Increase of power conversion efficiency in dye-sensitized solar cells through ferroelectric substrate induced charge transport enhancement

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Ferroelectric functionalized dye-sensitized solar cells were fabricated by using a positively-poled LiNbO3 substrate coated with ITO (ITO-LiNbO3) as a collector electrode and demonstrated enhanced power conversion efficiency. Surface potential properties of TiO2 nanoparticle film coated on the ITO-LiNbO3 (TiO2/ITO-LiNbO3) examined by Kelvin probe force microscopy (KPFM) confirmed that a large electric field (a few 10V/µm) generated from LiNbO3 can penetrate through the ITO layer and is applied to TiO2 film. This polarization-induced electric field leads to an increased photocurrent density by attracting and promoting electrons to direct transport through the mesoporous TiO2 network toward the collector electrode and a decreased charge recombination by facilitating electrons to pass through fewer boundaries of nanoparticles, resulting in high power conversion efficiency. The power conversion efficiency was enhanced by more than 40% in comparison with that without polarization-induced electric field. Incorporating functional ferroelectrics into photovoltaic cells would be a good strategy in improving photovoltaic performance and is applicable to other types of photovoltaic devices, such as perovskite solar cells.

The utilization of solar energy becomes increasingly important, as the fossil and mineral sources are not only limited but also the main sources of environmental pollution. Dye-sensitized solar cells (DSCs) are among the most promising low cost photovoltaic devices to substitute silicon solar cells, the latter is the dominant technology used for commercial solar panels at present1. The practical DSC contains broadly a mechanical support coated with transparent conductive oxides (TCOs) as a collector electrode; semiconductor film, usually TiO2; a sensitizer absorbed onto the surface of the semiconductor; an electrolyte containing a redox mediator; and a counter electrode capable of regenerating the redox mediator. A nanostructured TiO2 film with a high surface area can benefit efficient dye loading and create pathways for electron transport2,3. A high photocurrent density as much as 20 mA/cm2 can be generated as a result of good light harvesting and electron injection4,5. On the other hand, the nanostructured TiO2 film with high surface area can also promote charge recombination by decreasing electron diffusion length and hindering charge transport due to the highly random surfaces and boundaries.

Different with the other organic photovoltaic devices, in the DSC the charge generation is done at the TiO2-dye interface and the charge transport is completed by the TiO2 and the electrolyte. Sun light is absorbed...
by a dye monolayer located at the junction between the nanostructured TiO\(_2\) and the triiodide/iodide (I\(_3^-/I^-\)) redox electrolyte, leading to an excited sensitizer which injects electrons into the conduction band of the TiO\(_2\). The processes contributing to the photocurrent are the migration of electrons in the TiO\(_2\) film toward the collector electrode, the regeneration of oxidized sensitizers by redox couples in electrolyte, and the regeneration of the redox couples by a reduction occurring at the counter electrode. However, the injected electrons may also recombine either with the oxidized sensitizer or with the oxidized redox couple at the TiO\(_2\) surface, resulting in a loss of cell efficiency. Furthermore, in the DSC the charge transport is mainly forced by electron diffusion because there is no significant electric field existing in the system\(^6\). Due to trap and recombination limited transport, the electron diffusion through the nanostructured TiO\(_2\) film is much slower than that in the single crystal TiO\(_2\) film\(^7,8\). Extensive studies have shown that the rate of recombination depends on both the electron concentration and the film structure, which can be rationalized in terms of an exponential trap distribution model\(^9-11\). Enormous progresses have been made through design and synthesis of new dyes\(^12\), semiconductors\(^13\) and redox couples\(^14\), and optimization of semiconductor morphologies\(^3,15\), leading to a great advancement in power conversion efficiency (PCE). However, there is still a big gap between the practically achieved PCE and the theoretical maximum achievable one (~30%)\(^16\). Improving the charge transport has become one of the most important issues for approaching a higher efficiency of DSCs.

