

## Significant Improvement of Photovoltaic Performance of Dye-sensitized Solar Cells by Using 4-Trimethylsilylpyridine as Organic Additive to Electrolyte Solution

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The applicability of 4-trimethylsilylpyridine (4TMSpy) was investigated as an organic additive to the electrolyte solution of dye-sensitized solar cells. The N3-sensitized solar cell with 4TMSpy showed higher light-to-electric energy conversion efficiencies than that with the ordinary organic additive of 4-*tert*-butylpyridine by a factor of ca. 1.1. This improvement of the photovoltaic performance was considered to be due to the bulkiness and peculiar electronic properties of the trimethylsilyl group.

Dye-sensitized solar cells (DSSCs) consist of a nanocrystalline TiO<sub>2</sub> film electrode with porosity which is covered with a monolayer of a sensitizing dye, a redox electrolyte solution, and a counter electrode, and have been intensively studied as practical solar cells of the next generation because of its high possibility for lowering energy costs.<sup>1</sup> One of the approaches to improve the light-to-electric energy conversion efficiencies of DSSCs is the development of the electrolyte solutions, and various kinds of organic additives, over 150 compounds, to the electrolyte solutions have been examined to bring out higher photovoltaic performance from DSSCs.<sup>2,3</sup>

Among the organic additives, 4-*tert*-butylpyridine (4TBpy) is the most important and frequently used one, since it improves largely the open-circuit photovoltage ( $V_{oc}$ ), fill factor, and thus the light-to-electric energy conversion efficiency of DSSCs.<sup>3</sup> The increase of  $V_{oc}$  is recognized to be due to the shifts of the TiO<sub>2</sub> conduction band edge toward negative potentials by the adsorption of 4TBpy onto the bare TiO<sub>2</sub> surface, and due to the suppression of back electron transfer from the TiO<sub>2</sub> electrode to the electron acceptors in the electrolyte by the blocking effect of 4TBpy for the electron acceptors to approach the TiO<sub>2</sub> electrode surface.<sup>3,4</sup>

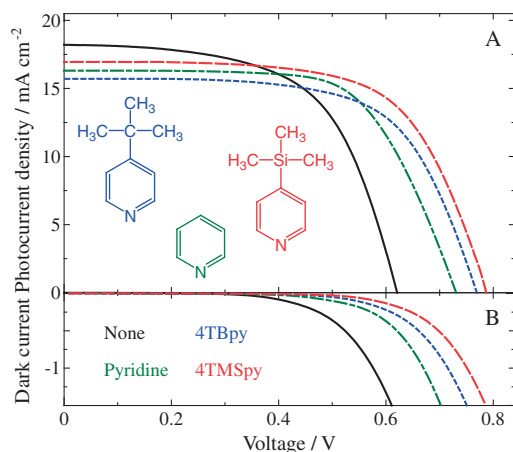
Alkylsilyl groups are bulkier substituents than the corresponding alkyl groups, possess high electron-donating properties, and give peculiar electronic effects to  $\pi$ -electron systems through  $\sigma$ - $\pi$  conjugations as the reflection of the characteristics of Si atom.<sup>5</sup> Therefore, by introducing an alkylsilyl substituent to pyridine other than an alkyl substituent such as the *tert*-butyl group and using the pyridine as the organic additive, further improvement is expected in the photovoltaic performance of DSSCs.

In this work, we thus examined the applicability of 4-trimethylsilylpyridine (4TMSpy) as the organic additive by comparing its improvement effect with those of pyridine and 4TBpy. The addition of 4TMSpy to the electrolyte solution actually improves the photovoltaic performance of the N3-

sensitized solar cell largely. The light-to-electric energy conversion efficiency over 8.5% of the cell with 4TMSpy was higher than that with the ordinary additive of 4TBpy by a factor of ca. 1.1.

4TMSpy was synthesized by lithiation of 4-bromopyridine hydrochloride followed by substitution with chlorotrimethylsilane. The nanocrystalline TiO<sub>2</sub> film electrodes for the cells were prepared on FTO-coated glass plates (25 × 50 mm<sup>2</sup>, 9–11  $\Omega$ sq<sup>-1</sup>; Asahi Glass) by spin-coating and screen-printing with subsequent sintering at 500 °C. The thickness of the porous TiO<sub>2</sub> film was estimated to be ca. 16.5  $\mu$ m by SEM observation. Adsorption of the *cis*-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylic acid)ruthenium(II) (N3 dye:<sup>1</sup> SOLARONIX) on the TiO<sub>2</sub> electrodes was performed by immersing the electrodes in a 3.0 × 10<sup>-4</sup> M ethanol solution of N3 dye at 70 °C for 15 h. Photovoltaic measurements were performed for the cells of an open sandwich type consisting of the N3-adsorbed TiO<sub>2</sub> electrode, a counter electrode, a polyethylene film spacer 30  $\mu$ m thick, and a redox electrolyte solution. A Pt-sputtered FTO glass plate was used as the counter electrode. The electrolyte solutions were composed of 0.5 M LiI, 0.05 M I<sub>2</sub>, and the 0.5 M organic additive of pyridine, 4TBpy, or 4TMSpy in acetonitrile. The photovoltaic performances of the cells were assessed from the  $I$ - $V$  properties of the cells measured with a solar simulator of OTENTO-SUN III (Bunkoh-Keiki) and a source meter of R6240A (Advantest). The aperture area of the cells was maintained at 1.20 × 1.20 cm<sup>2</sup> using a shading mask and the  $I$ - $V$  properties were measured under irradiation of AM-1.5G global-one sun condition (100 mW cm<sup>-2</sup>) at 25 ± 2 °C. The amount of the dye adsorbed on the TiO<sub>2</sub> electrode was confirmed to be the same among the cells after the measurements by visible absorption.

