

A High Voltage Dye-sensitized Solar Cell using a Nanoporous NiO Photocathode

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An np tandem dye-sensitized solar cell (np-DSC) comprising a titanium dioxide (TiO₂) anode and a nickel oxide (NiO) cathode prepared as porous nanostructured films by a sol-gel method using a triblock copolymer template (P123, HO(OCH₂-CH₂)₂₀(OCH(CH₃)CH₂)₇₀(OCH₂CH₂)₂₀OH)CH₂ exhibited a high open circuit voltage (V_{oc}) of 0.92 V that surpassed the long time champion data, ≈ 0.8 V for conventional DSC.

Since Grätzel and co-workers reported a highly efficient DSC,^{1,2} it has been extensively investigated as one of the most interesting alternatives to current solar cell technology for the conversion of sunlight into electrical energy. Typical DSC comprises a dye-adsorbing porous, nanocrystalline titanium dioxide film interpenetrated by a liquid electrolyte containing an I⁻/I₃⁻ red/ox couple. Because of n-type behavior of the dye-sensitized titanium oxide electrode, the conventional DSC is also called n-DSC. Although many researchers have tried to improve the performance, that is, V_{oc} , short circuit current density (J_{sc}), and the fill factor, reported more than ten years ago by Grätzel group,^{1,2} no one has significantly surpassed their data.

In this paper, we will report on an np-DSC exhibiting a V_{oc} , ≈ 0.92 V, significantly higher than the best V_{oc} , ≈ 0.8 V, of conventional DSC reported by Grätzel and co-workers.^{1,2} Replacement of a photo-inactive cathode of a Grätzel type cell by a dye-sensitized p-type semiconductor cathode results in an np-DSC. Figure 1 illustrates principle of photocurrent generation by np-DSC. V_{oc} of np-DSC is equal to $V_{oc1} + V_{oc2}$, where V_{oc1} is equal or close to V_{oc} of single n-DSC. Hence V_{oc} of np-DSC is intrinsically higher than that of conventional n-

DSC. When irradiated from the anode side, the solar light is partly absorbed by dye-1, yielding V_{oc1} . The light passing through the dyed anode and the electrolyte reaches the cathode and is absorbed by dye-2, yielding V_{oc2} . Thus an np-DSC is able to utilize wide spectrum of solar light when the dye-2 is designed to absorb the longer wavelength light in comparison with the dye-1. Lindquist and co-workers fabricated a np-DSC comprising a conventional TiO₂ dye-sensitized anode, an I⁻/I₃⁻ electrolyte and a dye-sensitized NiO cathode.³ V_{oc} of 0.73 V reported by them was, however, still lower than the best V_{oc} of n-DSC. In our work, the anode and the cathode are dye-sensitized TiO₂ and NiO films, respectively, as used by Lindquist and co-workers, but we prepared them differently, intending to increase dye-adsorbing surface area of NiO film. The both photoelectrodes were prepared by a sol-gel method using P123 triblock copolymer as a nanostructure template: P123 has been applied for preparation of crack-free nanoporous films.^{4,5}

