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Photocurrent Enhancement by TiCl_4 Post-Treatment for TiO_2 Nanoporous Film Electrode

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Abstract: Enhanced photocurrent in dye-sensitized photoelectrochemical cell was obtained by post-treating the TiO_2 nanoporous film electrode with TiCl_4 . By investigating the effect of the post-treatment on surface area, pore size distribution, laser pulse induced current transient of the film electrode, photocurrent increase by the post-treatment was assigned to the improved electron percolation resulting from broadening of interparticle neck.

Key words: Photoelectrochemical cell, Sensitization, TiO_2 , Electrode post-treatment

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1 Introduction

Dye-sensitized nanoporous TiO_2 photoelectrochemical cells have attracted much attention due to its merits in scientific, technical and economic aspects^[1~5]. The characteristic of this type of cells is the nanoporous thin film electrodes, i. e. the sintered network of TiO_2 nanoparticles, which serve as a matrix for attachment of sensitizer molecules and as the transfer layer for injected electrons. It is obvious that the property of the electrode is closely related to the cell performance. Methods of electrode modification or post-treatment have been subject to investigation aiming to improve cells performance further^[6].

We found in our experiments that TiCl_4 post-treatment of the film electrode led to repeatable increase in photocurrent. The mechanism of this improvement was explored by analysing surface area, pore size distribution, time-resolved photocurrent of the film electrodes with and without the post-treatment.

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2 Experimental

2.1 Electrode Preparation and Characterization

Preparation of TiO_2 nanoporous film electrode has been described in a previous work^[4]. TiO_2 film electrode was prepared by spread TiO_2 paste onto ITO conducting glass (Indium doped SnO_2 , sheet resistance $20 \text{ } \Omega \cdot \text{cm}^{-2}$, transmission $> 85 \%$ in the visible), followed by sintering at $450 \text{ } ^\circ\text{C}$ for 30 min. For the post-treatment, the prepared electrode was immersed in $0.5 \text{ mol } \cdot \text{L}^{-1} \text{ TiCl}_4$ for 2 h in a closed chamber, fully rinsed with deionized water, then heated again at $450 \text{ } ^\circ\text{C}$. Dye coating was carried out by soaking electrode just after heating in $0.3 \text{ mmol } \cdot \text{L}^{-1}$ Ru dye solution (cis-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium(II) in absolute ethanol) for 10h. Excess dye was removed by rinsing with ethanol.

Electrodes surface area and pore size distribution was studied using nitrogen adsorption-desorption apparatus (Model ASAP 2010, Micromeretics Instrument Corp.).

2.2 Photoelectrochemical Measurement

Sandwich-type cells were constructed with platinized ITO glass as counterelectrodes and $0.3 \text{ mol } \cdot \text{L}^{-1} \text{ LiI} / 0.03 \text{ mol } \cdot \text{L}^{-1} \text{ I}_2$ propylene carbonate solution as electrolyte. IPCE (incident photon-to-current conversion efficiency) was determined by measuring the short circuit photocurrent at various excitation wavelengths. The I-V curves were obtained at a scan rate of $5 \text{ mV } \cdot \text{s}^{-1}$ in two-electrode arrangement. A 150 W xenon lamp combining high-intensity grating monochromator served as light source. In current-voltage measurement, a 10 cm water filter and a 350 nm cut-off filter was placed in the beam, and 15% transmission loss in ITO glass was corrected.

Time-resolved photocurrent measurements were performed in a conventional three-electrode cell consisting of a quartz window. The working electrode was Ru dye coated film electrode, which is fixed parallel to the quartz window. The counter electrode and the reference electrode were a platinum plate and saturated calomel electrode (SCE). Saturated KI solution in MeCN was employed as electrolyte. The applied potential was held at 0 V vs SCE by a potentiostat (Princeton Applied Research, model 173). The light source was a YAG:Nd laser with a pulse duration of 6ns and wavelength of 532 nm at light intensity of $0.9 \text{ mJ } \cdot \text{cm}^{-2}$. Photocurrent transient was monitored by Digital Storage Oscilloscope (Tektronix TDS380).

