

Significant Efficiency Improvement of the Black Dye-Sensitized Solar Cell through Protonation of TiO₂ Films

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This paper describes the influence of acid pretreatment of TiO₂ mesoporous films prior to dye sensitization on the performance of dye-sensitized solar cells based on [(C₄H₉)₄N]₃[Ru(Htcterpy)(NCS)₃] (htcterpy = 4,4',4''-tricarboxy-2,2',2''-terpyridine), the so-called black dye. The HCl pretreatment caused an increase in overall efficiency by 8%, with a major contribution from photocurrent improvement. It is speculated, from the analysis of incident photon-to-electron conversion efficiency, UV-vis absorption spectra, redox properties of the dye and TiO₂, and the impedance spectra of the dye-sensitized solar cells, that photocurrent enhancement is attributed to the increases in electron injection and/or charge collection efficiency besides the improvement of light harvesting efficiency upon HCl pretreatment. Open-circuit photovoltage (*V*_{oc}) remained almost unchanged in the case of significant positive shift of flat band potential for TiO₂ upon HCl pretreatment. The suppression of electron transfer from conduction band electrons to the I₃[−] ions in the electrolyte upon HCl pretreatment, reflected by the increased resistance at the TiO₂/dye/electrolyte interface and reduced dark current, resulted in a *V*_{oc} gain, which compensated the *V*_{oc} loss due to the positive shift of the flat band. Using the HCl pretreatment approach, 10.5% of overall efficiency with the black dye was obtained under illumination of simulated AM 1.5 solar light (100 mW cm^{−2}) using an antireflection film on the cell surface.

Introduction

Dye-sensitized solar cells (DSSCs) have gained considerable attention since the landmark paper in 1991.¹ The DSSCs comprise four major parts: nanocrystalline metal oxide semiconductor film, dye sensitizer, redox electrolyte, and counter electrode. Usually, the dye-loaded semiconductor oxide is called the dye-sensitized photoelectrode, whose photoresponse can be extended to the visible region by dye sensitization. To harvest solar light efficiently, a lot of ruthenium complexes² and organic dyes³ have been designed and synthesized for dye sensitizers in DSSCs. The best dye sensitizer reported so far is the black dye (Figure 1) with visible absorption extending into the near-IR region up to 920 nm, producing an overall efficiency of 10.4%.⁴ Because the theoretical efficiency of

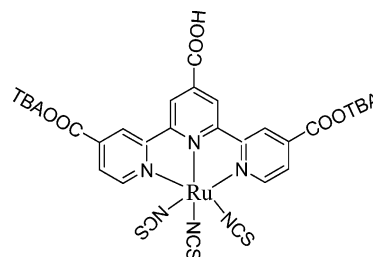


Figure 1. Structure of the black dye. TBA stands for tetrabutylammonium.

the black dye is calculated to be 19.6%,⁵ however, the challenge to optimize it still remains.

The device efficiency depends mainly on the redox properties of the dye and the semiconductor.⁶ The potential difference between the excited energy level of the dye and the conduction band edge minimum for TiO₂ determines the thermodynamic possibility of electron injection. Cations are known to influence semiconductor energetics and the efficiency of interfacial electron-transfer processes in nonaqueous aprotic solvent.¹ Fitzmaurice et al. reported that the flat band potential of TiO₂ was shifted positively by up to 1 V upon addition of 0.1 M LiClO₄ into the acetonitrile electrolyte,⁷ and, thus, the quantum yield of electron injection can be improved by cation adsorption on the TiO₂ surface.¹ However, in aqueous electrolytes, the flat band potential of TiO₂ depends on the pH. Proton adsorption on metal oxide semiconductor surfaces shifts the position of the conduction band edge minimum positively by 59 mV per pH unit.^{7,8} Therefore, the quantum

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yield for interfacial charge transfer can be tuned by adjusting the pH of the aqueous electrolyte. Several groups have studied the pH dependence of the charge-transfer efficiency for dye-sensitized nanocrystalline TiO_2 in aqueous solution.⁹ Although the charge-transfer efficiency can be tuned by adjusting the pH value, the aqueous electrolyte is not suitable in DSSCs because it is inferior to the nonaqueous aprotic one with respect to the cell efficiency and stability. Nevertheless, surface protonation of TiO_2 prior to dye sensitization has been proved to improve the photocurrent generation remarkably for organic dyes.¹⁰ Meyer et al. studied how proton adsorption influenced semiconductor energetics and electron injection.¹¹ They pointed out that protonation of the surface state was required for charge compensation and photocurrent production.¹²

