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Solar Cells

A Selenium-Based Cathode for a High-Voltage Tandem Photoelectrochemical Solar Cell**

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Dye-sensitized photoelectrochemical solar cells (DSCs) are one of the most promising alternatives to conventional inorganic devices owing to their potential low production costs and high conversion efficiencies.[1] In a typical DSC, a mesoporous n-type TiO_2 electrode, anchored with an electron-injecting sensitizer, acts as an photoanode for light absorption, and a platinized fluorine-doped tin oxide (FTO) glass as a passive cathode for catalysis of the electrolyte with a redox couple I^-/I_3^-, sandwiched between the two electrodes (n-DSC). In this n-DSC, light-induced electron injection from the excited sensitizer into the conduction band of TiO_2 is followed by hole injection into the electrolyte, generating a photovoltage defined by the difference in chemical potential between the TiO_2 photoanode and the electrolyte. On the other hand, a p-type semiconductor electrode (such as NiO) can be sensitized by a hole-injection sensitizer and used as a photocathode in combination with a Pt passive anode in a DSC (p-DSC). In this case, an opposite process occurs, with electron injection into the electrolyte and hole injection into the valence band of NiO, resulting in a photovoltage equal to the difference in chemical potential between the NiO photocathode and the electrolyte. With the combination of a photoanode and a photocathode in a single device (np-DSC), a tandem DSC has been advanced with a theoretical efficiency limitation well beyond that of a single junction DSC (n- or p-DSC). In this double junction tandem device, both the active electrodes are connected in series, and thus a high photovoltage, namely a sum of the photovoltages obtained in the corresponding p and n devices, can be expected, with the potential to dramatically improve the efficiency.[2–4]

Since the first report in 2000,[2] the p-type NiO semiconductor has been extensively investigated,[2–11] and efforts were mainly focused on the development of hole injection sensitizers for the electrode. In most reports, the NiO based p-DSCs gave the very limited photocurrent densities of 1–2 mA cm^{-2} and low open-circuit voltages V_{oc} of typically < 150 mV, resulting in efficiencies of < 0.2 %.[2,4–11] Recently, a record conversion efficiency of 0.41 % was achieved in a p-DSC through a combinational optimization of NiO electrode, electrolyte, and sensitizer.[3] The efficiency is encouraging, but is still low owing to the intrinsic limitation of the NiO electrode, where 30–40 % of photons are absorbed by the NiO electrode itself, but made almost no photocurrent contribution to the device. Furthermore, the V_{oc} is also limited by its high positive valence band energy level. Thus, it is necessary to develop new photocathodes to further improve the efficiency of the tandem device. Most recently, an acid-treated CdS quantum-dot-based electrode was reported as a photocathode, giving a photocurrent density (J_{sc}) of 0.1 mA cm^{-2} and open-circuit voltage of 111 mV.[12]

Herein, we present a selenium-based photocathode that was developed by deposition of selenium on the TiO_2 electrode by an electrochemical deposition method. With this photocathode, a photoelectrochemical solar cell was prepared using a Pt counter electrode and a standard I^-/I_3^- electrolyte, exhibiting a cathodic photocurrent of 3.73 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 318 mV, and an overall efficiency of 0.34 % under AM 1.5 (100 mW cm^{-2}) illumination. A tandem device was further constructed by replacing the Pt counter electrode with a conventional N719-sensitized TiO_2 anode, giving a J_{sc} of 2.72 mA cm^{-2}, a V_{oc} of 940 mV, and an overall efficiency of 0.98 %. The tandem device is represented with an energy scale[15] in Figure 1.

