

Composite Electrode SnO₂/TiO₂ for Dye-Sensitized Solar Cells

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Abstract: Composite nanoporous electrode SnO₂/TiO₂ was fabricated for the dye sensitized solar cell (DSSC) with N₃ (Cis-Ru). After introducing of TiO₂, the open-circuit photovoltage (Voc) was higher than that of the pure SnO₂ electrode, while short-circuit photocurrent (Isc) was varied with the ratio of the TiO₂. Appropriate content of the TiO₂ can be beneficial to the efficiency of the solar cell, and it gives negative impact on the composite electrode when the content of TiO₂ is higher.

Keywords: Dye sensitized solar cell, SnO₂/TiO₂ composite electrode, photoelectric conversion.

Much attention has been paid to improve the performance of the efficient photoelectron-chemical cells, since Grätzel and his co-workers reported a solar cell based on a ruthenium complex adsorbed on highly porous nanocrystalline TiO₂ film¹. Among them, the improvement of electrode is one of the important subjects, such as to search the alternative wide bandgap semiconductors^{2,3}, to modify the TiO₂ by doping or coating *et al.*^{4,5} SnO₂ is one of the extensively studied wide bandgap semiconductors. However, its overall yield is not higher than 3%. In this letter, we report the synthesis of the composite SnO₂/TiO₂ electrodes and their characteristics of the photo-electronic conversion.

Experimental

Fluorine-doped SnO₂-layered glass plates (20Ω/□)(SnO₂/F) were obtained from the Institute of Nonferrous Metals of China. Propylene carbonate (PC) was purchased from Acros. The redox electrode used in this work is 0.5 mol·L⁻¹ LiI + 0.05 mol·L⁻¹ I₂ + 0.1 mol·L⁻¹ *tert*-butylpyridine in a PC/MeCN (1:1, V/V) mixture solvent. Cis-Ru (N₃) was synthesized according to the literature⁶.

Large size of nanocrystalline SnO₂ colloid was prepared according to the procedure reported in the literature⁷, except that autoclaving was performing at 220°C for 30 h. After addition SnO₂ powder (1g) to 80 mL different concentration of TiCl₄ aqueous solution, the mixture was sonicated for about half an hour. The mixture was refluxed at 90°C for 4 hours under continuous stirring and then allowed to cool overnight. Part of the precipitate, washed with deionized water several times, was used to perform XRD analysis. The DSSC cells were fabricated with 10 μm thick films and monitored with the

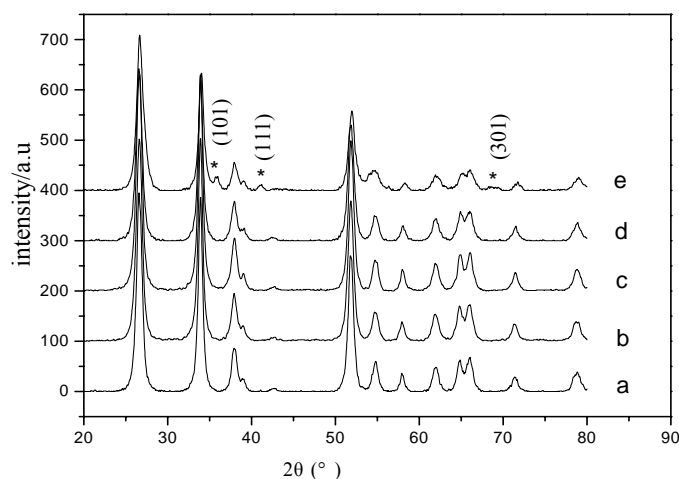
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method described in the literature⁸.

Results and Discussion

It can be seen from **Figure 1** that no pure TiO₂ rutile phase appears when the concentration of TiCl₄ is 0.01 mol·L⁻¹ or lower. With the Ti⁴⁺ content increasing to 0.05 mol·L⁻¹, a rutile phase of TiO₂ can be detected in composite electrode (in **Figure 1** curve e). It can be inferred from the results of XRD that when Ti⁴⁺ ion content is very low, Ti⁴⁺ ion should be adsorbed on to the surface of SnO₂ particles, and the rutile phase is formed when the concentration gets higher.

Figure 1 XRD pattern of SnO₂ and SnO₂/TiO₂ powder product.

