

Research Article

Al@SiO₂ Core-Shell Microflakes as Metal-Based Light Scattering Layer in Dye-Sensitized Solar Cells

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A metal-based light scattering layer (MLSL) for dye-sensitized solar cells (DSSCs) is formed from Al@SiO₂ core-shell microflakes prepared and coated on a thin porous TiO₂ electrode (approximately 4 μm thick). The DSSC corresponding to a TiO₂ electrode with an MLSL exhibits a low electron transport resistance in the TiO₂/electrolyte interface. Electron collection efficiency is greatly improved. Photovoltaic performance measurements indicate that the power conversion efficiency of the DSSC with the MLSL doubled from 1.37% to 2.96% (for an active area of 0.25 cm²), which is better than the 2.1% achieved by a DSSC with a conventional TiO₂-based light scattering layer (TLSL) obtained under identical experimental conditions.

1. Introduction

The dye-sensitized solar cell (DSSC) is expected to become the most cost-effective solar cell because of its low production cost and simplicity of fabrication. The photoactive dye in DSSC is the most important component because it controls the light-to-electricity conversion. Its price is one of the factors that dominate the cost of the DSSC. However, for cost-effective and large-scale DSSCs, dye use must be minimized. In practice, reducing the thickness of a TiO₂ electrode to several microns effectively reduces the amount of dye used [1], but it also reduces the number of electrons generated by illumination. Because of its poor light scattering capacity, the electrode transmittance of a thin TiO₂ electrode with a thickness of several microns usually exceeds 50% [2]. To compensate for low photon conversion and to improve light harvesting, a light scattering layer can be coated on the thin TiO₂ electrode [2–4]. Although studies have extensively discussed the optical performance of light scattering layers, none has elucidated the varying internal resistance and electron collection efficiency in DSSCs based on thin TiO₂ electrodes with and without light scattering layers. The literature also tends to focus on the use of TiO₂ particles to form a light scattering layer; this study is the first to consider the use of pure metal particles.

Aluminum (Al) microflakes are low-cost, plate-like metal microparticles with high optical reflectivity, which makes them suitable for use as the base material of a light scattering layer. However, reliability is important, and the prevention of corrosion of the Al microflakes by the electrolyte solution during long-term operation must be considered. This study evaluated the use of a protective SiO₂ shell layer coated directly onto the Al microflake surface to form Al@SiO₂ core-shell microflakes. These Al@SiO₂ core-shell microflakes coated on the thin TiO₂ electrode with an approximate thickness of 4 μm formed a metal-based light scattering layer (MLSL), which was expected to improve photovoltaic performance in a DSSC.

2. Experiment

2.1. Materials. Aluminum (Al) microflakes (flake size between 5 and 40 μm) were purchased from Titanex Corp. (Taiwan). Tetraethyl orthosilicate (TEOS) (99%, Aldrich), tetrabutyl orthotitanate (97%, Fluka), ammonium hydroxide solution (NH₃·H₂O) (25 wt%, Riedel-Dehaën), anhydrous ethanol (99.5%, J.T.Baker), Triton X-100 (J.T.Baker), chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O) (37.5% Pt basis, Sigma-Aldrich), citric acid (99.5%, Nihon Shiyaku

Industries, Ltd.), and TiO_2 powder (P25, Degussa) were used as received. Graphite powder (average size $2.7 \mu\text{m}$) was purchased from Homytech (Taiwan). Ru complex dye was Ruthenium 535 bis-TBA (N719), available at Solaronix (Switzerland). The FTO glass substrate (sheet resistance: $7 \Omega/\text{sq}$) was purchased from Hartford Glass Co. (USA). Rutile- TiO_2 nanopowder (particle size 250 nm) was supplied by ISK Taiwan Co., Ltd. (Taiwan).