3 Results and Discussion

Photocurrent action spectra of the Ru dye-sensitized electrode with and without TiCl_4 treatment are presented in Figure 1. IPCE represents the percentage of incident photon being converted to electrons at a certain wavelength. As shown in Figure 1, increased IPCE is obtained in the whole measured wavelength region by the post-treatment. The current-voltage curves of the Ru dye sensitized photoelectrochemical cells under $27 \text{ mW } \cdot \text{cm}^{-2}$ white light illumination are shown in Figure 2. It can be seen that short-circuit photocurrent is increased from $4.1 \text{ mA } \cdot \text{cm}^{-2}$ to 5.4

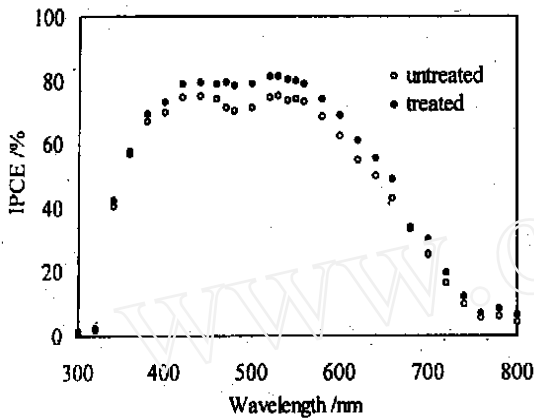


Fig. 1 Photocurrent action spectra of the Ru dye-sensitized electrodes

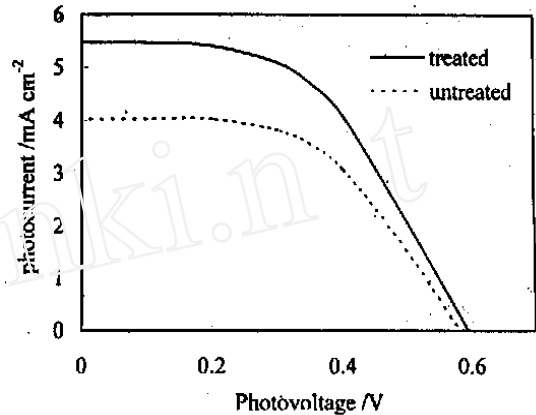


Fig. 2 Current-voltage curves of the Ru dye sensitized photoelectrochemical cells under 27 mW cm⁻² white light illumination

mA cm⁻² by the post-treatment. TiCl₄ post-treatment for the nanoporous film electrode is effective in increasing photocurrent as concluded from photocurrent action spectrum and I-V curve.

For the mechanism of this increase in photocurrent, it firstly occurred to us that in the post-treatment process, hydrolysis product of TiCl₄ nucleated on TiO₂ nanoparticles of the film electrode enlarges the interior surface area and the amount of dye absorbed, therefore, enhances the sensitized photocurrent. But contrary to this hypothesis, surface area and pore size distribution analysis of the electrodes with and without the post-treatment shows that TiCl₄ treatment decreases BET surface area from 127 m²·g⁻¹ to 119 m²·g⁻¹, and decreases average pore diameter from 13.3 nm to 12.5 nm. These results suggest that hydrolysis product of TiCl₄

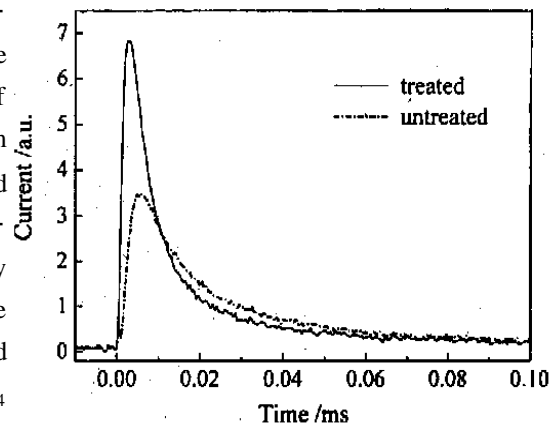


Fig. 3 Photocurrent transients of the Ru dye-sensitized electrodes

condenses at the interparticle neck, and electron percolation in the nanoporous film electrode is improved. For confirmation, time-resolved photocurrent was measured. It can be seen from Figure 3 that the decay of the current transient is faster and the amplitude is larger for the TiCl₄ treated electrode compared with the untreated one. This shows that TiCl₄ treatment facilitates electron transfer from one particle to another by broadening the interparticle neck.

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后处理对 TiO₂ 纳米晶膜电极光电性能的改善

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摘要: 利用 TiCl₄ 水溶液处理 TiO₂ 纳米晶膜电极, 可以提高光电流, 改善电极的光电转换性能. 对未经处理和处理后电极的比表面、孔分布, 以及瞬态光电流分析表明, 后处理改善了电荷在电极中的传输, 从而提高了光电流.

关键词: 光电化学电池; 敏化; TiO₂; 电极处理