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Water-based Dye-sensitized Solar Cells: Interfacial Activation of TiO_2 Mesopores in Contact with Aqueous Electrolyte for Efficiency Development

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Surface activation of TiO_2 mesopores in contact with aqueous electrolytes was conducted by hydrophilic conversion and reaction of chemical adsorbents. Water-based dye-sensitized solar cell was fabricated as an environmentally benign device. The solar cell yielded high conversion efficiency up to 2.2%.

Recent technical developments of dye-sensitized solar cell (DSSC) is making a new focus on low-temperature fabrication of mesoporous electrodes,[1] which enables manufacture of low-cost film-type cells and drastic reduction of environmental load. Green chemical fabrication of the cell is an important goal for DSSCs to compete with green processes for solid junction solar cells.[2] Use of organic volatile electrolytes and ruthenium bipyridyl complex dyes as sensitizers in DSSC achieves conversion efficiency of 10% or more that well competes with that of amorphous Si solar cells.[3] Volatile and flammable electrolytes, however, seriously degrades the durability and safety of the cell. To solve this, solidation and quasi-solidation of DSSC have been attempted in various ways by replacing the electrolytic layers with p-type semiconductors[4] (CuI, etc), polymer electrolytes,[5] and ionic liquids (imidazolium salts).[6] Among these alternatives, ionic liquids are considered most promising in cell performance.[6] However, imidazolium salts are of high cost and would likely involve high environmental load for preparation. In this regard, an expected direction for the electrolyte material is to utilize water as a green recyclable solvent. Except for the early experiments of Grätzel and co-workers,[7] little study has been attempted for construction of water-based DSSCs because aqueous electrolytes generally yield very low conversion efficiency ($<1\%$) compared with organic electrolytes. Activity of Ru complex dyes with excellent light-harvesting ability have been only available in acidic aqueous electrolyte solutions[7b,7c] that can barely stabilize the dye-TiO_2 binding. To solve this, goal of this communication is to report that interfacial activation of mesoporous TiO_2 films in contact with aqueous electrolyte is effective for constructing a water-based DSSC of relatively high efficiency and sufficient durability.

TiO_2 crystalline nanoparticle (F5) of average size 20–30 nm was supplied from Showa Titanium Co. It is anatase-rutile mixture (rutile content, 30%) of high crystallinity that is effective for reinforcing dye adsorption.[8] A viscous paste of the particle (TiO_2 content of 16 wt %) containing polyethylenglycol (MW 500000, 4 wt %) in ethanol (10%)-containing water was coated on a F-doped conductive transparent SnO_2 glass electrode (surface resistance of 7–9 $\Omega/\square$) and was sintered at 550 °C for 30 min to form a 20 μm-thick mesoporous TiO_2 film. Ru bipyridine complex sensitizers were used as supplied from Solaronix SA, one of which (Ru535 = $Ru[bpy(COOH)_2]_2(SCN)_2$) has four carboxylic acid groups as absorbable groups and the other (Ru535bisTBA = $Ru[bpy(COONBu_4)(COOH)]_2(SCN)_2$) has two carboxylic acid groups and two calboxylate with tetrabutylammonium. For dye adsorption, the TiO_2-coated electrode was dipped in 0.3 mmol/L solution of the dye in a mixture of acetonitrile:*tert*-butanol:ethanol (2:1:1 in volume) at 40 °C for 90 min.

In order to improve interfacial properties, two processes were carried out for TiO_2 mesopores. First, prior to dye adsorption, the mesoporous layer was treated with gaseous active oxygen. The TiO_2 electrode was set in a quartz tube under flowing of ozone-containing air (300 ppm) at rate of 1 L/min, ozone being produced by silent discharge of oxygen (99.9%). TiO_2 surface was exposed to UV light (254 nm) with a 13-W low-pressure mercury lamp for 60 min at a constant intensity of 22 mW/cm^2. Second, dye adsorption on TiO_2 was conducted in the presence of *tert*-butylpyridine (TBP) that had been mixed to the dye solution at concentration of 5 vol %. Neutral aqueous redox electrolyte was composed of 0.5 mol/L KI and 0.025 mol/L I_2 in water (pH 6–7). In this composition a portion of water was replaced by ethanol up to 35 vol% in an attempt to enhance photocurrent. Photoelectrochemical cell was constructed with platinum-deposited F/SnO_2 glass electrode as a counterelectrode. Thickness of the electrolyte layer was 50 μm by using a hot-seal type polyethylene film. Effective light-receiving area was 0.64 cm^2. Conversion efficiency was measured under simulated solar irradiation of 1 sun intensity (100 mW/cm^2, AM 1.5 G).

Dye-sensitized cells with aqueous iodide electrolyte, without undergoing the TBP and UV/ozone treatments to the mesoporous surface, yielded low photocurrent densities (J_{sc}) of 2.7 and 2.0 mA/cm^2 for sensitizers of Ru535 and Ru535bisTBA, respectively. Open-circuit voltage (V_{oc}) was in the range of 0.37 to 0.40 V, which was much lower than those normally obtained with organic liquid electrolytes (>0.7 V). It is noteworthy that with a substantially equal amount of dye molecules adsorbed per area, Ru535 dye with stronger adsorption power gave much higher J_{sc} than Ru535bisTBA. Ru535-adsorbed F5 TiO_2 film showed little release of the adsorbed dye into neutral aqueous electrolytes.