Figure 1A shows the results of  $I$ - $V$  measurements of the N3-sensitized solar cells with the electrolyte solutions containing pyridine, 4TBpy, or 4TMSpy as the organic additive, and with the solution containing no additive under the simulated sunlight irradiation. Photovoltaic parameters of the cells obtained by the  $I$ - $V$  measurements are listed in Table 1. Open-circuit photovoltages ( $V_{oc}$ ) were observed to be higher for the cells with the electrolyte solutions containing pyridine additives than for the cell without the additive. Although short-circuit photocurrent densities ( $J_{sc}$ ) of the cells with pyridine additives were less than that of the cell without the additive, the fill factors ( $FF$ ) were improved by the additives, resulting in higher light-to-electric energy conversion efficiencies ( $\eta$ ). Among the cells with pyridine additives, the enhancement of  $V_{oc}$  was most significant in the cell with 4TMSpy and the cell exhibited higher  $J_{sc}$  than



**Figure 1.** (A)  $I$ - $V$  properties of the N3-sensitized solar cells with the electrolyte solutions containing pyridine, 4TBpy, or 4TMSpy as the organic additive, and with the solution containing no additive under simulated sunlight irradiation of AM-1.5G global-one sun condition ( $100 \text{ mW cm}^{-2}$ ). (B) Dark current-voltage curves of the cells. The results were almost the same when using the electrolyte solutions kept at room temperature for 3 days.

**Table 1.** Photovoltaic parameters of the N3-sensitized solar cells with the electrolyte solution containing no additive, and with the solutions containing pyridine, 4TBpy, or 4TMSpy as the organic additive under simulated sunlight irradiation (AM-1.5G,  $100 \text{ mW cm}^{-2}$ )<sup>a</sup>

Additive	$J_{sc}/\text{mA cm}^{-2}$	$V_{oc}/\text{V}$	$FF$	$\eta/\%$
None	$18.21 \pm 0.02$	$0.622 \pm 0.003$	$0.591 \pm 0.002$	$6.69 \pm 0.03$
Pyridine	$16.30 \pm 0.02$	$0.732 \pm 0.002$	$0.653 \pm 0.002$	$7.79 \pm 0.02$
4TBpy	$15.72 \pm 0.02$	$0.770 \pm 0.002$	$0.659 \pm 0.003$	$7.98 \pm 0.03$
4TMSpy	$16.93 \pm 0.02$	$0.788 \pm 0.003$	$0.652 \pm 0.003$	$8.70 \pm 0.04$

<sup>a</sup>The parameters are the averaged values from the results of 3 experiments.

the cell with the ordinary additive of 4TBpy showing higher photocurrent density in the whole measured photovoltage region. The  $\eta$  of the cell with 4TMSpy was evaluated to be 8.70% under the present test conditions, which is higher than those of the cells with no additive, pyridine, and 4TBpy by factors of 1.30, 1.12, and 1.09, respectively.

Figure 1B shows the dark current-voltage curves of the cells. The onsets of the curves were observed to shift positively by the pyridine additives, and the shifts increased in the order from pyridine, 4TBpy, to 4TMSpy. This result indicates that 4TMSpy shifts the  $\text{TiO}_2$  conduction band negatively and diminishes the back electron transfer from the  $\text{TiO}_2$  electrode to  $\text{I}_3^-$  ions in the electrolyte solution more effectively than 4TBpy.

The above results exhibit clearly that the introduction of a trimethylsilyl (TMS) group to the organic additive of pyridine is more effective in the improvement of the conversion efficiency than that of a conventional *tert*-butyl group. The pyridine additives are thought to adsorb on the surface of the  $\text{TiO}_2$  electrode by the N atoms in the cells,<sup>2-4</sup> and the efficient improvement of the conversion efficiency by 4TMSpy is thought to be brought by the following reasons: The first is the bulkiness

of the TMS group which prevents the recombination reaction efficiently between the injected electrons into the  $\text{TiO}_2$  electrode and the electron acceptor of triiodide ions ( $\text{I}_3^-$ ) in the electrolyte solution,<sup>3</sup> the second is high electron donation of the TMS group which produces a large negative shift of the conduction band edge of the  $\text{TiO}_2$ ,<sup>3,4</sup> and the third is the rise of the HOMO level of the additive by the  $\sigma$ - $\pi$  conjugation between Si-C(methyl)  $\sigma$  orbitals of the TMS group and a  $\pi$  orbital of the pyridine ring,<sup>5</sup> which promotes the decrease of  $\text{I}_3^-$  concentration at the vicinity of the  $\text{TiO}_2$  surface through the formation of charge-transfer complexes between 4TMSpy and  $\text{I}_3^-$ .<sup>2,6</sup>

In this study, we examined for the first time the applicability of a pyridine derivative containing an alkylsilyl group as the organic additive to the electrolyte solution for DSSCs, and successfully revealed the effectiveness of 4TMSpy for improving the photovoltaic performance of the N3-sensitized solar cell. Such an improvement by 4TMSpy would also be possible for DSSCs using 4TBpy as the organic additive to the electrolytes. The results, along with those in our previous works,<sup>7</sup> show high potentials of organosilicon compounds as constituent materials for DSSCs.

This work was partly supported by the "Element Innovation" Project by Ministry of Education, Culture, Sports, Science and Technology in Japan.

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