In this study we report the optimization of DSSC based on the black dye through HCl pretreatment of TiO_2 films prior to dye sensitization. The effect of HCl pretreatment on the dye adsorption, redox properties of bare and dye-loaded TiO_2 films, the cell impedance, and their relation with the cell performance were discussed. Cell efficiency was improved remarkably upon HCl pretreatment, and 10.5% overall efficiency was achieved using this approach.

Experimental Section

Materials and Reagents. Dye sensitizer $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Ru}(\text{Htcterpy})(\text{NCS})_3]$ (tcterpy = 4,4',4''-tricarboxy-2,2',2''-terpyridine), the so-called black dye, was purchased from Solaronix SA and further purified by column chromatography on Sephadex LH-20 (Amersham Biosciences, Sweden) with 0.1 M tetrabutylammonium hydroxide aqueous solution as the eluent. All the other solvents and reagents with reagent grade were obtained from Wako.

Preparation of TiO_2 Photoelectrodes. TiO_2 films were fabricated on the fluorine-doped tin oxide ($\text{SnO}_2\cdot\text{F}$) covered glass substrate (TCO, Nippon Sheet Glass Co., Japan, $10\ \Omega/\square$) by screen printing. Anatase TiO_2 particles (23 and 100 nm) were prepared using a published method¹³ and employed to make various pastes for screen printing. TiO_2 pastes were prepared by dispersing TiO_2 particles in α -terpineol with ethyl cellulose as a binder. While paste N was composed of nanoparticles (23 nm), paste M' (M) contained a mixture of nanoparticles (23 nm) and large particles (100 nm) at a weight ratio of 8:2 (6:4). Transparent nanofilms were prepared by printing paste N on TCO glass while NM' films were fabricated by printing paste N, M', and M on the TCO glass subsequently.¹³ The film thickness was monitored with a Tenchor Alpha-Step 500 surface profiler. The apparent film size was 5 mm \times 5 mm. The films were calcined at 525 °C for 2 h with a rising rate of 10 °C/min and treated with 0.05 M TiCl_4 for 30 min at 70 °C followed by heating at 450 °C for 30 min.⁴ The TiCl_4 -treated TiO_2 films (denoted electrode A) were dipped in the 0.1 M HCl solution in ethanol for 2 h followed by washing with ethanol and dried with a N_2 flow, forming electrode B. Electrode A was immersed in the dye solution when the film was about 100 °C while electrode B was dipped in the dye solution at room temperature. Both electrodes were immersed in the dye solutions for at least 12 h. The 0.2 mM black dye containing 20 mM deoxycholic acid (DCA) in ethanol, which was testified to be the best condition for high efficiency, was employed for the coloration of the TiO_2 films.⁴ Although coadsorption of DCA

decreases the dye amount on TiO_2 , the mixed DCA/dye layer suppresses the dye aggregation effectively⁴ and results in enhanced photocurrent, photovoltage, and overall efficiency due to the suppressed charge recombination between the conduction band electrons and I_3^- ions.¹⁴

Photovoltaic Measurement. The sandwich-type solar cell was assembled by placing a platinum-coated conducting glass (counter electrode) on the dye-loaded TiO_2 (working electrode). The cell was sealed using a reported method.¹³ The redox electrolyte used was 0.1 M LiI, 0.05 M I_2 , 0.6 M dimethyl propyl imidazolium iodide, and 0.5 M *tert*-butylpyridine in dehydrated acetonitrile, which was obtained from Tomiyama Pure Chemical Industries, Ltd. The simulated AM 1.5 solar light was obtained from a solar simulator (Wacom Co., Japan, WXS-80C-3 with a 300-W Xe lamp and an AM 1.5 filter). *I*-*V* curves were measured with a direct current voltage current source/monitor (Advantest, R6243). The incident light intensity was calibrated with a standard Si solar cell equipped with a KG-3 filter, which was produced by Japan Quality Assurance Organization. Photocurrent action spectra, incident monochromatic photon-to-electron conversion efficiency (IPCE), plotted as a function of excitation wavelength, were recorded on a CEP-99W system (Bunkoh-Keiki Co., Ltd., Japan). The intensity of incident monochromatic light was calibrated with a Si photodiode (Bunkoh-Keiki Co., Ltd., Japan). To eliminate the reflected and refracted light from outside the active layer, the cell was masked with black paint around the dye-loaded TiO_2 film during *I*-*V* and IPCE measurement. The active area of the cell was measured with a Nikon digital camera controlled by a computer using an objective micrometer ruler as a reference.