2.2. Preparation of Al@SiO₂ Core-Shell Microflakes and TiO₂ Electrode with MLSL/TLSL. The Al@SiO₂ core-shell microflakes were prepared by Stöber method as described in the literature [5]. First, a solution of 3 g Al microflakes, 60 mL anhydrous ethanol, and 15 mL purified water was sonicated for 30 min to completely disperse the microflakes. Then, 4 mL tetraethyl orthosilicate (TEOS) and 2.5 mL $\text{NH}_3 \cdot \text{H}_2\text{O}$ were added to initiate a silica growth reaction at room temperature with continuous stirring for 12 h. The Al@SiO₂ core-shell microflakes were then filtered and washed with ethanol and then oven dried at 400°C for 1 h. A blending solution was prepared by mixing 2 g citric acid, 0.6 mL Triton X-100, and 1 mL tetrabutyl orthotitanate in 3 mL purified water. A paste was prepared by mixing the Al@SiO₂ core-shell microflakes with the blending solution at a weight ratio of 1 : 10 and then stirring for 30 min. The metal-based light scattering layer (MLSL) was obtained by coating the paste on the TiO_2 electrode (approximate active area and thickness, 0.25 cm^2 and $4 \mu\text{m}$, resp.) using doctor-blade method. The layer was then sintered at 400°C for 30 min. After sintering, measurement with an alpha-Step profilometer indicated that the thickness and covered area of the MLSL were about $7 \mu\text{m}$ and 0.36 cm^2 , respectively. For comparison, a TiO_2 electrode with a TLSL was also prepared here. A rutile- TiO_2 paste was prepared by mixing 4 g rutile- TiO_2 nanopowder, 2 g citric acid, 0.08 mL acetylacetone, 0.2 mL Triton X-100, and 0.3 mL tetrabutyl orthotitanate in 3 mL purified water and stirring for 30 min. The TiO_2 -based light scattering layer (TLSL) was obtained by coating the rutile- TiO_2 paste on the TiO_2 electrode and then sintering at 400°C for 30 min. The thickness and covered area of the TLSL were controlled same as the MLSL.

2.3. Graphite/Pt Counter Electrode. A mixture of graphite and platinum (Pt) was prepared to reduce the Pt loading and production cost of the DSSC. First, a solution for use as an adhesive solution was prepared by mixing 1 g citric acid, 0.2 mL Triton X-100, and 0.1 mL tetrabutyl orthotitanate in 1.5 mL purified water and stirring the mixture for 1 h. Then, 6 mg of chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was added to the adhesive solution, which was stirred for 30 min. Finally, 1 g of graphite powder was dispersed in the adhesive solution with stirring for 3 h to form a paste that contained graphite and Pt. The graphite/Pt counter electrode was prepared by coating the paste on an FTO glass substrate using the doctor-blade method and then sintering at 400°C for 30 min.

2.4. Assembly and Measurements of DSSCs. Three photo electrodes, a TiO_2 electrode, a TiO_2 electrode with an MLSL,

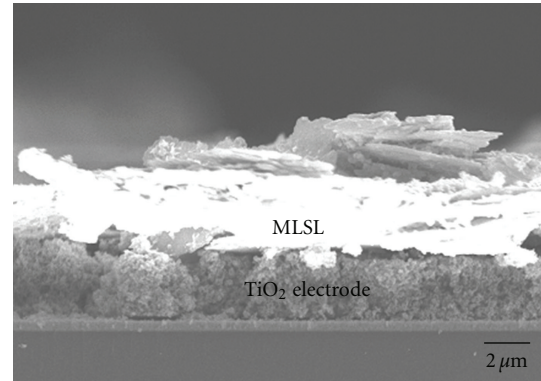
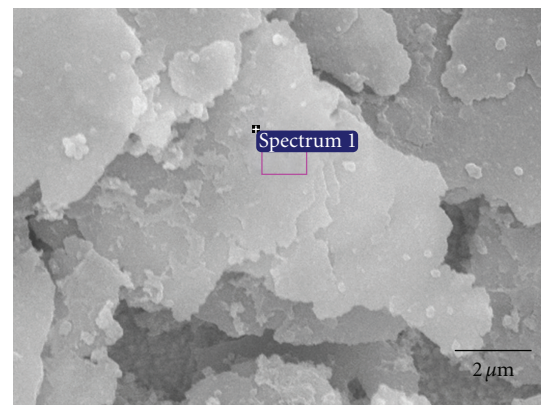
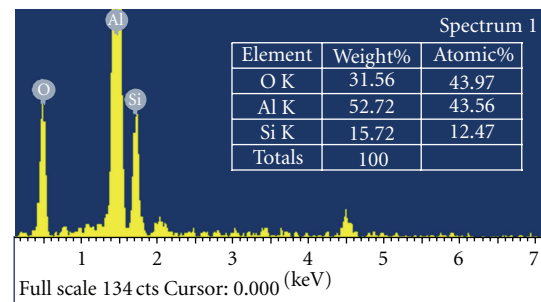


