

NANO EXPRESS

Open Access

Improvement in the photoelectrochemical responses of PCBM/TiO₂ electrode by electron irradiation

Seung Hwa Yoo¹, Jong Min Kum¹, Ghafar Ali^{1,2}, Sung Hwan Heo³ and Sung Oh Cho^{1*}

Abstract

The photoelectrochemical (PEC) responses of electron-irradiated [6,6]-phenyl-C61-butyric acid methyl ester (PCBM)/TiO₂ electrodes were evaluated in a PEC cell. By coating PCBM on TiO₂ nanoparticle film, the light absorption of PCBM/TiO₂ electrode has expanded to the visible light region and improved the PEC responses compared to bare TiO₂ electrode. The PEC responses were further improved by irradiating an electron beam on PCBM/TiO₂ electrodes. Compared to non-irradiated PCBM/TiO₂ 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/TiO₂ electrodes.

Keywords: photoelectrochemical cell, TiO₂, electron irradiation, PCBM, band-edge tuning

Introduction

TiO₂ 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 TiO₂ 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 TiO₂ 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-TiO₂ [12-14], fullerene-TiO₂ (C₆₀-TiO₂) [15-17], and graphene-TiO₂ [18,19] composites have been introduced by several groups and have shown enhanced

photocatalytic activities. Notably, C₆₀ has shown interesting effects when combined with TiO₂: facilitating the separation of photo-generated charge carriers from TiO₂ to C₆₀ [15,16] or sensitizing TiO₂ to absorb visible light [17]. However, the band-edge position of C₆₀ is unfavorable for a sensitizer of TiO₂ because the lowest unoccupied molecular orbital (LUMO) level of C₆₀ is lower than the conduction band of TiO₂ [17]. From the viewpoint of energy levels, [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is a better candidate than C₆₀ for the sensitization of TiO₂. We expect that the photo-excited electrons of PCBM can be transferred to TiO₂ more efficiently because the LUMO level of PCBM is slightly higher than the conduction band of TiO₂ [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

* Correspondence: socho@kaist.ac.kr

¹Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology, Daejeon, 305-701, South Korea
Full list of author information is available at the end of the article

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/TiO₂ electrodes using electron beam irradiation. The photocurrent density and open-circuit potential of PCBM/TiO₂ were respectively improved by 90% and 36% by electron irradiation. The effects of the electron irradiation on the PEC performances of PCBM/TiO₂ were systematically analyzed in this study.

Methods

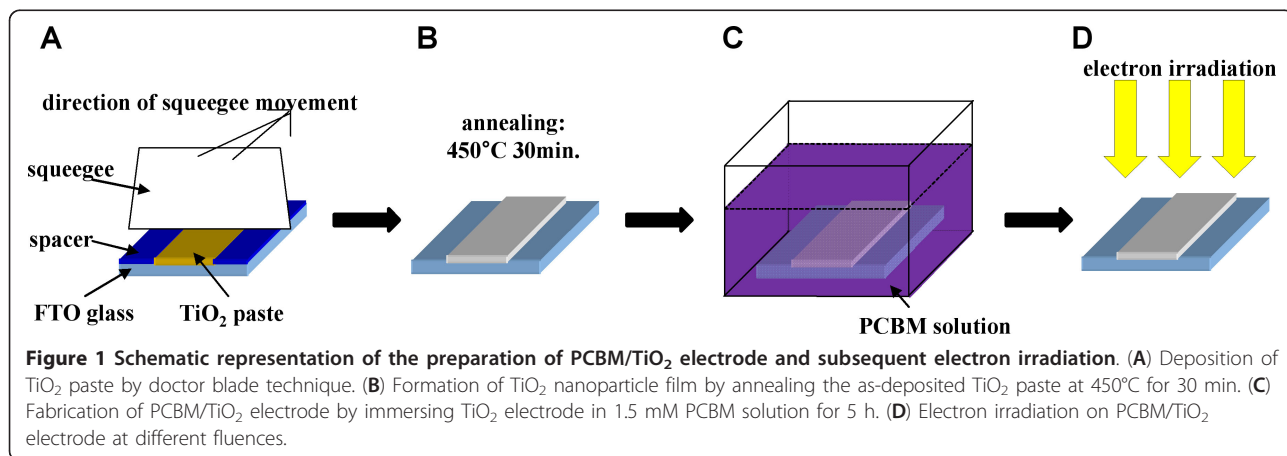
Figure 1 shows the schematic representation of the preparation of PCBM/TiO₂ electrode and subsequent electron irradiation. The as-received TiO₂ nanoparticle paste (DSL 18NR-T, Dyesol Industries Pty Ltd., Queanbeyan, New South Wales, Australia) was deposited on a fluorine-doped tin oxide (FTO) glass substrate (8 Ωm⁻², Dyesol) by a doctor blade technique. Before the deposition of TiO₂ paste, FTO glass substrates were cut by 1.0 × 2.5 cm² in dimension and were sonicated successively in acetone, isopropanol, ethanol, and deionized water for thorough cleaning and dried in N₂ gas stream. After the deposition of TiO₂ 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, TiO₂ nanoparticle film was formed. The as-prepared TiO₂ 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. Louis, MO, USA) solvent. After the immersion, the electrodes were washed in pure chlorobenzene several times and dried at ambient condition. As a result, PCBM/TiO₂ electrodes, where a thin layer of PCBM was coated on the TiO₂ nanoparticle electrodes, were prepared. Coating process of PCBM was carried out in darkness. The

