Photooxidized Polysilane Binders for Low Temperature Fabrication of Dye-sensitized Solar Cells

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(Received December 9, 2004; CL-041510)

Photooxidized polysilanes were evaluated as binders connecting nano-TiO_2 particles for low temperature baking process. Both of Jsc and Voc increased after TiO_2 nanoparticles (P25) were connected with photooxidized polysilanes. The amount of dyes adsorbed on TiO_2 layers, TiO_2 flat band potentials, electron diffusion co-efficient, electron life time were measured. The increases in the Jsc and Voc were associated with increases in electron diffusion coefficients and electron life time in TiO_2 layers.

Dye-sensitized solar cells (DSC) have been reported to show more than 10% photoenergy conversion efficiencies.[1] 450 °C is necessary to build up necking among TiO_2 nanoparticles.[2–5] Plastic solar cell is one of interesting research items. In order to fabricate nanoporous TiO_2 layers on plastic substrates, baking temperature has to be less than 150 °C. It has been reported that electron diffusion coefficient in TiO_2 layers decreases when TiO_2 layers were fabricated at low temperatures.[2] There are some reports on low temperature process to cause necking of TiO_2 particles.[6–12] Minoura and his co-workers have reported hydrothermal process for substrates on which TiO_2 paste was coated.[6] Miyasaka and his co-workers have reported electrophoretically deposited process for accumulation of TiO_2 nanoparticles.[7] They have also reported binder-free process to fabricate TiO_2 layers.[8] Lindstrom and his co-workers have reported compression process for TiO_2 layer fabrication at room temperature.[9–11] Kado and his co-workers have reported the use of low accelerated voltage electron beam showers.[12]

We have focused on binder polymers for TiO_2 porous layers. Commonly, polymer additives are added in the TiO_2 pastes.[13,14] They assist dispersion of TiO_2 nanoparticles in solutions. In 450 °C process, they burn out and make room for the diffusion of ionic species. On low temperature baking process, polymer binders play another role. It is required that polymers bind TiO_2 nanoparticles each other without disturbing ion diffusions. We report here new binders, photooxidized polysilanes.

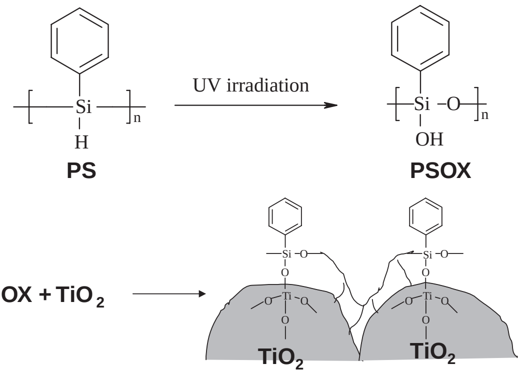

Figure 1. Reaction scheme.

Table 1. Abbreviation of cells and pastes and composition[1]

Cell	Paste	Binder PS	Binder EC[2]	P25	Ethanol	Water
Cell 1	Paste 1	4		100	100	100
Cell 2	Paste 2		4	100	100	100

1) Weight; 2) Ethylcellulose

Polysilane PS (Figure 1) was synthesized, according to a literature.[15] PS, P25 (Nippon Aerogel Co.) and ethyl alcohol were mixed in the dark (Table 1). Cell 1 was fabricated as follows. The paste was coated on SnO_2/F layered glasses (30 ohm/square, Nippon Sheet Glass Co. Ltd). The substrate was baked at 100 °C for 30 min and was exposed to deep UV light (365 nm, Funakoshi model UVGL-58) for 30 min to oxidize PS. The substrates were baked at 100 °C for 30 min to bind photooxidized polysilanes with TiO_2 nanoparticles. The substrates were immersed in *cis*-di(thiocyanato)-*N*,*N*′-bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) (Kojima Kagaku) solution in ethanol (0.1 wt %). Pt sputtered SnO_2/F layered glass substrates were used as counter electrodes. A plastic sheet (HIMILAN, Mitsui-Dupont Co. Ltd, 50 micron) was used as spacers. Electrolyte was injected in the cell at room temperature. Electrolyte composition was as follows: LiI: 500 mM, I_2: 40 mM, *t*-butylpyridine (*t*-BuPy): 580 mM in acetonitrile. The cell area was $1.0\,cm^2$. Cell 2 was fabricated by using ethyl cellulose (EC) as binders instead of PS. Photoelectrochemical measurements were performed using a solar simulator (YSS-50A, Yamashita Denso Co. Ltd., AM 1.5, $100\,mW/cm^2$). Electron diffusion coefficient (D_e) in TiO_2 layers was estimated with intensity modulated photocurrent spectroscopy (IMPS).[16–18] The samples were exposed to 680-nm wavelength light by use of a laser diode (Lab Lasers, Coherent Japan Inc.) A NF Corporation Frequency Response analyzer Model 5020 was used to control light modulation and to measure the modulation of photopotential. The amplitude of the sinusoidal modulation of the light intensity had an average value of 0.05 I_0. D_e was estimated by the following equation: $D_e = d^2 2\pi f_{min}$, where d and f_{min} stand for TiO_2 thickness and the frequency of minimum imaginary component in IMPS complex plane plot.[18] Electron life time (τ_n) was estimated by intensity-modulated photovoltage spectroscopy (IMVS),[17] as follows: $\tau_n = 1/\omega_{min}$, where, ω_{min} stands for the angular frequency of minimum imaginary component in IMVS complex plane. Experimental set up was the same as that for IMPS measurement. The details would be reported elsewhere. Flat band potentials of TiO_2 layers were discussed in the method described in the previous paper by use of absorption changes at 347 nm and 800 nm when