FIGURE 1: FE-SEM image of TiO_2 electrode with MLSL.



(a)



(b)

FIGURE 2: Characterization of Al@SiO₂ core-shell microflakes: (a) FE-SEM image and (b) EDS spectrum.

and a TiO_2 electrode with a TLSL, were soaked in a dye solution of 0.3 mM N719 dye in ethanol for 24 h at room temperature. The photo electrode and the graphite/Pt counter electrode were then clipped together, and an electrolyte solution of 0.1 M LiI, 0.05 M I_2 , and 0.5 M 4-tert-butylpyridine (TBP) in 3-methoxy propionitrile (MPN) was introduced into the cell to complete the assembly. A field-emission scanning electron microscope (FE-SEM, JEOL, JSM-6700F) equipped with an energy-dispersive spectrometer (EDS) was then used to characterize the TiO_2 electrode with the MLSL and the elemental composition

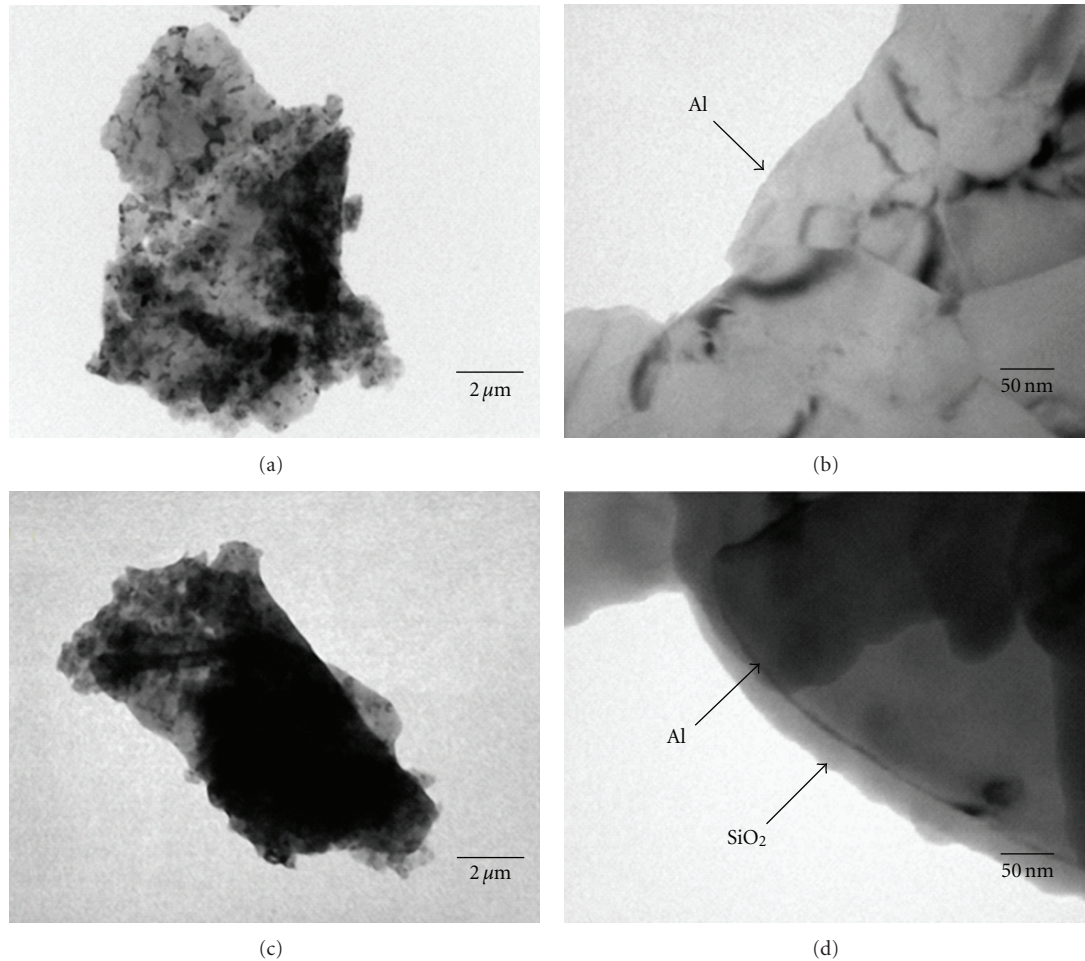


FIGURE 3: TEM images of (a) Al microflake without SiO_2 shell layer, (b) magnified view of (a), (c) Al microflake with SiO_2 shell layer, and (d) magnified view of (c).

of the Al@SiO_2 core-shell microflakes. The Al@SiO_2 core-shell microflake surface was viewed with a transmission electron microscope (TEM, PHILIPS, and CM-200 TWIN). Electrochemical impedance spectra (EIS) were measured using a computer-controlled potentiostat (EG&G, Model 273) equipped with a frequency response analyzer. The short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}) were measured by computer-controlled digital source meter (Keithley, Model: 2400) under one sun illumination (AM 1.5, 100 mW/cm^2).

3. Results and Discussion