For the preparation of the selenium-based photocathode, a 2.4 μm-thick porous TiO_2 layer was firstly coated on a FTO glass substrate by the doctor blade technique with TiO_2 paste (particle size 60 nm) synthesized according to a previous report.[13] Then a thin selenium layer on the mesoporous TiO_2 electrode was obtained by the electrochemical deposition method, which was widely used owing to its simplicity, good reproducibility, and controllable deposition fashion.[14] Elemental selenium was deposited inside the mesoporous TiO_2 film by reduction of selenite ions:[15]

$$SeO_3^{2-} + 4\,e^- \rightarrow Se + 3\,H_2O \qquad (1)$$

The average thickness of the overcoated selenium layer on the mesoporous TiO_2 film was estimated about 3–4 nm according to the total amount of charge (0.23 C cm^{-2}) passed during the deposition. The as-grown amorphous selenium (reddish brown) was annealed in air at 150 °C for 5 min to convert it into gray metallic-colored crystalline material. As shown in Figure 2, the XRD pattern obtained after the deposition and annealing of the selenium shows the diffrac-

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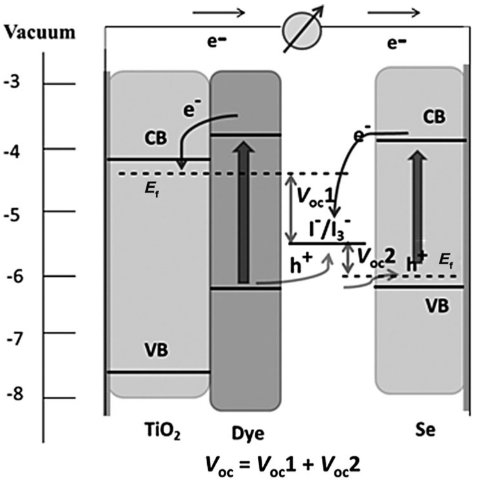

Figure 1. Representation of a selenium-based tandem device, where a selenium-coated TiO_2 active cathode and a N719 dye-sensitized TiO_2 anode were employed with a standard I^-/I_3^- electrolyte sandwiched between the two electrodes. CB = conduction band, VB = valence band, E_F = Fermi energy level, h = hole, V_{OC} = open-circuit voltage. *y* axis: energy vs. vacuum [eV].

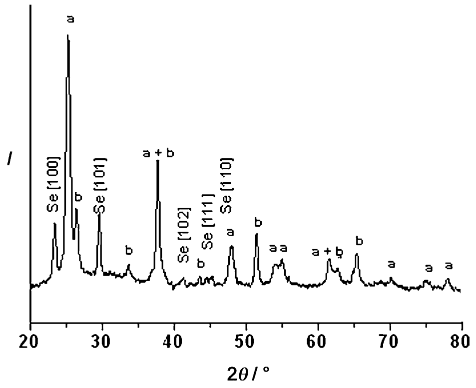

Figure 2. XRD pattern of selenium-coated TiO_2 film on FTO glass. a = anatase TiO_2, b = fluorine-doped tin oxide (FTO) substrate.

tion peaks at $2\theta = 23.7$, 29.8, 41.4, 43.9, and 45.5° are for the (100), (101), (110), (102), and (111) reflections of the pure hexagonal phase of selenium (JCPDS 06-0362), respectively.[16] Hexagonal selenium is stable with a high conductivity.[17]

A single-junction device (denoted p-device) was constructed by the selenium-based photocathode, a Pt counter electrode, and a standard I^-/I_3^- electrolyte (0.6 M 1-propyl-3-methylimidazolium iodide, 0.1 M LiI, 0.05 M I_2, and 0.5 M *tert*-butylpyridine in the mixture of acetonitrile and valeronitrile (1:1, v/v)). Photons absorbed by the selenium (right part of Figure 1) create electrons in the conduction band and holes in the valence band, followed by electron collection by redox species in the electrolyte and hole collection at the FTO back contact, resulting in a cathodic photocurrent and a photovoltage ($V_{oc}2$). The photoelectrochemical properties of the p device was evaluated by recording the curve of the photocurrent density–voltage (*J–V)* under AM 1.5 G 100 mW cm^{-2}

