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Light scattering of nanocrystalline TiO_2 film used in dye-sensitized solar cells*

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This paper studies the light scattering and adsorption of nanocrystalline TiO_2 porous films used in dye-sensitized solar cells composed of anatase and/or rutile particles by using an optical four-flux radiative transfer model. These light properties are difficult to measure directly on the functioning solar cells and they can not be calculated easily from the first-principle computational or quantitative theoretical evaluations. These simulation results indicate that the light scattering of 1–25 nm TiO_2 particles is negligible, but it is effective in the range of 80 and 180 nm. A suitable mixture of small particles (10 nm radius), which are resulted in a large effective surface, and of larger particles (150 nm radius), which are effective light scatterers, have the potential to enhance solar absorption significantly. The rutile crystals have a larger refractive index and thus the light harvest of the mixtures of such larger rutile and relatively small anatase particles is improved in comparison with that of pure anatase films. The light absorption of the 10 μm double-layered films is also examined. A maximal light absorption of double-layered film is gotten when the thickness of the first layer of 10 nm-sized anatase particles is comparable to that of the second larger rutile layer.

Keywords: light scattering, modelling, films, dye-sensitized solar cells
PACC: 4225F, 6146

1. Introduction

Applications of TiO_2 colloids and films are numerous, such as electroluminescence, photocatalysis, photochromic, photovoltaic and sensors. Nanocrystalline TiO_2 is applied to dye-sensitized solar cells (DSSC) as material of porous films, since the landmark paper reported by O'Regan *et al* in 1991.[1,2] The performance of DSSC depends on the nature of porous nanocrystalline TiO_2 films, including its crystalline phase and particle size particularly. The typical 10-μm-thick electrode film in a DSSC is composed of a three dimensional network of interconnected 15–20 nm sized nanoparticles, which permits efficient light harvesting for the large surface area. Now this relatively low cost solar cell technology has just experimentally achieved overall light-to-electricity conversion efficiencies of over 11% (under AM 1.5),[1,3,4] which is still under its theoretical conversion efficiency 33%.[5] One of the problems to the relatively low efficiencies compared to conventional semiconductor solar cells is the poor absorption of solar radiation. Effective ways to enhance the light absorption include the enlargement of the surface area of the nanocrystalline film, and the importation of light scatterers into the films to prolong the light path length.[6] Experimental and theoretical studies indicated that multiple scattering of light in the porous films can increase the light path length and the light absorptance of dye sensitizer, and hence improve the conversion efficiencies of DSSC.[7]

However, the light scattering in inhomogeneous TiO_2 film is generally a very complex phenomenon because of the rescattering and the interaction of scattered light.[8,9] Thus, quantitative theoretical evaluations or first-principle calculations of the light scattering are usually very difficult. Several groups have attempted to evaluate the experimental results employing empirical values of the crucial parameters.[8,10−17] Most researches focused on the parameters of monolayer and single crystal of titania film. Usami and Ozaki[8] proposed a simplest Monte Carlo model for nanocrystalline TiO_2 films. Their results showed that both the increase of light path length in the films and the optical confinement in the cells improved light absorption and quantum efficiency. Tachibana *et al*[18]

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studied the optical simulation of a nano-anatase TiO_2 film for solar cell applications. However, up to now the light scattering and absorption in binary TiO_2 nanoparticulate films still remain relatively unknown, leaving many questions unanswered with regard to their dependence to solar cell efficiency. In this paper, we discussed the light scattering and absorption in the pure anatase and/or rutile films and their binary films. An optical four-flux radiative transfer model for light properties in the porous films was employed. It aimed at an optical effect of single crystal of TiO_2 films and the mixing proportion on light absorption in DSSC electrode.

