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Improvement in the photoelectrochemical responses of PCBM/TiO_2 electrode by electron irradiation

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Abstract

The photoelectrochemical (PEC) responses of electron-irradiated [6,6]-phenyl-C61-butyric acid methyl ester (PCBM)/TiO_2 electrodes were evaluated in a PEC cell. By coating PCBM on TiO_2 nanoparticle film, the light absorption of PCBM/TiO_2 electrode has expanded to the visible light region and improved the PEC responses compared to bare TiO_2 electrode. The PEC responses were further improved by irradiating an electron beam on PCBM/TiO_2 electrodes. Compared to non-irradiated PCBM/TiO_2 electrodes, electron irradiation increased the photocurrent density and the open-circuit potential of PEC cells by approximately 90% and approximately 36%, respectively at an optimum electron irradiation condition. The PEC responses are carefully evaluated correlating with the optical and electronic properties of electron-irradiated PCBM/TiO_2 electrodes.

Keywords: photoelectrochemical cell, TiO_2, electron irradiation, PCBM, band-edge tuning

Introduction

TiO_2 has been widely used for photocatalysts because of its good chemical- and photostabilities to convert photon energy to electrical and chemical energies [1]. However, due to its wide bandgap, the light absorption is limited only to the ultraviolet (UV) region of the solar spectrum. Hence, sensitizing TiO_2 with small bandgap semiconductors, such as quantum dots or organic dyes, has been extensively studied to harvest more photons in the visible light region of solar spectrum for the applications to quantum dot-sensitized solar cells [2-4], dye-sensitized solar cells [5-7], and photoelectrochemical (PEC) cells [8-10].

Along with this current research trends, combining TiO_2 with carbonaceous nanomaterials has attracted much interest, and studies on these materials are increasing exponentially these days [11]. For instance, high performance photocatalysts such as carbon nanotube-TiO_2 [12-14], fullerene-TiO_2 (C_{60}-TiO_2) [15-17], and graphene-TiO_2 [18,19] composites have been introduced by several groups and have shown enhanced photocatalytic activities. Notably, C_{60} has shown interesting effects when combined with TiO_2: facilitating the separation of photo-generated charge carriers from TiO_2 to C_{60} [15,16] or sensitizing TiO_2 to absorb visible light [17]. However, the band-edge position of C_{60} is unfavorable for a sensitizer of TiO_2 because the lowest unoccupied molecular orbital (LUMO) level of C_{60} is lower than the conduction band of TiO_2 [17]. From the viewpoint of energy levels, [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is a better candidate than C_{60} for the sensitization of TiO_2. We expect that the photoexcited electrons of PCBM can be transferred to TiO_2 more efficiently because the LUMO level of PCBM is slightly higher than the conduction band of TiO_2 [20]. In our previous study, we have found that the band-edge positions as well as the bandgap of PCBM can be tuned by electron irradiation at different fluences [21]. We believe that electron irradiation technique can be an alternative and unique method to modify the molecular structure and tune the bandgap [22,23] compared to the conventional methods such as adjusting the particle size of quantum dots [24,25] or modifying the molecular structure of the dyes [26] for larger light absorption. In addition to the bandgap, the band-edge positions can also be tuned by electron irradiation compared to the

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conventional methods such as ionic adsorption for specific quantum dots [27] or by varying the conjugation linkers in organic dyes [28].

Based on our previous findings, we present here a novel approach to improve the PEC performance of PCBM/TiO_2 electrodes using electron beam irradiation. The photocurrent density and open-circuit potential of PCBM/TiO_2 were respectively improved by 90% and 36% by electron irradiation. The effects of the electron irradiation on the PEC performances of PCBM/TiO_2 were systematically analyzed in this study.