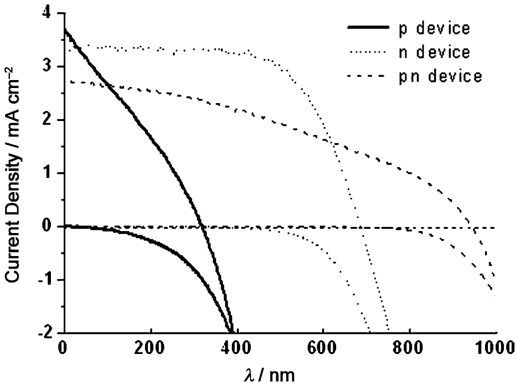

Figure 3. Current-density–voltage (*J–V*) curves for the selenium/TiO_2 based p device, N719/TiO_2-based n device, and the tandem pn device. A simulated AM 1.5 light (100 mW cm^{-2}) was was employed to illuminate from the anode side.

conditions (Figure 3), and the resulting photovoltaic data were summarized in Table 1. The preliminary experiment gives a short-circuit current density (J_{sc}) of 3.73 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 318 mV, a fill fact (FF) of 0.29, and a conversion efficiency (η) of 0.34 %. These values are comparable with those obtained in the optimized NiO-based device,[3] and are much higher than those in the QD-based device.[12] It is worth pointing out that after the selenium is excited by the light, there are two ways for the electron transfer from an energetic point of view: 1) electron transfer from the conduction band of selenium to the conduction band of TiO_2, and hole transfer from the valence band of selenium to the electrolyte; or 2) electron transfer from the conduction band of selenium to the electrolyte, and hole transfer through the selenium film directly to the FTO substrate. The observed cathodic photocurrent means that the second way seems to dominate in the operation, and may be explained by the larger driving force of the electron transfer in the second way, as compared to that in the first way. Therefore, selenium functions as both light-harvesting material and hole-transport material in the device. It should be noted that the deposition of selenium on the mesoporous n-type TiO_2 can be easily realized with a conformal coating on TiO_2 surface owing to the semiconductive properties of TiO_2 (Figure 4). Furthermore, a SiO_2-based substrate was also prepared for selenium deposition, but Se was only deposited on naked FTO surface, and could not be deposited on the surface of SiO_2. In the case of a flat FTO electrode, only a thin layer of Se can be deposited on the substrate owing to the poor conductivity of Se, which limited its further deposition. With the flat FTO/Se

Table 1: Photovoltaic performance of the p device, the n device, and the pn device under an AM 1.5 G 100 mW cm^{-2} conditions.

Sample	J_{sc} [mA cm^2]	V_{oc} [V]	FF	η [%]
p device	3.73	318	0.29	0.34
n device	3.39	685	0.64	1.51
pn device	2.72	940	0.39	0.98