2. Modelling of the nano-TiO_2 films

The photoelectrode of DSSC is composed of a dye-sensitized TiO_2 porous film sintered on the conducting glass substrates. Platinum covered conducting glass acts as the cathode and closes the cell. The light absorption by the sensitizer promotes it to an excited state, which injects an electron into the semiconductor. To increase the light adsorption, the optical properties of nanocrystalline solar cell can be optimized by application of the light scattering effects of nanocrystalline TiO_2 films. The light scattering and absorption in the nanocrystalline TiO_2 particle films have been studied by the radiative transfer equation.[19−21] Numerical solution of the radiative transfer equation using an approximation method has the advantage of easy computation.

Many-flux models, which are an approximation for the transfer equation, seem better suitable to the present purpose.[10] Since the reflectance and transmittance of the film have to be calculated a large number of times and compared with experimental data in a non-linear least squares parameter optimization scheme, the availability of an analytical solution for the problem is an important advantage over a numerical solution. This restricts the many-flux model to a small number of fluxes. At a given wavelength, the absorption and scattering are described in this case with a small number of parameters. The simplest two-flux model, Kubelka–Munk model, is questionable in the case of collimated illumination.[22] A four-flux model has been developed.[16] It separates the total light flux into four distinct fluxes, two collinear fluxes, one travelling in the forward direction and the other in the backward direction, and two diffuse fluxes, one travelling in the forward direction and the other in the backward direction. This model has been compared with numerical solutions of the transfer equations using the discrete ordinate approximation or Monte Carlo simulations, and has been found to be a satisfactory approximation for the calculation of the reflectance and the transmittance. This model, described in Ref.[23], will be adopted here. The variation of the fluxes within an infinitesimal slab of thickness $\mathrm{d}x$ can be established by considering the energy balance for forward scattering, backward scattering and absorption.

$$\frac{\mathrm{d}A(x)}{\mathrm{d}x} = (k+s)A(x), \tag{1}$$

$$\frac{\mathrm{d}B(x)}{\mathrm{d}x} = -(k+s)B(x), \tag{2}$$

$$\begin{aligned}\frac{\mathrm{d}C(x)}{\mathrm{d}x} =& -\zeta sA(x) - (1-\zeta)sB(x) \\ &+ k\varepsilon C(x) + \varepsilon(1-\zeta)sC(x) \\ &- \varepsilon(1-\zeta)sD(x),\end{aligned} \tag{3}$$

$$\begin{aligned}\frac{\mathrm{d}D(x)}{\mathrm{d}x} =& (1-\zeta)sA(x) + \zeta sB(x) \\ &- k\varepsilon C(x) + \varepsilon(1-\zeta)sC(x) \\ &- \varepsilon(1-\zeta)sD(x),\end{aligned} \tag{4}$$

where, k and s are the wavelength-dependent absorption coefficient and scattering coefficient, respectively (in unit of length^{-1}). The factor ε is the equivalent path length for the diffuse fluxes, ζ is the forward scattering ratio coefficient, and x is the distance from the substrate. x=0 corresponds to the location of light entrance and x=z the location of light exit. In this work, however, ε and ζ will be considered as empirical parameters which are determined from reference data, since the number of parameters has to be kept at a minimum. If the particles are well separated, the wavelength-dependent absorption (or scattering) coefficient can be calculated as the production of absorption (or scattering) cross-section and the number density of the centres by employing the Mie theory.[10] According to the Mie theory, the cross-section depends on the refractive index of the TiO_2 nanoparticle films. For a single crystal TiO_2 nanoparticle films, it has refractive index n_{anatase}=2.52 or n_{rutile}=2.76. The average refractive index of binary particle mixtures is obtained by using the following equation which is de-

scribed in Refs.[8, 24, 25]:

$$n = n_{\mathrm{A}} \left[1 + \frac{3 f_{\mathrm{R}} \dfrac{n_{\mathrm{R}} - n_{\mathrm{A}}}{n_{\mathrm{R}} + 2n_{\mathrm{A}}}}{1 - f_{\mathrm{R}} \dfrac{n_{\mathrm{R}} - n_{\mathrm{A}}}{n_{\mathrm{R}} + 2n_{\mathrm{A}}}} \right], \tag{5}$$

where f_{R} is the volume fraction of rutile, and n_{A} and n_{R} were indexes of anatase and rutile, respectively.

