

An Efficient Dye-sensitized Photoelectrochemical Solar Cell Made from CaCO₃-coated TiO₂ Nanoporous Film

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A convenient—and quick to realize—approach for the synthesis of an ultrathin overlayer of CaCO₃ on TiO₂ thin films is suggested. Since dye-sensitized photoelectrochemical investigations on CaCO₃-thin-layer-coated TiO₂ nanoporous films are hitherto unreported, we performed such investigations by sensitizing our TiO₂-CaCO₃ films with tetrabutylammonium *cis*-di(thiocyanato)-*N,N'*-bis(4-carboxylato-4'-carboxylic acid-2,2'-bipyridine)ruthenate(II) and achieved power conversion efficiencies over 9.3% under illumination of AM 1.5 simulated sunlight (95 mW/cm²).

Dye-sensitized solar cells (DSSCs) based on nanoporous films of TiO₂ are gaining much attention as promising solar energy conversion devices.¹⁻⁴ The performance of these devices mainly depends on the nanoporous semiconductor film material, film morphology, structural properties of the sensitizer, and the redox couple used. In addition, the interfacial recombinations of the electrons injected by the photoexcited dye with the dye-cations or redox couple are also limiting the efficiency of the DSSCs. Recently, it has been suggested that the growth of insulating thin overlayers on the surfaces of nanoporous films may be an important approach to suppress the interfacial recombination in DSSCs.⁵⁻¹¹ The main intention of this overcoat is to increase the physical separation of injected electrons and redox couple/oxidized dye molecules and thereby retarding the recombination reactions.⁵ Perusal of results also reported the procedures for the coating of nanocrystalline metal oxide films with thin overlayer of different metal oxide with a higher conduction band edge, and demonstrated that this coating resulted in both retardation of interfacial recombination dynamics and improvement in device performance.^{7,8,10,12} To further exploit this approach, we prepared new kind of insulating layer other than the metal oxides, i.e., CaCO₃. We attempted a simple approach for the fabrication of CaCO₃-coated TiO₂ nanoporous film from calcium oxalate, by simply mixing it with TiO₂ powder during the paste preparation. To the best of our knowledge, this is the first example for the fabrication of CaCO₃-thin-layer-coated TiO₂ films and their application to dye-sensitized photoelectrochemical properties.

The nanoporous bare TiO₂ and CaCO₃ overlayer-coated TiO₂ films were prepared by using the following procedure. First the nitric acid-adsorbed TiO₂ (P-25) powder¹³ was mixed with water and homogenized it for 10 min using ultrasonic homogenizer. Finally, [Ti(OH)_x(OOH)_y] and Triton X 100 were added into this paste and stirred for 1 h using a magnetic stirrer. For the coatings of CaCO₃ on TiO₂, by and large, we followed the procedure, which was used for the bare TiO₂ paste preparation with the exception of mixing the calcium oxalate (Wako chemicals). In addition, for preparing various thickness of CaCO₃-containing TiO₂ films, various wt % of calcium oxalate was added

during the TiO₂ paste preparation. Thus obtained paste was deposited on the FTO conducting glass (SnO₂:F) using bar coater method. The resulting layer was sintered for 30 min at 500 °C.

The thickness of both the thin-layer-coated and uncoated electrodes were measured and it was ca. 8 μm. The sintered films were characterized by X-ray diffractometry (Figure is not shown). The absence of CaO formation and the presence of CaCO₃ on the TiO₂ films were clearly observed in the X-ray diffractogram. Further, the CaCO₃ could not be observed when the amount is less in the film. In order to check the formation of CaCO₃ on TiO₂, we prepared thick layer of CaCO₃ by adding 10 wt % of calcium oxalate. The amount of CaCO₃ loaded on TiO₂ film (Ca/Ti) was measured by the XPS analysis and then the average thickness of CaCO₃ was calculated.⁸ For the thickness calculation, we assumed all the added calcium oxalate was converted into CaCO₃ and deposited uniformly on TiO₂ owing to the specific adsorption of Ca²⁺.

For dye-sensitized photoelectrochemical investigations, a sandwich-type configuration was employed. A Pt-coated slide glass was used as a counter electrode, and 0.1 M LiI + 0.05 M I₂ + 0.6 M dimethylpropylimidazolium iodide + 0.5 M *tert*-butylpyridine in methoxypropionitrile was used as electrolyte. The dye tetrabutylammonium *cis*-di(thiocyanato)-*N,N'*-bis(4-carboxylato-4'-carboxylic acid-2,2'-bipyridine)ruthenate(II) (N719, Solaronix) was adsorbed by immersing the electrodes in a 0.3 mM ethanolic solution of the dye (reflux treatment).