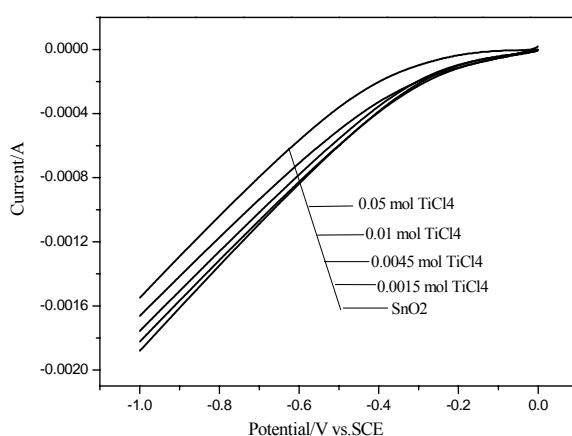


(a) SnO₂, (b) SnO₂/0.0015 mol TiCl₄, (c) SnO₂/0.0045 mol TiCl₄, (d) SnO₂/0.01 mol TiCl₄ and (e) SnO₂/0.05 mol TiCl₄

Table 1 summarized some parameters obtained from a thin-layer sandwich-type solar cell under illumination of white light from Xe lamp (67.2 mW·cm⁻²) and the effective illumination area is 0.182 cm². We can see in **Table 1** that open-circuit photovoltage (Voc) and the fill factor (FF) of the solar cells fabricated by composite electrodes are higher than those of pure SnO₂. At an appropriate content Ti⁴⁺ coated SnO₂, although the sample d cell gave a short-circuit photocurrent (Isc) of 13.5 mA·cm⁻², which is lower than that of pure SnO₂, it got a much higher open-circuit photovoltage (Voc) of 492 mV and a better fill factor (FF) of 0.44. Therefore, higher Voc and FF of the composite electrode offset the decrease of Isc and result in the overall yield (η) 4.33 %, which is superior to the efficiency of pure SnO₂ cell.

Table 1 Electrode characteristics and parameters for their DSSCs

electrode	molar ratio of Ti:Sn	dye molar/cm ²	η (%)	Voc(mV)	Isc(mA)	FF
SnO ₂	/	0.76×10^{-7}	2.31	299	16.3	0.32
SnO ₂ /0.0015 mol TiCl ₄	1: 70.2	1.15×10^{-7}	2.82	352	17.5	0.31
SnO ₂ /0.0045 mol TiCl ₄	1: 23.	1.06×10^{-7}	2.81	388	14.3	0.34
SnO ₂ /0.01 mol TiCl ₄	1:10.5	1.65×10^{-7}	4.33	492	13.5	0.44
SnO ₂ /0.05 mol TiCl ₄	1: 2.1	1.24×10^{-7}	0.84	489	1.9	0.59

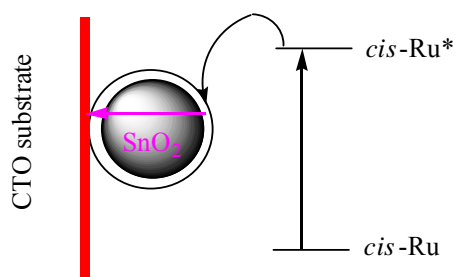
Figure 2 Dark current of the bare SnO₂ electrode and the composite SnO₂/TiO₂ electrodes.

Scan rate is 10 mV/s, and the electrolyte is $0.5 \text{ mol}\cdot\text{L}^{-1}$ LiI, $0.05 \text{ mol}\cdot\text{L}^{-1}$ I₂, $0.1 \text{ mol}\cdot\text{L}^{-1}$ 4-*tert*-butylpyridine in 1:1 acetonitrile-propylene carbonate.

Figure 2 shows the dark current of the electrodes. Data show that the dark current of all composite electrodes is lower than that of the bare SnO₂ electrode under the same bias voltage used, and that the more concentration of the Ti⁴⁺, the lower the dark current gets. This phenomenon indicates that electron recombination rate decreases, which might attribute to the energy barrier formed after TiO₂ coating. The coating layer TiO₂ serves as the energy barrier between the excited cis Ru(II) and SnO₂ layer. When the ratio of Ti:Sn is small, the electrons transport from Ru(II)* to TiO₂, and then inject into SnO₂. In this situation, the SnO₂ is close to the CTO substrate, therefore, the injected electrons easily reach to the substrate. Such scene can be illuminated in the **Scheme 1**. With the ratio Ti:Sn is increasing greatly, the SnO₂ particles might disperse around TiO₂ particles. In this case, these injected electrons in the TiO₂ cannot reach to the substrate but transfer to the electron collector tank, SnO₂ nanoparticles. Then these SnO₂ nanoparticles serve as trap centers to annihilate injected electron. It is unfavorable for these trapped electrons to reach the CTO substrate with 0.3 V energy difference between the rutile TiO₂ and SnO₂ particles. In this circumstance, such structure does not favor electron transfer. Therefore appropriate content TiO₂ layer plays an important role in decreasing electron

recombination rate and the optimized SnO₂/TiO₂ composite electrode to give better performance than that of pure SnO₂.

Scheme 1 The electron transfer way when the TiO₂ coating layer is thin.



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