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Short communication

Synthesis of reflective TiO_2/SiO_2 multilayer flakes for solar cell application

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ABSTRACT

A novel technique for preparing TiO_2/SiO_2 multilayer flakes has been developed to synthesize an optical interference pigment active in visible light. As this process does not require a core layer such as mica, the thickness of the flakes can be <1 μm, this being much thinner than conventional interference flakes. As a potential application, the flakes were employed as light-scattering particles in dye-sensitized solar cells to improve light-harvesting efficiency. Although the improvement in the incident photon-to-electron conversion efficiency was limited to a wavelength range <600 nm, the flakes enhanced the short-circuit current under illumination as much as conventional scattering particles of a low aspect ratio.

1. Introduction

Dye-sensitized solar cells (DSCs) [1] attract research attention as low-cost alternatives to conventional solar cells. It is known that light-scattering particles incorporated in photoelectrodes enhance the photovoltaic conversion efficiency of DSCs, since these particles enhance light-harvesting efficiency by confining light within the cells [2]. A variety of materials and designs for light confinement have been investigated, such as submicrometer particles of anatase TiO_2, rutile TiO_2, ZrO_2 and SiO_2 [3–6] and inverse opal structures [7]. The light-scattering particles have been used either as additives in photoelectrodes or as reflectors on the back side of photoelectrodes. Of these techniques, a back reflector composed of submicrometer TiO_2 particles seems most practical, considering their resultant effect and simple processing. For a back reflector, however, reflective particles would be more effective than conventional submicrometer particles with weak back scattering. This paper concerns a novel technique for preparing reflective flakes designed as light-scattering particles for DSCs.

2. Design of reflective flakes

According to classical theory of optical interference, alternating layers of high and low refractive index materials yield strong reflection of light [8]. For a multilayer film of materials A and B, which have refractive indices n_A and n_B ($n_A > n_B$) and layer thicknesses t_A and t_B, the maximum reflectance is obtained at a wavelength $\lambda = 4n_At_A$, if the thickness $t_B = n_At_A/n_B$ and the outermost layers of the film are composed of material A. The reflectance of multilayer films can be calculated by iteratively applying Fresnel equations [8]. If $n_A = 2.0$, $n_B = 1.5$, $t_A = 75$ nm and $t_B = 100$ nm are assumed as an example, five alternating layers (A/B/A/B/A) placed in air exhibit a maximum reflectance of 73% at $\lambda = 600$ nm for normal incident light.

Similarly, multilayer flakes exhibit strong reflectance and are produced in industry by coating a core, such as glass flakes or mica. However, the incorporation of cores increases the thickness of the flakes to more than 1 μm, which unfavorably increases the thickness of the reflecting layer in DSCs. In this work, we prepare coreless multilayer flakes by detaching a sol-gel multi-coated film from a substrate.

3. Experimental

For high and low refractive index materials, we used TiO_2 and SiO_2, respectively. Alternating five-layered TiO_2/SiO_2 flakes were synthesized using two steps: sol-gel deposition and a lift-off process as shown in Fig. 1. Precursor solutions of TiO_2 and SiO_2 for the sol-gel process were prepared by hydrolyzing ethanolic solutions of Ti-tetraisopropoxide (TTIP, Wako) and tetraethyl orthosilicate (TEOS, Tokyo Chemicals). An aqueous solution of 1 M HNO_3 was added to TTIP and TEOS in the molar ratios of $H_2O/TTIP = 2$ and $H_2O/TEOS = 4$. The non-ionic surfactant Triton X-100 (Wako) was added to both solutions at

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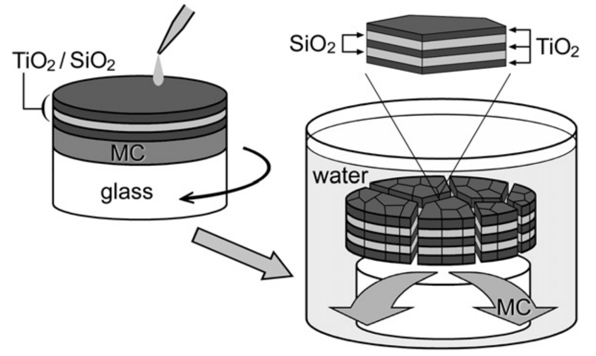

Fig. 1. A schematic diagram of the preparation process of the multilayer flakes.

a concentration of 0.1% to improve the wettability [9]. Prior to coating, the glass substrate was covered with a 1-μm thick methylcellulose (MC, Wako) by spreading and drying its aqueous solution. The TiO_2 and SiO_2 precursor solutions were then alternately spin-coated on the substrate. The MC layer showed no sign of dissolution during the process. The SiO_2 precursor films needed heating at 120 °C for 10 min to avoid mixing with subsequent deposits, while those of TiO_2 rapidly solidified during spin-coating. The thickness of each layer was controlled by adjusting the spin-coating conditions and concentrations of the precursors. For example, coatings of 0.2 M TiO_2 and 0.5 M SiO_2 precursor solutions yielded 40 nm and 105 nm thick films respectively, by spin-coating at 2000 rpm for 15 s. The multilayer films were baked at 120 °C for 1 h and then immersed in water. Once immersed, the films were lifted off from the substrate into flakes, as the water dissolved the MC layer. Finally, these flakes were sintered on an aluminum plate at 450 °C for 30 min.