irradiation of an electron beam on PCBM/TiO₂ 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/TiO₂ electrodes were irradiated by 1, 2, and 4 h which correspond to electron fluence of 3.6 × 10¹⁶, 7.2 × 10¹⁶, and 1.44 × 10¹⁷ cm⁻², respectively. Diffuse reflectance UV-visible (VIS) spectra of electron-irradiated PCBM/TiO₂ 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/TiO₂ electrodes, a custom-made PEC cell was constructed to measure the PEC responses of electron-irradiated PCBM/TiO₂ 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 N₂ 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/TiO₂ photo-anodes of PEC cells. TiO₂ nanoparticles (NPs) were firstly deposited to



form a film on a FTO glass substrate. A uniform TiO₂ NP film was formed by annealing the as-deposited TiO₂ paste at 450°C for 30 min. The TiO₂ NP film was submerged in a PCBM solution for 5 h, and consequently, the TiO₂ NP film was coated with PCBM. Subsequently, the PCBM/TiO₂ 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/TiO₂ 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/TiO₂ film. TiO₂ 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 TiO₂ NPs were well interconnected with one another, forming a rigid film that is strongly attached to the FTO glass substrate. The thickness of the TiO₂ NP film was approximately 16.5 μm.

We observed that transparent TiO₂ 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 TiO₂ NP films. When PCBM was coated on TiO₂, visible light absorption of TiO₂ 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/TiO₂ 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/TiO₂ 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/TiO₂ electrodes. The measurement results of the PEC responses of bare TiO₂, PCBM/TiO₂, and electron-irradiated PCBM/TiO₂ 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 TiO₂ 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 TiO₂ nanoparticles, the PEC performance was improved: J_{ph} and E_{ocp} of PCBM/TiO₂ 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 TiO₂. After electron irradiation of PCBM/TiO₂ 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/TiO₂ electrode was further improved through electron irradiation of increased electron fluence. Both J_{ph} and E_{ocp} of electron-irradiated PCBM/TiO₂ 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/TiO₂ electrode was improved by electron fluence is interesting because electron irradiation increases the bandgap of