Methods

Figure 1 shows the schematic representation of the preparation of PCBM/TiO_2 electrode and subsequent electron irradiation. The as-received TiO_2 nanoparticle paste (DSL 18NR-T, Dyesol Industries Pty Ltd., Queanbeyan, New South Wales, Australia) was deposited on a fluorine-doped tin oxide (FTO) glass substrate (8 Ωm^{-2}, Dyesol) by a doctor blade technique. Before the deposition of TiO_2 paste, FTO glass substrates were cut by 1.0 × 2.5 cm^2 in dimension and were sonicated successively in acetone, isopropanol, ethanol, and deionized water for thorough cleaning and dried in N_2 gas stream. After the deposition of TiO_2 paste, subsequent annealing process was performed at 450°C for 30 min with a temperature increase rate of 1°C min^{-1}. After the annealing, TiO_2 nanoparticle film was formed. The as-prepared TiO_2 electrodes were immersed vertically in a chlorobenzene solution containing 1.5 mM PCBM for 5 h while stirring. PCBM solution was prepared by dissolving PCBM (99.5% purity, Nano-C, Inc., Westwood, MA, USA) powder into chlorobenzene (≥99.5% purity, Sigma-Aldrich, St. Luois, MO, USA) solvent. After the immersion, the electrodes were washed in pure chlorobenzene several times and dried at ambient condition. As a result, PCBM/TiO_2 electrodes, where a thin layer of PCBM was coated on the TiO_2 nanoparticle electrodes, were prepared. Coating process of PCBM was carried out in darkness. The irradiation of an electron beam on PCBM/TiO_2 electrodes was carried out at room temperature and in vacuum lower than 2 × 10^{-5} Torr. An electron beam was generated from a thermionic electron gun with electron energy of 50 keV, and current density of the electron beam was 1.6 μA cm^{-2}. The electron fluence was varied by adjusting the irradiation time. PCBM/TiO_2 electrodes were irradiated by 1, 2, and 4 h which correspond to electron fluence of 3.6 × 10^{16}, 7.2 × 10^{16}, and 1.44 × 10^{17} cm^{-2}, respectively. Diffuse reflectance UV-visible (VIS) spectra of electron-irradiated PCBM/TiO_2 powders were measured on a spectrometer (S-4100, SCINCO CO., LTD., Seoul, South Korea) by scratching the nanoparticle film off the FTO glass substrate.

After electron irradiation of PCBM/TiO_2 electrodes, a custom-made PEC cell was constructed to measure the PEC responses of electron-irradiated PCBM/TiO_2 electrodes, which act as photo-anodes of PEC cells. The PEC cell has a three-electrode configuration comprising a photo-anode, a Pt wire as a cathode, and a saturated calomel electrode (SCE) (0.242 V vs. NHE, BAS Inc., West Lafayette, IN, USA) as a reference electrode. An aqueous solution of 1 M NaOH (Junsei Chemical Co., Ltd., Chuo-ku, Tokyo, Japan) was used as a supporting electrolyte after 30 min purging with N_2 gas. The PEC response of the electrodes was recorded on a potentiostat (Model SP-50, BioLogic, Claix, France) by sweeping the potential from -1.2 to 0.5 V (vs. SCE) at a sweep rate of 100 mV s^{-1}. The photo-anodes were illuminated with a solar simulator (Model LS-150, Abet Technologies, Inc., Milford, CT, USA) equipped with AM 1.5 filter. The illumination power was estimated as 80 mW cm^{-2} at the photo-anode surface by a digital photometer (ILT1400-A, International Light Technologies, Inc., Peabody, MA, USA).

Results and discussion

Figure 1 displays the schematic representation for the preparation of the PCBM/TiO_2 photo-anodes of PEC cells. TiO_2 nanoparticles (NPs) were firstly deposited to

