [6] Maeda, K., Teramura, K., Lu, D., Takata, T., Saito, N., Inoue, Y. and Domen, K. (2006) Photocatalyst Releasing Hydrogen from Water. *Nature*, **440**, 295. <https://doi.org/10.1038/440295a>

- [7] Zou, Z., Ye, J., Sayama, K. and Arakawa, H. (2001) Direct Splitting of Water under Visible Light Irradiation with an Oxide Semiconductor Photocatalyst. *Nature*, **414**, 625-627. <https://doi.org/10.1038/414625a>
- [8] Maruyama, Y., Irie, H. and Hashimoto, H. (2006) Visible Light Sensitive Photocatalyst, Delafossite Structured  $\alpha$ -AgGaO<sub>2</sub>. *The Journal of Physical Chemistry B*, **110**, 23274-23278. <https://doi.org/10.1021/jp063406s>
- [9] Amao, F., Nogami, K., Abe, R. and Ohtani, B. (2008) Preparation and Characterization of Bismuth Tungstate Polycrystalline Flake-Ball Particles for Photocatalytic Reactions. *The Journal of Physical Chemistry C*, **112**, 9320-9326. <https://doi.org/10.1021/jp801861r>
- [10] Paola, A. D., Palmisano, L. and Augugliaro, V. (2000) Photocatalytic Behavior of Mixed WO<sub>3</sub>/WS<sub>2</sub> Powders. *Catalysis Today*, **58**, 141-149. [https://doi.org/10.1016/S0920-5861\(00\)00249-2](https://doi.org/10.1016/S0920-5861(00)00249-2)
- [11] Long, M., Cai, W., Cai, J., Zhou, B., Chai, X. and Wu, Y. (2006) Efficient Photocatalytic Degradation of Phenol over Co<sub>3</sub>O<sub>4</sub>/BiVO<sub>4</sub> Composite under Visible Light Irradiation. *The Journal of Physical Chemistry B*, **110**, 20211-20216. <https://doi.org/10.1021/jp063441z>
- [12] Bessekhoud, Y., Robert, D. and Weber, J.-V. (2005) Photocatalytic Activity of Cu<sub>2</sub>O/TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> and ZnMn<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> Heterojunctions. *Catalysis Today*, **101**, 315-321. <https://doi.org/10.1016/j.cattod.2005.03.038>
- [13] Gao, B., Ma, Y., Cao, Y., Yang, W. and Yao, J. (2006) Great Enhancement of Photocatalytic Activity of Nitrogen-Doped Titania by Coupling with Tungsten Oxide. *The Journal of Physical Chemistry B*, **110**, 14391-14397. <https://doi.org/10.1021/jp0624606>
- [14] Kim, H.G. and Jeong, E.D. (2006) Photocatalytic Ohmic Layered Nanocomposite for Efficient Utilization of Visible Light Photons. *Applied Physics Letters*, **89**, Article ID: 064103. <https://doi.org/10.1063/1.2266237>
- [15] Tada, H., Mitsui, T., Kiyonaga, T., Akita, T. and Tanaka, K. (2006) All-Solid-State Z-Scheme in CdS-Au-TiO<sub>2</sub> Three-Component Nanojunction System. *Nature Materials*, **5**, 782-786. <https://doi.org/10.1038/nmat1734>
- [16] Iwase, A., Ng, Y.H., Ishiguro, Y., Kudo, A. and Amal, R. (2011) Reduced Graphene Oxide as a Solid-State Electron Mediator in Z-Scheme Photocatalytic Water Splitting under Visible Light. *Journal of the American Chemical Society*, **133**, 11054-11057. <https://doi.org/10.1021/ja203296z>
- [17] Kobayashi, R., Tanigawa, S., Takashima, T., Ohtani, B. and Irie, H. (2014) Silver-Inserted Heterojunction Photocatalysts for Z-Scheme Overall Pure-Water Splitting under Visible-Light Irradiation. *The Journal of Physical Chemistry C*, **118**, 22450-22456. <https://doi.org/10.1021/jp5069973>
- [18] Kobayashi, R., Kurihara, K., Takashima, T., Ohtani, B. and Irie, H. (2016) A Silver-Inserted Zinc Rhodium Oxide and Bismuth Vanadium Oxide Heterojunction Photocatalyst for Overall Pure-Water Splitting under Red Light. *Journal of Materials Chemistry A*, **4**, 3061-3067. <https://doi.org/10.1039/C5TA08468G>
- [19] Kobayashi, R., Takashima, T., Tanigawa, S., Takeuchi, S., Ohtani, B. and Irie, H. (2016) A Heterojunction Photocatalyst Composed of Zinc Rhodium Oxide, Single Crystal-Derived Bismuth Vanadium Oxide, and Silver for Overall Pure-Water Splitting under Visible Light up to 740 nm. *Physical Chemistry Chemical Physics*, **18**, 27754-27760. <https://doi.org/10.1039/C6CP02903E>
- [20] Hara, Y., Takashima, T., Kobayashi, R., Abeyrathna, S., Ohtani, B. and Irie, H. (2017) Silver-Inserted Heterojunction Photocatalyst Consisting of Zinc Rhodium Oxide and Silver Antimony Oxide for Overall Pure-Water Splitting under Visible