Recent years, ferroelectric materials have attracted extensive attention for solar cells owing to their unique surface/interface charge properties attributed to spontaneous polarization. The integration of ferroelectrics was initially done with polymer solar cells (PSCs). Yuan et al.\(^17\) and Nalwa et al.\(^18\) obtained an enhanced PCE by introducing a ferroelectric polyvinylidene fluoride (PVDF) layer into PSCs, the former demonstrated an increased open-circuit voltage (\(V_{oc}\)) resulting from an internal electric field ensured by the ferroelectric polymer layer and the later verified an enhanced photocurrent density (\(J_{sc}\)) and fill factor (\(FF\)) owing to enhanced exciton dissociation by the local electric field of ferroelectric dipoles. Lan et al.\(^19\) observed an increased PCE from inverted PSCs by adopting a dual phase SrTiO\(_3/ZnO\) nanocomposite films as a cathodic buffer layer and claimed that spontaneous polarization of SrTiO\(_3\) induce a self-built electric field to impede charge recombination at the interface of the active layer and buffer layer. By applying BaTiO\(_3/TiO_2\) nanocomposite films as photoanodes, our recent work\(^2\) demonstrated enhanced PCEs in the DSCs. We concluded that performance improvement in BaTiO\(_3\) nanocrystalline incorporated cells was due to the increase of electron mobility and decrease of charge recombination caused by the local electric field of ferroelectric BaTiO\(_3\) dipoles. Moreover, in perovskite solar cells, ferroelectric polarization was demonstrated to improve charge separation inside the absorber and to promote charge transport from CH\(_3\)NH\(_2/PbI\(_2\) to TiO\(_2\),\(^20\) resulting in enhanced photovoltaic performance.

In this paper, we propose a design of ferroelectric functionalized DSCs using a positively-poled (\(+Z\)) LiNbO\(_3\) substrate coated with ITO (ITO-LiNbO\(_3\)) as a collector electrode. Figure 1 illustrates the schematic of the proposed device. After poling, LiNbO\(_3\) single crystal exhibits a large spontaneous polarization (\(P \sim 75\ \mu C/cm^2\)) along the crystallographic Z-axis\(^21\) which generates high density bound charges at the surface\(^22,23\). When the poled surface of LiNbO\(_3\) single crystal is deposited with an ITO layer followed by the coating of a TiO\(_2\) nanoparticle film, the bound charges at the poled surface are partially or completely compensated by the ITO and the screening charge sheet generates an electric field penetrating into the nanostructured TiO\(_2\) film. It is worth mentioning that, at the interface of ITO-LiNbO\(_3\) and nanostructured TiO\(_2\) film, the polarization-induced charges will not be fully compensated by the low-concentration free charges in semiconductor, which leads to the formation of an uncompensated internal field in the TiO\(_2\) nanoparticles. Such a polarization-induced electric field is anticipated to favor charge transport in DSCs. LiNbO\(_3\) single crystal is employed for this study because of its advantages in
material characteristics such as (1) the possession of a large spontaneous polarization (P) of 75 \( \mu \)C/cm\(^2\) arising from the ionic displacements within the crystal lattice, which is highly stable due to a large coercive field (21 kV/mm, the electric field for polarization reversal of congruent LiNbO\(_3\)), resulting in a permanent polarization without change of orientation and magnitude, and (2) its high Curie temperature (1140 °C, the phase transition point from paraelectrics to ferroelectrics) which enables to maintain ferroelectric properties through a sintering process at the temperature ranging of 350–500 °C to form a mesoporous TiO\(_2\) network that provides pathways for charge transport. In addition, non-doped congruent LiNbO\(_3\) single crystal shows a good optical transmittance in the visible region (Figure S1). In our work, by using the ITO-LiNbO\(_3\) (+Z) as a collector electrode, the PCE of DSCs increases by 42.9% resulted from both increased photocurrent density (\(J_{sc}\)) and fill factor (FF). The possible mechanism and influences of the polarization-induced electric field on the PCE have been discussed.