The four boundary conditions needed to integrate Eqs.(1)–(4) were determined by taking into account the incident irradiation and back reflections at the interfaces.[10,26] The solution of Eqs.(1)–(4) subjected to the described boundary conditions could now be calculated in a closed form. The absorption of the light in the medium was determined once the optimal values of the parameters were obtained. The local rate of light absorption $g(x, \lambda)$ and the total wavelength-dependent absorption $G(\lambda)$ over whole film thickness were evaluated, respectively.

$$g(x, \lambda) = kA + kB + \varepsilon kC + \varepsilon kD, \tag{6}$$

$$G(\lambda) = \int_0^Z g(x, \lambda) \mathrm{d}x. \tag{7}$$

In the light scattering simulations of the nanocrystalline TiO_2 films, k and s were calculated from Mie theory, and they were taken as 1.8 and 0.5 for the transparent film and 1.6 and 0.8 for the scattering film, respectively.[26]

3. Results and discussions

3.1. Light absorption of single crystal TiO_2

Figure 1 is the macroscopic absorption and scattering coefficients, $k(\lambda)$ and $s(\lambda)$, as a function of TiO_2 particle radius from 1 nm to 5 μm at wavelength 550 nm. It was observed that scattering of 1–25 nm TiO_2 particles was negligible. Effective Mie scatterers were the particles with sizes in the range of 80–800 nm. For both of anatase and rutile particles with size ranging in 80–180 nm the scattering coefficients were more than 10 $\mu\mathrm{m}^{-1}$. The scattering coefficient of anatase particles was smaller than that of rutile particles when the particle size was less than 100 nm. But for the sizes between 100 to 5000 nm, both the scattering coefficients of anatase and rutile decreased with the increase of TiO_2 radius. As were mentioned in Section 2, the absorption and scattering coefficients were the product of the cross-section of the scatterers and their number density:

$$k(\lambda) = \sigma_{\mathrm{abs}} n_{\mathrm{abs}}, \tag{8}$$

$$s(\lambda) = \sigma_{\mathrm{scat}} n_{\mathrm{scat}}, \tag{9}$$

where σ was the cross-section and n was the number density for absorption and scattering. Their scattering intensity descended with the radius of TiO_2 particles, because the particle number density decreased. It was confirmed from Fig.1 that the scattering intensity of larger particles with radius greater than 200 nm decreased gradually from 5 $\mu\mathrm{m}^{-1}$ to 0 $\mu\mathrm{m}^{-1}$.

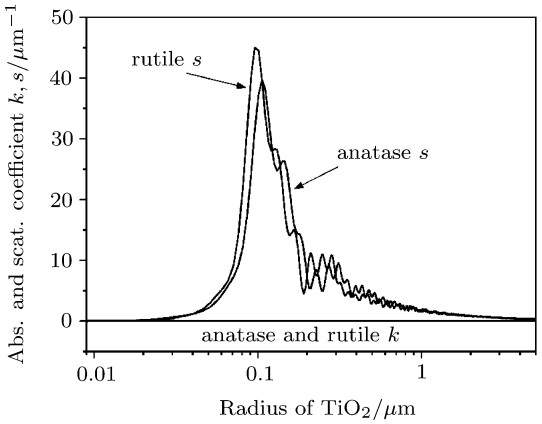


Fig.1. Absorption and scattering coefficient k and s as a function of TiO_2 radius. Mie calculations were done for single crystal TiO_2 particles at light wavelength = 550 nm, the refractive indices of anatase and rutile are 2.52 and 2.76, respectively.