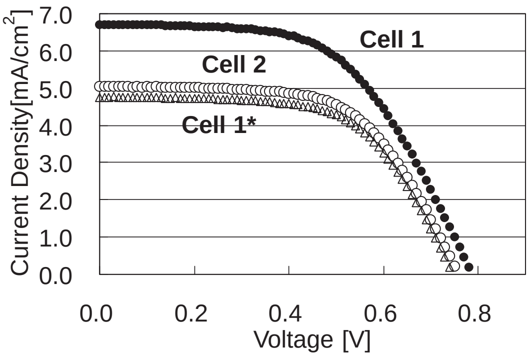

Figure 2. I–V curves for Cells 1, 1*, and 2 AM 1.5, 1 sun, 1 cm^2, 1*: before UV irradiation, Electrolyte: see experimental section.

Table 2. Differences between Cell 1 and Cell 2

	Unit	Cell 2	Cell 1
The amount of dye adsorbed on TiO_2 layers	$[mol/cm^2/\mu m]\ 10^{-7}$	0.08	0.09
FB-Potential[a]	V	−1.18	−1.05
Electron life time (τ_n)[b]	s	0.58	0.71
Electron diffusion coefficient (D)[2]	$[cm^2/s]\ 10^{-6}$	2.81	4.55

[a] Measured with Ag/Ag^+ in MeCN (1 M $LiClO_4$).
[b] 0.17 mW/cm^2, 680 nm.

potential was applied to TiO_2 electrodes.[19–23] Ag/Ag^+ reference electrode was used. I^-/I_3^- redox potential was measured by using a Ag/AgCl electrode as the reference electrode.

It has been reported that polysilanes are photooxidized to form polysiloxanes bearing Si–OH groups (Figure 1).[24] Our idea is summarized in Figure 1. Figure 2 shows I–V curves for DSCs. Jsc and Voc for Cell 1 increased from 5.0 to 6.7 mA/cm^2 and from 0.76 to 0.79 V, compared with those for Cell 2. The PV performance for unexposed cell (Cell 1*) was almost the same as that for Cell 2, showing that UV-exposure is necessary. The amount of dyes adsorbed on TiO_2 layers and flat band potentials for Cell 1 were almost the same as those for Cell 2. Electron diffusion constant in TiO_2 layers for Cell 1 was 4.55×10^{-6} cm^2/s at 0.17 mW/cm^2 (680 nm). This was larger than that of Cell 2 (2.81×10^{-6} cm^2/s). This trend did not change when the exposure strength was changed from 0.17 to 1.2 mW/cm^2. The larger electron diffusion coefficients for Cell 1 may be explained by improved binding strength among TiO_2 nanoparticles by the aid of photooxidized polysilanes. The strong binding properties were measured by the following experiment. Adhesive tapes were put on TiO_2 layers and the tapes were peeled off to see surface at which part exfoliation occurred. The exfoliation occurred within the TiO_2 layers for Cell 2. However, exfoliation of TiO_2 layers for Cell 1 did not occur within TiO_2 layers. This implies the strong binding effects of photooxidized polysilanes for TiO_2 particles. In addition, surface modification of TiO_2 with SiOH may improve the electron diffusion properties, because surface modifications of TiO_2 with carboxylic acids have been reported to be effective for burying surface electron traps and increasing electron diffusion constants.[23,25] Electron life time for Cell 1 was 0.71 s, which was larger than that of Cell C2 (0.58 s). Electron life time has been reported to decrease by the increase in back electron transfer reactions from TiO_2 to I_2 in electrolytes.[16–18] Off set potential of dark currents for Cell 1 was larger than that for Cell 2, suggesting that back electron transfers were relatively retarded.

In conclusion, photooxidized polysilane binders improved Jsc and Voc. This was explained by increases in electron diffusion coefficients and electron life time in TiO_2 layers, and retardations of back electron transfer reactions.

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Published on the web (Advance View) April 2, 2005; DOI 10.1246/cl.2005.650