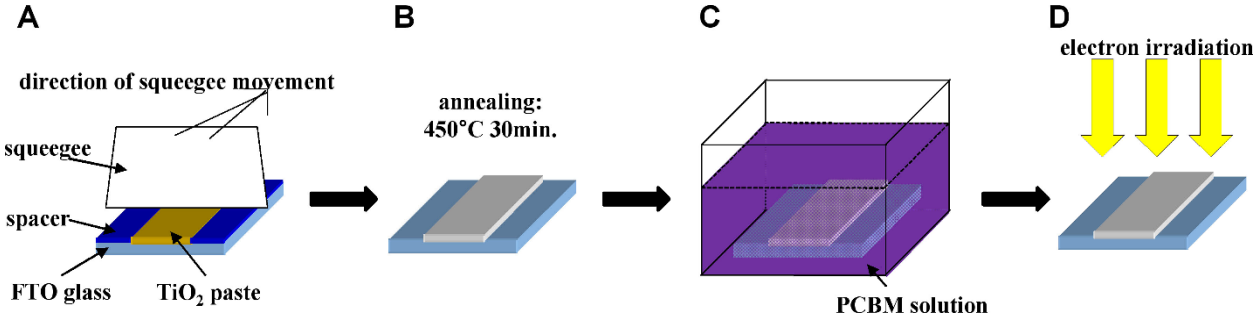

Figure 1 Schematic representation of the preparation of PCBM/TiO_2 electrode and subsequent electron irradiation. (**A**) Deposition of TiO_2 paste by doctor blade technique. (**B**) Formation of TiO_2 nanoparticle film by annealing the as-deposited TiO_2 paste at 450°C for 30 min. (**C**) Fabrication of PCBM/TiO_2 electrode by immersing TiO_2 electrode in 1.5 mM PCBM solution for 5 h. (**D**) Electron irradiation on PCBM/TiO_2 electrode at different fluences.

form a film on a FTO glass substrate. A uniform TiO_2 NP film was formed by annealing the as-deposited TiO_2 paste at 450°C for 30 min. The TiO_2 NP film was submerged in a PCBM solution for 5 h, and consequently, the TiO_2 NP film was coated with PCBM. Subsequently, the PCBM/TiO_2 electrodes were irradiated with an electron beam. The energy of the electron beam was 50 keV, and the electron fluence was changed by controlling the irradiation time. These electron-irradiated PCBM/TiO_2 films on FTO glass substrates were used as photo-anodes of PEC cells for water splitting. Figure 2 shows the field emission scanning electron microscopy (FESEM) images of the fabricated PCBM/TiO_2 film. TiO_2 NPs with the diameter of approximately 20 nm were deposited on a FTO glass substrate (see details in the 'Methods' section). As shown in the FESEM image, the TiO_2 NPs were well interconnected with one another, forming a rigid film that is strongly attached to the FTO glass substrate. The thickness of the TiO_2 NP film was approximately 16.5 μm.

We observed that transparent TiO_2 NP film became slightly yellowish after the PCBM coating. The UV-VIS absorption spectra shown in Figure 3 more clearly characterize the optical properties of the TiO_2 NP films. When PCBM was coated on TiO_2, visible light absorption of TiO_2 in the wavelength range of 390 to 800 nm was increased, while absorption of UV in the range of 300 to 360 nm was decreased. In addition, when PCBM/TiO_2 was irradiated with an electron beam, the absorbance in both UV and visible light region decreased gradually as the electron fluence increased. In our previous work, we reported that the bandgap of electron-irradiated PCBM increased as the electron fluence was increased. The modification of the bandgap was attributed to the change in the molecular structure of PCBM by electron irradiation. From these facts, we could conclude that the effective bandgap of electron-irradiated PCBM/TiO_2 also increased as the electron fluence increased (Figure 4).

In order to investigate the band-tuning effect caused by the electron irradiation, we tried to characterize the PEC cell device performances using the electron-irradiated PCBM/TiO_2 electrodes. The measurement results of the PEC responses of bare TiO_2, PCBM/TiO_2, and electron-irradiated PCBM/TiO_2 electrodes are listed on Table 1, and the typical current density-potential curves of the electrodes are shown in Figure 5. The saturated current density at 0 V vs. saturated calomel electrode under dark conditions of all the electrodes was less than 15 μA cm^{-2}. Under illumination of simulated solar light, bare TiO_2 nanoparticle electrode shows saturated photocurrent density (J_{ph}) of 176 μA cm^{-2} and open-circuit potential (E_{ocp}) of -0.85 V vs. SCE. After coating PCBM on TiO_2 nanoparticles, the PEC performance was improved: J_{ph} and E_{ocp} of PCBM/TiO_2 electrode increased to 234 μA cm^{-2} and -1.05 V vs. SCE, respectively. The improvement in J_{ph} and E_{ocp} is attributed to the increment of visible light absorption of PCBM compared to that of TiO_2. After electron irradiation of PCBM/TiO_2 electrode at electron fluence of 3.6×10^{16} cm^{-2}, J_{ph} and E_{ocp} increased from 234 to 306 μA cm^{-2} and -1.05 to -1.16 V vs. SCE, respectively. The PEC performance of PCBM/TiO_2 electrode was further improved through electron irradiation of increased electron fluence. Both J_{ph} and E_{ocp} of electron-irradiated PCBM/TiO_2 were increased with increasing the electron fluence. J_{ph} increased to 333 μA cm^{-2}, and E_{ocp} increased to -1.16 V vs. SCE at the electron fluence of 7.2×10^{16} cm^{-2}.