Mesoporous and transparent electrodes of nanocrystalline TiO_2 (nc-TiO_2) were prepared on conducting glass substrates (F-doped SnO_2 overlayer, 10 Ω/sq, Nippon Sheet Glass) by painting a commercial paste of TiO_2 particles with a diameter of ~20 nm (PST-18NR, JGC Catalysts and Chemicals). A back reflecting layer was formed on the nc-TiO_2 layer by painting a paste that comprised TiO_2/SiO_x flakes (20%), nc-TiO_2 (5–8%), ethylcellulose (5–8%) and α-terpineol. For comparison, conventional electrodes with back reflectors of submicrometer TiO_2 (μ-TiO_2) crystals were also prepared using a PST-400C paste (JGC Catalysts and Chemicals). The electrode size was 0.22 cm^2. After sintering at 470 °C for 50 min, the optical properties of these photoelectrodes were measured with a spectrometer (HR2000+, Ocean Optics) equipped with an integral sphere. Film thicknesses were measured by a stylus profilometer (SE1200, Kosaka Laboratory).

The ruthenium complex dye Ruthenium 535 bis-TBA (Solaronix), *cis*-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium (II) bis(tetrabutylammonium), was loaded on the sintered electrodes by immersion in a 0.4 mM ethanolic solution for 24 h. The photoelectrodes were attached to Pt-coated indium tin oxide substrates and an electrolyte was injected between the electrodes. The electrolyte contained 50 mM of I_3^- in acetonitrile (AN-50, Solaronix).

I–V characteristics were measured under an AM1.5 simulated sunlight emitted from a filtered 150 W xenon lamp. The light intensity was calibrated using an a-Si standard cell designed for DSCs (BS-520, Bunko-Keiki). The incident photon-to-electron conversion efficiency (IPCE) was measured under constant monochromatic light between 400 and 780 nm with intensities of 0.5–1.4 mW cm^{-2}.

4. Results and discussion

Crystallographic and optical properties of the TiO_2 and SiO_2 layers prepared by sol-gel processes were examined for films sintered on a glass substrate. The TiO_2 layer had an anatase structure and the SiO_2 was amorphous, as determined by X-ray diffraction. The refractive indices (n) of the TiO_2 and SiO_2 films were estimated at 2.06 ± 0.03 and 1.45 ± 0.01, respectively, by fitting transmittance data in the 500–800 nm region to theoretical values [8], which allowed use of n and the film thickness (t) as adjustable parameters.

According to the refractive indices of the TiO_2 and SiO_2 layers, the layer thicknesses were fixed at $t(TiO_2) = 75$ nm and $t(SiO_2) = 105$ nm in the flakes of five alternating layers, so that the flakes exhibited maximum reflectance at a wavelength of 600 nm ($= 4nt$). Control of the layer thickness was achieved with an error of a few percent.

Fig. 2 shows reflectance of the photoelectrodes of the DSCs before loading dyes. The test cells contained an nc-TiO_2 transparent layer (7 μm thick) with and without a back reflector (3 μm thick). In contrast to the weak wavelength dependence of the μ-TiO_2 back reflector, the flakes exhibited a reflectance peak around 600 nm as a result of optical interference. The maximum reflectance of 52% in Fig. 2 seems significantly smaller than the theoretical value of 66% calculated from experimentally obtained n and t data at normal incidence. This may be due to a variation of flake orientation and inaccuracy of thickness control.

Fig. 3 shows optical and scanning electron micrographs of flakes in a back reflector. The lateral dimensions of the flakes were in the 10–100 μm range. The yellow/green color of the flakes observed in the optical reflection images changed into blue/purple in the transmission images, as is characteristic of interference pigments.