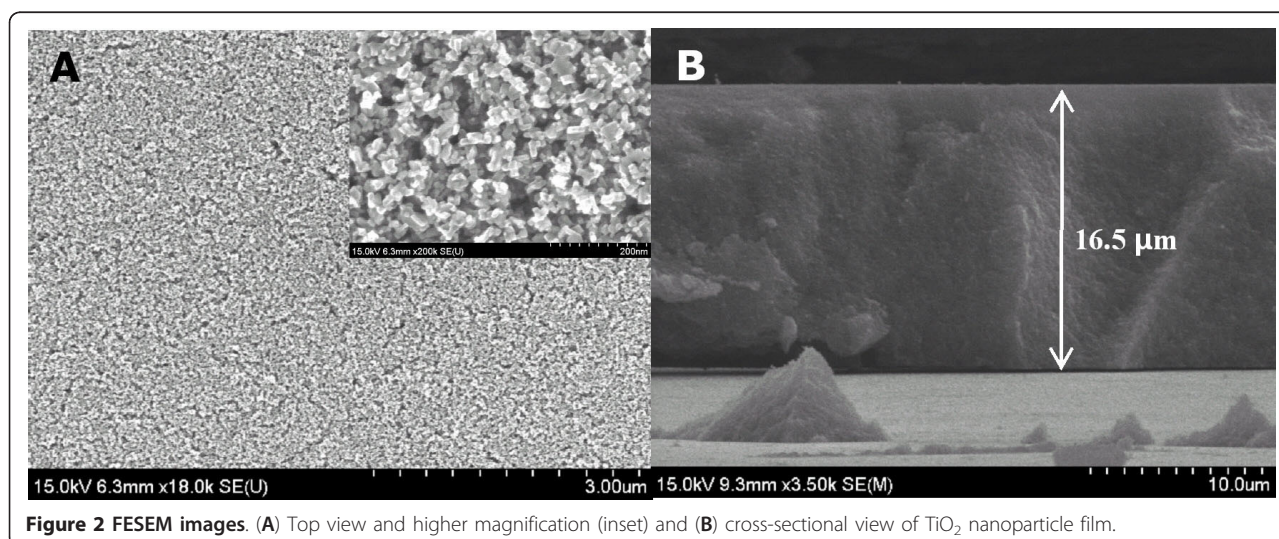


Figure 2 FESEM images. (A) Top view and higher magnification (inset) and (B) cross-sectional view of TiO₂ nanoparticle film.

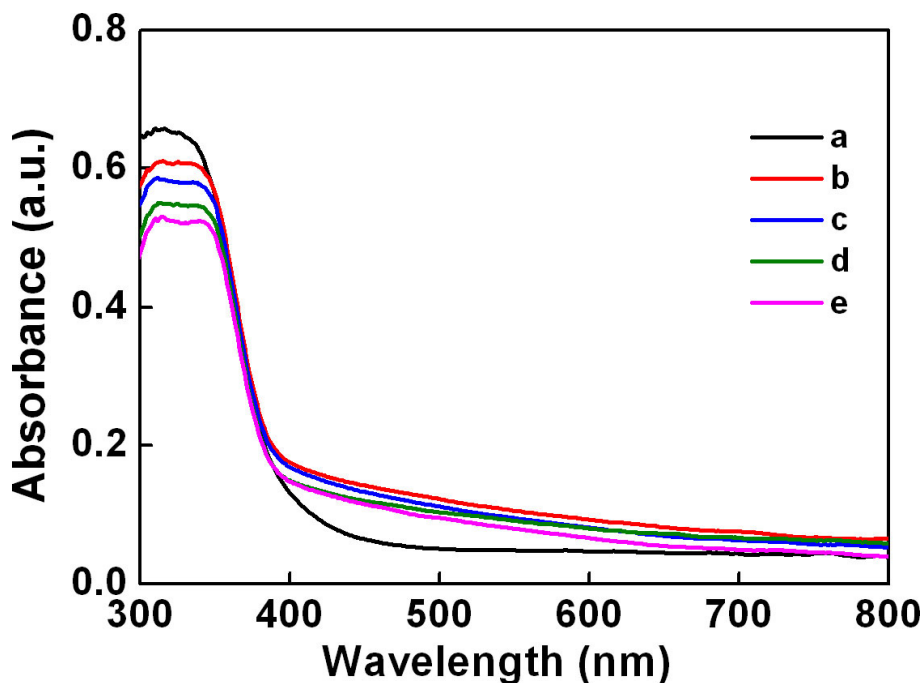


Figure 3 Diffuse reflectance UV-VIS spectra. (a) TiO₂ and (b) PCBM/TiO₂. PCBM/TiO₂ irradiated at (c) 3.6×10^{16} , (d) 7.2×10^{16} , and (e) $1.44 \times 10^{17} \text{ cm}^{-2}$.

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 TiO₂, electron-hole pairs produced in PCBM can contribute to the increase in the photo-current of TiO₂. However, the energy difference between the LUMO energy level of PCBM and the

