Solid State Dye-Sensitized TiO_2 Solar Cell with Polypyrrole as Hole Transport Layer

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Solid type dye-sensitized solar cell was fabricated using photodepositing polypyrrole onto the surface of porous TiO_2 electrode anchored by photosensitizing molecules of a ruthenium complex. Polypyrrole in the porous medium successfully works as hole transport layer connecting the sensitizer dye molecules to a counter electrode. Doping density of the polypyrrole conducting layer was optimized to improve the efficiency of the system.

Photovoltaics using dye photosensitizer in ordered mono molecular layer on porous semiconductor has attracted much interests as a novel type solar cell because of their high efficiency and the feasibility of the preparation.[1] Recent studies proved that the dye-coated porous electrode with the high surface area improves optical pathlength of incident light, achieving high photoenergy conversion efficiency comparable with those in solid solar cells with p/n junction. The remaining problem of the system is the stability of the liquid phase used for hole transport from dye molecules to a counter electrode. The system consists of mixed solvent such as ethylene carbonate and acetonitrile containing redox couple, I_3^-/I^-. The liquid phase often causes the problem of leaks leading to decrease in lifetime and efficiency of the system. Although several attempts were made to improve long term stability using devices with electrolyte support made of capillary pores[2] and the room temperature molten salt,[3] it should be desirable to construct the system without organic solvent medium. Recently, ionic conducting polymers were applied for the system to fabricate solid state cells.[4,5] Difficulty in the fabrication is to construct homogeneous hole transport phase in such porous structure. In this paper, we attempt the fabrication of solid state TiO_2 solar cell using photoelectrodeposited polypyrrole as hole transport layer (Figure 1), and report the effect of doping density of the layer on photocurrent-voltage characteristics of the system.

The dye, *cis*-di(thiocyanato)-N,N'-*bis*(2,2'-bipyridyl-4,4'-dicarboxylic acid)ruthenium(II) complex ($[RuL_2(NCS)_2]$), anchored porous TiO_2 electrode was prepared by the previously reported procedure.[6] Before dye adsorption, surface of TiO_2 electrode (mean diameter of TiO_2 particle = ca. 20 nm, thickness = 11 μm, roughness factor = 1100) on F doped SnO_2 conducting glass was treated by anodic polarization in 0.05 M (1 M = 1 mol dm^{-3}) $TiCl_3$ at pH 2.5 aqueous solution for 1 h at current density of 0.05 $mA{\cdot}cm^{-2}$. The dye was adsorbed onto the surface in an ethanol solution of the dye (3×10^{-4} M) by refluxing for 15 min under nitrogen atmosphere (quantity of the adsorbed dye per unit area = 7×10^{-7} $mol{\cdot}cm^{-2}$). Electrodeposition of polypyrrole onto the dye adsorbed porous TiO_2 electrode was carried out in a 0.1 M $LiClO_4$ acetonitrile solution containing 0.1 M pyrrole by potentiostatic procedure (-100 mV vs. Ag/Ag^+) under the illumination by 500 W Xe lump (400 ~ 1000 nm, 22 $mW{\cdot}cm^{-2}$). Total charges for the anodic deposition was 100 $mC{\cdot}cm^{-2}$. After the electrodeposition procedure, the doping density of polypyrrole was controlled by treatment as follows. The electrode was immersed in a 0.1 M $LiClO_4$ acetonitrile solution under visible light irradiation, and was kept at the doping potential of -300 mV or 100 mV for 30 min. After drying of the resulting electrode, the side of electrodeposited polypyrrole was covered by gold deposited through evaporation (rate = 0.05 nm sec^{-1}, thickness = 100 nm). Partial deposition of SiO_2 onto polypyrrole surface was carried out to prevent direct electronic contact between TiO_2 electrode and the connecting wire, which might be caused by the penetration of silver paste for the connection. Figure 2 shows schematic presentation of the vertical sectional view of the solid type solar cell. Photoelectrochemical measurements were performed according to the reported procedures.[6]

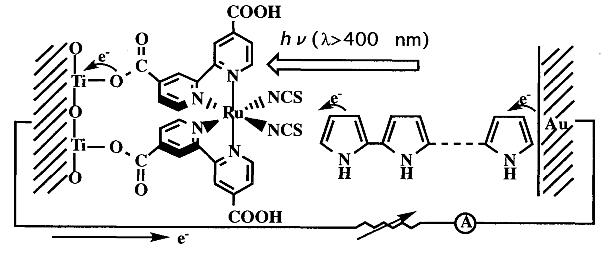

Figure 1. Schematic presentation of solid sate dye-sensitized solar cell.

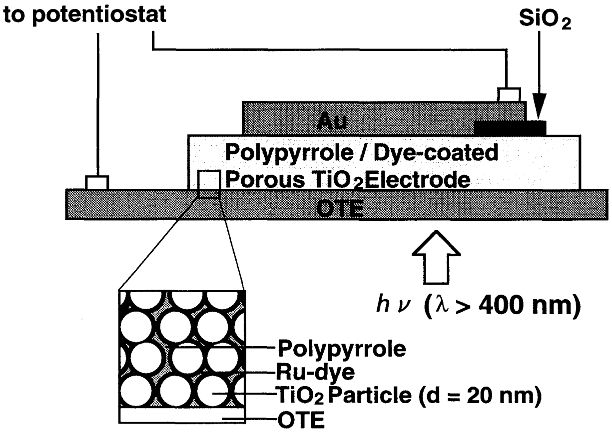

Figure 2. Vertical sectional view of the solid cell.

