Nanocrystalline TiO_2 Electrodes Prepared by Water-Medium Screen Printing Technique

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A water-medium screen printing technique was developed for making mesoporous TiO_2 electrodes by using two types of commercial nanocrystalline TiO_2 powders and three types of water-soluble cellulosic thickeners. Treatment of the electrodes with a $TiCl_4$ aqueous solution improved the overall conversion efficiency of the dye-sensitized solar cells based on these mesoporous TiO_2 electrodes.

Grätzel cells[1,2] based on nanocrystalline TiO_2 electrodes sensitized to visible light with dye molecules have been proved as one of the promising inexpensive solar cells. Upon absorption of light, the dye adsorbed on the surface injects an electron into the conduction band of the TiO_2 electrode. The oxidized dye molecule is then regenerated by a redox couple of I^-/I_3^- present in an electrolyte solution. In the system, the three-dimensional mesoporous network of the nanocrystalline TiO_2 through internecking is very important for the performance of the cell.[3]

In order to fabricate such nanocrystalline TiO_2 films for the dye-sensitized solar cell (DSC), a doctor-blade technique is generally used for coating colloidal TiO_2 paste on transparent conductive glasses.[1–3] As an extended technique of the doctor blade one, a terpineol-medium screen printing technique is an alternative approach aiming at large scale production of the TiO_2 electrodes.[4–6] A screen printing technique not only can meet the purpose of large-scale production, but also enable ones to control thickness of films and to reproduce easily high-quality films.

In this paper, we report a water-medium screen printing method using commercial TiO_2 powders and only a small amount of non-toxic cellulosic thickeners. The screen printing technique provided cracking-free films with different film thickness after sintering at 450 °C. The high conversion efficiency of the cell based on these electrodes has been obtained by treatment of the mesoporous electrode with a $TiCl_4$ aq solution.

Nanocrystalline TiO_2 electrodes were made using two types of TiO_2 powder; one was "F-6" (Showa Denko, Japan, 5% rutile and 95% anatase, BET surface area 94 m^2/g, particle size 16 nm), and the other was "P25" (Degussa, Germany, 30% rutile and 70% anatase, BET surface area 55 m^2/g, particle size 25 nm). The viscosity of the water-medium paste containing only polyethylene glycol (M_W 20000)[1–3] was insufficient for applying the paste to the screen printing. So the viscosity of TiO_2 dispersion (TiO_2 paste) was increased by addition of cellulosic thickeners which had different viscosities (Figure 1); the three types of the commercial cellulosic thickeners (60MP-50, M-400 or 65MP-4000, Matsumoto Yushi-Seiyaku, Japan) gave 100, 1000 or 10000 mPa·s in the 2.5 wt% aq solutions, respectively.

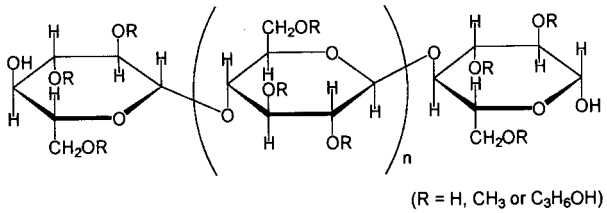

Figure 1. Structure of water-soluble cellulosic thickeners. The Rs of each thickner were randomly substituted in the different ratio for the three thickners.

The nanocrystalline TiO_2 powder (3 g, F6 or P25) and the 2.5 wt% cellulosic thickener aqueous solution (20 g) were added into Milli-Q water (100 g) for the printing paste. After dispersed by an ultrasonic bath, the colloidal suspension was intermittently treated with a titanium ultrasonic horn (Nihonseiki Kaisha Ltd., US-300T, 300 W) for 20 min by repetition of 20-s irradiation and 20-s rest. The suspension was introduced into a rotary evaporator and condensed at 30 °C (for F6) or 37 °C (for P25) and then transferred directly to a three roller grinding mill (Exakt Model-50, Otto Herrmann Ceramic, Germany) to obtain a final TiO_2 concentration of 21–30 wt%. The hydrophilic structures of the high-viscosity polymers may contribute to stabilized dispersion of the TiO_2 nanoparticles. By a screen printing technique (screen printing machine: AISI 304, plane weaving, 150 mesh, Mesh Industrial Co., Ltd., Japan), the TiO_2 film was prepared and then sintered at 450 °C for 30 min. The TiO_2 films were white and completely opaque. The opacity of these films would increase the conversion efficiency by the internal diffusion of the incident light.[3] The thickness and the area of each electrode were 10 μm and 0.2 cm^2, respectively. The still warm electrode (80 °C) was immersed in an ethanol solution of *cis*-bis(4,4'-dicarboxy-2,2'-bipyridine)bis(thiocyanato)ruthenium(II), N3 dye (0.5 mM) overnight at room temperature. This dye-sensitized electrode was employed as a working electrode and platinized conductive glass as a counter electrode for assembling a sandwich-type dye cell. The electrolyte was 0.1 M LiI, 0.3 M 1,2-dimethyl-3-propylimidazolium iodine, 0.05 M I_2 and 0.5 M *tert*-butylpyridine in methoxyacetonitrile. Photocurrent–voltage measurements were described elsewhere.[7]

