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A high-voltage dye-sensitized photocapacitor of a three-electrode system†

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A high-voltage photo-rechargeable capacitor (photocapacitor) of three-electrode configuration, comprising a dye-sensitized mesoporous TiO_2 electrode, two carbon-coated electrodes, and two liquid electrolytes, attained a charge-state voltage of 0.8 V and high energy density per area of 47 μW h cm^{-2} which is five times larger than the previous two-electrode photocapacitor.[1]

Self-rechargeable photovoltaic cells, which can directly store the electric energy generated by light, have been studied by several groups[1–6] and are becoming a recent topic in the solar energy science and industries. To ensure *in situ* electric storage function, structurally, a photocell should possess electrochemical interfaces where photonic energy is converted to electrochemical potential. Using the redox system of secondary batteries, photo-rechargeable cells can be devised by combining a dye-sensitized semiconductor layer with intercalation materials such as WO_3 or polypyrrole.[3–6] Energy storage can also be performed by electric double-layer capacitors (EDLC) without the use of redox reactions. EDLC are particularly suitable as storage devices for solar cells and wind force power generators because of their high charge–discharge durability and rapid discharge performance.[7,8] We have first constructed a photo-rechargeable capacitor, a photocapacitor,[1] in which photogenerated positive and negative charges at the semiconductor–electrolyte interface are directly stored as double-layer charges on the surface of active carbon. With a two-electrode configuration (photoelectrode and counter-electrode), the photocapacitor produces 0.45 V in the charged state and yields 75 mC cm^{-2} as a discharge capacity. A problem of this method, however, is a high internal resistance that retards the discharge process because electrons returning to the photo-electrode should go through the space charge Schottky barrier at the TiO_2 layer.[9] To make a photorechargeable secondary battery with dye-sensitized TiO_2, Nagai and Segawa have used an additional electrode for operation of efficient discharge by redox reaction.[6] Based on this practice, we show in this report a new configuration for high-voltage photocapacitor by introduction of an internal bifunctional electrode between working and counter electrodes, which conducts redox electron transfer on one side and charge storage on the other side. This three-electrode configuration achieves a large energy output, five times more than the two-electrode system, with a high charge-state voltage of 0.8 V.

The three-electrode type (3E) photocapacitor is a liquid-junction cell where one internal electrode is in junction with two different electrolytes and works as cathode and anode, simultaneously, for two outer electrodes. This 3E structure is shown in Fig. 1, and comprises the dye-sensitized mesoporous TiO_2 layer on the transparent conducting glass as a photoelectrode (PE), the activated carbon layer coated on one side of a platinum plate as an internal electrode (IE), activated carbon layer coated on the platinum-spattered conducting glass as a counter-electrode (CE), and two layers of liquid ionic electrolytes, where a redox electrolyte containing I^-/I_3^- and a non-redox electrolyte constitute the PE–IE and IE–CE junctions, respectively.

Preparation of the dye-sensitized photoelectrode (PE) and the carbon-coated counter-electrode (CE) basically follows the method described previously[1,10] (see ESI†). For PE, Ru bipyridyl complex dye, N719, was used as a sensitizer adsorbed on the TiO_2 layer on an F-SnO_2 conductive glass. The TiO_2 layer at the PE and the activated carbon layer at the IE and CE have thicknesses of 10 μm and 200–300 μm, respectively. A porous polycarbonate membrane was inserted between the PE–IE and between the IE–CE to protect against short circuits, along with setting of a polyethylene film spacer (50 μm thick) surrounding the electrolyte layers. The apparent surface areas of the dye-sensitized TiO_2 film on the PE and the activated carbon layers on the IE and CE were *ca.* 0.64 cm^2 (0.8 cm × 0.8 cm) and 1.21 cm^2 (1.1 cm × 1.1 cm), respectively. The redox electrolyte for the PE–IE unit consisted of 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide, 0.5 M 4-*tert*-butylpyridine, 0.1 M LiI, and 0.05 M I_2 in methoxyacetonitrile and the redox-free electrolyte for the IE–CE unit was 15 wt% tetraethylammonium tetrafluoroborate solution in propylene

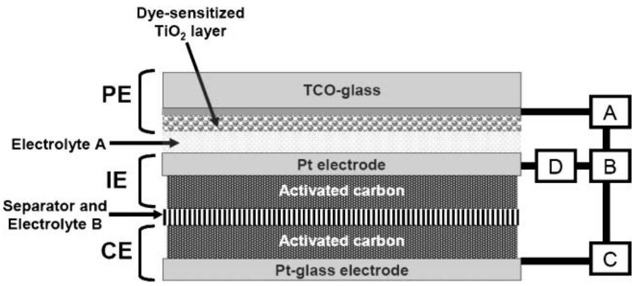

Fig. 1 Structure of the three-electrode photocapacitor. The cell consists of a dye-sensitized TiO_2 photoelectrode (PE), a Pt-plate inner electrode (IE) and a Pt-coated glass counter-electrode (CE) covered with activated carbon (AC), spacer, separator, and redox and redox-free electrolytes. The spacer and redox electrolyte (I^-/I_3^-) are inserted between the PE and IE. The separator and redox-free electrolyte occupy the space between the IE and CE.

