Simple approach for enhancement of light harvesting efficiency of dye-sensitized solar cells by polymeric mirror

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Abstract: A Polymeric mirror from 1D photonic crystal exhibiting full specular reflection is applied on the exterior of the counter electrode of a dye-sensitized solar cells (DSSCs). Reflection of exiting light from the cell allows for the reuse of the light and thereby significantly increases the efficiency of the DSSCs (from 8.07% to 8.85%). Furthermore, it is also found to be effective even with incorporation of an internal scattering layer, which is widely used within a TiO_2 anode layer for enhancing light trapping in DSSCs (from 9.17% to 9.53%).

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A dye-sensitized solar cell consisting of a nanoporous TiO_2 photoanode with a monolayer of ruthenium complex based dye, a Pt counter electrode, and an electrolyte with redox couple is one of the most promising configurations to utilize solar energy via photovoltaic technology owing to various advantages such as low cost, a simple fabrication process, and the feasibility of large scale production [1]. In addition, flexible solar cells, which are beneficial for mobile applications and complex systems, can be realized by the implementation of flexible electrodes (*e.g.*, plastic films) into DSSCs [2,3]. However, the lower power conversion efficiency of DSSCs as compared to silicon-based solar cells remains a challenging issue, and much research is being focused on the optimization of materials and the configuration of components to improve light utilization efficiency [4]. Since the dye injects the photogenerated electrons to the conduction band of the nanocrystalline TiO_2 when it absorbs visible light, it is critical to increase light harvesting in order to improve power conversion efficiency. This implies that efficient light trapping within solar cells by optical manipulation without modifying the material or configuration inside the cell can lead to further improvement of cell efficiency. For this purpose, scattering layers or photonic crystal structures have been applied inside the titania layer, and it has been demonstrated that these approaches can improve harvesting within dye absorbed TiO_2 electrode [5]. In these cases, the enhancement of optical absorption is attributable to the increased optical path in the active layer (TiO_2 layer absorbing the light), which confers greater possibility of photon absorption by the dye molecule. In particular, deposition of dense layers with alternating refractive indices enables the formation of lossless and highly efficient mirrors over a range of wavelengths if Bragg diffraction is fulfilled. Furthermore, porous Bragg reflectors consisting of silica and TiO_2 nanoparticles applied onto the anode layer allow for interpenetration of liquid electrolytes through both the Bragg structure and the TiO_2 layer, which is appealing for application to DSSCs [6]. Indeed, Míguez et al. reported remarkably improved light utilization using one-dimensional photonic crystals of a multilayer coupled inside a cell based on inorganic nanoparticles [7–9]. Recently, photonic crystals based on a latex sphere were reported as a concentrator for DSSCs. With this approach, it is possible to circumvent difficulties of fabricating a large area anode with photonic crystals, and reflected light is utilized to enhance DSSC efficiency [10]. While, there have been significant efforts to maximize light utilization, little attention has been paid to preventing loss of light from the cell through the counter electrode. Extension of the concept using 1D photonic crystals with high reflection at the exterior of the DSSC not only increases the optical path but also prohibits a portion of light leaving the cell without being used. Previous works have shown that photonic crystals based on particles inside cell are effective at the restricted wavelength among the visible region according to the particle size yet proven to enhance DSSC performance. This supports the idea that photonic crystals showing broad-band reflection in the visible region possess strong potential for light utilization. It will be more advantageous if the 1D photonic crystals are based on a multilayer polymer mirror that is flexible under bending stress. In this work, we investigated the enhancement of efficiency of a DSSC using polymeric 1D photonic crystals with broadband high reflection on the exterior of a Pt counter electrode. We also compared the effect of the reflection mode using specular and diffuse reflection films. Ease of conformable attachment of the polymeric film confirms the

possibility of extension of the system to flexible DSSC. The conceptual illustration of the work is shown in Fig. 1.
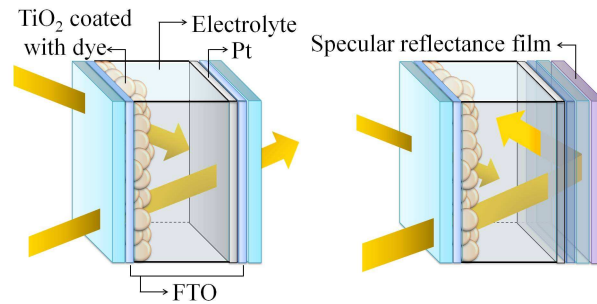

