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Fabrication of Dye-Sensitized Solar Cells with an Open-Circuit Photovoltage of 1 V

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Solar energy conversion by photoelectrochemical devices is being intensively investigated as an alternative energy source instead of conventional fossil-fuel-based energy systems. Of the several different types of solar cells under development today, dye-sensitized solar cells (DSSCs) have attracted considerable interest because of their significantly high photoconversion ability and low material and production costs.[1,2] As the energy conversion efficiency (η) is calculated from the short-circuit current density (J_{sc}), the open-circuit voltage (V_{oc}), the fill factor (FF) and the intensity of incident light (P), a simultaneous improvement of the three parameters, J_{sc}, V_{oc} and FF, is needed in order to improve η [Eq. (1)].

$$\eta = (J_{sc}\, V_{oc}\, \mathrm{FF})/P \qquad (1)$$

Since the landmark paper on DSSCs reported by Grätzel and O'Regan appeared in 1991,[1] a number of studies have focused on enhancing the efficiency of the cells by using new materials and/or improving the device structure, which has led to significant improvements in J_{sc} or FF.[3–7] However, with regard to V_{oc}, only a slight enhancement has been accomplished so far, although it is clearly expected that an increase in V_{oc} offers a great opportunity for a substantial enhancement of η. This is probably because of the utilization of TiO_2 electrodes and electrolytes containing iodide and triiodide (I^-/I_3^-) ions, which are considered as the best electron-transfer mediators in DSSCs. As the maximum V_{oc} is determined by the difference between the Fermi level of the electrode under illumination and the redox potential of the electrolyte, in the case of TiO_2 electrodes and iodide-based electrolytes, V_{oc} is definitely limited to about 0.9 V.[2,8,9]

With regard to the sensitizer, Ru complex dyes exhibit the highest photoconversion efficiencies of up to 11% under AM 1.5 irradiation (100 mW cm^{-2}).[2,6,9] However, the development of organic dyes instead of Ru complex dyes remains important because the materials and processes required in the synthesis of Ru dyes are expensive and the limitation of Ru resources is a critical issue. Synthetic organic dyes have many advantageous features such as the diversity of the dye structure, high extinction coefficients, low cost of the material and facile preparation as well as purification processes. One additional and quite noticeable feature of organic dyes is that some dyes, for instance, phenyl-conjugated organic dyes,[10,11] have much higher lowest unoccupied molecular orbitals (LUMOs) as compared to Ru complex dyes, which may bring about an enhancement in the V_{oc} value used in DSSCs. Herein, we report a major advancement in the enhancement of V_{oc} of DSSCs by the combined use of cyanoacrylic acids as the photosensitizer and nanocrystalline Mg-containing titanium oxides as the electrode. The obtained cells generated a significantly high V_{oc} of 1.00 V, the highest value reported so far generated by a single DSSC.

Magnesium-modified titanias were prepared by heating the appropriate amounts of titanium tetraisopropoxide and $Mg(CH_3COO)_2{\cdot}4H_2O$ in 1,4-butanediol at 300 °C for 2 h in an autoclave.[12–14] The products obtained are designated as Mg(x)-TiO_2, where x is the Mg/Ti charged ratio. X-ray diffraction (XRD) analysis shows that Mg(0)-TiO_2 (pure TiO_2) and Mg(0.1)-TiO_2 have anatase structures and no indication of the presence of other phases. It was also shown that the peak positions were shifted by the addition of Mg, and these results indicate that the Mg ions are incorporated in the anatase structure.

The UV/Vis absorption spectra of the Mg(x)-TiO_2 samples are depicted in Figure 1. Relative to that of Mg(0)-TiO_2, the optical absorption edges shift to shorter wavelengths with increasing

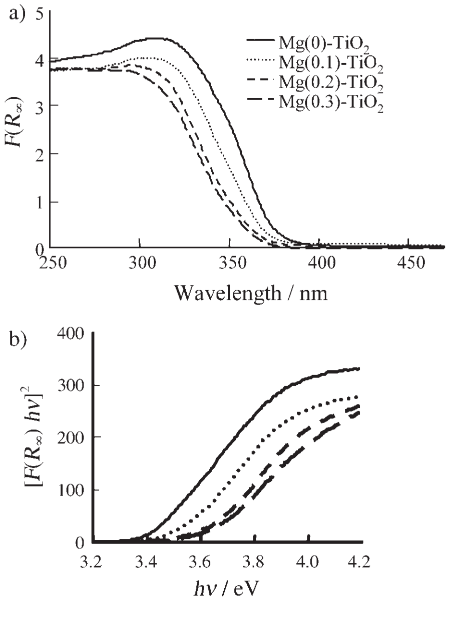

Figure 1. UV/Vis absorption spectra of Mg(x)-TiO_2: a) as a function of wavelength and b) as a function of energy.