Instrumentation. UV-vis absorption spectra of dye-loaded films were recorded with a Shimadzu model 3100 UV-vis-near-IR spectrophotometer in transmission mode. Impedance spectra for DSSCs under illumination of simulated AM1.5 light (100 mW cm^{-2}) were measured with an impedance/gain-phase analyzer (Solartron SI 1260) connected with a potentiostat (Solartron SI 1286). The spectra were scanned in a frequency range of 0.1–10⁵ Hz at room temperature. The applied bias and alternating current amplitude were set at open-circuit condition and 10 mV, respectively.

Results and Discussion

Solar Cell Performance. In nonaqueous aprotic electrolyte, the efficiency of DSSCs depends on the nature of cations. For example, IPCE was increased from 68% for tetrapropylammonium iodide to 84% for lithium iodide.¹ LiI is usually employed in the redox electrolyte for DSSCs. Recently, it was reported that protonation of the TiO_2 surface was effective to increase photocurrent and efficiency for DSSCs consisting of acetonitrile electrolyte.^{10,11} As the anions in the acids may affect the cell performance, various acids (0.1 M) were screened to seek the best efficiency. The strong acids such as HCl, HNO_3 , and H_2SO_4 yielded a similar improvement, while the acids such as HAc and H_3PO_4 diminished the efficiency. This is because they resulted in different dye adsorptions, which will be discussed later. Among the acids improving the cell performance, hydrochloric acid is a simple and non-oxidative acid. On the basis of this consideration, hydrochloric acid was chosen to pretreat TiO_2 films prior to dye sensitization in the following studies unless specified.

The performance data for electrodes A and B are summarized in Table 1. While the short-circuit photocurrent (J_{sc}) and fill factor (FF) were increased, open-circuit photovoltage (V_{oc}) remained almost unchanged, resulting in an increase in overall efficiency (η) by 24%.

Figure 2 depicts the IPCE action spectra for the untreated and HCl pretreated photoelectrodes. IPCE values for electrode B are much higher than those for

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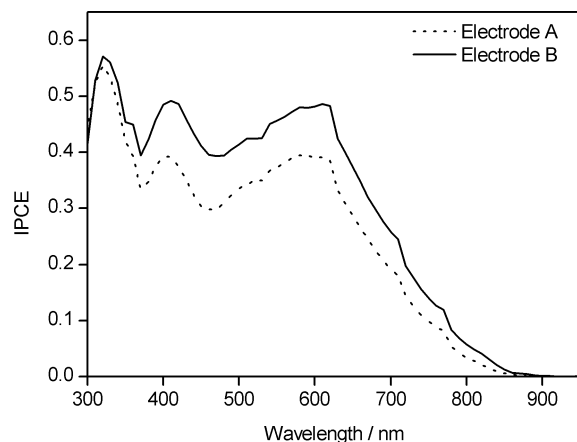
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Table 1. Photocurrent–Photovoltage Characteristics of DSSCs^a

electrode	$E_{\text{fb}} - \text{LUMO}$ (eV)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	η (%)
A	0.15	7.62	0.751	0.728	4.2 ± 0.1
B	0.31	9.31	0.749	0.741	5.2 ± 0.1

^a Dye-sensitized 6 μm nanofilms were measured under 100 mW cm⁻² of simulated AM 1.5 solar light.

**Figure 2.** IPCE action spectra for untreated (electrode A) and HCl pretreated (electrode B) DSSCs. The 6 μm TiO₂ nanofilms were used.

electrode A in the whole visible region. The maximum IPCE was increased by 24% from 39.1 to 48.6%.

