Since the first report of a dye-sensitized solar cell (DSSC) by Grätzel, they have been seen as a promising solution for many impending energy and environmental problems, due to their inexpensive fabrication, eco-friendly characteristics, and reasonable efficiency (>11%).[1–4] Furthermore, DSSCs with thin, light-weight substrates may allow for the creation of innovative mobile IT tools.[5] However, the efficiency of DSSCs is low compared with crystalline Si (24.7%) or thin-film CIGS (copper indium gallium selenide, 20.0%), which restricts their potential application.[4] There have been many attempts to improve the efficiency of DSSCs. Researchers have mainly concentrated their attention on electrode materials, novel sensitizers, electrolyte additives, and nanostructures for enhanced light scattering.[6–10] However, relatively few reports have focused on the interface between the electrode material and the current-collecting substrates—in particular, DSSCs with metal substrates. Hayase et al. demonstrated improved efficiency by mechanical treatment of the substrate.[11] However, this earlier study investigated a DSSC with a F/SnO$_2$ (FTO) glass substrate, and the increase in the efficiency was small. We previously reported a DSSC that used a metal substrate, rather than the commonly used conductive-layer-coated plastic films. In addition, we found that the interface between TiO$_2$ and metal substrates plays an important role.[12–15]

In this communication, we report that acid (HNO$_3$-HF) treatment of the Ti substrate for the photo-anode significantly improved the efficiency of DSSCs. Prior to spreading the TiO$_2$ paste on the substrates with a doctor blade, the Ti substrates were chemically treated with aqueous HNO$_3$-HF. With the exception of cleaning, no additional pre- or post-treatment was performed. The proposed surface-treatment method simultaneously improved the electrical and optical behavior (Scheme 1), resulting in a highly increased performance in terms of all figures of merit: open-circuit voltage, $V_{oc}$, short-circuit current density, $J_{sc}$, fill factor, FF, and power conversion efficiency.

![Scheme 1. A schematic diagram of the electrical and optical variations of the Ti substrates due to the HF-HNO$_3$ treatment.](image-url)
The detailed crystal structure of the thermally oxidized layer were characterized using a field-emission transmission electron microscope (FE-TEM) and a fast Fourier transform (FFT) analysis. The FE-TEM images showed a thicker and more variable than that of the HNO$_3$-HF-treated substrates, irrespective of the same oxidation conditions (Figure 1d–g).
exhibited various oxide forms including anatase, rutile, and titanium oxide. However, only rutile was observed in the oxide layer of the HNO₃-HF-treated Ti substrate. Furthermore, almost all the peaks for oxide and Ti were sharpened after HNO₃-HF treatment. The microstructural analysis subsequently confirmed that the finer-grained disordered layer of the non-treated Ti substrate unevenly accelerated the oxygen diffusion and the defects were retained after oxidation, producing a disordered oxidized layer. However, a high degree of crystallinity in the oxidized layer was produced after elimination of the finer-grained disordered layer by HNO₃-HF treatment.

Figure 2. High-resolution FE-TEM image with FFT diffractogram of the thermally oxidized layer of a) non-treated Ti substrate (shown in Figure 1d) and b) HNO₃-HF-treated Ti substrate (Figure 1e). c) By use of a 2θ scan method (Supporting Information), XRD patterns of non-treated and HNO₃-HF-treated Ti substrates after thermal annealing at 550 °C for 30 min. Note: The FFT diffractograms shown in the insets of (a) and (b) were obtained from the full image of (a) and (b).
After HNO₃-HF treatment, the $V_{oc}$, $J_{sc}$ and $FF$ all increased, resulting in highly increased efficiency (Figure 3d). Specifically, the overall conversion efficiency increased from 5.90 to 9.20% after HNO₃-HF treatment. The other variations in the characteristics were as follows: $V_{oc}$ from 807 to 839 mV; $J_{sc}$ from 10.7 to 14.9 mA cm⁻²; and $FF$, from 68.2 to 73.4%. In the evaluation of the illumination intensity effect on the performance factors, the $V_{oc}$ and $J_{sc}$ exhibited logarithmic and linear dependence, respectively. However, $FF$ decreased under stronger illumination intensity (see Supporting Information). According to Snaih et al., an increased charge-generation rate increases the chemical potential within a device and thus increases $V_{oc}$ under strong illumination.[24] However, compared with the $V_{oc}$ variation of the DSSCs with non-treated and HNO₃-HF-treated Ti substrate, i.e. from 807 mV to 839 mV, the amount of the increased $V_{oc}$ under various illumination was too small. Furthermore, the $FF$ also improved from 68.2 to 73.4% after HNO₃-HF treatment. These consequences suggest that the improved performance of the DSSC with the HNO₃-HF-treated substrate cannot be attributed to the enhanced optical reflection alone. Rather, we believe that the greater part of this improvement could be attributed to a reduced back reaction of the electrons with $I_3^−$ ions at the interface of the conductive substrate and electrolyte because the thickness of the nano crystalline TiO₂ layer is about 15 μm. For a device with a > 10 μm thick TiO₂ layer, performance increases due to reflection are restricted to wavelengths above 580 nm where the absorption of the N719 dye is weak.[13]