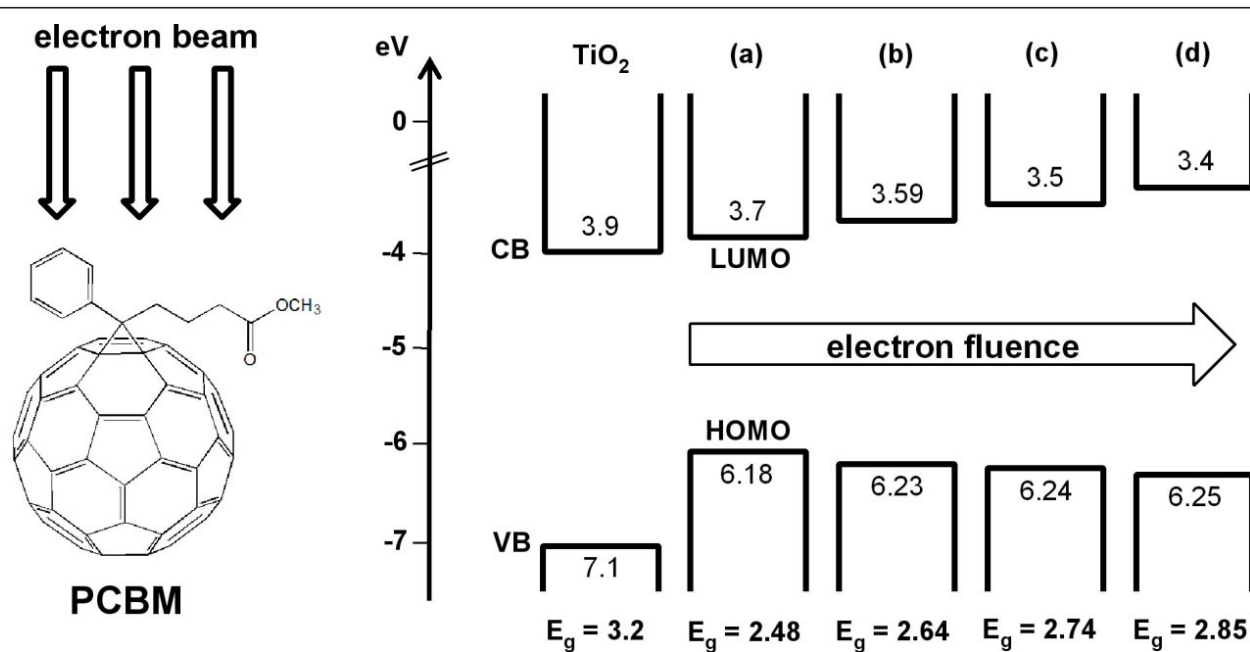


Figure 4 Band structure of PCBM after electron beam irradiation of different fluences. (a) Non-irradiated PCBM. (b) Irradiated PCBM at 3.6×10^{16} , (c) 7.2×10^{16} , and (d) $1.44 \times 10^{17} \text{ cm}^{-2}$.

Table 1 Photoelectrochemical performance of various electrodes investigated

	J_{ph} ($\mu A\ cm^{-2}$)	E_{ocp} (V) vs. SCE
TiO ₂	176	-0.85
PCBM/TiO ₂	234	-1.05
PCBM/TiO ₂ ($3.6 \times 10^{16}\ cm^{-2}$)	306	-1.16
PCBM/TiO ₂ ($7.2 \times 10^{16}\ cm^{-2}$)	333	-1.16
PCBM/TiO ₂ ($1.44 \times 10^{17}\ cm^{-2}$)	285	-1.10

conduction band edge minimum of pure TiO₂ is 0.2 eV, which might not be high enough for efficient electron transfer from PCBM to TiO₂ [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 TiO₂ [25]. This can explain why J_{ph} of electron-irradiated PCBM/TiO₂ 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 TiO₂ 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 $1.44 \times 10^{17}\ cm^{-2}$, the PEC performance of electron-irradiated PCBM/TiO₂ 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 TiO₂. 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/TiO₂, 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 TiO₂ at an optimum electron fluence at $7.2 \times 10^{16}\ cm^{-2}$.

Conclusions

Using the fact that the electronic band structure of PCBM can be modified by electron irradiation, PCBM/TiO₂ electrodes were fabricated and tested in a PEC cell. We observed that electron irradiation on PCBM/TiO₂ 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