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Mg addition, which is a clear indication of the change in the band-gap energy. It is known that $MgTiO_3$ and $MgTi_2O_5$ have higher band gaps than pure TiO_2.[15,16] Therefore, the observed shifts suggest the formation of Mg-Ti mixed oxides; however, the local structure of Mg ions is not elucidated sufficiently. For oxides not containing partly filled d levels, the relationship between the flat-band potential V_{fb}(NHE) and the band gap E_g is given by Equation (2).[15] Accordingly, the flat-band potentials of the Mg(x)-TiO_2 samples are expected to lie at more negative positions than that of pure TiO_2.

$$V_{fb}(\text{NHE}) = 2.94 - E_g \qquad (2)$$

Table 1 lists the photoelectrochemical properties of DSSCs with Mg(x)-TiO_2 electrodes using three sensitizing dyes: *cis*-dithiocyanato-bis(4,4′-dicarboxy-2,2′-bipyridine)ruthenium(II) bis(tetrabutylammonium) salt (N719), 2-cyano-5-(4-*N*,*N*-diphenylaminophenyl)-*trans*,*trans*-penta-2,4-dienoic acid (NKO-007) and 2-cyano-3-(4-*N*,*N*-diphenylaminophenyl)-*trans*-acrylic acid (NKY-003). With N719, the V_{oc} values increased slightly using Mg-containing TiO_2 electrodes. On the contrary, the V_{oc} values were markedly enhanced from 0.75 V to about 0.9 V for NKO-007, and from 0.73 V to over 0.9 V for NKY-003. As the maximum V_{oc} value for the DSSCs using TiO_2 electrodes and I^-/I_3^-electrolytes is known to be around 0.9 V,[2,8,9] the V_{oc} values higher than 0.9 V obtained in this study are noteworthy. To the best of our knowledge, the highest V_{oc} value of 1.00 V, attained for the combined use of Mg(0.1)-TiO_2 and NKY-003, is the highest V_{oc} reported so far generated by a single DSSC. These results indicate that the Fermi levels of these electrodes under working conditions are negatively shifted as compared to those of pure TiO_2, which is consistent with the above-mentioned shift of the flat-band potential estimated from the band-gap energy [Eq. (1)].

Table 1. Performance of DSSCs using Mg(x)-TiO_2 electrodes.

Dye	Electrode	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF	η [%]
N719	Mg(0)-TiO_2	6.45	0.67	0.72	3.1
	Mg(0.1)-TiO_2	7.78	0.75	0.74	4.4
	Mg(0.2)-TiO_2	7.79	0.75	0.75	4.4
NKO-007	Mg(0)-TiO_2	3.02	0.75	0.70	1.6
	Mg(0.1)-TiO_2	4.51	0.89	0.76	3.1
	Mg(0.2)-TiO_2	4.09	0.90	0.79	2.9
NKY-003	Mg(0)-TiO_2	2.41	0.73	0.70	1.2
	Mg(0.1)-TiO_2	3.48	1.00	0.71	2.5
	Mg(0.2)-TiO_2	2.47	0.92	0.80	1.8

The energy diagrams of the NKY-003-sensitized Mg(0.1)-TiO_2 solar cell and a conventional N719-sensitized TiO_2 solar cell are illustrated in Figure 2. One may assume that thin layers of an Mg-containing phase act as barrier layers, which prohibit the recombination reaction, hence increasing V_{oc}.[17–21] However, it is known that only a very small amount of the barrier layers, for instance, about 0.5 wt %, is effective to function as a blocking layer, whereas increased amounts of MgO coating result in a drastic decrease in J_{sc}.[20,21] In the case of the Mg(x)-TiO_2 samples, the amounts of MgO used were 4.8 and 9.2 wt % for $x = 0.1$ and 0.2, respectively, which are too large as the effective coating layers. Furthermore, high V_{oc} values over 0.9 V cannot be explained just because of the effect of the coating models. Therefore, it is reasonable to conclude that the enhanced V_{oc} values are a result of the Mg ions incorporated in the anatase lattice. As significant increases in V_{oc} were obtained in the NKY-003/Mg(x)-TiO_2 and NKO-007/Mg(x)-TiO_2 systems and not in