Fig. 1. Schematic diagram showing the concept of highly reflectance film supported DSSC. (a) DSSC configuration used for reference cell. (b) Modification of reference by applying polymeric reflective film at the exterior of counter electrode. FTO is fluorine-doped tin oxide.

Multilayer polymeric films with an alternating quarter-wavelength thick high refractive index and a low index material can be used to fabricate omnidirectional mirrors [11,12]. Reflection of a polymeric mirror follows Eq. (1) and increases with the number of stacked multilayers, resulting in specular reflection.

$$R = \left[\frac{1 - \left(n_{low}/n_{high} \right)^{2m}}{1 - \left(n_{low}/n_{high} \right)^{2m}} \right]^2 \qquad (1)$$

R, n_{low}, n_{high}, and m in the Eq. (1) represent reflectivity of polymeric mirror, low and high refractive index of stacked material, and number of periods of the stacked layer, respectively. On the other hand, metallic foils such as aluminum film also show specular reflection. However, a polymeric mirror consisting of a distributed Bragg reflector exhibits sharp angular width of the specular peak (constant intensity at the reflection angle equal to the incident angle) [13] and is free from oxidation at the surface. Owing to its superior reflective properties, multilayers fabricated by the continuous multilayer coextrusion process are currently used as highly reflective films in mobile liquid crystalline display (LCD) devices. Since reflection can be classified into specular and diffuse reflection, we selected diffuse reflective polymeric film for comparison in this work. The reflection (total, specular, and diffuse reflection) characteristics of polymeric reflective films are measured using a Cary 600i UV-Vis-NIR spectrometer (Varian) and the results are shown in Fig. 2. A polymeric mirror (Thickness: 65 μm, Vikuiti^{TM} ESR, 3M), and a white diffuse reflective film (RP14, SKC) are used as representative specular and diffuse reflective films, respectively. The two reflective films showed almost the same reflectivity over the visible wavelength region. The polymeric mirror showed very similar values of total reflection and specular reflection, thus illustrating that the reflection is fully specular. In the case of the diffuse reflective film, the total reflection originates mainly from diffuse reflection and a small amount of specular reflection.
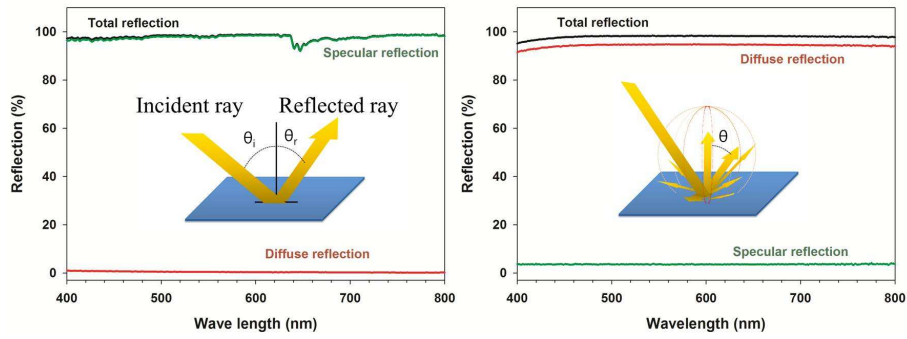
Fig. 2. Reflectance spectra of (a) polymeric mirror and (b) white diffuse reflection film in the range of visible wavelength region. Angle of incidence is 7° where normal incidence is set to 0° and the total and diffuse reflectance were measured with detector varying the angle. Specular reflectance is calculated by the difference of total and diffuse reflectance.
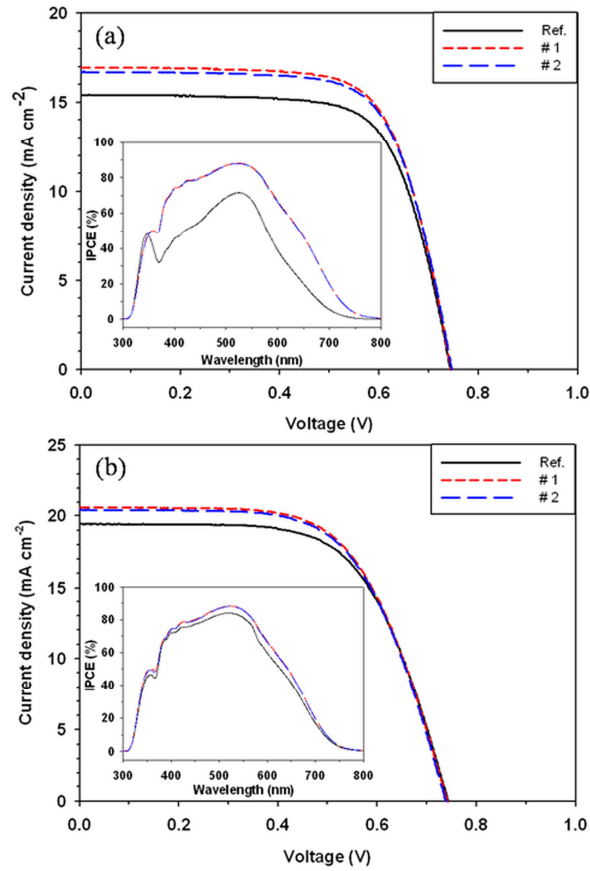