**Results and Discussion**

**Polarization-induced electric field.** Ferroelectric materials have spontaneous polarization without the need of an external electric field. The spontaneous polarization charges can be presented as \(\sigma_{pol} = P \cdot n\), where \(P\) is the polarization vector and \(n\) is the unit normal to the surface. When a ferroelectric surface contacts with a conductive layer (i.e., ITO), polarization charges at the ferroelectric surface will be screened by free charges in the conductive layer. The distribution of screening charges in the conductive layer, very near the interface with the ferroelectric, leads to several important thickness-dependent electrical phenomena in ferroelectrics. A depolarization field can be formed due to the slight offset between the polarization charges at the ferroelectric surface and the screening charges in the conductive layer\(^{24-26}\). Assume that the ferroelectric is homogeneously-polled, the interface states and space charge in the ferroelectric may be ignored\(^{25}\), so that the polarization charges are localized at the ferroelectric/conductive-layer interface. The depolarization field \(E_d\) in the ferroelectric can be represented as

\[
E_d = -\frac{P}{\varepsilon_f} \left( \frac{2\varepsilon_f/d}{2\varepsilon_f/d + \varepsilon_c l_s} \right)
\]

where \(d\) is the thickness of ferroelectric plate, \(l_s\) is the screening length (space charge extent in conductive layer), and \(\varepsilon_f\) and \(\varepsilon_c\) are the relative dielectric constants of the ferroelectric and the conductor, respectively\(^{25}\). It is clear that the magnitude of the depolarization field is strongly plate thickness dependent. In our work, we used 0.3-mm-thick LiNbO\(_3\) (i.e., \(d = 0.3\) mm) and 50 nm-thick ITO (which gives rise to \(l_s = 0.05\) nm)\(^{27}\), i.e., \(d \gg l_s\) and thus the depolarization field is predicted to disappear. In this case, screening charges reside at the ferroelectric/conductive-layer interface, completely compensating for the spontaneous polarization \(P\) in the ferroelectric. The screening charges \(\sigma_f, |\sigma_f| = |\sigma_{pol}|\), generates an electric field \(E\) within the adjacent TiO\(_2\) layer, which is related to the polarization-induced electric field on the ferroelectric surface.

To verify the electric field induced by the spontaneous polarization of LiNbO\(_3\) and whether it can penetrate through the ITO layer and TiO\(_2\) film, surface potential properties of the photoanode after subjected to the sintering process were investigated with Kelvin probe force microscopy (KPFM). As shown in Fig. 2, surface potential of the TiO\(_2\)/ITO-LiNbO\(_3\) (+Z, Fig. 2b) was much larger than that of the TiO\(_2\)/ITO-glass (Fig. 2c), indicating a

![Figure 2. (a) Schematic of the Kelvin probe force microscopy (KPFM) measurement. Surface potential images of TiO\(_2\)/ITO-LiNbO\(_3\) (b) and TiO\(_2\)/ITO-glass (c). Topographic images of TiO\(_2\)/ITO-LiNbO\(_3\) (d) and TiO\(_2\)/ITO-glass (e). The images (b–e) were taken after subjected to the sintering process.](image-url)
potential enhancement on the TiO$_2$ film due to the employment of LiNbO$_3$. Topographic images (Fig. 2d and e) display a very similar morphology of TiO$_2$ nanoparticles for these two samples, suggesting that topography effect on the surface potential is negligible. The electric field generated from the LiNbO$_3$ at the tip scanning level can be estimated to be a few 10 V/µm. Variations of surface potential over the scan area were observed from both samples, which might be caused by an AC voltage generally applied to the tip while scanning. KPFM though is not for a quantitative measurement of surface potential, the results clearly confirmed that the electric field originating from the LiNbO$_3$ is significantly large and can penetrate through the ITO layer and TiO$_2$ film. In other words, the TiO$_2$ film is “immersed” in an electric field in view of the spontaneous polarization of LiNbO$_3$.

To demonstrate that the polarization-induced electric field can be introduced into DSCs for charge transport promotion, two types of cells were fabricated and studied in this work: ferro-based cell has a configuration of TiO$_2$/ITO-LiNbO$_3$ (+Z), while glass-based cell is composed of TiO$_2$/ITO-glass. For each type, more than five cells were adopted for characteristics of charge transport properties and photovoltaic performance.