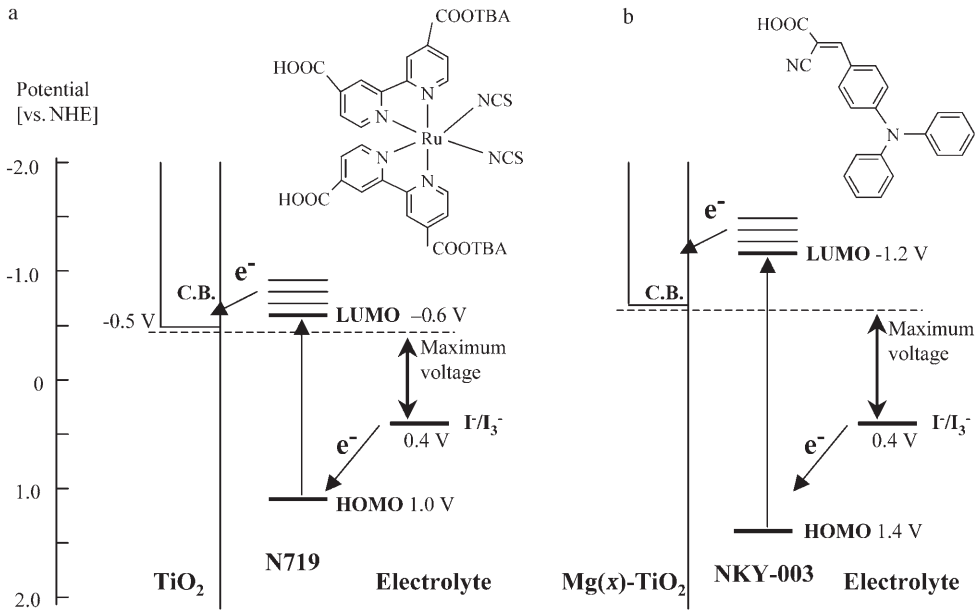

Figure 2. Schematic energy diagrams of the dye-sensitized solar cells (NHE = normal hydrogen electrode; TBA = tetrabutylammonium). a) In the case of conventional TiO_2 electrode and iodide electrolyte, the maximum voltage is lower than 0.9 V. b) The conduction band (CB) edge of the Mg-containing TiO_2 electrode is located at a more negative position relative to the conventional TiO_2 electrode. A dye sensitizer with a higher LUMO energy level can effectively inject the photoexcited electrons into the electrode, and a higher V_{oc} is obtained.

the N719/Mg(x)-TiO_2 system, the combined use of the organic dyes with higher LUMO energy levels together with Mg-containing TiO_2 electrodes seems to be a critical factor in the generation of high V_{oc} values.

As for the J_{sc} value, however, the DSSCs using the organic dyes provided relatively lower values. This is mainly due to the low accordance of the absorption spectra of the organic dye with the solar spectrum. Although further examination is necessary to improve the energy-conversion efficiency, it should be noted that enhanced V_{oc} values higher than 0.9 V were attained with efficiencies of 2–3 %.

In conclusion, we demonstrated in this study for the first time that a single DSSC consisting of a conjugated acid organic sensitizer, NKY-003, and a nanocrystalline Mg-containing TiO_2 electrode generated a high open-circuit voltage of 1 V with a considerable energy conversion efficiency of 2.5 %. The obtained results address a new and promising concept—the combined use of a sensitizer with a high LUMO level together with an electrode with a higher conduction band—for the design of high-performance DSSCs with enhanced open-circuit voltages.

Experimental Section

Nanocrystalline Mg-containing TiO_2 samples were synthesized by the thermal reaction of titanium tetraisopropoxide and magnesium acetate tetrahydrate in 1,4-butanediol: Titanium tetraisopropoxide (25 g), magnesium acetate tetrahydrate (0, 1.88, 3.77 and 5.66 g for $x=0$, 0.1, 0.2 and 0.3, respectively) and 1,4-butanediol (100 mL) were added to a 300 mL autoclave. The atmosphere in the autoclave was replaced with nitrogen, and then the assembly was heated at 300 °C for 2 h.[12–14] After cooling, solid products dispersed in the organic solvent were washed with acetone and then air-dried. They were calcined in a box furnace in air at 450 °C for 30 min. The products thus obtained are designated as Mg(x)-TiO_2, where x is the Mg/Ti charged ratio. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT 2000 diffractometer using CuKα radiation and a carbon monochromator. UV/Vis absorption spectra were recorded on a JASCO V-650 spectrophotometer.

Paste preparation and fabrication of thin-layer electrodes were carried out based on a reported procedure.[22] No scattering layer was used in this study. A solution composed of 0.1 M tetrapropylammonium iodide and 0.05 M I_2 in a mixture of acetonitrile and ethylene carbonate (6:4 v/v) was used as the electrolyte solution. The devices were irradiated at 100 mW cm^{-2} with a light source simulating AM 1.5 global solar radiation.

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Keywords: dye-sensitized solar cells · energy conversion · magnesium · sensitizers

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