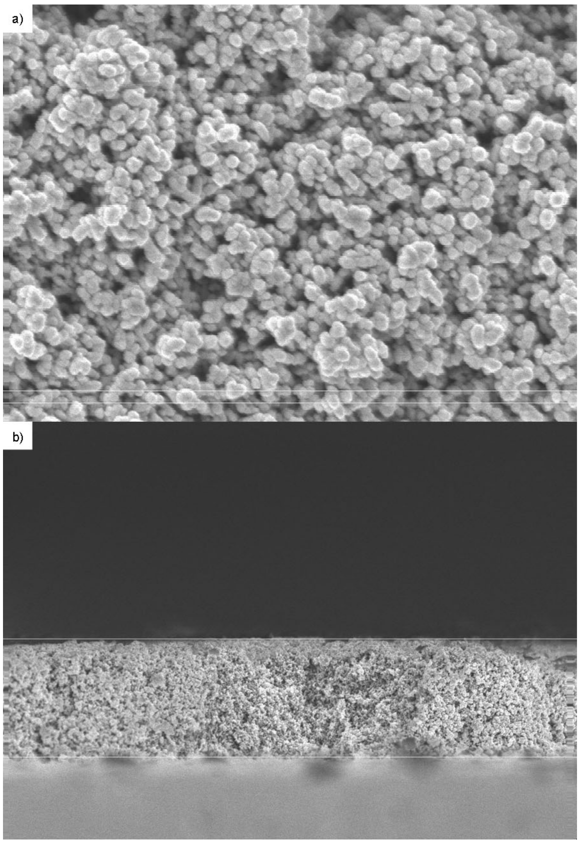

Figure 4. Scanning electron micrographs of Se-TiO_2 film on FTO glass after annealing in air for 5 min at 150 °C: a) top view, b) cross-sectional view.

electrode, a cathodic photoresponse still can be recorded, but gave a relatively weak photocurrent of 0.42 $mA\,cm^{-2}$, with a V_{oc} of 285 mV, a FF of 0.23, and an efficiency η of 0.03 %. Thus, we think the mesoporous n-type TiO_2 film may work as a semiconductive substrate for effective Se deposition, and the large surface area of the mesoporous TiO_2 coated with the layer of Se favors light harvesting and charge separation and transfer.

For the fabrication of the selenium-based tandem device, a typical N719-sensitized TiO_2 electrode was employed, where the TiO_2 electrode consists of about 40 nm-thick dense TiO_2 blocking layer and 1.2 μm-thick mesoporous TiO_2 (particle size: 20 nm) layer on FTO glass substrate.[18] A single-junction device was first constructed by the dye-sensitized d TiO_2 anode and a Pt counter electrode (denoted n device). Under illumination, photons absorbed by the dye N719 (left part of Figure 1) is followed by the electron transfer to the conduction band of TiO_2 and hole transfer to the electrolyte, resulting in a photovoltage of 685 mV ($V_{oc}1$). Finally, a tandem device was constructed with the selenium-based cathode and the N719-sensitized TiO_2 anode in a simple sandwich configuration (denoted pn device). With light illumination through the photoanode side, the tandem pn device gives a J_{sc} of 2.72 $mA\,cm^{-2}$, a V_{oc} of 940 mV, a FF of 0.39, and an efficiency η of 0.98 %. The high V_{oc} value (940 mV) in the tendem pn device is almost equal to the sum of the photovoltages measured in the p device ($V_{oc}2 =$ 318 mV) and the n device ($V_{oc}1 = 685$ mV). As compared to both the single junction devices, the photocurrent for the tandem pn-device is relatively lower owing to the overlap of the photoresponse spectra in both the photoanode and photocathode (as discussed below).

A preliminary stability test was carried out for the pn device, which was aged in the dark at room temperature. The changes of J_{sc}, V_{oc}, FF, and η with time were shown in Figure 5. The values for them were slowly decreased with time, and the efficiency kept about 64 % of the initial value after 96 h.