To clarify which factors contribute to the IPCE improvement, let us consider the following equation

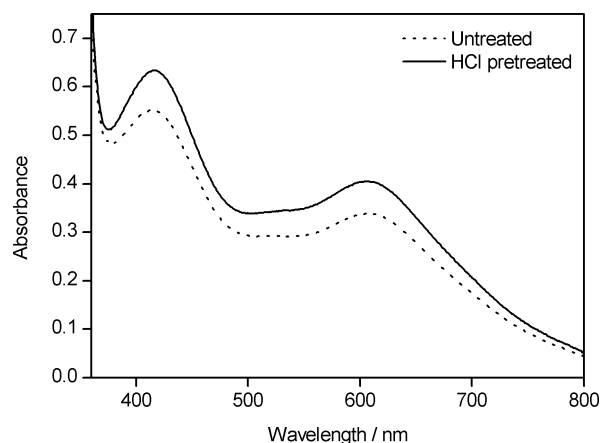
$$\text{IPCE} = \text{LHE} \times \phi_{\text{inj}} \times \phi_{\text{coll}} \quad (1)$$

IPCE is expressed by the product of light harvesting efficiency (LHE) of the photoelectrode, the quantum yield of electron injection (ϕ_{inj}), and the efficiency of collecting the injected electron (ϕ_{coll}) at the conducting glass substrate. The LHE at the maximum absorption wavelength can be estimated using the following equation

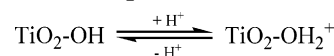
$$\text{LHE} = 1 - 10^{-A} \quad (2)$$

where A is the absorbance of the dye on TiO₂ at the maximum wavelength. To explain the IPCE improvement, the effect of HCl pretreatment on LHE, electron injection, and charge collecting efficiency will be discussed in the following.

UV–Vis Absorption Spectrum. It was found that the HCl pretreatment accelerated the dye adsorption and reduced the time to reach saturation of dye adsorption. On the other hand, the HCl pretreatment resulted in a significant increase of the maximum absorbance by ~20% without shift of the maximum absorption peak, as shown in Figure 3. It is no doubt that the increased dye adsorption contributes to the LHE and, hence, the IPCE improvement. The other strong acids such as HNO₃ and H₂SO₄ also increased the dye adsorption with a similar increasing ratio. However, HAc and H₃PO₄ decreased the dye amount on TiO₂. Carboxylate in HAc and phosphate in H₃PO₄ are strong anchoring groups, and their adsorption occupies part of the surface, which accounted for the significantly decreased dye adsorption and, hence, the poor IPCE. Although the NO₃⁻ and SO₄²⁻ groups can also attach to the TiO₂ surface to some extent, the anchoring group in the dye, that is, -COO⁻, is stronger than them and may

**Figure 3.** UV–vis absorption spectra for the dry dye-loaded untreated (dotted line) and HCl pretreated (solid line) films. A bare TiO₂ film was used as a reference.

Scheme 1. Proton Adsorption/Desorption Equilibrium



replace them easily. The increased dye surface concentration after the strong acid treatment verifies this hypothesis.

On the basis of the above observations, it is the proton adsorption on the TiO₂ surface that results in the IPCE improvement. To confirm this, we first treated the TiO₂ film with hydrochloric acid and then removed HCl by heating the treated film at 450 °C before dipping in the dye solution. It was found that the efficiency after this treatment, which was similar to that for the untreated cell, was decreased remarkably compared to that for the HCl pretreated cell. One can easily conclude that the proton adsorption on the TiO₂ surface is essential to the efficiency improvement.

In acidic solutions the TiO₂ surface tends to be protonated and has a positive charge. There is a surface proton adsorption/desorption equilibrium on the TiO₂ surface as shown in Scheme 1. The dyes were chemically adsorbed onto the TiO₂ surface through the carboxylate groups. The electrostatic attraction between the negatively charged dye molecules and the positively charged TiO₂ surface may assist the dye uptake and, thus, accelerate the dye adsorption. On the other hand, the formed positive charge upon HCl pretreatment may screen the negative charge on the dye molecules and render a compact layer. This may explain the increased dye adsorption after HCl pretreatment.