- Light. *Applied Catalysis B: Environmental*, **209**, 663-668. <https://doi.org/10.1016/j.apcatb.2017.03.040>
- [21] Mayer, M.T., Du, C. and Wang, D. (2012) Hematite/Si Nanowire Dual-Absorber System for Photoelectrochemical Water Splitting at Low Applied Potentials. *Journal of the American Chemical Society*, **134**, 12406-12409. <https://doi.org/10.1021/ja3051734>
- [22] Khaselev, O., Bansal, A. and Turner, J.A. (2001) High-Efficiency Integrated Multi-junction Photovoltaic/Electrolysis Systems for Hydrogen Production. *International Journal of Hydrogen Energy*, **26**, 127-132. [https://doi.org/10.1016/S0360-3199\(00\)00039-2](https://doi.org/10.1016/S0360-3199(00)00039-2)
- [23] Reece, S.Y., Hamel, J.A., Sung, K., Jarvi, T.D., Esswein, A.J., Oijpers, J.J.H. and Nicera, D.G. (2011) Wireless Solar Water Splitting Using Silicon-Based Semiconductors and Earth-Abundant Catalysts. *Science*, **334**, 645-648. <https://doi.org/10.1126/science.1209816>
- [24] Arai, T., Yanagida, M., Konishi, Y., Iwasaki, Y., Sugihara, H. and Sayama, K. (2007) Efficient Complete Oxidation of Acetaldehyde into CO<sub>2</sub> over CuBi<sub>2</sub>O<sub>4</sub>/WO<sub>3</sub> Composite Photocatalyst under Visible and UV Light Irradiation. *Journal of Physical Chemistry Letters*, **111**, 7574-7577. <https://doi.org/10.1021/jp0725533>
- [25] Jia, Q., Iwase, A. and Kudo, A. (2014) BiVO<sub>4</sub>-Ru/SrTiO<sub>3</sub>: Rh Composite Z-Scheme Photocatalyst for Solar Water Splitting. *Chemical Science*, **5**, 1513-1519. <https://doi.org/10.1039/c3sc52810c>
- [26] Yamane, S., Kato, N., Kojima, S., Imanishi, A., Ogaea, S., Yoshida, N., Nonomura, S. and Nakato, Y. (2009) Efficient Solar Water Splitting with a Composite “*n*-Si/*p*-CuI /*n*-*i*-*p* a-Si/*n*-*p* GaP/RuO<sub>2</sub>” Semiconductor Electrode. *The Journal of Physical Chemistry C*, **113**, 14575-14581. <https://doi.org/10.1021/jp904297v>
- [27] Deki, S., Beleke, A.B., Kotani, Y. and Mizuhata, M. (2010) Synthesis of Tungsten Oxide Thin Film by Liquid Phase Deposition. *Materials Chemistry and Physics*, **123**, 614-619. <https://doi.org/10.1016/j.matchemphys.2010.05.024>
- [28] Tanaka, H., Shimakawa, T., Miyata, T., Sato, H. and Minami, T. (2004) Electrical and Optical Properties of TCO-Cu<sub>2</sub>O Heterojunction Devices. *Thin Solid Films*, **469-470**, 80-85. <https://doi.org/10.1016/j.tsf.2004.06.180>
- [29] Irie, H., Watanabe, Y. and Hashimoto, K. (2003) Nitrogen-Concentration Dependence on Photocatalytic Activity of TiO<sub>2-x</sub>N<sub>x</sub> Powders. *The Journal of Physical Chemistry B*, **107**, 5483-5486. <https://doi.org/10.1021/jp030133h>
- [30] Bamwenda, G.R., Sayama, K. and Arakawa, H. (1999) The Effect of Selected Reaction Parameters on the Photoproduction of Oxygen and Hydrogen from a WO<sub>3</sub>-Fe<sup>2+</sup>-Fe<sup>3+</sup> Aqueous Suspension. *Journal of Photochemistry and Photobiology A: Chemistry*, **122**, 175-183. [https://doi.org/10.1016/S1010-6030\(99\)00026-X](https://doi.org/10.1016/S1010-6030(99)00026-X)
- [31] Torimoto, T., Nakamura, N., Ikeda, S. and Ohtani, B. (2002) Discrimination of the Active Crystalline Phases in Anatase-Rutile Mixed Titanium(IV) Oxide Photocatalysts through Action Spectrum Analyses. *Physical Chemistry Chemical Physics*, **4**, 5910-5914. <https://doi.org/10.1039/B207448F>
- [32] Irie, H., Miura, S., Kamiya, K. and Hashimoto, K. (2008) Efficient Visible Light-Sensitive Photocatalysts: Grafting Cu(II) Ions onto TiO<sub>2</sub> and WO<sub>3</sub> Photocatalysts. *Chemical Physics Letters*, **457**, 202-205. <https://doi.org/10.1016/j.cplett.2008.04.006>
- [33] Abe, R., Takami, H., Murakami, N. and Ohtani, B. (2008) Pristine Simple Oxides as Visible Light Driven Photocatalysts: Highly Efficient Decomposition of Organic Compounds over Platinum-Loaded Tungsten Oxide. *Journal of the American Chemical Society*, **130**, 7780-7781. <https://doi.org/10.1021/ja800835q>



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