The fact that the PEC performance of PCBM/TiO_2 electrode was improved by electron fluence is interesting because electron irradiation increases the bandgap of

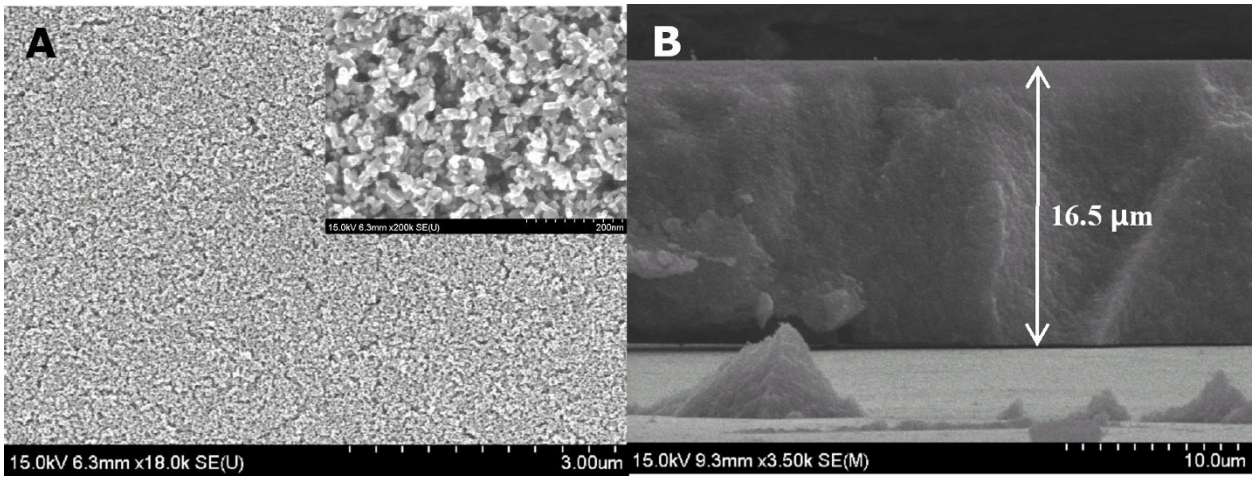

Figure 2 FESEM images. (**A**) Top view and higher magnification (inset) and (**B**) cross-sectional view of TiO_2 nanoparticle film.