The effect of the reflecting layer on the DSC performance was studied by examining *I–V* characteristics. The short-circuit current density (J_{sc}) was increased by the incorporated flakes as depicted in Fig. 4, whereas either the open-circuit voltage (V_{oc}) or the fill factor (FF) showed no noticeable difference. For a DSC containing a 3 μm thick back reflector of flakes on a 10 μm thick nc-TiO_2 layer, typical values of J_{sc}, V_{oc}, FF and conversion efficiency were 15.7 mA cm^{-2}, 0.70 V, 0.71 and 7.8%, respectively, under simulated sunlight (100 mW cm^{-2}). The layer of flakes are expected to be less effective in generating photoelectrons than the nc-TiO_2 layer, considering fewer dye molecules loaded on a smaller surface area of flakes. Therefore the flake layer increased J_{sc} values mainly via confining light in the nc-TiO_2 layer.

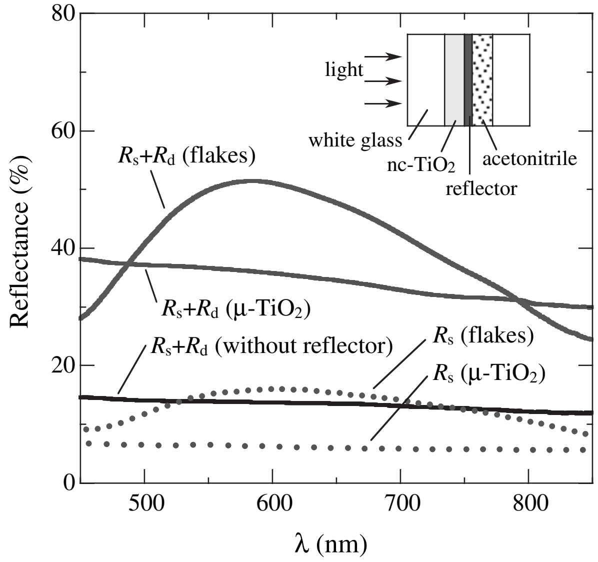

Fig. 2. Reflectance of test cells with and without back reflectors (dotted line, specular reflectance (R_s); solid line, sum of R_s and diffuse reflectance (R_d)). The inset shows the cell structure. Reflection from the air/glass and glass/nc-TiO_2 interfaces is not subtracted.

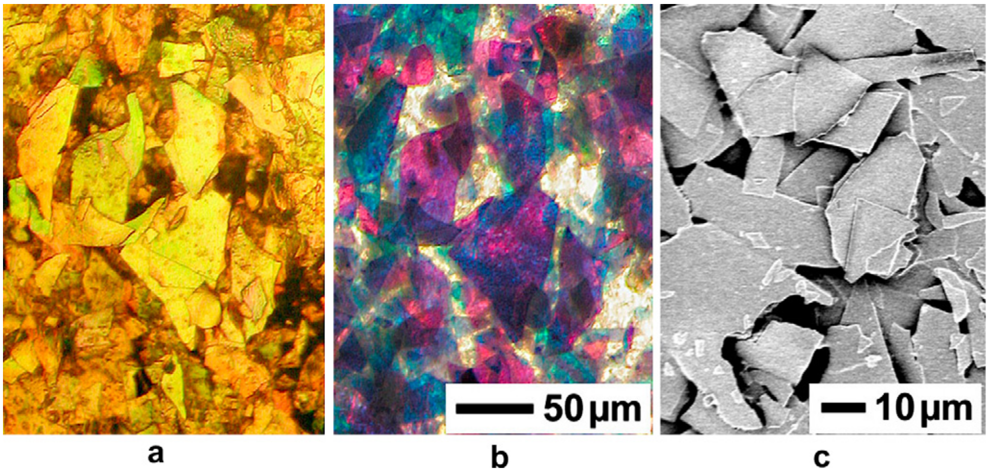

Fig. 3. Micrographs of a reflecting layer of flakes. Optical photos of (a) reflection, (b) transmission and (c) a SEM image.

Fig. 5 shows the IPCE spectra measured for DSCs with and without reflectors. At wavelengths below 600 nm, the flakes enhanced the IPCE most efficiently as a result of large reflectance (Fig. 2). This effect, however, seems inactive above 600 nm, compared to the μ-TiO_2 reflector. It is speculated from the SEM photograph (Fig. 3c) that flat planes of the flakes accumulate nearly parallel to the substrate. A large fraction of the normal incident light is then reflected vertically, while diffusive μ-TiO_2 particles scatter light in random directions, as schematically shown in Fig. 6. Thus the flakes may yield a smaller increase in the path-length of light compared with μ-TiO_2. Nevertheless, the flakes may enhance the IPCE at wavelengths below 600 nm, where photoelectrodes loaded with N719 dye absorb light sufficiently [10] to consume the incident light within the increased light path.