TBP treatment of the TiO_2 mesoporous improved the photoelectric performance for both dyes. A large increase in J_{sc} and V_{oc} occurred for Ru535 when 5% TBP-containing dye solution was used for dye adsorption. The result is shown in Table 1. It has been established that TBP added in electrolyte or dye solution improves V_{oc} in organic electrolyte-based DSSC.[9] Since TBP is insoluble in aqueous electrolytes, we used TBP on the step of dye adsorption and found that J_{sc} is also significantly enhanced. We consider that TBP adsorbed on the TiO_2 surface accelerates deprotonation of the dye carboxyl group to reinforce the dye-TiO_2 binding and thus raises electron injection efficien-

Table 1. Photoelectric performances of water-based DSSCs with different conditions for electrolyte solvent, sensitizing dye, and TBP treatment under exposure to simulated solar irradiation of 1 sun (100 mW/cm^2, AM 1.5 G). Electrolyte contained 0.5 mol/L KI and 0.025 mol/L I_2

Electrolyte Solvent	Dye	J_{sc} /mA cm^{-2}	V_{oc} /V	η %
Water	Ru535	2.70	0.37	0.6
	Ru535 with TBP	3.61	0.47	1.1
	Ru535bisTBA	2.00	0.40	0.5
	Ru535bisTBA with TBP	2.14	0.44	0.6
35% aqueous ethanol solution	Ru535	4.68	0.47	1.3
	Ru535 with TBP	4.94	0.55	1.7
	Ru535bisTBA	4.04	0.48	1.1
	Ru535bisTBA with TBP	4.24	0.51	1.3

cy. Aqueous electrolyte containing 35% ethanol also yielded higher photoelectric performance for Ru535 than Ru535bisTBA in the presence of TBP. Conversion efficiency (η) with the former dye reached 1.7% with $J_{sc} = 4.9$ mA/cm^2 and $V_{oc} = 0.55$ V under irradiation of 100 mW/cm^2, which is fairly high as a water-based dye-sensitized cell using neutral aqueous electrolyte. Table 1 summarizes photoelectric data obtained for both Ru dyes with and without the TBA treatment.

With aqueous electrolytes, however, the surface of TiO_2 showed hydrophilicity not high enough to allow efficient permeation of aqueous redox electrolyte into the mesoporous structure due to high surface tension of water compared to organic electrolytes. To improve wettability of the mesoporous layer, ozone/UV post-treatment was carried out. Figure 1 shows I–V characteristics of dye-sensitized cells (aqueous 35% ethanol electrolyte) with and without the ozone/UV treatment. The electrode with ozone/UV-treatment yielded J_{sc} of 5.8 mA/cm^2, which was 20% larger than J_{sc} of nontreated electrode. This J_{sc} recovery was accompanied by substantial increase in V_{oc} by 50 mV. The conversion efficiency under 1 sun (100 mW/cm^2) was increased to 2.2%, a level of efficiency 4 times larger than the initial performance of the dye with neutral water-based electrolyte.

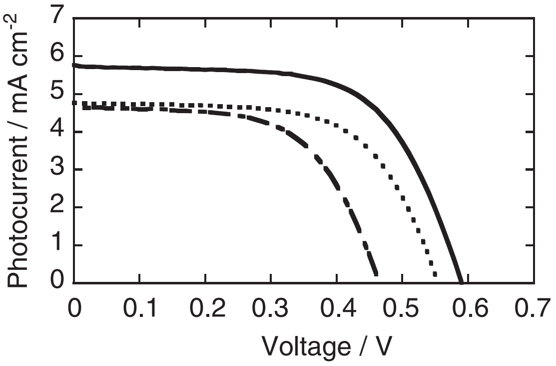

Figure 1. Photocurrent density-voltage characteristics for DSSCs with and without ozone/UV treatment of TiO_2 mesopores. — Ozone/UV treated TiO_2 layer before dye adsorption; ---- TiO_2 layer without ozone/UV treatment; -—- TiO_2 layer without ozone/UV treatment and TBP treatment. Incident power density, 1 sun (100 mW/cm^2, AM 1.5 G). Light-receiving area, 0.64 cm^2. All DSSCs except for the last were treated with TBP in dye sensitization. Aqueous electrolyte was 35% ethanol-containing neutral water with 0.5 mol/L KI and 0.025 mol/L I_2.

Water contact angle measurements using single crystal TiO_2 samples clarified that hydrophilic conversion by the present ozone/UV treatment decreases contact angle from 71 to 7 (rutile (100) surface) and 71 to 22 (anatase (100) surface).

Preservation stability was examined for a DSSC made of pure water-based electrolyte and Ru535-adsorbed F5 film. Photocurrent amplitude decreased to half the initial level during 2.5 months of preservation of the cell at room temperature, without substantial lowering in V_{oc}. It has been investigated that deterioration of dye-sensitized cells can proceed via water-assisted decomposition of iodide in organic electrolytes.[10] We detected bleaching of iodine for some of sample cells (not all cases) and agree that the lifetime of water-containing electrolytes can be shorter than non-aqueous organic electrolytes. Even if it matters, a significant merit of DSSC is insisted that electrolyte itself can be exchanged to recover the cell performance. In combination of water-based electrolytes with low temperature electrode fabrication,[1] greener process for DSSC fabrication can be designed for realization of environmentally benign dye solar cells.

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References and Notes

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