The binding mode of the dye on the TiO₂ surface is one of the factors influencing electron injection.¹⁵ We observed a carboxylate binding mode for both HCl pretreated and untreated cases from FT-IR data (see Supporting Information). Thus, the influence of the binding mode difference on electron injection can be excluded.

According to Figure 3, the maximum absorbance was increased from 0.338 to 0.405 upon HCl pretreatment. The LHE at the maximum absorption was increased by 13% according to eq 2. The increase in LHE is much lower than that in maximum IPCE (24%). Obviously, the LHE improvement cannot be responsible for the IPCE increase completely. According to eq 1, we conclude that the electron injection yield and/or the charge collection yield are also improved upon HCl pretreatment.

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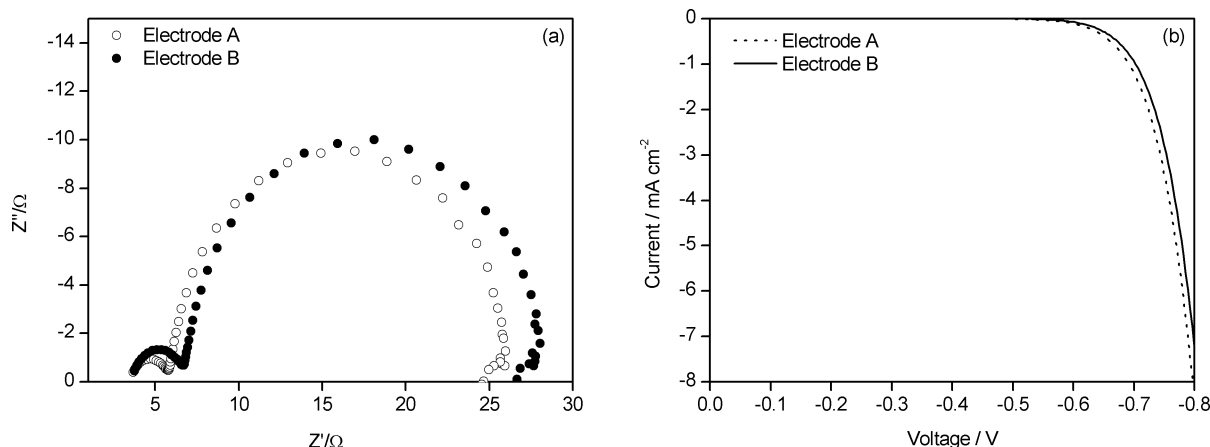


Figure 4. (a) Electrochemical impedance spectra and (b) dark current with applied potential for untreated (electrode A) and HCl pretreated (electrode B) DSSCs.

Interfacial Electron Transfer. Photocurrent generation depends on electron injection, charge collection, and charge recombination. Here we discuss the effect of HCl pretreatment on the three factors qualitatively. The relative position of the excited energy level of the dye and the conduction band edge minimum is essential to the electron injection. The redox potentials ($E_{1/2}$) of the dye and the flat band potential (E_{fb}) for TiO_2 were obtained from cyclic voltammogram and spectro-electrochemical measurement.¹⁶ $E_{1/2}$ was 0.62 V versus SCE (same below) for the dye on both HCl pretreated and untreated films, but E_{fb} was -0.84 V for electrode A and -0.68 V for electrode B.¹⁶ The flat band potential (-0.84 V) obtained for the untreated TiO_2 is in good agreement with the reported value (-0.90 V).⁷ The proton adsorption/desorption equilibrium accounts for the positive shift of the flat band potential upon HCl pretreatment.^{7,8} The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels are essential parameters for electron injection and dye regeneration. LUMO is determined to be -0.99 V by

$$\text{LUMO} = \text{HOMO} - E_{0-0} \quad (3)$$

where E_{0-0} (1.61 eV) is the 0–0 transition energy, which is cited from the reference,¹⁷ and $E_{1/2}$ is taken as the HOMO. The driving force for electron injection (see Table 1), $E_{fb} - \text{LUMO}$, was increased from 0.15 eV for electrode A to 0.31 eV for electrode B.