The blocking layer (compact TiO₂) at the interface of the TiO₂ particles/conductive substrates has been studied[25,26] and several groups concluded that recombination occurs predominantly near the conductive substrate and not across the entire TiO₂ film.[27] In the DSSCs with metal substrates, the oxidized layer is naturally formed at the interface of the TiO₂ particles/conductive substrate during thermal annealing. Furthermore, this oxidized layer can act as a blocking layer, retarding the back-reaction of electrons with $I_3^−$ ions.[28] However, it seems that the low quality oxidized layer induced poor blocking behavior of the DSSCs with the non-treated Ti substrates. The recombination kinetics were investigated by the evaluation of the rate of photovoltage decay under open-circuit conditions. According to Zaban et al., the rate of photovoltage decay under open-circuit conditions is inversely proportional to the lifetime of the photoelectron in the DSSCs, and the lifetime of the electron is inversely proportional to the rate of recombination.[29] As shown in Figure 3b, the HNO₃-HF treatment of the Ti substrates strongly influenced the rate of the photovoltage decay. However, the initial rapid decay of the photovoltage was much less sensitive to the HNO₃-HF treatment. Electron back transfer to $I_3^−$ ions via the conductive substrate may significantly contribute to the overall

---

**Figure 3**. a) Optical reflectance of Ti substrates measured with UV-VIS-NIR spectro-photometers combined with an integrated sphere before and after thermal annealing at 550 °C for 30 min. Baseline calibration was performed with a standard specimen composed of polytetrafluoroethylene (PTFE). b) open-circuit voltage decay measurements, c) electrochemical impedance spectra, and d) current–voltage ($J−V$) curves of DSSCs with non-treated and HNO₃-HF-treated Ti substrates.
recombination current at longer times (i.e. lower photovoltages) but that pathway becomes less significant by covering the conductive substrate with a compact TiO₂ blocking layer.[30]

The electron recombination may lead to a lowering of the photocurrent, but also to a decrease in the photovoltage by lowering the quasi-Fermi level for the electrons under illumination due to a kinetic argument.[31,32] Furthermore, the FF is a measure of the increase in recombination (decrease in photocurrent) with increasing photovoltage.[33] If the improved optical reflection at the substrate were a dominant element in the HNO₃-HF solutions at 25 ºC, followed by another ultrasonic water using an ultrasonic bath. The cleaned Ti foil was immersed in the HNO₃-HF treatment of the Ti substrate. This result is similar to the FTO-glass-based DSSC structures of the oxidized layers determine the blocking ability, the significantly decreased size of the 2nd semicircle could be attributed to a highly decreased charge recombination by virtue of improved micro-structure after HNO₃-HF treatment of the Ti substrate. This result is similar to the FTO-glass-based DSSC after introduction of a highly crystalline blocking layer at the interface of the FTO glass and TiO₂ electrode.[34]

We have introduced a very simple, but highly effective, surface-treatment method for the use of Ti foil as a substrates for photoelectrode in DSSCs. When a Ti substrate was treated with an aqueous HNO₃-HF solution, both the surface morphology and the crystalline structure of the thermally oxidized layer were varied. The simultaneous improvements in Vₜₜ, Jₜ, and FF cannot be attributed primarily to an enhanced optical reflection. Rather, the modified crystalline structure of the oxidized layer might have a critical influence on cell properties such as electron recombination and electrochemical impedance. Consequently, an overall efficiency of 9.20% was achieved by use of DSSCs with the HNO₃-HF-treated substrates.

Experimental Section

Preparation: Ti foils (GoodFellow, 99.6 wt.% purity) were prepared in the form of 15 × 15 × 0.1 mm³ specimens. Prior to chemical treatment, the surfaces were cleaned in both acetone and deionized water using an ultrasonic bath. The cleaned Ti foil was immersed in the HNO₃-HF solutions at 25 ºC, followed by another ultrasonic cleaning process. The DSSCs with non-treated and HNO₃-HF-treated substrates were fabricated according to a method described in our previous work.[15]

Characterization: Surface morphology of the Ti substrate and thickness of the TiO₂ layer were inspected using SEM (FEI, SIRION). The cross-sectional micro-structure was characterized by a high-resolution STEM (Hitachi, HD2300A) and a FE-TEM (FEI, Tecnai G² F30 S-Twin). The variations of phase and degree of crystallinity were observed with a fast fourier transformation (FFT) diffractogram (Gatan, DigitalMicrograph ver. 1.7138) and X-ray diffractometer (RIGAKU, D/MAX-2500) using a 2θ scan method. Optical reflectance was identified with UV-VIS-NIR spectrophotometers combined with an integrated sphere (Varian, Cary 100 & DRA-CA-300). Under a xenon lamp light source (Oriel, 91193), the j–V characteristics, electrochemical impedance, and voltage decay were measured using a Keithley 2400 source meter and potentiostat/galvanostat (Gamry, Reference600). The illumination intensity (100 mW cm⁻²) was adjusted with a standard solar cell composed of a crystalline Si capped with a KG-5 glass.