**Optical transmittance of collector electrodes.** Optical properties of ITO-LiNbO$_3$ and ITO-glass were measured and compared, and their UV-vis transmittance spectra were shown in Fig. 3. It was found that both electrodes have good optical transmittance in the effective absorption wavelength region of N719, although the collector electrode of ITO-LiNbO$_3$ shows a lower transmittance at the wavelength range of 320–600 nm.

**Charge transport properties.** Effects of polarization-induced electric field on the charge transport properties in the DSCs were investigated by electrochemical impedance spectroscopy (EIS). As a well-established technique, the EIS has been widely employed to study the kinetics of electrochemical and photoelectrochemical systems including DSCs. Under the EIS measurement with a forward bias in dark, electrons are injected into the conduction band of TiO$_2$ nanoparticles from the collector electrode and then transported through the mesoscopic TiO$_2$ network. At the same time, some of the injected electrons react with I$_3^-$ in the electrolyte, which is related to the recombination process. The Nyquist plot typically consists of two semicircles, which is fitted by an equivalent circuit inserted in Fig. 4(a). The first small semicircle corresponds to the charge transport resistance at counter electrode/electrolyte interface ($R_1$) at a high frequency (>10$^3$ Hz). The second large semicircle corresponds to the charge transport resistance within the TiO$_2$ film ($R_t$) at 10$^3$-10$^2$ Hz and the charge transfer resistance at the TiO$_2$/electrolyte interface ($R_{ct}$) around 10$^1$ Hz. $R_t$ denotes how effective the electrons in the conduction band of TiO$_2$ network move along with the TiO$_2$ network, while $R_{ct}$ reflects the charge recombination.

Under the open circuit condition ($V_{oc}$), a relatively high carrier density results in a low diffusion resistance, the $R_t$ is not usually detected in Nyquist plot due to its small value compared to other two charge transfer resistances $R_1$ and $R_{ct}$. Therefore, the second large semicircle is mainly attributed to the charge transfer resistance $R_{ct}$.

Figure 4 shows the representative results of EIS measurements at the $V_{oc}$. An increase of $R_{ct}$ was obtained from the ferro-based cell with the use of LiNbO$_3$ as shown in Fig. 4a. The larger the amount of $R_{ct}$, the more difficult the recombination of the electrons and holes, which results in decreased charge recombination. Figure 4b shows the Bode plots of the cells, indicating a longer lifetime for the ferro-based cell (32 ms) than the glass-based cell (24 ms). The electron lifetime ($\tau$) can be determined by using the curve peak of the spectrum following equation:

$$\tau = \frac{1}{2\pi f_{peak}}$$

where $f_{peak}$ is the peak frequency at the minimum phase angle, 4.915 Hz for the ferro-based cell and 6.478 Hz for the glass-based cell. Both the increases in the $R_{ct}$ and $\tau$ lead to a reduced interface charge recombination in ferro-based cells.

Figure 4c displays $J-V$ curves of the cells measured under dark conditions, showing dark currents caused by the reaction of injected electrons with I$_3^-$ in the electrolyte. The dark current was smaller in the ferro-based cell than in the glass-based cell.
than that in the glass-based cell. This is in keeping with the EIS results, which further demonstrates that charge recombination was impeded by the polarization-induced electric field in ferro-based cells.

Photovoltaic performance. Figure 5 shows the photocurrent density-voltage ($J$-$V$) characteristics and the corresponding incident monochromatic photon-to-electric current conversion efficiency (IPCE) spectra of the ferro-based and glass-based cells, and their photovoltaic performance parameters are summarized in Table 1. Ferro-based cell had a PCE of 4.46%, which is 42.9% higher than that of 3.12% for glass-based cell. Such an efficiency enhancement in ferro-based cells was mainly attributed to the increased $J_{sc}$. It is known that $J_{sc}$ is the integration of the IPCE over the absorption range. As expected, ferro-based cells show higher IPCE values comparing with glass-based cells, despite the lower optical transmittance in LiNbO$_3$, which is in a same trend to that of $J_{sc}$. The increased $J_{sc}$ can be ascribed to the existence of a polarization-induced electric field from ferroelectric LiNbO$_3$ in the ferro-based cell, in which electrons transport along the TiO$_2$ network are enforced by the electric field toward the electron collection electrode and consequently the transport involves less charge recombination at the TiO$_2$/electrolyte interfaces (Fig. 5d), resulting in a larger photocurrent density.