3.1. Characteristics of MLSL and Al@SiO_2 Core-Shell Microflakes. Figure 1 is an FE-SEM image of the TiO_2 electrode with MLSL. The Al@SiO_2 core-shell microflakes were stacked individually to form the MLSL, which was then secured to the TiO_2 electrode. Figure 2 presents the EDS spectrum of the Al@SiO_2 core-shell microflakes, which was obtained by measuring the energy and intensity distribution of X-ray signals generated by a focused electron beam on the

Al@SiO_2 core-shell microflakes. The elemental composition of Al@SiO_2 core-shell microflakes was thus obtained, and the SiO_2 shell layer on the Al microflake surface was verified. Figure 3 presents the TEM image of Al microflakes with and without the SiO_2 shell layer. The SiO_2 shell layer on the Al microflake surface was homogeneous and about 50 nm thick.

3.2. Optical Spectra Analysis. To realize the potential of the MLSL as an effective collector of the solar intensity in the cell, the UV-VIS transmittance spectra of the three photo electrodes were obtained as shown in Figure 4. This figure clearly reveals that the TiO_2 electrode was semitransparent in the visible and near-infrared regions. However, the transmittance of the TiO_2 electrode with the MLSL was observably lower than that without, probably because the MLSL effectively scattered the light that penetrated the TiO_2 electrode.

3.3. Photovoltaic Performance Measurement. Table 1 presents the photovoltaic performance of DSSCs based on different photo electrodes. Figure 5 plots the characteristic curves of

TABLE 1: Photovoltaic performance, peak frequency (f_p) of middle-frequency semicircle, and electron lifetime (τ) of DSSCs based on different photo electrodes.