Fig. 3. J-V characteristics of a cell for a DSSC cell (a) without and (b) with scattering layers. Each figure contain inset figure exhibiting IPCE versus wavelength (λ). Inset figure exhibit IPCE versus wavelength. Ref, #1, and #2 in the figure represent reference cell, polymeric mirror attached onto reference cell and white diffuse reflection film attached onto reference cell.

A DSSC is prepared to investigate the effects of integrating a reflective film at the exterior of the cell. The fabrication materials and methods have been reported in previous publications [14–17]. The dye used is N719 from Solaronix. The J-V characteristics of the cells were recorded with a computer-controlled digital source meter (Keithley 2400) by applying external potential bias to the cell under AM 1.5 sunlight intensity. The incident photon to current conversion efficiency (IPCE) spectra were measured as a function of wavelength from 400 nm to 900 nm using an IPCE system (PV Measurement, Inc.). All experiements were performed using a black mask and polymeric reflective films were attached onto the counter electrode part. Measured J-V and IPCE spectra are illustrated in Fig. 3.

It can be easily concluded from the J-V curves that simple attachment of a reflective film at the exterior of the Pt counter electrode increased J_{SC}, while leaving the open circuit voltage, V_{OC}, unaltered. This phenomenon was observed from both of the polymeric mirror and the white diffuse reflective film (Fig. 3(a)). However, specular reflection from the polymeric mirror was more effective in improving J_{SC} compared to diffuse reflective films despite similar total reflection ability. With respect to participation of the reflected light in the increasing light efficiency, the reflected light should reach dye on the titanium particles to generate electrons. It is speculated that slight increase of the reflected light absorbed by the electrolyte (triiodide species) [18] or small portion of light loss through the edge of the cell owing to the change of reflection angle by the the diffuse reflective film is the cause of reduced amount of light reaching the titanium particles compared to that of a polymeric mirror. IPCE spectra also indicate an increase of J_{SC} when a reflective film is applied. The maximum value of IPCE is obtained around the wavelength of 540 nm, which corresponds to maximum absorption for N719. With the reflective film attached to the exterior of the counter electrode, IPCE increased over the range of the visible region.