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† Electronic Supplementary Information (ESI) available: Preparation of TiO_2-coated PE and carbon-coated CE; light source and setups for measuring charge-discharge characteristics. See http://www.rsc.org/suppdata/cc/b5/b503122b/

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carbonate. The 2E-photocapacitor, as a reference cell, was constructed of AC-coated dye-sensitized TiO_2 electrode (AC–PE) and AC-coated Pt-glass counter-electrode (CE) according to our previous method.[1] Specifically, the PE was improved by introducing a hole trapping lithium iodide layer at the TiO_2–AC interface.[1] In the 2E-photocapacitor, the sole electrolyte layer binding PE and CE was the redox-free composition, which is same as the non-redox electrolyte used for the present 3E-photocapacitor.

The photocapacitor was charged under the visible light irradiation at intensity of 100 mW cm^{-2} for 1.8 ks in the short-circuit condition by connection of PE and CE. The photo-charged capacitor was subjected to a galvanostatic discharge to the limit voltage of 0 V in the condition of connecting CE and IE. The current density is expressed as the current per area of the dye-sensitized TiO_2 unless otherwise indicated. Measurement of charging voltage was conducted using an electrometer for monitoring of the voltage accumulated between the IE and CE. Charge and discharge properties of the cells under illumination and in the dark, respectively, were evaluated for the changes of charging current density, charging voltage, and discharging voltage. These characteristics were compared with those of the 2E-photocapacitor.

To conduct photocharging, PE and CE were short-circuited by closing the junctions of A, B, and C and opening the junction D (see Fig. 1). On visible light illumination, an anodic photocurrent exceeding 13 mA cm^{-2} occurred and it decreased with time exhibiting an exponential curve (Fig. 2 A). The initial photocurrent density, for a few seconds after the onset of photocharging, was comparable with the amplitude of the dye-sensitized solar cell, which is obtained on this circuit by connecting the PE and IE. The anodic response of photocurrent indicates that electrons flowing from PE to CE are accumulated at the surface of the AC as a double-layer negative charge.[1] At the dye-sensitized TiO_2 electrode, photogenerated holes of the dye (oxidized dye) are trapped by iodide anions in the electrolyte to regenerate the dye, following the conventional scheme of a dye-sensitized photocell.[10,12,13] The oxidized state of iodide, triiodide (I_3^-), is supposed to be reduced at the surface of the inner platinum electrode (IE) to regenerate I^- ion, where the holes produced by this electron transfer move to the surface of the AC layer, coated on the back side of the IE, and are stored as a double-layer positive charge. On the photocharging process, the total charge that flowed in the external circuit (A,B,C) for first 30 min of charging was measured to be 1.12 C cm^{-2}. This value proved to be over three times as high as that obtained by the 2E-photocapacitor (354 mC cm^{-2}),[1] indicating that a considerably higher quantity of electrons and holes were stored at the AC electric double-layer on the CE side and on the IE side, respectively.

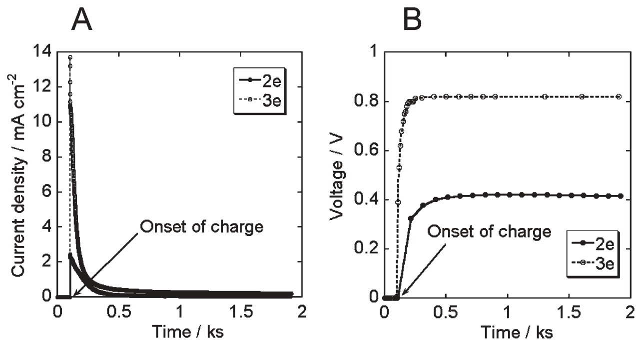

Fig. 2 Charging photocurrent (A) and open-circuit voltage (B) as a function of irradiation time for the 2E- and 3E-photocapacitors. Photocharging started at 100 s.