In addition to the increase in $J_{sc}$, fill factor ($FF$) of ferro-based cells also increases and contributes to the higher PCE. The FF reflects electrical and electrochemical losses occurring during operation of the DSC, it can be contributed by series and shunt resistance in the device. The shunt resistance ($R_{sh}$) is for the resistance related to the back electron transfer across the TiO$_2$/electrolyte interface$^{39}$, and the series resistance ($R_s$) is mainly attributed to the sheet resistance of TCO substrates. Increasing $R_{sh}$ and decreasing $R_s$ will lead to a higher $FF$, thus resulting in a greater efficiency. The $R_{sh}$ and $R_s$ can be obtained by calculating the inverse of the slopes of $J$-$V$ characteristics near $J_{sc}$ and $V_{oc}$ respectively. Compared with the glass-based cell, the ferro-based cell presents a slightly larger $R_s$ but an apparently larger $R_{sh}$, resulting in a larger $FF$ (Table 1). The larger $R_{sh}$ originating from reduced charge recombination can be ascribed to the field-assisted charge collection which leads to less opportunities for the electrons to back react at the TiO$_2$/electrolyte interfaces. It should also be noted that the overall PCEs are not high due to the small $FF$. The large $R_s$ caused by the ITO might be the reason for the small $FF$. To confirm this speculation, resistivity of the ITO and FTO (commonly used as a TCO of collector electrodes in DSCs) before and after the sintering process were measured and compared. The results show that the resistivity of the ITO increased slightly after subjected to the sintering process (2.767 and 2.865 $\Omega$·cm respectively, before and after sintering), however, it is 2.2 times of that of FTO (1.293 $\Omega$·cm after the same sintering process). The comparatively large resistivity of the ITO leads to the small $FF$ thus the overall low PCEs from this work.
Conclusions

In summary, we report ferroelectric functionalized DSCs, in which a positively-poled LiNbO$_3$ single crystal coated with ITO was used as a collector electrode, have better performance due to higher photocurrent density and fill factor. The large spontaneous polarization of LiNbO$_3$ generates an electric field that can penetrate through the ITO layer and into TiO$_2$ film, giving rise to two impacts on electron transport in the mesoporous TiO$_2$ network: enhanced photocurrent density by attracting electrons to transport through the mesoporous TiO$_2$ network toward the collector electrode and decreased recombination chance by facilitating electrons to pass through fewer boundaries of TiO$_2$ nanoparticles. Further work is necessary to optimize the incorporation of ferroelectrics into solar cells in order to take full advantages of polarization-induced electric field to further enhance the PCE of DSCs.

Materials and Methods

Preparation of collector electrodes. LiNbO$_3$ single crystal of congruent composition (YAMAJYU Ceramics Co., Ltd, Japan) was uniformly poled along with the crystallographic Z-axis and cut perpendicular to the polar axis, and then polished to a plate with the thickness of 0.3 mm. Following the polishing, the plate was diced into $2 \times 2$ cm pieces and ultrasonic cleaned in acetone, methanol and deionized (DI) water sequentially, and then blown dry with nitrogen. After cleaning, a 50-nm-thick indium tin oxide (ITO) film was sputtered onto the positively-poled (+Z) surface of LiNbO$_3$ single crystals. For comparison, ITO-coated glasses were also prepared following the same process.