At the initial stage of DSSC research, only a nanofilm composed of narrow size-distributing particles was used to study the cell performance. O'Regan and Grätzel studied the conversion efficiency of solar cells with 20 μm-thick film composed of about 10 $\sim$ 30 nm TiO_2 particle, and a conversion efficiencies of about 7% was gotten.[1] But the monolayer nanofilm was transparent and had no light scattering effect, solar cells with such nanoparticles generated relatively low energy conversion efficiency.[27] The larger particles, though with less surface area, had longer light path lengths because of greater scattering effect. Figure 1 showed that 100–200 nm TiO_2 particles had their highest scattering coefficient. In this paper, 10 nm and 150 nm TiO_2 particles were employed as transparent and scattering particles, respectively. Figure 2 showed the scattering coefficient of anatase and rutile particles as a function of light wavelength. It showed that the scattering coefficient $s(\lambda)$ of anatase TiO_2 particles was comparable to that of rutile. The scattering

coefficient of scattering particles was much larger. For an instance, $s(\lambda)$ of the scattering particles were 80 and 90 times larger than that of transparent particles at wavelength 500 nm for anatase and rutile, respectively. The scattering coefficient of the 150 nm TiO_2 particles increased as a whole with the increase of light wavelength, except the maxima peak at about 560 nm (anatase) and 610 nm (rutile).

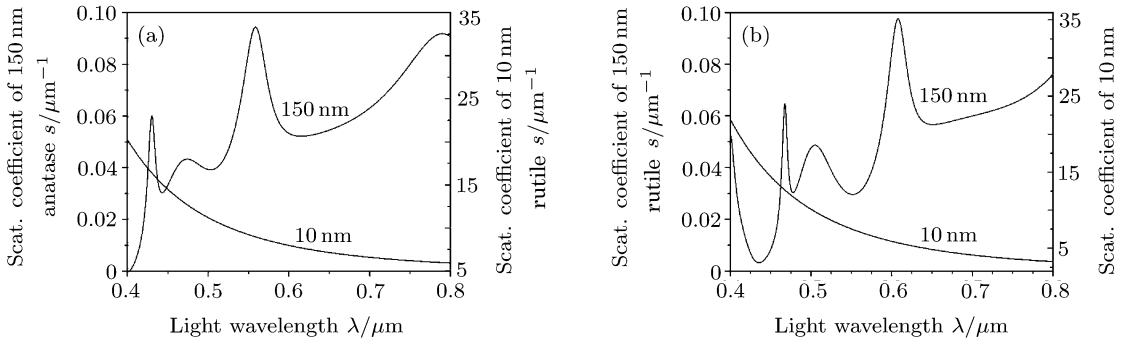


Fig.2. Scattering coefficient s of (a) anatase and (b) rutile as a function of incident light wavelength. The same Mie calculations parameters were used as Fig.1.

The light absorption of the single crystalline TiO_2 film at a constant thickness 10 μm could be confirmed by evaluating the local absorption rate $g(x, \lambda)$ in the film. Figure 3 showed the local rate of light absorption over the whole film thickness in the light range 400 nm to 800 nm. As shown in Fig.3, for 10 nm particles, the light absorption for anatase crystalline film was more than that for rutile film near the light incident surface,