DSSC modules	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	f_p (Hz)	τ (s)
TiO ₂ electrode	2.65	0.746	0.692	1.37	17.44	0.057
TiO ₂ electrode with TLSL	3.92	0.778	0.687	2.10	14.36	0.070
TiO ₂ electrode with MLSL	5.51	0.785	0.683	2.96	11.91	0.084

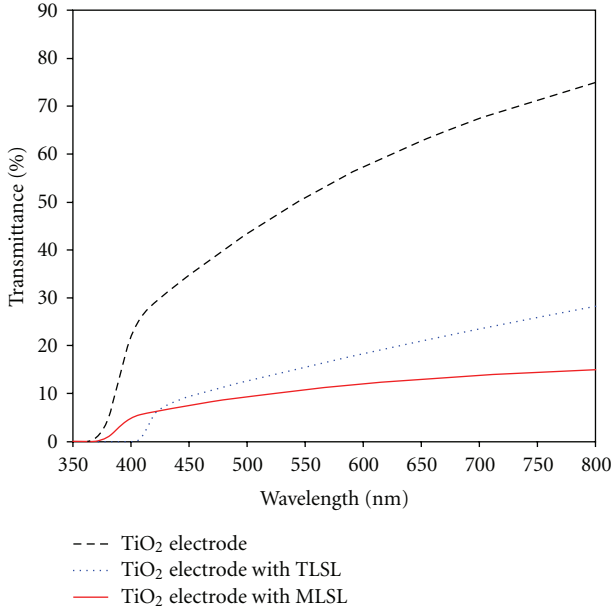


FIGURE 4: Transmittance spectra of three photo electrodes (undyed TiO₂ electrode: 4 μ m thick; TLSL: 7 μ m thick; MLSL: 7 μ m thick).

current density versus voltage. Under one sun illumination (AM 1.5, 100 mW/cm²), the DSSC based on the TiO₂ electrode without a light scattering layer has an open-circuit voltage (V_{oc}) of 0.746 V, a short-circuit current density (J_{sc}) of 2.65 mA/cm², a fill factor (FF) of 0.692, and a power conversion efficiency (η) of 1.37%. For the TiO₂ electrode with the TLSL, J_{sc} and η were improved to 3.92 mA/cm² and 2.1%, respectively. When the MLSL was coated on the TiO₂ electrode, J_{sc} and η were improved to 5.51 mA/cm² and 2.96%, respectively, which values are greater than those obtained with the TLSL.

3.4. EIS Analysis. Figure 6 presents the EIS with Nyquist plots and Bode phase plots of DSSCs based on the TiO₂ electrode with and without the light scattering layer, which were obtained under a forward bias of -0.68 V in the dark. The impedance data were analyzed by Zahner software through fitting the data with Randles equivalent circuit [6]. The Nyquist plots of the EIS confirm that the diameter of the middle-frequency semicircle for the TiO₂ electrode with MLSL was smaller than that of the electrode without. However, the diameter of the middle-frequency semicircle for the TiO₂ electrode with the TLSL was larger than that of

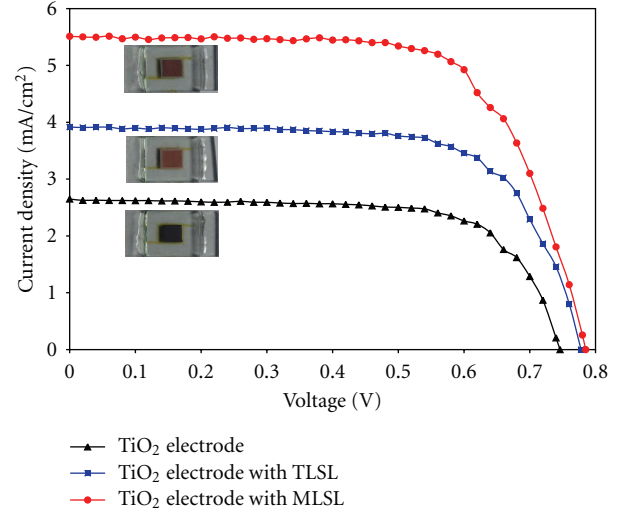


FIGURE 5: Photocurrent density-voltage curves for DSSCs based on different photo electrodes.

the electrode without. Accordingly, the use of a light scattering layer greatly changes the middle-frequency semicircles. Additionally, the middle-frequency semicircle is associated with electron transport in the TiO₂/electrolyte interface, and its diameter usually equals the electron transport resistance [7], so the use of the MLSL reduced the electron transport resistance in the TiO₂/electrolyte interface while the use of the TLSL increased it. Since the electron transport resistance in the TiO₂/electrolyte interface was critical to the total internal resistance of the DSSC, and since DSSC performance improves as this total internal resistance is reduced [8], the MLSL effectively improves DSSC performance.