Several studies revealed that increasing the interfacial concentration of Li^+ and H^+ resulted in a greater yield of electron injection from the excited dye molecules.^{11,18,19} This effect was reported to be due to the positive shift of the flat band potential of TiO_2 .¹⁸ The electron injection yield depends on the driving force. Katoh et al. reported

that electron injection occurs efficiently when the LUMO of the dye is located sufficiently far above the conduction band edge minimum for TiO_2 .²⁰ Hara et al. found that 0.2 eV of driving force was the minimum threshold for high IPCEs.²¹ On the basis of their results, the LUMO of the untreated electrode is not high enough to efficiently inject electrons. However, after HCl pretreatment, the driving force of 0.31 eV is greater than the 0.2 eV threshold. Therefore, we speculate that the electron injection yield is increased after HCl pretreatment.

The J_{sc} improvement is also related to the charge collection efficiency. After HCl pretreatment, the TiO_2 surface is protonated and positively charged. The positive charge at the TiO_2 surface may provide charge compensation of injected electrons. Therefore, improvement of charge collection efficiency is also expected upon surface protonation of TiO_2 .¹²

The V_{oc} is theoretically the difference of the flat band potential of TiO_2 and the redox potential of the redox couple in the electrolyte. Therefore, a 0.16 V decrease in V_{oc} should be expected after HCl pretreatment. Contrasting to this expectation, the V_{oc} remained almost unchanged (Table 1). Charge recombination between conduction band electrons and the I_3^- ions at the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface, which is associated with the V_{oc} , is analyzed by impedance spectroscopy and dark current.

Figure 4a shows the impedance spectra of DSSCs at open-circuit condition under illumination of simulated AM 1.5 solar light (100 mW cm^{-2}). A large semicircle at low frequencies and a small one at high frequencies were observed for both HCl pretreated and untreated solar cells. Responses in the frequency regions 10^3 – 10^5 , 1 – 10^3 , and 0.1 – 1 Hz are assigned to charge-transfer processes occurring at the Pt/electrolyte interface and $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface, in Nernst diffusion within the electrolyte, respectively.²² The semicircle in the 0.1 – 1 Hz range is overlapped with that in the medium-frequency region. The resistance at the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface was increased to some extent upon HCl pretreatment as shown in Figure 4a. The increased resistance at the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface may indicate the suppression of reaction between conduction band electrons and I_3^- ions.

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(16) The cyclic voltammogram was performed with a three-electrode cell containing the dye-loaded TiO_2 film, platinum wire, and Ag/Ag^+ ($0.01 \text{ M AgNO}_3 + 0.1 \text{ M tetrabutylammonium perchlorate}$ in acetonitrile) as the working, counter, and reference electrodes, respectively. Spectro-electrochemistry was carried out using a typical three-electrode cell made of quartz, in which the transparent TiO_2 film ($6 \mu\text{m}$), a platinum wire, and an Ag/AgCl /saturated KCl in contact with a KCl salt bridge acted as the working, counter, and reference electrodes, respectively. The supporting electrolyte was 0.1 M LiClO_4 in dry acetonitrile. The potentials of the reference electrodes were calibrated with ferrocene, and all the potentials reported in this study are converted to values against saturated calomel electrode (SCE).

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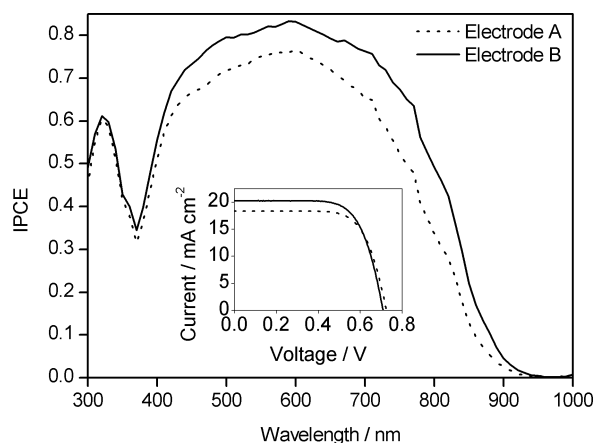


Figure 5. IPCE action spectra for DSSCs with scattering films (32 μm). The inset shows the corresponding I – V curves.

In addition, the dark currents for DSSCs were measured and are shown in Figure 4b. Upon HCl pretreatment, the dark current onset potential remained almost same while the magnitude of the dark current was reduced to some extent. The unchanged dark current onset potential explains well the fact that the open-circuit photovoltage was not changed noticeably. The dark current at potentials more negative than the dark current onset potential was reduced upon HCl pretreatment, which also indicates that the reaction between triiodides and conduction band electrons was suppressed.