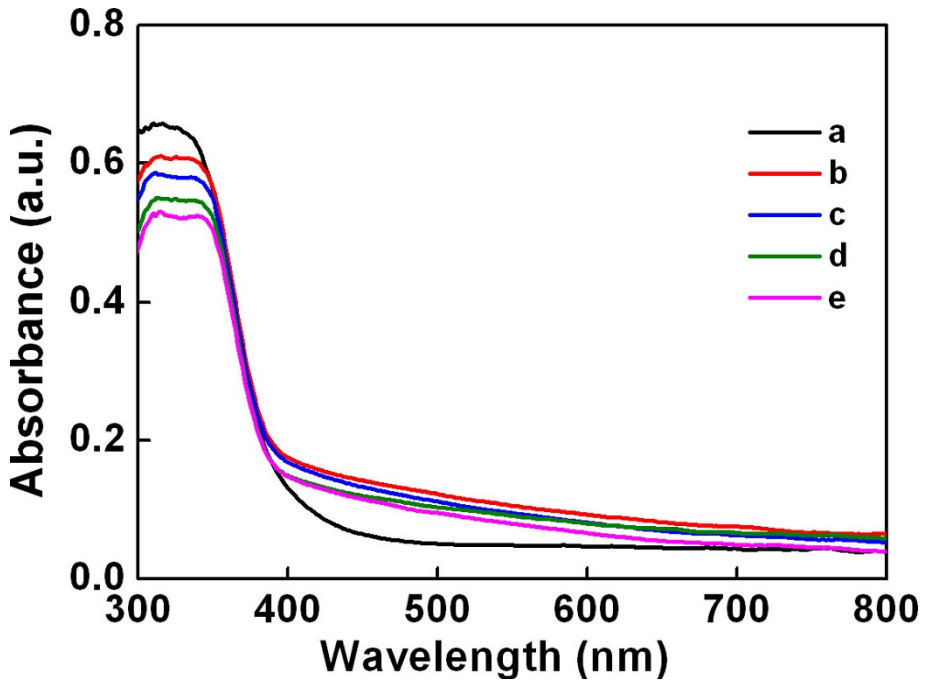

Figure 3 Diffuse reflectance UV-VIS spectra. (a) TiO_2 and (b) PCBM/TiO_2. PCBM/TiO_2 irradiated at (c) 3.6×10^{16}, (d) 7.2×10^{16}, and (e) 1.44×10^{17} cm^{-2}.

PCBM and accordingly decreases the light absorption. As verified in our previous work, the LUMO level of PCBM shifts upward to the vacuum energy level as electron fluence increases. Since the bandgap of PCBM is much lower than that of TiO_2, electron-hole pairs produced in PCBM can contribute to the increase in the photo-current of TiO_2. However, the energy difference between the LUMO energy level of PCBM and the

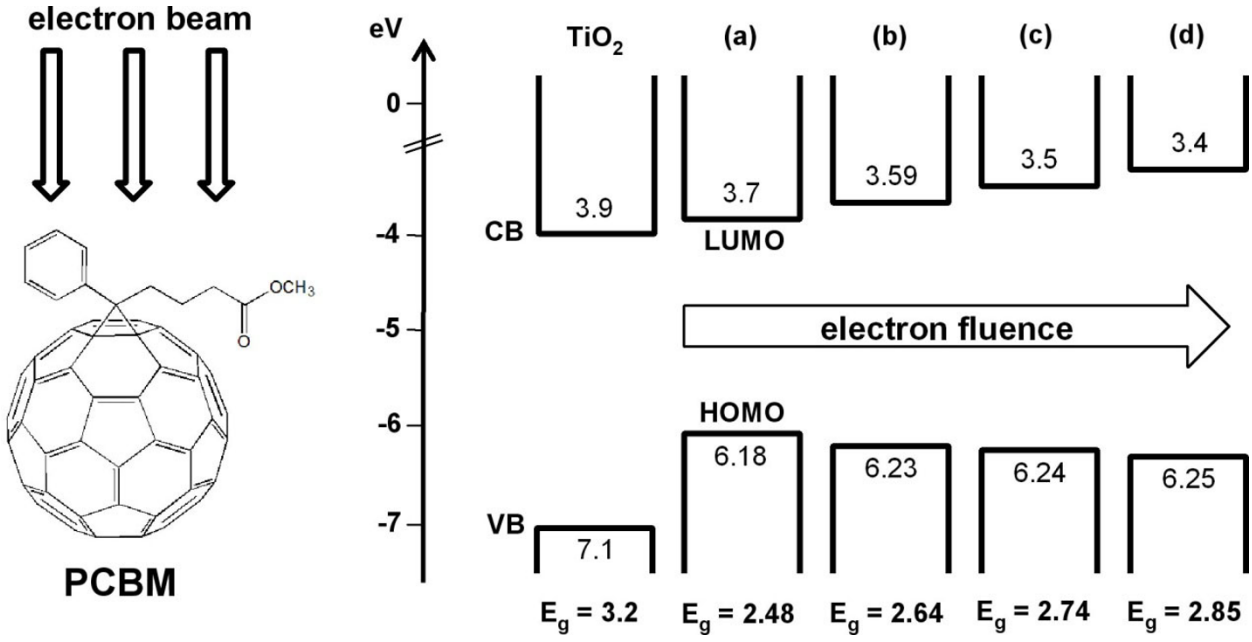

Figure 4 Band structure of PCBM after electron beam irradiation of different fluences. (a) Non-irradiated PCBM. (b) Irradiated PCBM at 3.6×10^{16}, (c) 7.2×10^{16}, and (d) 1.44×10^{17} cm^{-2}.