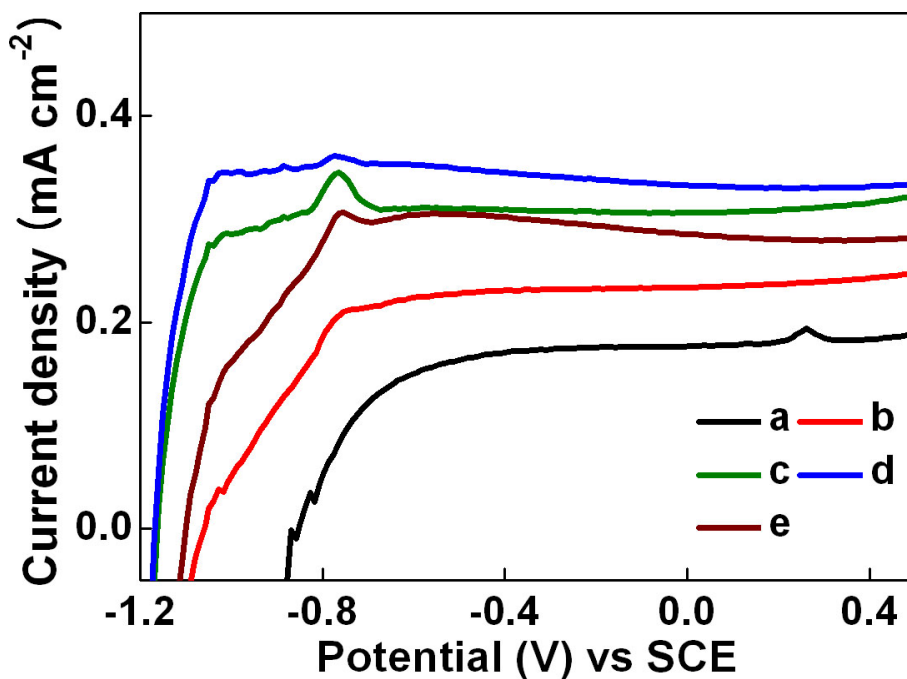


Figure 5 Current density-potential curves of TiO₂ and PCBM/TiO₂ electrodes irradiated at different electron fluences under illumination. (a) Non-irradiated TiO₂ and (b) PCBM/TiO₂. PCBM/TiO₂ irradiated at (c) 3.6×10^{16} , (d) 7.2×10^{16} , and (e) $1.44 \times 10^{17}\ cm^{-2}$.

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.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MEST) (no. 2011-0020764).

Author details

¹Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology, Daejeon, 305-701, South Korea
²Nanomaterials Research Group, Physics Division, PINSTECH, Islamabad, 45650, Pakistan
³Particla Co. Ltd., Daejeon, 306-220, South Korea

Authors' contributions

The work was carried out by the collaboration between all authors. SOC initiated the idea of electron irradiation on PCBM/TiO₂ 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/TiO₂ electrodes. JMK and SHH carried out the diffuse reflectance UV-VIS spectroscopy measurements of electron-irradiated PCBM/TiO₂. SOC and SHY analyzed the data and suggested the mechanism of improvement of electron-irradiated PCBM/TiO₂ electrodes. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