The data of impedance spectra and dark current provide persuasive evidence that the protonation of TiO_2 films suppresses the charge recombination between triiodides and conduction band electrons. Such suppression of charge recombination would result in a V_{oc} gain compensating the V_{oc} loss due to the positive shift of the flat band for TiO_2 .

Optimization. Scattering particles are usually employed to increase the path–depth length of monochromatic light in the near-IR region and, hence, to increase LHE.¹³ The 10.4% efficiency for the black dye was obtained with a scattering film.⁴ It is, therefore, interesting to investigate the protonation effect on the scattering film. Three-layer films, with structure of N/M', were employed for the optimization of the cells.¹³ The thicknesses were 15, 12, and 5 μm for layers N, M', and M, respectively. Upon HCl pretreatment, the surface dye concentration was increased by 15% from 1.3×10^{-7} to 1.5×10^{-7} M cm^{-2} , in agreement with the increase (20%) in the nanofilm.

The photocurrent action spectra for both untreated and HCl pretreated photoelectrodes are compared in Figure 5. It is evident that the HCl pretreatment is still effective for the scattering film. Upon HCl pretreatment, the maximum IPCE was increased from 76.8% to 83.3% by 8%. However, the increased ratio (8%) in the scattering film is lower than that (24%) in the nanofilm. Because the maximum absorbance is greater than 2 for the untreated

electrode, the LHE there is above 99% and, thus, its improvement should be less than 1%. Again the enhanced IPCE should be mainly attributed to the improved injection, charge collecting, or both.

The inset of Figure 5 shows the I – V curves of DSSCs before and after HCl pretreatment. J_{sc} was increased from 18.33 to 20.24 mA cm^{-2} by 10%, and overall efficiency was improved from 9.3% to 10.0% by 8%. In agreement with the IPCE result, the photocurrent increase (10%) in the scattering film is also smaller than that (22%, see Table 1) in the nanofilm. The main reason for this difference is that the LHE improvement in the scattering film is less significant than that in the nanofilm. The integrated photocurrent for electrode B from the IPCE action spectrum and the standard AM 1.5 solar emission spectrum is calculated to be 21.02 mA cm^{-2} . Therefore, the spectral mismatch between the simulated and the true solar spectrum is about 4% [$=(21.01 - 20.24)/21.01$].

When an antireflection layer film ($\text{SiO}_2/\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{MgF}_2$, Tokai Optical Co., Ltd., Japan) was applied on the cell surface, the light reflection by the TCO glass can be reduced and, thus, J_{sc} was further enhanced by about 5%. The HCl pretreated solar cell with such an antireflection film produced 21.49 mA cm^{-2} of J_{sc} , 0.700 V of V_{oc} , and 0.699 of FF, corresponding to an energy conversion efficiency of 10.5%, under illumination of simulated AM 1.5 solar light (100 mW cm^{-2}).

In summary, we successfully optimized the black dye toward efficiency in both nano- and scattering films. The HCl pretreatment resulted in a significant increase of dye adsorption, a positive shift of the flat band for TiO_2 , reduced dark current, and increased resistance at the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface. These changes contributed to the efficiency improvement, and an efficiency of 10.5% was achieved. Such a simple technique is also effective to improve the overall efficiency of DSSC with N719.²³ The HCl pretreatment appears to be general and may improve the efficiency of DSSCs with other dyes. To elucidate the protonation effect on the efficiency of DSSCs, future studies will focus on the kinetics of electron injection and charge transport in the nanoporous TiO_2 film.

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Supporting Information Available: FT-IR data for the black dye powder, dye-loaded untreated, and dye-loaded HCl pretreated TiO_2 films (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(23) The HCl pretreatment is also effective to improve the overall efficiency of N719 dye-sensitized 6 μm nano- TiO_2 solar cell from 5.8 to 6.6% by 14% with major contribution from the photocurrent enhancement. However, the overall efficiency of the N719-based cell was not increased significantly in the scattering film with this approach. The detailed study of the protonation effect on the N719-based solar cell is under way.