Visible-light Energy Storage by Ti^{3+} in TiO_2/Cu_2O Bilayer Film

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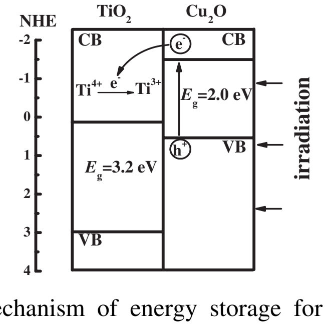
Ti^{3+} in TiO_2/Cu_2O bilayer film is demonstrated to show energy storage ability. UV–vis absorption spectrum and XPS characterization are carried out to confirm that there are Ti^{3+} ions formed and that more than 74% Ti^{4+} ions are reduced to Ti^{3+} ions after visible-light irradiation. More than $10^{-2}\,C\,cm^{-2}$ electrons are detected in the bilayer film as determined by H_2 evolution. This study provides a new way to harvest and store excess energy from solar light in the daytime.

Photoresponsive semiconductors are promising materials for the conversion of light energy to chemical or electrical energy, but they are unable to store energy and only function under light illumination. As a solution to this limitation, a few research groups in Japan have developed several semiconductor composite systems for energy storage, such as TiO_2/WO_3,[1] TiO_2/MoO_3,[2] and $TiO_2/Ni(OH)_2$.[3] The energy can be stored either in reduced WO_3, MoO_3 or in oxidized $Ni(OH)_2$ under UV-light irradiation. The visible-light responsive Au–TiO_2 photocatalyst was also demonstrated to store energy in a reductive energy storage material, such as WO_3 or MoO_3.[4] Recently, Yasomanee et al.[5] have reported that TiO_2/Cu_2O composite film led to the continuous generation of H_2 from water splitting in the dark after UV–vis light irradiation stopped. This inspired us to believe that TiO_2/Cu_2O could be a good energy storage material.

In this investigation, Ti^{3+} in TiO_2/Cu_2O bilayer film is demonstrated to store energy under visible light. It is well known that the band gap of TiO_2 is about 3.2 eV and that the conduction band of TiO_2 is about -0.2 eV.[6] Cu_2O is a semiconductor with one of the highest conduction bands. The band gap of Cu_2O is about 2.0 eV, and the potential of its conduction band is -1.4 eV.[7]

As shown in Scheme 1, the photogenerated electrons from the conduction band of Cu_2O were captured by Ti^{4+} ions in TiO_2 and Ti^{4+} ions were further reduced to Ti^{3+} ions. The Ti^{3+} ions have a long lifetime and bear the photogenerated electrons as a form of energy. The electron-transfer process is shown in eqs 1 and 2.



Scheme 1. Mechanism of energy storage for Ti^{3+} in TiO_2/Cu_2O bilayer film.

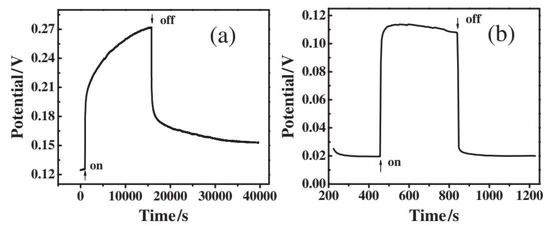


Figure 1. Photovoltage measured as a function of time for $TiO_2/Cu_2O/FTO$ (a) and Cu_2O/FTO (b) electrodes.

$$Cu_2O + h\nu\ (\lambda > 400\,nm) \longrightarrow {h_{vb}}^{+} + {e_{cb}}^{-} \quad (1)$$

$${e_{cb}}^{-} + Ti^{4+} \longrightarrow Ti^{3+} \quad (2)$$

The preparation of TiO_2/Cu_2O bilayer film on fluorine-doped SnO_2 (FTO) conducting glass was conducted according to refs 8 and 9. The XRD patterns and SEM images (cross section for the bilayer film) of TiO_2 film, Cu_2O film, and TiO_2/Cu_2O bilayer film are shown in Figures S1 and S2 in Supporting Information, respectively.[10]

Figure 1 shows the photovoltage measured as a function of time under visible-light irradiation for $TiO_2/Cu_2O/FTO$ and Cu_2O/FTO electrodes. The figure was measured by using a PARSTAT 2273 electrochemical station (Princeton Applied Research) in 1.0×10^{-3} M air-saturated aqueous Na_2SO_4 solution with a three-electrode system ($TiO_2/Cu_2O/FTO$ and Cu_2O/FTO electrode as working electrodes, platinum wire, and saturated calomel electrode as counter and reference electrode, respectively). The light source was a halogen lamp (300 W) with an optical filter ($\lambda \leq 420$ nm).

It can be seen that the potential for both of the two electrodes shifted positively under the same irradiation. The positive potential shift may be due to holes generated on Cu_2O, which is one of p-type semiconductors. As TiO_2 has no response to visible light, the photopotential of TiO_2/Cu_2O bilayer film almost results from Cu_2O. This result is similar to the report in ref 5. The net positive photovoltage comes from the interfacial potential difference of electrostatic double layer formed between the holes on the surface of Cu_2O and the ${SO_4}^{2-}$ layer in electrolyte.