The observed variation of IPCE spectra may also be related to a photovoltaic reaction in reflecting layers. Since dye-loaded μ-TiO_2 films can generate and transport considerable photoelectrons [6], J_{sc} is enhanced by photovoltaic generation in the μ-TiO_2 reflector. This would be significant at wavelengths above 600 nm, where N719 dye has low absorbance and most of the incident light can reach the reflecting layer. By contrast, photoelectrons should diffuse around the outermost TiO_2 layer in the case of TiO_2–SiO_2 multilayer flakes, which have poorer crystallinity than single crystals, as expected from lower refractive indices. Owing to the poor electron transport, electrons generated around flakes inefficiently contribute to J_{sc}.

To improve the IPCE at longer wavelengths, one needs to increase the scattered light propagating in the lateral direction of the electrodes. An intermediate layer composed of a mixture of μ-TiO_2 and nc-TiO_2 may be suitable for this purpose [4]. Alternatively, smaller flakes are favorable in terms of both light reflection

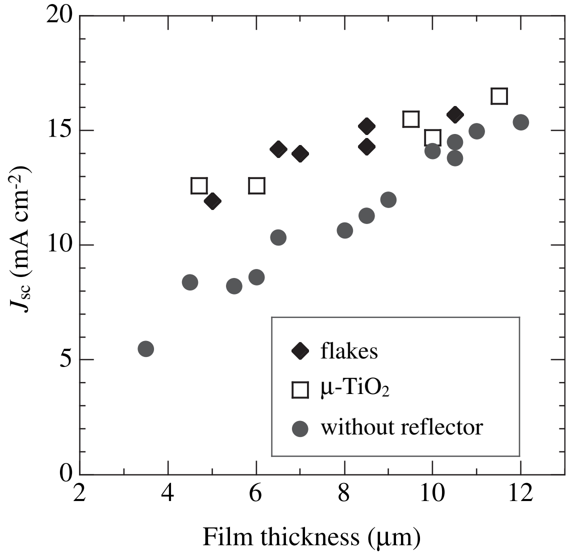

Fig. 4. Short-circuit current density of DSCs containing different reflecting layers. The data are plotted as a function of the nc-TiO_2 layer thickness.

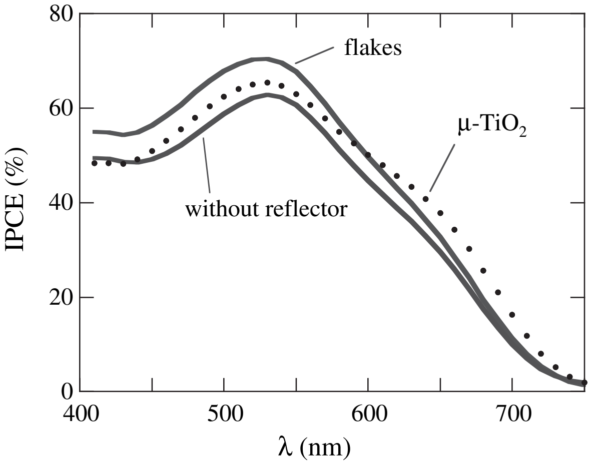

Fig. 5. IPCE spectra of DSCs containing different reflecting layers. The thickness of the nc-TiO_2 layer was 10 μm in all of the samples.

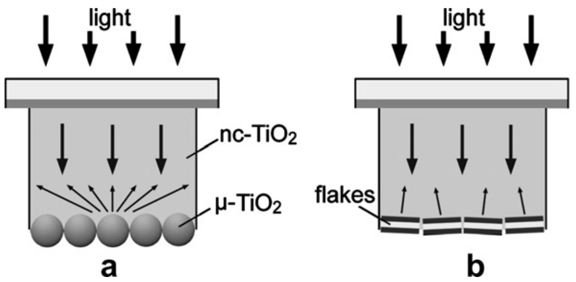

Fig. 6. Schematic diagrams of the light paths obtained from (a) a diffuse reflective layer and (b) a specular reflective layer.

and electron transport discussed above. First, small flakes should show weak orientation, giving rise to reflection of light in various directions. Second, reduction of size would shorten a diffusion path of electrons around flakes. In fact, our recent experiment showed that a back reflector of flakes of a smaller diameter ($\sim 10\ \mu m$) enhanced the IPCEs around 650 nm, with comparable performance to a μ-TiO_2 reflector. The optimum size of flakes is possibly a few micrometers, below which reflective interference would be lost.

5. Conclusions

We have successfully prepared optical interference flakes composed of five alternating layers of TiO_2 and SiO_2. Although the flakes were useful in confining light in DSCs, the effect was limited to wavelengths below 600 nm. Higher DSC performance will be attained by tuning the reflection spectra and the grain size of the flakes. Since the flakes can reflect light in a selected wavelength range, they may also work as a reflecting layer in a tandem cell [11], reflecting short wavelength light back to a top cell and transmitting long wavelength light to a bottom cell.

Acknowledgments

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