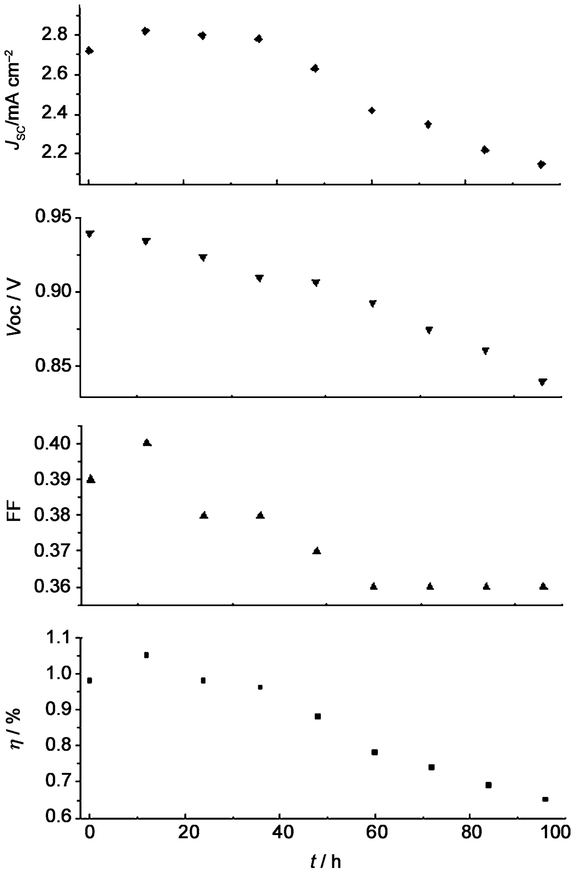

Figure 5. Preliminary stability test for the pn device aged in the dark at room temperature. The corresponding data (J_{sc}, V_{oc}, FF, and η) were recorded under a simulated AM 1.5 light (100 $mW\,cm^{-2}$).

The incident photon-to-electron conversion efficiencies (IPCE) of the three devices were measured as shown in Figure 6. For the p device, the IPCE spectrum shows a strong and broad photoresponse with an onset at 700 nm, similar to that observed in the selenium-based heterojunction solar cell.[19] The n device gives a broad photoresponse spectrum with a strong peak at 535 nm, corresponding to the absorption spectrum of N719 dye.[20] Both the single-junction devices present a similar photoresponse in the range of 400 nm to 700 nm. In spite of this, the tandem pn device features both the distinct IPCE spectra observed in the p device and the n device, exhibiting a broad and strong spectrum with a peak

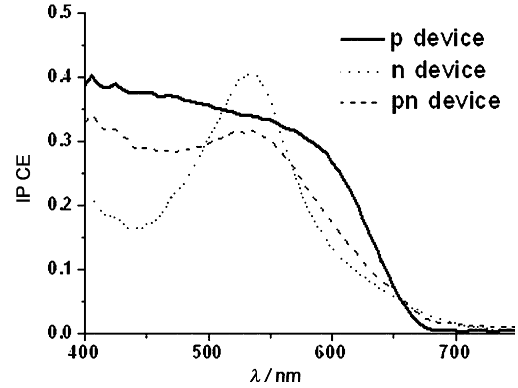

Figure 6. Incident photon-to-current conversion efficiency (IPCE) spectra of the p device, the n device, and the tandem pn device.

at 535 nm. This shows that both the electrodes can effectively absorb photons and contribute to the photocurrent, and an enhanced efficiency can be expected by employing a near-IR absorbing dye for the anode to realize a panchromatic photo response along with the selenium-based active cathode.

In conclusion, a thin layer of selenium was deposited on a mesoporous TiO_2 electrode by an electrochemical deposition method, and the selenium-based TiO_2 electrode was used as a photocathode in a single-junction photoelectrochemical solar cell for the first time, which gave a high V_{oc} of 318 mV and an efficiency of 0.34%. Moreover, a double-junction tandem solar cell was realized with the selenium-based cathode and an N719-sensitized TiO_2 anode, and it presented a high V_{oc} of 940 mV and an efficiency of 0.98%. The preliminary results are satisfactory, and further improvement can be expected through optimization of the selenium-based cathode and electrolyte composition, and the development of near-IR-absorbing dyes in the system. The utilization of selenium-based photocathode opens a new path of research on tandem solar cells.

Experimental Section

A thin selenium layer on a mesoporous TiO_2 electrode was obtained by electrochemical deposition, where a 2.4 μm-thick TiO_2 (particle size, 60 nm) electrode was employed as an anode and a gold plate as a cathode with an aqueous solution of selenium dioxide (0.3 M aqueous solution). The average thickness of the overcoated selenium layer was estimated to be about 3–4 nm according to the total amount (0.23 $C\,cm^{-2}$) of charge passed during the deposition. The as-grown amorphous selenium (reddish brown) was annealed in air at 150 °C for 5 min to convert it into gray metallic-colored crystalline material. The absorption spectra and the XRD patterns obtained before and after the annealing are available in the Supporting Information.

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