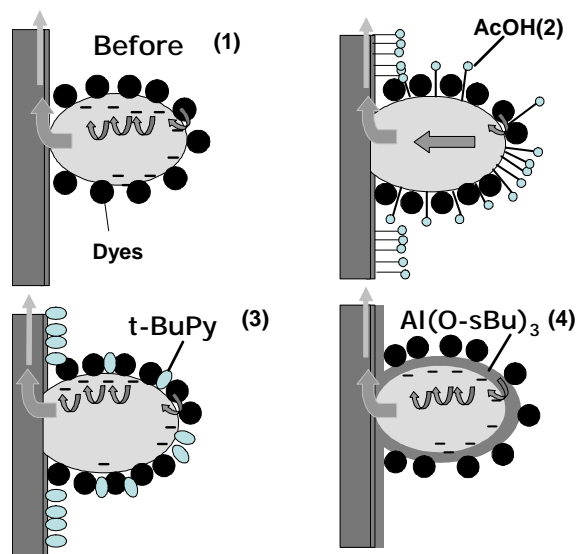


## Variations in electron diffusion coefficient caused by surface modification of nano-porous TiO<sub>2</sub> layers in DSC

T.Kato, T.Kado, S.Sakaguchi, D.Kosugi, U.Ogomi, W.Takashima, K.Kaneto, and S.Hayase  
 Kyushu Institute of Technology, 2-4, Wakamatsu-ku, Kitakyushu 808-0196 Japan.  
 Fax: 093-695-6005; Tel: 093-695-6054  
 Email: kato-h-takehito@edu.life.kyutech.ac.jp

**1. Introduction:** Dye sensitized solar cells have been attracted interests due to their high energy conversion efficiencies<sup>1,2</sup>. Surface modifications of nano-TiO<sub>2</sub> electrodes are one of the effective methods to increase the energy conversion efficiencies. Previous reported surface modifications contribute to retardations of back electron transfer from TiO<sub>2</sub> to I<sub>2</sub>, leading to increasing the Voc<sup>3-6</sup>. Recently, we have reported that surface modifications with carboxylic acids are effective to increase Jsc without decreasing Voc<sup>7</sup>. We report new results that electron diffusions in porous TiO<sub>2</sub> layers varied by how to modify the TiO<sub>2</sub> surfaces<sup>3</sup>.

**2. Experimental:** Electrolyte composition employed was as follows: I<sub>2</sub> 300mM, t-BuPy 580mM, LiI 500mM in Methylpropylimidazoliumiodide (MePrImI) containing 5% of H<sub>2</sub>O. Ti-Nanoxide D paste (Solaronix SA), SnO<sub>2</sub>/F layered glasses (30 ohm/square, Nippon Sheet Glass Co. Ltd), N3 (Solaronix SA), and thermally supported Pt were employed for the cell fabrication. The cell area was 1cm<sup>2</sup>. t-BuPy-treated TiO<sub>2</sub> electrodes were fabricated in the same procedure except that acetic acid is replaced with t-BuPy.



**Figure 1** Various surface modifications

Tris(*s*-Butoxy)aluminium was coated by dipping the heat treated TiO<sub>2</sub> electrodes in 0.5% solution in toluene. After the substrate was rinsed with toluene, the substrate was dipped in the ethanol solution of N3 dye (0.1%) at room temperature over night. Acetic acid surface treatment was carried out by dipping stained TiO<sub>2</sub> electrodes in 0.5% acetic acid solution in toluene (Figure 1).

**3. Results and discussion:** Results are summarized in Table 1. After TiO<sub>2</sub> was modified with acetic acid, De and Jsc increased. On the contrary, in case of t-BuPy-modification, De and Jsc decreased. Concerning Jsc and De, the influence for AcOH-modification is opposite to that for t-BuPy-modification. Increases in De after AcOH modifications are considered to be associated with the increases in Jsc. Voc and electron life times were constant or somehow decreased

after Acetic acid modification. In contrast, Voc and electron life times increased after t-BuPy modification. Electron life times are determined by recombination rates between electrons in TiO<sub>2</sub> and I<sub>2</sub> species in electrolytes. Increases in Voc after t-BuPy modification are explained by increases in electron life time, because back electron transfers (dark currents) are retarded by the adsorption of t-BuPy as is reported in the previous papers.

It has been reported that Jsc increases but Voc decreases seriously when acetic acid was added directly in the electrolytes because of positively shifted flat band potential of TiO<sub>2</sub> caused by adsorptions of H<sup>+</sup>. AcOH-modification was completely different from the acetic acid-addition to electrolytes because the flat band potential shifted negatively a little from -1.07 to -1.11 (Ag/Ag<sup>+</sup>) after AcOH-modification. AcOH groups form ester linkages (Ti-O-CO-CH<sub>3</sub>) with TiO<sub>2</sub> surface. The presence of H<sup>+</sup> becomes negligible for AcOH-modification. This prevents the serious Voc decrease. In case of BuOAl-modification, the increase in Voc is explained by the increase in electron life times. Electron diffusion coefficients decreased after the BuOAl - surface modification. These phenomena were similar to those for t-BuPy-modification.

**Table 1** Dye sensitized solar cell properties and electron diffusion behaviors

Modification	Dye bonding		Before	After
AcOH	on TiO <sub>2</sub>	Voc(V)	6.3	→ 6.2
		life time(s)	0.14	→ 0.12
		Jsc(mA/cm <sup>2</sup> )	6.9	↑ 8.8
		De(cm <sup>2</sup> /s) 10 <sup>-5</sup>	4	↑ 5.2
t-BuPy	on TiO <sub>2</sub>	Voc(V)	5.9	↑ 6.3
		life time(s)	0.08	↑ 0.1
		Jsc(mA/cm <sup>2</sup> )	6.8	↓ 4
		De(cm <sup>2</sup> /s) 10 <sup>-5</sup>	3.5	↓ 2.8
BuAlO	on Al <sub>2</sub> O <sub>3</sub>	Voc(V)	5.9	↑ 6.2
		life time(s)	0.08	↑ 0.16
		Jsc(mA/cm <sup>2</sup> )	5.9	→ 5.8
		De(cm <sup>2</sup> /s) 10 <sup>-5</sup>	3.5	↓ 2.9

The AcOH modifications increased De and the others decreased De. The De increases were supported by the results that the interfacial resistances in the porous TiO<sub>2</sub> layers decreased from 19.1 to 3.4 after AcOH-modification. Ti-O-H moieties on the surfaces are considered to be associated with electron traps. The number of traps would decrease or traps become shallow because Ti-OH moieties are converted to Ti-O-CO- by AcOH-modifications. However, in the other modifications, formations of such linkages are not expected.

**4 Conclusion:** We found that electron diffusions are controlled by selecting the way of modification. What we stress is the fact that carboxylic acid-modification exceptionally increases electron diffusion coefficient.

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