It can also be seen that the potential for the Cu_2O/FTO electrode jumped to the maximum instantly and remain unchanged. It indicates that the generation and recombination of e^-–h^+ pairs in Cu_2O established a dynamic equilibrium. However, it took the $TiO_2/Cu_2O/FTO$ electrode about 4 h to reach its maximum. It indicates that there was a process for the accumulation of holes in $TiO_2/Cu_2O/FTO$ electrode. As we know, both photogenerated electrons and holes were produced in Cu_2O under the irradiation. So, there was a process for the accumulation of electrons in $TiO_2/Cu_2O/FTO$ electrode, too. The photogenerated electrons in Cu_2O have much energy due to the absorption of visible light. Thus, when these electrons are transferred to the conduction band of TiO_2 and trapped by Ti^{4+}, they are seen as Ti^{3+} and are stored as a form of energy in the bilayer film. The holes still stay in Cu_2O. The longer the irradiation time, the more electrons were generated by Cu_2O and injected into TiO_2 and thereafter the more energy stored. This process did not stop until the potential of the TiO_2/Cu_2O electrode reached the maximum.

After the irradiation was removed, the potential for both of these electrodes shifted negatively. The potential for Cu_2O/FTO electrode dropped instantly to the minimum, the original potential before the irradiation. It indicates that the photogenerated electrons and holes are recombined completely. However, it took TiO_2/Cu_2O/FTO electrode a long time (above 7 h) to reach its minimum, which was still 20 mV higher than the original potential before the irradiation. It indicates that there are still holes in TiO_2/Cu_2O/FTO electrode and that the photogenerated electrons and holes may not be recombined completely because a little amount of electrons are still trapped by Ti^{3+}.

Additionally, under the same irradiation, the potential increment for TiO_2/Cu_2O/FTO electrode was 140 mV, much higher than 80 mV for Cu_2O/FTO electrode. It demonstrates that much more photogenerated holes and electrons were present in the bilayer film. The better photoelectric properties of the bilayer film than that of Cu_2O film suggests that the bilayer films have improved abilities for charge separation and charge carrier lifetime and can store energy.

To confirm the existence of Ti^{3+} supporting the above mechanism, XPS measurement was carried out to obtain surface information of the bilayer film to prove the presence of Ti^{3+}. The analytic result is shown in Figure S3[10] and in accordance with the reported data.[11]

UV–vis diffuse reflectance measurement was further carried out to identify the conversion of Ti^{4+} to Ti^{3+} in the bilayer film after the irradiation. The data are shown in Figure 2. The absorbance of the bilayer film became weaker in the short wavelength range ($200 \leq \lambda \leq 350$ nm) while becoming stronger in the long wavelength range ($350 < \lambda \leq 800$ nm) after the irradiation. It is confirmed based on the above data that Ti^{3+} ions were produced in the bilayer film after the irradiation. Because Ti^{4+} has no response to visible light while Ti^{3+} does,[12] the presence of Ti^{3+} ions leads to the weaker absorbance of bilayer film in the short wavelength range while stronger in the long wavelength range. It was found that the transparent TiO_2 film turned blue under the irradiation as shown in Figure S4.[10] The phenomenon is similar to the J. P. Yasomanee' report[5] and also demonstrates the presence of Ti^{3+}.

As for the application of the energy stored in Ti^{3+}, a preliminary attempt was taken to reduce H^+ for the formation of H_2 from water splitting. A home-made Pyrex glass reactor and gas chromatograph instrument (GC-2014, SHIMADZU) were used for photocatalytic H_2 evolution and gas analysis, respectively. Figure S5[10] shows the curve of H_2 yield as a function of time, it can be found that H_2 evolution was still noticeable after the irradiation stopped until the third hour. This result is also similar to the J. P. Yasomanee' report.[5] We believe that the electrons trapped in Ti^{3+} ions as stored energy lead to evolve H_2 from H_2O in the dark. According to Figure S5,[10] we can see that

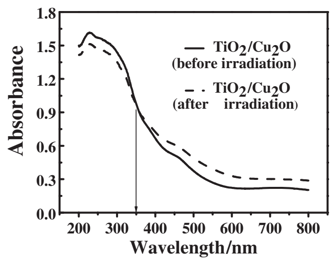


Figure 2. UV–vis diffuse reflectance spectra of TiO_2/Cu_2O bilayer film before (solid line) and after irradiation (dashed line).

more than 10^{-2} C cm^{-2} electrons were stored in TiO_2/Cu_2O film under 4 h visible-light irradiation.

In summary, Ti^{3+} in TiO_2/Cu_2O bilayer film has energy storage ability under visible-light irradiation. More than 74% Ti^{4+} ions are reduced to Ti^{3+} ions after 6 h visible-light irradiation. At least 10^{-2} C cm^{-2} electrons are detected in the bilayer film by H_2 evolution. The system may be potentially applied to portable devices charged at daytime and used at night without extra storage cells.

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