Table 1 Photoelectrochemical performance of various electrodes investigated

	J_{ph} (μA cm^{-2})	E_{ocp} (V) vs. SCE
TiO_2	176	-0.85
PCBM/TiO_2	234	-1.05
PCBM/TiO_2 (3.6×10^{16} cm^{-2})	306	-1.16
PCBM/TiO_2 (7.2×10^{16} cm^{-2})	333	-1.16
PCBM/TiO_2 (1.44×10^{17} cm^{-2})	285	-1.10

conduction band edge minimum of pure TiO_2 is 0.2 eV, which might not be high enough for efficient electron transfer from PCBM to TiO_2 [29]. Since LUMO energy level of PCBM is up-shifted by electron irradiation, electron-irradiated PCBM provides higher driving force of electron injection from PCBM to TiO_2 [25]. This can explain why J_{ph} of electron-irradiated PCBM/TiO_2 electrodes was increased by increasing the electron fluence. Moreover, the increase in the energy difference between the LUMO energy level of electron-irradiated PCBM and the conduction band edge minimum of TiO_2 provides efficient charge separation of the photo-excited electron-hole pairs, thereby improving E_{ocp} [30].

However, when the electron fluence was further increased to 1.44×10^{17} cm^{-2}, the PEC performance of electron-irradiated PCBM/TiO_2 became worse. As shown in Figure 4, the LUMO energy level of PCBM was constantly up-shifted toward the vacuum energy level as the electron fluence was increased. The up-shift in the LUMO energy level of electron-irradiated PCBM increases the driving force of electron injection from PCBM to TiO_2. With the up-shift in the LUMO energy level, the bandgap of the electron-irradiated PCBM also increases with increasing the electron fluence. The increase in the bandgap reduces the light absorption of PCBM and consequently deteriorates the PEC performance. Therefore, electron irradiation induces the two contradictory effects on the PEC performance of the electron-irradiated PCBM/TiO_2, and this suggests that there is an optimum electron fluence at which the PEC performance is maximized. In our experiments, J_{ph} increased by approximately 90% and E_{ocp} increased by approximately 36% compared to bare TiO_2 at an optimum electron fluence at 7.2×10^{16} cm^{-2}.

Conclusions

Using the fact that the electronic band structure of PCBM can be modified by electron irradiation, PCBM/TiO_2 electrodes were fabricated and tested in a PEC cell. We observed that electron irradiation on PCBM/TiO_2 electrodes led to an increase in J_{ph} by approximately 90% and E_{ocp} by approximately 36% at an optimum electron irradiation condition. These results show that electron irradiation approach can be a good tool to