Figure 3 shows photocurrent-voltage characteristics of the cells under white light illumination from 500 W Xe lump (400 nm ~ 1000 nm, 22 $mW{\cdot}cm^{-2}$). Anodic photocurrent response was observed at the cell treated at -300 mV. Open circuit voltage (V_{oc}) and short-circuit photocurrent (i_{sc}) of the cell were 285 mV and 22 $\mu A{\cdot}cm^{-2}$, respectively. The response proved that the electrodeposited polypyrrole on the dye coated porous TiO_2 electrode works as hole transport layer electronically connecting the dye molecules to a gold counter electrode, *i.e.*, electron was injected to the excited dye molecules successfully from polypyrrole. It was confirmed that any photoresponse was not

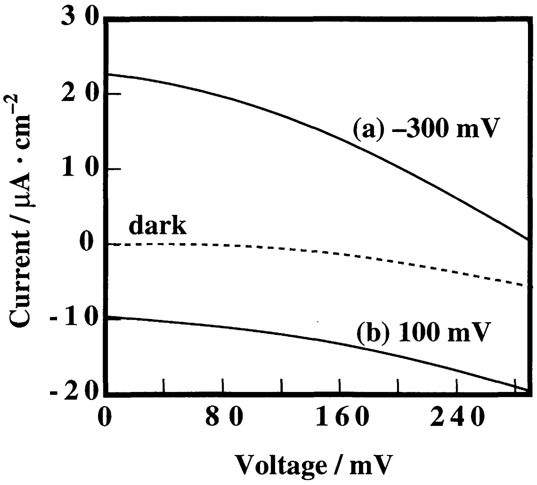

Figure 3. Photocurrent-voltage characteristics of the solid cell using polypyrrole treated at -300 mV (a), and 100 mV (b).

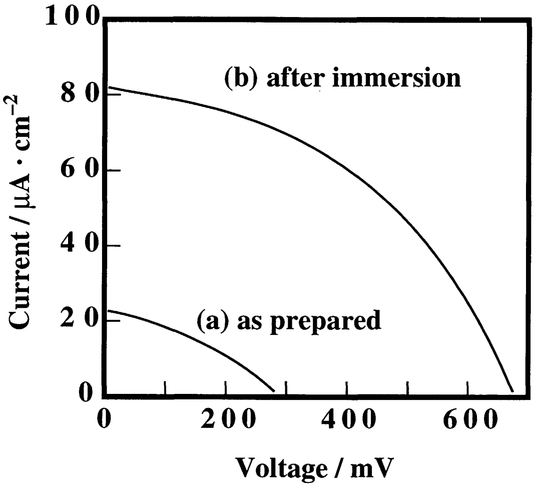

Figure 4. Photocurrent-voltage characteristics of the solid cell using polypyrrole treated at -300 mV; (a) as prepared, and (b) after immersion treatment.

observed for the cell prepared without the dye molecules. Photocurrent measurement was also carried out using the polypyrrole-deposited cell treated at 100 mV. In this system, cathodic photocurrent was observed, contrary to our expectation. Relatively low photocurrent at short-circuit potential was -10 $\mu A \cdot cm^{-2}$. The cathodic photocurrent increased as the electrode potential became positive. The difference in the photoresponse depending on the doping potential should be due to the difference of the oxidation state of polypyrrole. The doping density of polypyrrole treated at -300 mV should be lower than that treated at 100 mV. Thus, Fermi level of polypyrrole treated at -300 mV became higher than that treated at 100 mV. This difference resulted in effective electron injection from polypyrrole to excited dye molecules. Lower Fermi level in polypyrrole treated at 100 mV should induce back-electron transfer from the excited dye molecules to polypyrrole rather than expected electron injection from polypyrrole.

The above results suggest that optimum oxidation state of polypyrrole should be chosen to induce effective electron injection to dye molecules. The lower doping density, however, often decreases the conductivity of polypyrrole. In the present system, higher conductivity should be achieved keeping the optimum oxidation state of polypyrrole. We have also successfully attempted to improve the conductivity of polypyrrole treated at -300 mV by immersion treatment into a 0.2 M $LiClO_4$ acetonitrile solution for 1 h. Dopant, *i.e.*, ClO_4^-, as well as Li^+ was expected to diffuse into polypyrrole during this immersion. The effect of the improved conductivity was clearly observed as improvement of the photocurrent-voltage characteristics as shown in Figure 4. Both V_{oc} and i_{sc} were improved to 670 mV and 82 $\mu A \cdot cm^{-2}$, respectively. Energy conversion efficiency of the cell was ca. 0.1 %. Higher concentration of ClO_4^- in polypyrrole should contribute to improvement of charge mobility in the polymer chain of polypyrrole.

In conclusion, we successfully fabricate a solid type dye sensitized solar cell using photodeposited polypyrrole onto the surface of porous TiO_2 electrode coated by photosensitizer molecules of a ruthenium complex. Polypyrrole in the porous medium was confirmed to work as hole transport layer. Oxidation state as well as doping density of the polypyrrole layer was controlled and optimized. It was proved that the increase of doping density keeping the optimum oxidation state is important to improve photocurrent-voltage characteristics.

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