Figure 2 shows the photocurrent–voltage characteristics of the cells based on the different electrodes of F-6 with the three different cellulosic thickeners. The F-6 electrode with a high viscosity cellulosic thickener of 65MP-4000 showed the best performance among the three: the short-circuit photocurrent (I_{sc}) was 9.54 mA/cm^2; the open-circuit voltage (V_{oc}) was 0.7 V; the fill factor (ff) was 66% and the overall conversion efficiency (η) was 4.4%.

The performance of the cells based on the different electrodes of P25 with the three different cellulosic thickeners is

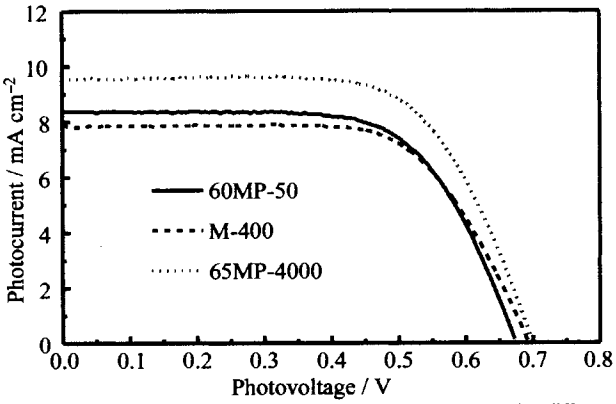

Figure 2. Current-voltage characteristics of cells based on the different electrodes of F-6 with three different cellulosic thickeners. The cells were irradiated by a solar simulator with 100 mW/cm^2.

Table 1 Performance characteristics of photovoltaic cells based on the different electrodes of P25 with three different cellulosic thickeners

Cellulosic thickener	I_{sc} / mA cm^{-2}	V_{oc} / mV	ff / %	η / %
60MP-50	9.16	700.8	69.5	4.5
M-400	9.29	704.0	68.1	4.5
65MP-4000	9.48	695.4	64.2	4.3

The cells were irradiated by a solar simulator with 100 mW/cm^2.

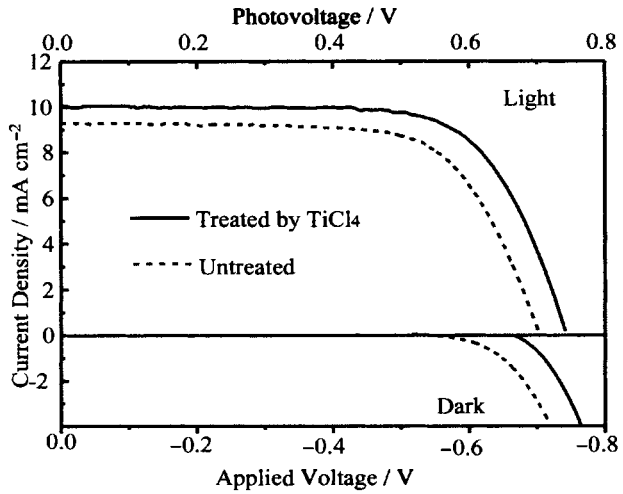

Figure 3. Current–voltage characteristics of cells based on P25 electrodes with M-400 cellulosic thickener before (dash line) and after (solid line) $TiCl_4$ treatment. The cells were irradiated by a solar simulator with 100 mW/cm^2.

shown in Table 1. The conversion efficiencies of the three different P25 electrodes were nearly the same, suggesting that the three different cellulosic thickeners all could produce good films. We also treated the three different electrodes by a $TiCl_4$ aq solution and found that the efficiency of the P25 electrode with M-400 cellulosic thickener was increased to 5.2%. The $TiCl_4$ treatment increased the efficiencies of the other two electrodes by 0.2%. Figure 3 shows that the treatment improved both photocurrent and photovoltage of the cells, while the dark current was decreased. According to the literature, the $TiCl_4$ treatment can increase the necking between the nanoparticles, facilitating the electrons transportation, and can also form a very thin film under the micropores which would suppress the recombination between electrons in the conduction band of TiO_2 and I_3^- in the electrolyte.[3,8]

In conclusion, the mesoporous TiO_2 electrodes with good performance as DSC were prepared for the first time[9] using the water-based TiO_2 paste obtained by powerful mixing of TiO_2 powder only with cellulosic thickener employing the ultrasonic horn and three roller grinding mill. The method is superior to the terpineol-medium screen printing one[4–6] from environmental point of view.

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