Preliminary Study for Development of Dye-Sensitized Solar Cells by using Functionalized Carbon Clusters

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A dye-sensitized solar cell known as a new kind of photoelectrochemical solar cells has recently attracted considerable attention (Fig.).[1] The cell generally consists of a structured nanoporous TiO_2 electrode sensitized by a Ruthenium-complex dye with high absorption in the visible part of the solar spectrum, an iodine-iodide electrolyte, and a Pt counter electrode. Although a large number of studies about improvement of the dye and electrolyte parts have been reported, development of organic counter electrode materials has been hardly investigated, unexpectedly.

Herein, we examined dye-sensitized solar cells with several functionalized carbon clusters, such as fullerene (C_{60}) and single wall carbon nano tube (CNT) derivatives, as the new counter electrode material. Incidentally, C_{60} and CNT are hitherto known to have relatively large photoconductivity and electroconductivity, respectively.

In the present study, several types of functionalized C_{60}s **1-3,** which were readily soluble in common organic solvents including toluene and $CHCl_3$, were synthesized via Bingel, Prato, and Diels-Alder reactions, respectively (Scheme), since C_{60} itself hardly soluble in organic solvents: the functionalization is indispensable to increase the solubility and processability. At first, we were carried out the I/V-measurement of the cells with the counter electrodes applied with the C_{60} derivatives instead of Pt. In Table 1, the optimum preparation conditions of the counter electrodes were investigated under different concentrate and solvent conditions, in which [60]methanofullerene **1a** was used as the representative C_{60} derivative (Table 1). As a result, it was found that the efficiency increased with increase of the concentration and that the case with 10^{-2} M of $CHCl_3$ solution of the derivative **1a** was the most suitable conditions.

Table 2 shows the results of the I/V-measurement of the cells with various C_{60} derivatives. As a result, the derivative **3** was unfortunately found to indicate the similar efficiency to that of unmodified ITO counter electrode itself, probably due to existence of no polar group, which should enhance the adhesion to ITO. In deed, the efficiency of the other derivatives bearing ester, carboxyl, amino, and pyridyl groups indicated higher than that of the derivative **3**. In addition, the result that the derivative **1a** indicated the highest efficiency among these derivatives **1-3** can be considered as follows. Since the derivative **1a** that is known to electronically convert to unsubstituted C_{60} via so-called retro Bingel reaction,[2] C_{60}, which should have higher photoconductivity than those of the other functionalized derivatives, might be regenerated in this case, at least partially.

In conclusion, we can demonstrate that the possibility of the utilization of functionalized C_{60} derivatives as the counter electrode, although the solar to electric energy conversion efficiency is relatively low at this stage, even in the case of the derivative **1a**. Besides the further investigation, the similar examination by using functionalized CNT are now in progress, and will be reported at the present presentation.

[1] O'Reagan and Grätzel, *Nature*, **1991**, 353, 737.
[2] Kessinger et al. *J. Am. Chem. Soc.*, **1998,** *120*, 85458.

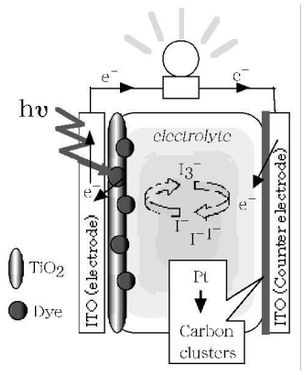
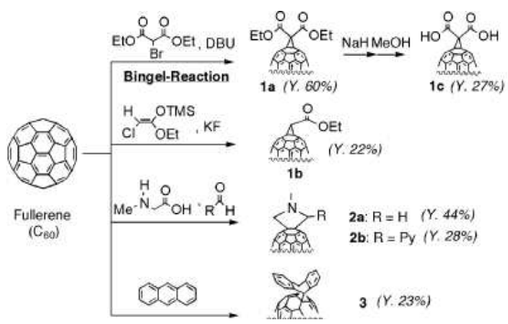


Fig. Dye-sensitized solar cell



Scheme

Table 1. The results of the electric energy conversion efficiency of 1a

Solv. (Conc.)	Isc (mA/cm^2)	Voc (V)	Pmax ($\mu W/cm^2$)	F.F. (%)
Toluene				
(10^{-4} M)	0.80	0.31	35.6	14.4
(10^{-3} M)	1.05	0.39	76.6	18.9
(10^{-2} M)	1.67	0.40	121.1	18.3
Chloroform				
(10^{-4} M)	0.82	0.31	35.5	14.0
(10^{-2} M)	2.13	0.43	166.8	18.6

[Conditions] Light source : Xe lamp; Cell size : 1.0 x 1.0 [cm^2]; Photosensitizer : N_3 Dye; Electrolyte: ethylene carbonate (2.4 mL); MeCN (0.6 mL); I_2 (7 mg); KI (83 mg); TPAI (16 mg); tBuPy (135 mg).

Table 2. The results of the electric energy conversion efficiency of 1-3

C_{60} derivative	Jsc (mA/cm^2)	Voc (V)	Pmax ($\mu W/cm^2$)	F.F. (%)
1a	2.81	0.48	309.2	23.0
1b	0.49	0.18	11.2	12.8
1c	0.90	0.33	40.5	13.6
2a	0.58	0.31	28.5	15.7
2b	1.08	0.38	82.3	20.4
3	0.44	0.24	12.6	11.8
-	0.48	0.33	17.3	10.9

[Conditions] Light source : Xe lamp; Cell size : 1.0 x 1.0 [cm^2]; Photosensitizer : N_3 Dye; Electrolyte: ethylene carbonate (2.4 mL); MeCN (0.6 mL); I_2 (7 mg); KI (83 mg); TPAI (16 mg); tBuPy (135 mg).