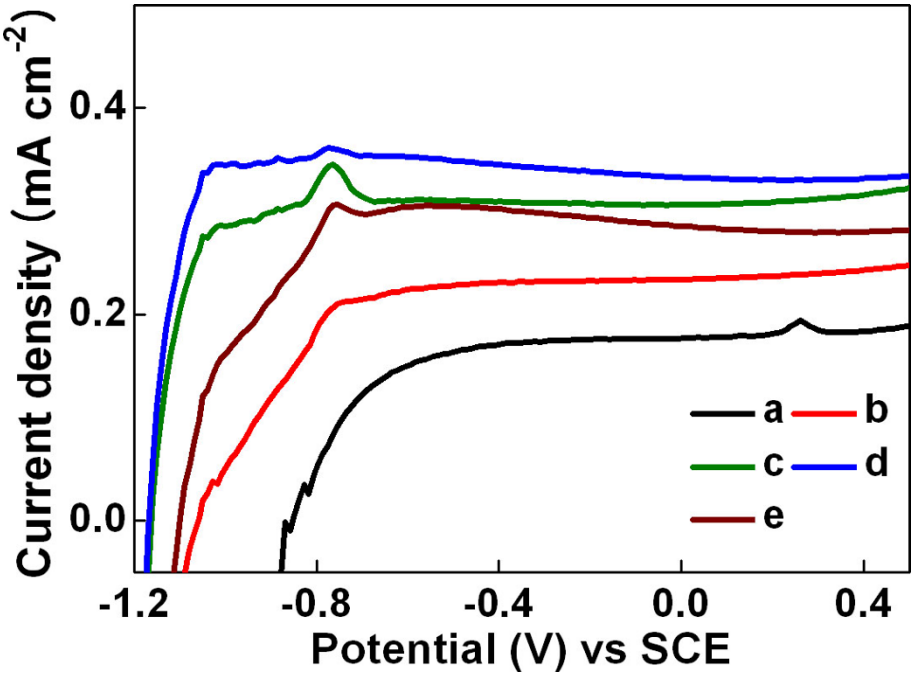

Figure 5 Current density-potential curves of TiO_2 and PCBM/TiO_2 electrodes irradiated at different electron fluences under illumination. (a) Non-irradiated TiO_2 and (b) PCBM/TiO_2. PCBM/TiO_2 irradiated at (c) 3.6×10^{16}, (d) 7.2×10^{16}, and (e) 1.44×10^{17} cm^{-2}.

tune the bandgap and the band-edge positions of PCBM and provide an evidence that the approach is useful for PEC device application. We believe that the electron irradiation strategy can also control the electronic band structures of other organic semiconducting materials, and thus, this strategy can improve the performances of PEC and photocatalytic devices.

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Authors' contributions
The work was carried out by the collaboration between all authors. SOC initiated the idea of electron irradiation on PCBM/TiO_2 electrodes. SHY performed the electron irradiation experiments. SHY and GA performed the construction of PEC cell and measurement of PEC responses of electron-irradiated PCBM/TiO_2 electrodes. JMK and SHH carried out the diffuse reflectance UV-VIS spectroscopy measurements of electron-irradiated PCBM/TiO_2. SOC and SHY analyzed the data and suggested the mechanism of improvement of electron-irradiated PCBM/TiO_2 electrodes. All authors read and approved the final manuscript.

Competing interests
The authors declare that they have no competing interests.