The preparation of photoanode TiO₂ film is described briefly in the following. 1.25 g of P123 was added to 3 g of titanium isopropoxide dissolved in a mixed solvent of acetyl acetone and 2-propanol, and stirred for 3 h. Then the solution was spin-coated (400 rpm for 3 s, then 2000 rpm for 10 s) on SnO₂: F conducting glass (FTO) (Asahi glass co. Ltd., 10 $\Omega/\square$), and dried at room temperature. This process was repeated three times. The FTO substrate was immersed in an alkaline bath for 2 h before the spin coating. Finally, the spin-coated precursor film was calcined at 450 °C for 30 min in air. Nanostructured NiO film for photocathodes was similarly prepared by a sol-gel method using NiCl₂ as a source material and P123 as a template. The TiO₂ and NiO films were immersed into dehydrated ethanol solution containing 10⁻⁴ M of *cis*-di(thiocyanato)bis(4,4'-dicarboxy-2,2'-bipyridine) ruthenium(II) (Kojima Chemicals Co. Ltd., Ru(dcbpy)₂(NCS)₂) or 3-carboxymethyl-5-[2-(3-octadecyl-2-benzothiazolylidene)ethylidene]-2-thioxo-4-thiazolidine (MC, Hayashibara Biochemical Laboratories, Inc.)⁶ for 12 h, respectively. Ru(dcbpy)₂(NCS)₂ and MC were used without purification. Prior to fabrication of DSC, the dye-coated TiO₂ and NiO films were rinsed with dehydrated ethanol and dried using dry N₂ gas. Counter electrodes for n- and p-DSC were prepared by depositing Pt/Pd on ITO by sputtering with Pt/Pd (7:3) target. DSC were fabricated by coupling the TiO₂ anode with the counter-electrode for n-DSC, the counter electrode with the NiO cathode for p-DSC, and the TiO₂ anode with the NiO cathode for np-DSC, and filling the space between the both electrodes with an I⁻/I₃⁻ electrolyte PN50 (Solaronix SA). The active cell area was 0.12 cm². The cells were irradiated at 100 mWcm⁻² with a light source simulating AM 1.5 global solar radiation. The photocurrent-bias voltage characteristics were obtained using a standard three-electrode setup. Scanning rate was 10 mVs⁻¹.

FE-SEM images, reported elsewhere,⁷ of the TiO₂ (anatase

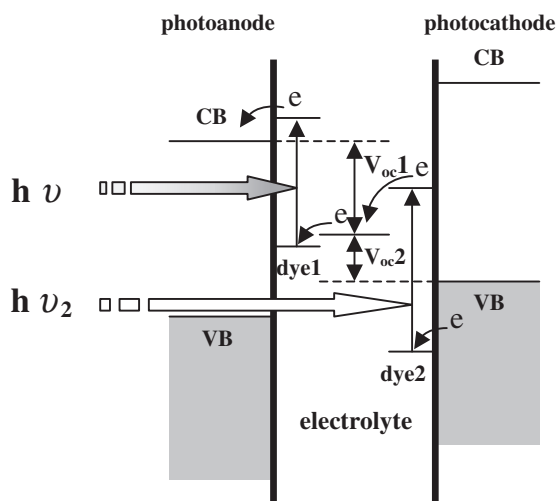


Figure 1. Principle of photocurrent generation by np-DSC.