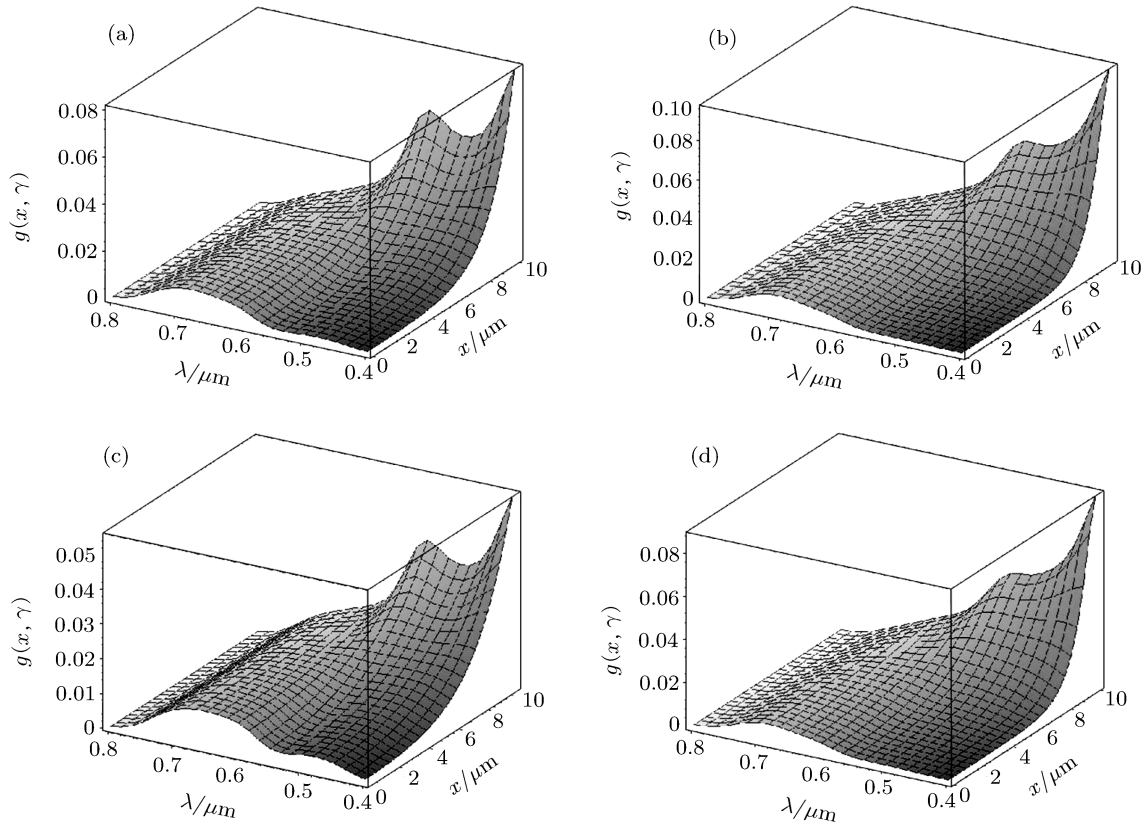


Fig.3. The local rate of light absorption $g(x, \lambda)$ over whole film thickness. Mie calculations of single crystalline TiO_2 particles are (a) anatase particles with a radius of 10 nm; (b) rutile particles, 10 nm; (c) anatase particles, 150 nm and (d) rutile particles, 150 nm. The same Mie calculations parameters were used as Fig.1.

especially in the longer wavelength range (600–800 nm). With the increasing distance from incident surface, the absorption for anatase film was gradually increased, which could be obviously seen in short wavelength region. In the film near the light exit surface, the absorption increasing rate for the rutile film was quicker than that for the anatase film. At the exit surface the quantities of the local light absorption were 0.1 and 0.08 for rutile film and anatase film, respectively. In the rutile films, the scattering effect resulted in the lengthening of the light path. So the local light absorption in the rutile films was more than that in the anatase films. For the larger particle films with radius 150 nm, the similar phenomena were shown in Fig.3. For the films composed with single crystal TiO_2, larger particle films had less local light absorption. For instance, the local absorptions at the light exit surface for 150 nm and 10 nm pure anatase films were 0.055 and 0.08, respectively. Obviously, the absorption for 150 nm film was only 84% of that for 10 nm film. The larger particles were in favour of light scattering, which increased the light path length. However, the number density in the unit volume decreased, so did the scattering and absorption coefficients according to Eq.(8).