Fabrication of solar cells. TiO$_2$ paste was prepared based on the literature using commercial TiO$_2$ powder (P25). Doctor-blading method was adopted to make a TiO$_2$ film onto the ITO-LiNbO$_3$ or ITO-glass. The film was

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Figure 5. (a) Photocurrent density-voltage ($J$-$V$) curves and (b) incident photon-to-current conversion efficiency (IPCE) spectra of the ferro-based and glass-based cells under AM 1.5 with 100 mW/cm$^2$. Schematics illustrating electron transport through the TiO$_2$ network in ferro-based (c) and glass-based (d) cells.

| device         | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF    | $\eta$ (%) | $R_s$ (k$\Omega$ cm$^2$) | $R_{sh}$ (k$\Omega$ cm$^2$) |
|----------------|----------------------|--------------|-------|------------|------------------------|--------------------------|
| ferro-based    | 12.27                | 0.7          | 0.52  | 4.46       | 0.0210                 | 0.522                    |
| glass-based    | 11.12                | 0.7          | 0.44  | 3.12       | 0.0278                 | 0.232                    |

Table 1. Photovoltaic performance parameters of ferro-based and glass-based cells.
first dried at 150 °C for 30 min and then annealed at 350 °C for 1 h at the heating rate of 10 °C/min to remove the organic additives and to create a mesoporous network of TiO2. Owing to the thermal restriction of ITO, 350 °C for 1 h was applied to anneal the TiO2 films in this work. It has been confirmed that, the organic residues can be entirely removed, and anatase TiO2 phase structure can be formed after annealing at 350 °C.[30]

The resulting TiO2 film was then sensitized with a 0.3 mM solution of N719 dye (Solaronix) for 24 h. The N719 dye was dissolved in ACN and IBA (volume ratio of 1:1) as a standard dye solution. The sensitized film was assembled with a counter electrode made of a Pt-coated silicon after removing excess dye with ethanol and drying with air flow. A 30-μm-thick spacer was used to separate the sensitized film and the counter electrode, and the gap between them was filled with an electrolyte composed of 0.6 M tetrabutylammonium iodide, 0.1 M lithium iodide, 0.1 M iodine and 0.5 M 4-tert-butylpyridine in acetonitrile.

Characterization. The morphology of the glass, LiNbO3, ITO-glass and ITO-LiNbO3 (Figure S2) was characterized by atomic force microscopy (AFM, Asylum Research Cypher S) at an ac mode. The surface potential properties of TiO2 film coated on collector electrodes after the sintering process were characterized by Kelvin probe force microscopy (KPFM, Asylum Research Cypher S), the corresponding surface morphology of the films can be obtained simultaneously with the KPFM. A conductive cantilever with a spring constant of 2 N/m and tip radius of 10 nm was used. Surface potential properties were characterized by scanning the TiO2 films with the conductive tip at a constant level of 50 nm from the film.

The optical transmittance of the LiNbO3 (Figure S1), ITO-glass and ITO-LiNbO3 was characterized by UV-vis spectrometer. Electrochemical impedance spectroscopy (EIS) was performed using a Solartron 1287 A equipped with a Solartron 1260 FR as a Impedance analyzer to investigate charge transport properties in the DSCs. The frequency range was set from 10−1 to 105 Hz and the oscillation potential amplitude was 10 mV. The photovoltaic performance of the DSCS was characterized by using a HP 4155 A programmable semiconductor parameter analyzer equipped with an AM 1.5 simulated sunlight with a power density of 100 mW/cm². The incident monochromatic photon-to-electron conversion efficiency (IPCE) plotted as a function of excitation wavelength were recorded on a QTest Station 1000 ADI system (Crowntech, Inc.) equipped with a 300 W Xe lamp. The monochromatic photocurrent-wavelength measurements were carried out by placing a monochromator, assisted by an automatic filter wheel, between the DSCs and the light source. A mask was used to enable an illuminated active area of 0.196 cm².

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Author Contributions
X.Y.L. designed the study, interpreted the data, and wrote the main manuscript text. G.Z.C. and Q.F.Z. interpreted the data and wrote the part of manuscript text. X.T. carried out the impedance experiments. J.Y.L. and N.V. made a great contribution in the process of revise the manuscript.

Additional Information
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