Charging voltage is essential for determining the maximum energy stored by the capacitor. The presently used, redox-free organic electrolyte allows for charging voltages up to 2.5 V.[14] For the iodide/triiodide-based dye-sensitized photocell, however, the maximum photovoltage is limited to a range of 0.7–0.85 V.[10–12] Our previous 2E-photocapacitor gave a maximum charging voltage of around 0.45 V,[1] which was much lower than the photovoltage of the dye-sensitized photocell. This was greatly improved by the present 3E-photocapacitor. The open-circuit voltage developed between the IE and CE by photocharging was measured as a function of charging time. The result is shown in Fig. 2B. The voltage of IE *vs.* CE, which had been reset to 0 V in the dark, increased rapidly after the onset of photocharge and reached 0.82 V after 300 s of illumination. The voltage obtained is approximately twice as large as that of the 2E-photocapacitor. The time required for the saturation of voltage is found to be shorter than the 2E-photocapacitor. The latter may indicate an increased rate of electron and hole diffusion from dye to the AC surfaces, which is improved in the present system by using iodide as reducing agent.

The charged photocapacitor was left in the open-circuit condition by disconnecting A for a rest time of 500 s. Discharge of the photocapacitor was carried out through the external circuit combining the IE and CE by connecting the junction B, C, and D. Here, the IE and CE act as positively and negatively charged electrodes, respectively. Discharge current was galvanostatically controlled at 47 μA cm^{-2}. Fig. 3 exhibits a profile of the discharging voltage. During the rest time in the open-circuit condition, the charge-state voltage (rest voltage) gradually decreased with time. This indicates the occurrence of a self discharge. With a loss of 80 mV, the starting voltage for discharge was 0.72 V. Subsequent discharge showed a constant decrease with time. The total charge released by the discharge to 0 V was 470 mC cm^{-2}, which is more than twice as high as that attained by

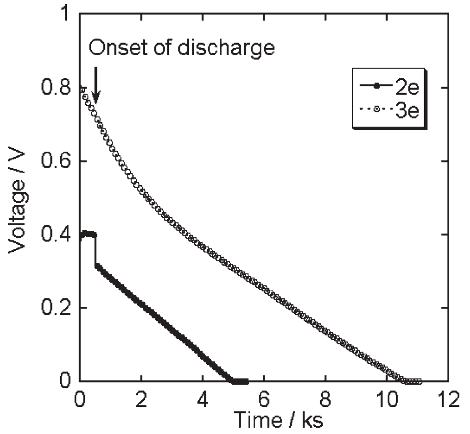

Fig. 3 Change of discharging voltage in the dark under galvanostatic discharge at 47 μA cm^{-2} for the 2E- and 3E- photocapacitors. Discharge started at 500 s.

the 2E-photocapacitor (211 mC cm^{-2}). The coulombic efficiency for charge–discharge of the 3E-photocapacitor was 42%. On the basis of the slope of the discharge curve, capacitance of the 3E-photocapacitor is calculated as 0.65 F cm^{-2}. It should be noted that, as shown in Fig. 3, the 3E-photocapacitor causes only a small drop in the voltage on the onset of discharge, while the 2E-photocapacitor exhibited a significant voltage drop. This drop, ΔV, is a sign of the internal resistance (R) of the capacitor[7,8] as expressed by the equation, $\Delta V = IR$ (I denotes photocurrent). The internal resistance is estimated as 330 Ω, which was much lower than 2.6 kΩ measured for 2E-photocapacitor.

A large reduction in ΔV that leads to increased coulombic capacity was realized by the use of the IE, which has dual functions and performs redox electron transfer on one side and charge storage on the other side. Calculated energy densities of discharge per unit area of electrode are 47 μW h cm^{-2}, which is five times more than that of the 2E-photocapacitor, 9.3 μW h cm^{-2}. The main cause of this improvement is efficient transfer of electrons and holes at the bifunctional IE; in the charge process, holes generated at the exited dye oxidize I^- to form I_3^-, which diffuses to the IE to inject holes to be accumulated as double-layer charge on AC and, in the discharge process, electrons accumulated at the AC on the CE move to the AC on the IE without interruption by a potential barrier, which had existed in the PE (TiO_2) when using the 2E system. The 3E photocapacitor, however, showed a relatively low coulombic efficiency in the charge–discharge process presumably due to self-discharge. This self-discharge can be associated with the back electron transfer at the IE by partial quenching of the holes accumulated in the AC by iodide anions in the electrolyte.

In conclusion, we have devised a dye-sensitized photocapacitor capable of a high charging voltage up to 0.8 V and direct storage of light energy for 47 μW h cm^{-2}, using a three-electrode system to facilitate electron and hole transfer in the charge–discharge processes. The photocapacitor is capable of cyclic photocharge and discharge, similar to the performance of the 2E photocapacitor.[1]

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