3.2. Films of binary particle mixtures

On simulating the single crystalline TiO_2 layers, it was found that the light absorption was highest when the internal surface was largest. And for the same particle size, it was observed that the scattering in the larger refractive films enhanced the absorbed fraction of the incident light, by increasing the optical path length in the film. To maximize the amount of absorbed light over the whole film thickness, now binary particle mixtures were investigated. Calculation results at wavelength λ=550 nm were presented in Fig.4. It showed the light absorption $g(x, \lambda)$ of the films made of anatase and rutile TiO_2 particles admixtures. Figure 4 showed that for the mono-sized particle films c and d, the light absorptance decreased with the increased volume fraction of rutile particles. For instance, the light absorptance of film c was 0.02758 at f_{rutile}=10%, 0.02710 at f_{rutile}=50% and less than 0.02632 at f_{rutile}=90%. It was confirmed that the light absorption of pure anatase TiO_2 crystal film was greater than that of pure rutile film. The magnitudes for the pure anatase TiO_2 film were 1.06 and 1.17 times larger than that for the pure rutile TiO_2 for films c and d, respectively. Films a and b were TiO_2 mixtures that were produced from nanoscale anatase particles (radius 10 nm) mixed with different fractions of larger particles (150 nm). As could be seen in Fig.4, an optimal mixture was obtained with an admixture of about 50% rutile particles. The maximum light absorptance of film b was comparable to that of film a. But if there were too many large particles, not only the effective internal surface decreased, but mainly there were too much back-scatterings.[8] In this case, the reflectance of the film was enhanced, not its absorptance.

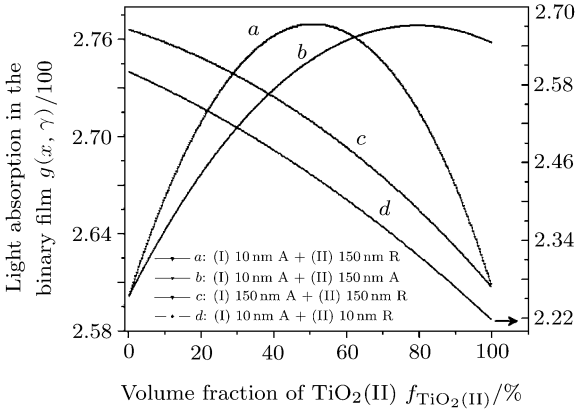


Fig.4. The local light absorption $g(x, \lambda$=550 nm) over the binary particle film at location x=8.4 μm. The light absorption value of curve d is on the right axis. The overall film thickness is 10 μm.

Another idea was to simulate a double layer to enhance light absorption. Compared with the monolayer structures, we found that the two-layered structure showed a broader action spectrum and resulted in a better energy-conversion performance.[27] As was discussed in the above section, solely increasing the film thickness failed to improve the maximum light absorption. The strong back-scattering of light due to the large particles near the exit surface may result unavoidably in a light loss. In order to reduce or suppress the light loss ascribed to the back-scattering, double-layer-films were studied. Since the visible light can completely penetrate the transparent film, it is wise to deposit the suitable particles firstly on the substrate followed by a second layer for light scattering. Figure 5 was the total light absorption over two types of double-layered films. When the light propagates through the double-layered film, it firstly penetrates the first layer and reaches at the interface of the first layer and the second one. It diffuses through the second layer before it leaves the exit surface. The anatase particle sizes for the first layers in Figs.5(a) and 5(b)

were 10 nm and 150 nm, respectively. Figure 5 showed that the light absorption of the first layer in the film a was slightly more than that of film b. When the thickness of the first layer increased from 1 μm to 4 μm, the light absorptions increased up to 0.12 for film a and 0.115 for film b, respectively. For the larger thickness of the first layer, the light gain was smaller.