When comparing electron collection efficiencies of the DSSCs based on the TiO₂ electrode with and without the light scattering layer, the crucial parameter is electron lifetime, which increases with the electron collection efficiency [9]. The electron lifetime can be determined by the following equation [10]:

$$\tau = \frac{1}{f_p}, \quad (1)$$

where f_p denotes the peak frequency of the middle-frequency semicircle in the Nyquist and Bode phase plots. Table 1 presents the peak frequency of the middle-frequency semicircle and the electron lifetime of DSSCs based on different photo electrodes. The MLSL increases electron lifetime and

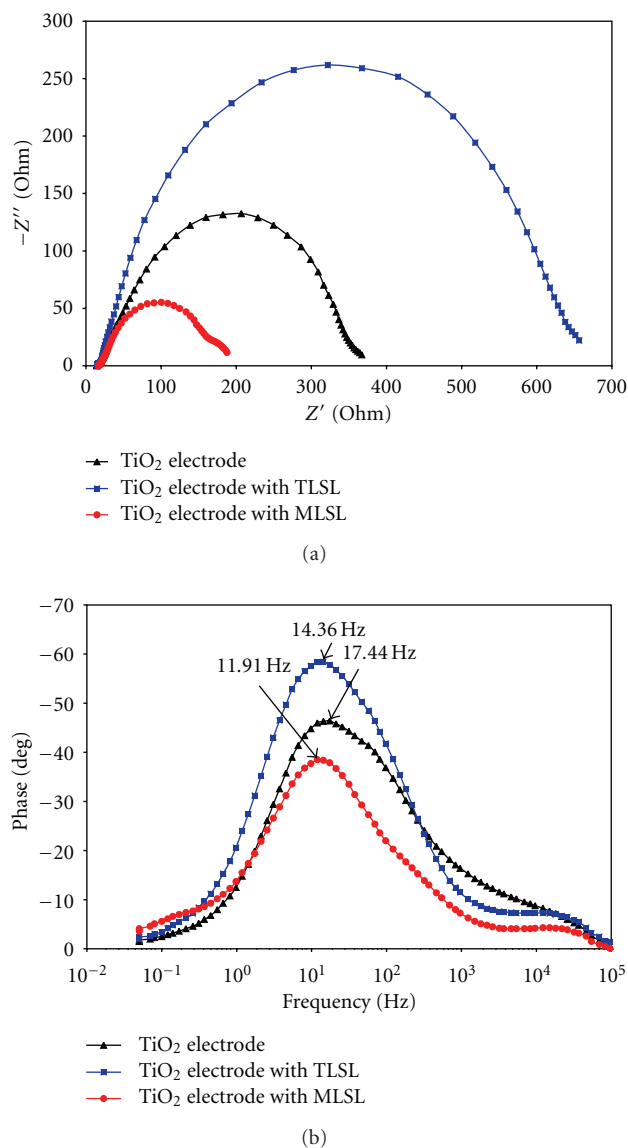


FIGURE 6: Electrochemical impedance spectra for DSSCs based on different photo electrodes. (a) Nyquist plot and (b) Bode phase plot.

ultimately increases electron collection efficiency in the DSSC.

4. Conclusion

In this study, Al@SiO₂ core-shell microflakes were developed and used directly to form the metal-based light scattering layer (MLSL) in dye-sensitized solar cells. Because the MLSL reduces electron transport resistance in the TiO₂/electrolyte interface, it improves electron collection efficiency and thereby increases power conversion efficiency by 116% (from 1.37% to 2.96%). Therefore, the photovoltaic performance of the DSSC based on TiO₂ electrode with MLSL was superior to that of DSSC based on TiO₂ electrode with TLSL.

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