Received: 21 October 2011 Accepted: 20 February 2012

Published: 20 February 2012

References

- Hoffmann MR, Martin ST, Choi W, Bahnemann DW: Environmental applications of semiconductor photocatalysis. *Chem Rev* 1995, **95**:69.
- Lee YL, Huang BM, Chien HT: Highly efficient CdSe-sensitized TiO₂ photoelectrode for quantum-dot-sensitized solar cell applications. *Chem Mater* 2009, **20**:6903.
- Xie Y, Ali G, Yoo SH, Cho SO: Sonication-assisted synthesis of CdS quantum-dot-sensitized TiO₂ nanotube arrays with enhanced photoelectrochemical and photocatalytic activity. *ACS Appl Mater Interfaces* 2010, **2**:2910.
- Chen C, Ali G, Yoo SH, Kum JM, Cho SO: Improved conversion efficiency of CdS quantum dot-sensitized TiO₂ nanotube-arrays using CuInS₂ as a co-sensitizer and an energy barrier layer. *J Mater Chem* 2011, **21**:16430.
- O'regan B, Grätzel M: A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature* 1991, **353**:737.
- Bach J, Lupo D, Comte P, Moser JE, Weissörtel F, Salbeck J, Spreitzer H, Grätzel M: Solid-state dye-sensitized mesoporous TiO₂ solar cells with high photon-to-electron conversion efficiencies. *Nature* 1998, **395**:583.
- Law M, Greene LE, Johnson JC, Saykally R, Yang P: Nanowire dye-sensitized solar cells. *Nature Mater* 2005, **4**:455.
- Hodes G: A thin-film polycrystalline photoelectrochemical cell with 8% solar conversion efficiency. *Nature* 1980, **285**:29.
- Heller A: Conversion of sunlight into electrical power and photoassisted electrolysis of water in photoelectrochemical cells. *Acc Chem Res* 1981, **14**:154.
- Grätzel M: Photoelectrochemical cells. *Nature* 2001, **414**:338.
- Leary R, Westwood A: Carbonaceous nanomaterials for the enhancement of TiO₂ photocatalysis. *Carbon* 2011, **49**:741.
- Yao Y, Li G, Ciston S, Lueptow RM, Gray KA: Photoreactive TiO₂/carbon nanotube composites: synthesis and reactivity. *Environ Sci Technol* 2008, **42**:4952.
- Gao B, Peng C, Chen GZ, Li Puma G: Photo-electro-catalysis enhancement on carbon nanotubes/titanium dioxide (CNTs/TiO₂) composite prepared by a novel surfactant wrapping sol-gel method. *Appl Catal B* 2008, **85**:17.
- Xia XH, Jia ZJ, Yu Y, Liang Y, Wang Z, Ma LL: Preparation of multi-walled carbon nanotube supported TiO₂ and its photocatalytic activity in the reduction of CO₂ with H₂O. *Carbon* 2007, **45**:717.
- Krishna V, Noguchi N, Koopman B, Moudgil B: Enhancement of titanium dioxide photocatalysis by water-soluble fullerenes. *J Colloid Interface Sci* 2006, **304**:166.
- Long Y, Lu Y, Huang Y, Peng Y, Lu Y, Kang SZ, Mu J: Effect of C₆₀ on the photocatalytic activity of TiO₂ nanorods. *J Phys Chem C* 2009, **113**:13899.
- Meng ZD, Zhu L, Choi JG, Chen ML, Oh WC: Effect of Pt treated fullerene/TiO₂ on the photocatalytic degradation of MO under visible light. *J Mater Chem* 2011, **21**:7596.
- Zhang H, Lv X, Li Y, Wang Y, Li J: P25-graphene composite as a high performance photocatalyst. *ACS Nano* 2010, **4**:380.
- Zhou K, Zhu Y, Yang X, Jiang X, Li C: Preparation of graphene-TiO₂ composites with enhanced photocatalytic activity. *New J Chem* 2011, **35**:353.
- Kamat PV, Haria M, Hotchandani S: C₆₀ cluster as an electron shuttle in a Ru(II)-polypyridyl sensitizer-based photochemical solar cell. *J Phys Chem B* 2004, **108**:5166.
- Yoo SH, Kum JM, Cho SO: Tuning the electronic band structure of PCBM by electron irradiation. *Nanoscale Research Letters* 2011, **6**:545.
- Lee HM, Kim YN, Kim BH, Kim SO, Cho SO: Fabrication of luminescent nanoarchitectures by electron irradiation of polystyrene. *Adv Mater* 2005, **17**:120.
- 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.
- Kongkanand A, Tvrdy K, Takechi K, Kuno M, Kamat PV: Quantum dot solar cells. Tuning photoresponse through size and shape control of CdSe-TiO₂ architecture. *J Phys Chem C* 2008, **112**:18737.
- Kamat PV: Quantum dot solar cells. Semiconductor nanocrystals as light harvesters. *J Phys Chem C* 2008, **112**:18737.
- Robertson N: Optimizing dyes for dye-sensitized solar cells. *Angew Chem Int Ed* 2006, **45**:2338.
- Peter LM, Wijayantha KGU, Riley DJ, Waggett JP: Band-edge tuning in self-assembled layers of Bi₂S₃ nanoparticles used to photosensitize nanocrystalline TiO₂. *J Phys Chem B* 2003, **107**:8378.
- 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.
- Wang ZS, Yamaguchi T, Sugihara H, Arakawa H: Significant efficiency improvement of the black dye-sensitized solar cell through protonation of TiO₂ films. *Langmuir* 2005, **21**:4272.
- Lin CJ, Lu YT, Hsieh CH, Chien SH: Surface modification of highly ordered TiO₂ nanotube arrays for efficient photoelectrocatalytic water splitting. *Appl Phys Lett* 2009, **94**:113102.

doi:10.1186/1556-276X-7-142

Cite this article as: Yoo et al.: Improvement in the photoelectrochemical responses of PCBM/TiO₂ electrode by electron irradiation. *Nanoscale Research Letters* 2012 **7**:142.

Submit your manuscript to a SpringerOpen® journal and benefit from:

- Convenient online submission
- Rigorous peer review
- Immediate publication on acceptance
- Open access: articles freely available online
- High visibility within the field
- Retaining the copyright to your article

Submit your next manuscript at ► springeropen.com