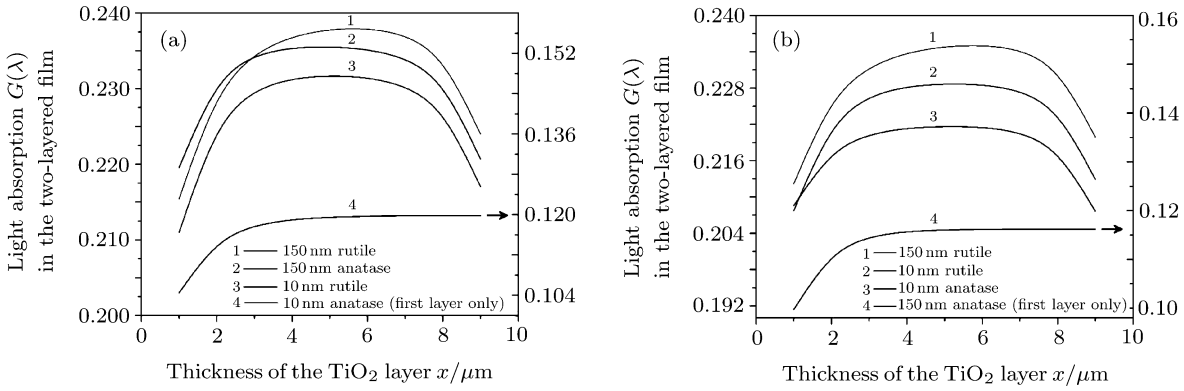


Fig.5. The total light absorption $G(\lambda$=550 nm) over double-layered film. The y-axis of the first titania layer is at the right. The thickness of first layer is $x\,\mu$m, the second layer $(10-x)\,\mu$m, so that the whole film is kept 10 μm thick.

A further enhancement of light absorption was gotten by combining the second layer onto the first one. For instance of the film a, when the first layer thickness was 1 μm and the corresponding second layer thickness is 9 μm, the overall absorptions of incident light were 0.2241, 0.2206 and 0.2174 for curve 1, 2 and 3, respectively. The total light absorptions increased with the first layer thickness till about x=5 μm, owing to the light scattering effect of the larger particles or the more refractive particles. When the two layers' thicknesses were comparable, they reached the maximum absorption. The calculation results of film b were approximately similar to that of film a. It was found that for a 10 μm thick double-layered film at light wavelength 550 nm, both films had an optimal light absorptance when the first film thickness was about 5 μm. Figure 5 showed that 150 nm rutile particles which composed the second layer achieved the highest light gain with the value 2.380. Another feature according to the calculation results was that the incident orientation of light had influence on the light absorption. In the 10 μm two-layered anatase film, when the first layer was 5-μm-thick layer with particle radius 10 nm and the second layer with 150 nm, the total light gain was 0.2356. While the first layer was 5 μm-thick layer with radius 150 nm and the second with 10 nm, the corresponding value turned out to be 0.2191.

The light absorption model described above can be extended to estimate the light absorption in systems fitted with a specular or a diffuse back reflector placed behind the exit surface. To solve the differential Eqs.(1)–(4) the corresponding boundary conditions must be changed. A possible configuration is composed of two or more porous layer with different scattering properties. It may be achieved by taking the best mixture determined above and putting a larger particle film with an optimal thickness behind it. However, this relatively small extra gain does not justify the enormous extra effort in cell preparation.[10,13]

4. Conclusion

In this work the four-flux model was described with several parameters to simulate the light scattering and absorption in the nanocrystalline TiO_2 porous films which were used in electrodes of DSSC. They were difficult to measure directly on the functioning solar cells and they could not be calculated easily from the first-principle computation. These simulations of light scattering in the TiO_2 electrodes of DSSC indicated that light scattering of 1–25 nm TiO_2 particles was negligible. However, light scattering was effective in the particle size range of 80 to 180 nm. A suitable mixture of small particles (10 nm), which resulted in a large effective surface, and of larger particles (150 nm), which were the effective light scatterers, had the po-

tential to enhance solar absorption significantly. The rutile crystals had a larger refractive index and thus the light harvest of the mixtures of such larger rutile particles was improved. The light absorption of the double-layered films was examined. It showed that a maximal light absorption was gotten when the thickness of the first layer of 10 nm-sized anatase particles was comparable to that of the second 150 nm-sized rutile layer.

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