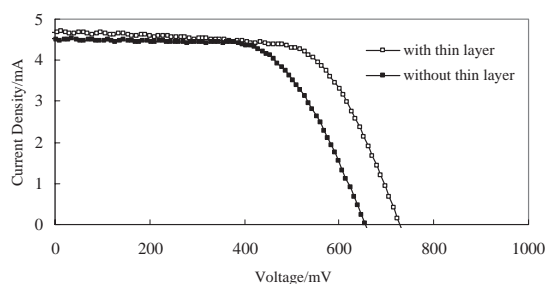


Figure 1. Photocurrent–voltage curves of dye-sensitized solar cell with (open square) and without CaCO₃ thin layer (filled square) under illumination of AM 1.5 simulated sunlight (95 mW cm⁻²). (Illumination area; 0.25 cm²).

Table 1. Comparison of the photoelectrochemical performance parameters of the cells based on TiO₂ and TiO₂/CaCO₃ films (Light intensity; 95 mW cm⁻². Illumination area; 0.25 cm²)

	Voc/mV	Jsc/mA cm ⁻²	F.F	η/%
TiO ₂	674	16.56	0.695	8.1
TiO ₂ /CaCO ₃	728	18.69	0.651	9.3

Table 2. Comparison of the photoelectrochemical performance parameters of the cells based on TiO₂ and TiO₂/CaCO₃ films, wt % of added calcium oxalate, calculated thickness of CaCO₃ layer, and amount of loaded dye (Light intensity; 95 mW cm⁻². Illumination area; 1 cm²)

Calcium oxalate /wt %	Calculated thickness of CaCO ₃ /nm	Dye amount × 10 ⁻⁸ mol/cm ²	<i>J</i> _{sc} /mA cm ⁻²	<i>V</i> _{oc} /mV	<i>F.F.</i>	<i>η</i> /%
0	0	2.46	8.6	728	0.50	3.2
1	0.06	5.43	9.7	749	0.48	3.5
2.5	0.14	5.25	10.4	755	0.48	3.8
5	0.28	6.53	8.0	776	0.51	3.5
10	0.54	5.52	7.9	782	0.58	3.6

The dye-coated electrodes were rinsed quickly with acetonitrile and used as such for photovoltaic measurements. The amount of dye adsorbed on the electrode was measured by UV-vis absorption of the electrode. Photocurrent-voltage characteristics of solar cells were measured by using EIKO Model MP-160S IV-tracer and Wacom solar simulator equipped with AM 1.5 filter was used as a light source. Light intensity was measured by using EIKO-SEIKI MS-802 thermopile.

A comparison of two typical DSSCs that differ in their type of electrode was described here. One cell contained the new CaCO₃-thin-layer-coated (ca. 0.14 nm) TiO₂ electrode and the other one served as a reference, consisting of a standard nanoporous TiO₂ electrode. To ensure fair comparison, both cells were studied under similar conditions. Figure 1 showed the photocurrent-voltage characteristics of the cells constructed from TiO₂ porous film with and without thin layer. The performance of thin layer-containing cell is superior to the standard one with respect to all cell parameters such as short circuit current (*J*_{sc}), open circuit voltage (*V*_{oc}), and efficiency (*η*) and the results were shown in Table 1. The suppression of the interfacial recombination may be responsible for the significant increase of *V*_{oc} and fill factor as reported earlier.^{4,7-10} It is pertinent to point out here that the improvement of *J*_{sc} is observed in the CaCO₃-coated TiO₂ electrode containing cell in spite of the fact that the existence of CaCO₃ layer tends to minimize the efficiency of electron injection from excited dye molecules into the conduction band of TiO₂. The increased dye amount on CaCO₃-coated TiO₂ films (see Table 2) should be responsible for this enhancement of photocurrent. The better dye adsorption on CaCO₃-coated TiO₂ surface may be due to the more basic nature of CaCO₃, which favors attachment of the dye molecules through its carboxylic acid groups.

In order to investigate further the effect of barrier layer on DSSCs performance when its thickness exceeds certain critical level, a various thick CaCO₃ layer containing TiO₂ films were prepared. The DSSCs were constructed in the same way as mentioned above and for the I-V measurements; the light illumination area was kept at 1 cm² for all the cells. The photoelectrochemical performance parameters of all the cells, calculated thickness of CaCO₃ layer and amount of loaded dye on the films are shown in Table 2. The cell constructed with the electrodes of thicker CaCO₃ layer show higher *V*_{oc} and fill factor, which also confirms the blocking behavior of CaCO₃ layer. The sharp decreases in the *J*_{sc} value may be due to the reduction of tunneling

probability of electrons across the thicker CaCO₃ barrier layer. Similar result was observed in the case of DSSCs made with MgO-coated SnO₂ electrodes.⁵

The results presented above clearly demonstrate that the CaCO₃-thin-overlayer-coated TiO₂ electrodes are superior (when the thickness is optimum) to the standard thin layer uncoated TiO₂ electrodes in terms of the performance of DSSCs. These results suggest that the improvement is achieved by the formation of an energy barrier at the TiO₂ electrode-electrolyte interface, which slows or minimizes the recombination process. In conclusion, for the first time we demonstrated a simple method to coat CaCO₃ thin barrier layer on TiO₂ porous film, and have shown that such layer improves the performance of DSSCs remarkably.

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