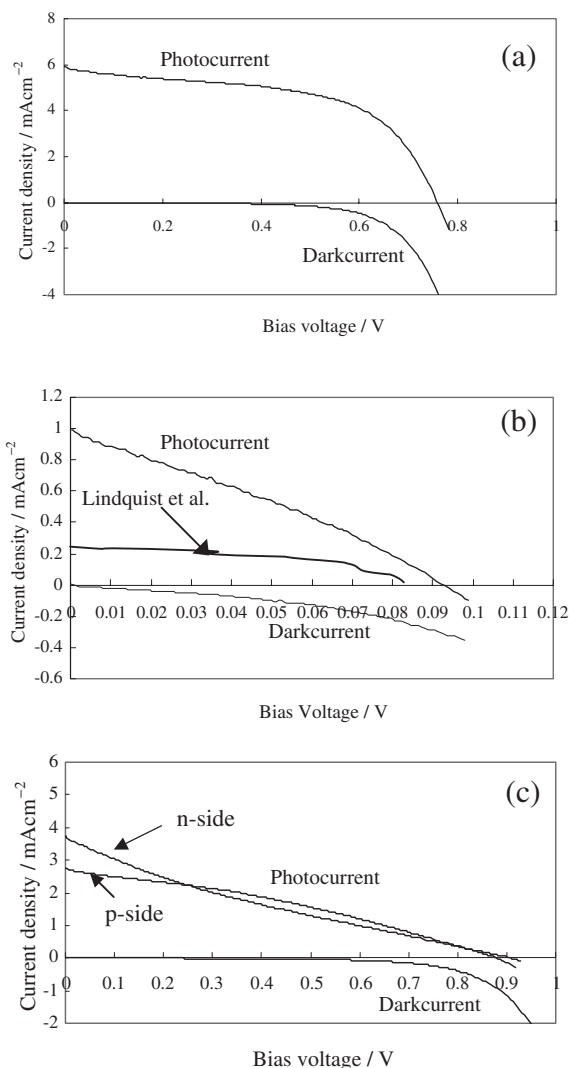


Figure 2. The photocurrent vs bias voltage of various type DSCs. (a) n-DSC, (b) p-DSC, (c) np-DSC, and n-side and p-side shows illumination direction.

phase) and NiO films indicated the formation of nanoparticles of 10–30 and 30–40 nm diameters, respectively.

The photocurrent density–bias voltage curves of n-, p-, and np-DSC are shown in Figure 2. The n-DSC exhibited a V_{oc} of 0.76 V (Figure 2a), which is comparable to that of well-prepared conventional n-DSC. The result indicated that the sol–gel method using P123 as a template could be an alternative method for preparing nanostructured TiO_2 anodes of n-DSC. Although the J_{sc} of our n-DSC was low, we expect that further increase in the film thickness to 10 μm from $\sim 1 \mu m$ of this work would raise J_{sc} to the level of conventional n-DSC. The photocurrent density–bias voltage curve of our p-DSC is shown together with that of the pioneering work by Lindquist and co-workers (Figure 2b); J_{sc} and V_{oc} are fivefold and by $\approx 15\%$, respectively, larger than their results.³ We presumed that the improvement of NiO nanostructure owing to the application of the sol–gel method using P123 increased dye-adsorption surface area, which enhanced light absorption, resulting in increased number of photoactivated electrons.

Table 1. The characterization of various type DSCs

type	J_{sc} / $mAcm^{-2}$	V_{oc} /V	FF ^b /–	η^c /%
n	5.83	0.762	0.53	2.360
p	1.00	0.093	0.30	0.027
np (n-side) ^a	3.62	0.918	0.19	0.660
np (p-side) ^a	2.73	0.887	0.32	0.780

All data collected with 100 $mWcm^{-2}$ solar illumination.

^aparagraph is illumination side.

^bFF is fill factor.

^c η is photoconversion efficiency.

The np-DSC exhibited V_{oc} of 0.92 V which is higher than the best V_{oc} , ≈ 0.8 V, of conventional DSC (Figure 2c). This result demonstrated that the np tandem would be a suitable structure for a high voltage type DSC. J_{sc} and V_{oc} of our np-DSC were higher by approximately 70 and 27%, respectively, than the reported np-DSC data.³ J_{sc} of our np-DSC, 3.7 $mAcm^{-2}$, was smaller than that of our n-DSC, which was presumably due to the insufficient number of carriers generated by the photocathode. We expect that increase of NiO film thickness would enhance dye adsorption, resulting in a higher current density. Choice of dyes is also important to increase the current density. The combination of dyes, $Ru(dcbpy)_2(NCS)_2$ as dye-1 and MC as dye-2, applied in this work is not optimal, because the absorption edge of dye-2, 589 nm, was shorter than that of dye-1, 750 nm.

Difference of the irradiation direction, from p- or n-side, did not make significant difference of the np-DSC performance. This suggested that the cathode absorbed minor amount of the light, giving insignificant difference of irradiation intensity at the anode whether it was irradiated directly or through the cathode.

The performance of n-, p-, and np-DSC is summarized in Table 1.

In conclusion, np-tandem DSC can generate a V_{oc} higher than n-DSC. When carrier generation at the photocathode is augmented to a level at the photoanode of conventional n-DSC, J_{sc} and the solar-to-electricity conversion efficiency (η) of np-DSC would approach and surpass, respectively, those of conventional n-DSC. Further development including enhancement of dye adsorption at the cathode and choice of optimum combination of dyes is required to increase cathode photocurrent.

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