Table 1. Photocurrent-voltage characteristics of DSSC

Group[a]	Samples[b]	V_{OC}(V)	J_{SC}(mAcm^{-2})	FF	η(%)
Without scattering layer	Reference	0.74	15.40	0.70	8.07
	#1	0.74	16.95	0.70	8.85
	#2	0.75	16.70	0.70	8.74
With scattering layer	Reference	0.74	19.45	0.64	9.17
	#1	0.74	20.60	0.62	9.53
	#2	0.74	20.45	0.63	9.45

[a] Illumination conditions: 100 mWcm^{-2} (AM 1.5). [b] #1 is for polymeric mirror and #2 is for white diffuse reflection film on the counter electrode. VOC, JSC, FF, and η refer to open circuit voltage, short-circuit current, fill factor, and power conversion efficiency, respectively.

From the J-V curves, η (power conversion efficiency) was calculated using the equation $\eta = (FF \times J_{SC} \times V_{OC})/P_i$, where FF is the fill factor, P_i is the power density of the incident light. The values are summarized in Table 1. The power conversion efficiency increased from 8.07% in the reference cell to 8.85% or 8.74% after attaching the polymeric mirror and diffuse reflective film, respectively. Since the same reference cell is used, it is clear that almost 10% efficiency improvement can be achieved by reusing the light exiting from the cell. As aforementioned, incorporation of the scattering layer and 1D photonic crystals coupled inside the cell is an effective means of improving light harvesting efficiency (LHE), reference cells with a scattering layer were fabricated and the influence of applying a reflective film has been investigated and the results are shown in Fig. 3(b). A scattering layer was formed using 400nm TiO$_2$ (CCIC, Japan) particles. The incorporation of the scattering layer inside the cell increased J_{SC} due to internal light trapping. A reflective film (polymeric mirror and diffuse reflective film are compared) was applied to the exterior of the same cell and an increased value of J_{SC} was obtained. Although the degree of improvement was smaller than that of cells without scattering layer, additional improvement was also observed from cell with internal scattering layer. This clearly indicates that there is a limitation of light trapping by using a scattering layer only and that loss of light is unavoidable. It is well known that the size of nanoparticles comprising 1D photonic crystals or a scattering layer is closely related with the wavelength of light reflection and that a maximum wavelength of reflection exists. Because

the polymeric film used here shows high reflection through the wavelength of the visible region, untrapped light reaching counter electrode can be reused. Combining the light utilization effects of the scattering layer and polymeric mirror led to remarkably enhanced power conversion efficiency (from 8.07% to 9.54%).

To investigate the effect of specular reflection on the increase of the light pass in the cell, power conversion efficiency was measured varying the angle of incidence. Polymeric mirror and aluminum foil were used as specular reflectors and the result is illustrated in Fig. 4. Reference cell exhibiting 6.0% efficiency was used and the similar trend of increasing power conversion efficiency compared to reference cell with 8.07% efficiency was obtained. Interestingly, additional increase of the power conversion efficiency was observed when the incident angle was 20° (normal incident angle is 0°) when the specular reflector was applied onto the reference cell. This optimal trend of power conversion is originated from the competence of increase of the light reflection at the surface of glass anode and increase of the light passway. This two factors oppositely affect power conversion efficiency. The former deteriorate power conversion efficiency. Severe reflection from glass anode after 40° eliminated the effect of specular reflector.
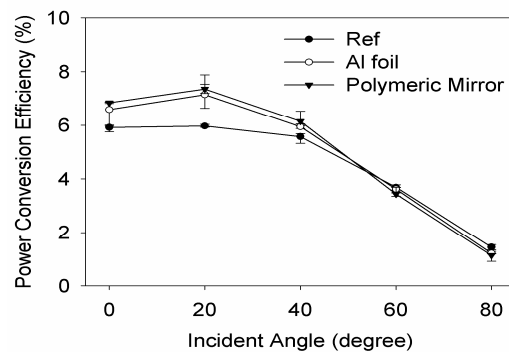

Fig. 4. Power coversion efficiency of DSSC with varying angle of the incident light.

In conclusion, we have suggested a simple but powerful approach of utilizing a reflective film at the exterior of the cell in order to enhance the power conversion efficiency. Specular reflection via multilayer stacking of a polymeric film with alternating refractive indices increased J_{SC} and the resulting η. Broad-band reflection and conformable properties of 1D photonic crystals based on the polymeric mirror can potentially be applied to other solar cell systems and flexible DSSCs where reflection is important.

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