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References

1. Hoffmann MR, Martin ST, Choi W, Bahnemann DW: **Environmental applications of semiconductor photocatalysis.** *Chem Rev* 1995, **95**:69.
2. Lee YL, Huang BM, Chien HT: **Highly efficient CdSe-sensitized TiO_2 photoelectrode for quantum-dot-sensitized solar cell applications.** *Chem Mater* 2009, **20**:6903.
3. Xie Y, Ali G, Yoo SH, Cho SO: **Sonication-assisted synthesis of CdS quantum-dot-sensitized TiO_2 nanotube arrays with enhanced photoelectrochemical and photocatalytic activity.** *ACS Appl Mater Interfaces* 2010, **2**:2910.
4. Chen C, Ali G, Yoo SH, Kum JM, Cho SO: **Improved conversion efficiency of CdS quantum dot-sensitized TiO_2 nanotube-arrays using $CuInS_2$ as a co-sensitizer and an energy barrier layer.** *J Mater Chem* 2011, **21**:16430.
5. O'regan B, Grätzel M: **A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films.** *Nature* 1991, **353**:737.
6. Bach J, Lupo D, Comte P, Moser JE, Weissörtel F, Salbeck J, Spreitzer H, Grätzel M: **Solid-state dye-sensitized mesoporous TiO_2 solar cells with high photon-to-electron conversion efficiencies.** *Nature* 1998, **395**:583.
7. Law M, Greene LE, Johnson JC, Saykally R, Yang P: **Nanowire dye-sensitized solar cells.** *Nature Mater* 2005, **4**:455.
8. Hodes G: **A thin-film polycrystalline photoelectrochemical cell with 8% solar conversion efficiency.** *Nature* 1980, **285**:29.
9. Heller A: **Conversion of sunlight into electrical power and photoassisted electrolysis of water in photoelectrochemical cells.** *Acc Chem Res* 1981, **14**:154.
10. Grätzel M: **Photoelectrochemical cells.** *Nature* 2001, **414**:338.
11. Leary R, Westwood A: **Carbonaceous nanomaterials for the enhancement of TiO_2 photocatalysis.** *Carbon* 2011, **49**:741.
12. Yao Y, Li G, Ciston S, Lueptow RM, Gray KA: **Photoreactive TiO_2/carbon nanotube composites: synthesis and reactivity.** *Environ Sci Technol* 2008, **42**:4952.
13. Gao B, Peng C, Chen GZ, Li Puma G: **Photo-electro-catalysis enhancement on carbon nanotubes/titanium dioxide (CNTs/TiO_2) composite prepared by a novel surfactant wrapping sol-gel method.** *Appl Catal B* 2008, **85**:17.
14. Xia XH, Jia ZJ, Yu Y, Liang Y, Wang Z, Ma LL: **Preparation of multi-walled carbon nanotube supported TiO_2 and its photocatalytic activity in the reduction of CO_2 with H_2O.** *Carbon* 2007, **45**:717.
15. Krishna V, Noguchi N, Koopman B, Moudgil B: **Enhancement of titanium dioxide photocatalysis by water-soluble fullerenes.** *J Colloid Interface Sci* 2006, **304**:166.
16. Long Y, Lu Y, Huang Y, Peng Y, Lu Y, Kang SZ, Mu J: **Effect of C_{60} on the photocatalytic activity of TiO_2 nanorods.** *J Phys Chem C* 2009, **113**:13899.
17. Meng ZD, Zhu L, Choi JG, Chen ML, Oh WC: **Effect of Pt treated fullerene/TiO_2 on the photocatalytic degradation of MO under visible light.** *J Mater Chem* 2011, **21**:7596.
18. Zhang H, Lv X, Li Y, Wang Y, Li J: **P25-graphene composite as a high performance photocatalyst.** *ACS Nano* 2010, **4**:380.
19. Zhou K, Zhu Y, Yang X, Jiang X, Li C: **Preparation of graphene-TiO_2 composites with enhanced photocatalytic activity.** *New J Chem* 2011, **35**:353.
20. Kamat PV, Haria M, Hotchandani S: **C_{60} cluster as an electron shuttle in a Ru(II)-polypyridyl sensitizer-based photochemical solar cell.** *J Phys Chem B* 2004, **108**:5166.
21. Yoo SH, Kum JM, Cho SO: **Tuning the electronic band structure of PCBM by electron irradiation.** *Nanoscale Research Letters* 2011, **6**:545.
22. Lee HM, Kim YN, Kim BH, Kim SO, Cho SO: **Fabrication of luminescent nanoarchitectures by electron irradiation of polystyrene.** *Adv Mater* 2005, **17**:120.
23. Li Y, Lee EJ, Cai W, Kim KY, Cho SO: **Unconventional method for morphology-controlled carbonaceous nanoarrays based on electron irradiation of polystyrene colloidal monolayer.** *ACS Nano* 2008, **2**:1108.
24. Kongkanand A, Tvrdy K, Takechi K, Kuno M, Kamat PV: **Quantum dot solar cells. Tuning photoresponse through size and shape control of CdSe-TiO_2 architecture.** *J Phys Chem C* 2008, **112**:18737.
25. Kamat PV: **Quantum dot solar cells. Semiconductor nanocrystals as light harvesters.** *J Phys Chem C* 2008, **112**:18737.
26. Robertson N: **Optimizing dyes for dye-sensitized solar cells.** *Angew Chem Int Ed* 2006, **45**:2338.
27. Peter LM, Wijayantha KGU, Riley DJ, Waggett JP: **Band-edge tuning in self-assembled layers of Bi_2S_3 nanoparticles used to photosensitize nanocrystalline TiO_2.** *J Phys Chem B* 2003, **107**:8378.
28. Hagberg DP, Marinado T, Karlsson KM, Nonomura K, Qin P, Boschloo G, Brinck T, Hagfeldt A, Sun L: **Tuning the HOMO and LUMO energy levels of organic chromophores for dye sensitized solar cells.** *J Org Chem* 2007, **72**:9550.
29. Wang ZS, Yamaguchi T, Sugihara H, Arakawa H: **Significant efficiency improvement of the black dye-sensitized solar cell through protonation of TiO_2 films.** *Langmuir* 2005, **21**:4272.
30. Lin CJ, Lu YT, Hsieh CH, Chien SH: **Surface modification of highly ordered TiO_2 nanotube arrays for efficient photoelectrocatalytic water splitting.** *Appl Phys Lett* 2009, **94**:113102.

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