Effect of Hydroquinone Dderivatives in Electrolytes on Dye-Sensitized Solar Cell Performance

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Abstract

New kinds of hydroquinone derivatives were synthesized and along with a azo dye applied as additives in the iodide/iodine redox electrolyte for dye-sensitized solar cells and their effect on the short-circuit photocurrent of dye sensitized solar cells was investigated. Addition of 0.05 M a hydroquinone derivative in the electrolyte comprising 0.5 M 1-methyl-3-propylimidazolium iodide (MPII) and 0.05 M I$_2$ in a mixture of acetonitrile and valeronitrile (volume ratio, 85:15) enhanced significantly photocurrent density from 11.1 to 12.8 mA/cm^2, and voltage increased from 0.66 to 0.68 V. As a result, overall conversion efficiency increased from 4.4% to 4.8%, corresponding to increment of 10.9%.

1. Introduction

Dye-sensitized solar cells (DSSCs) are photoelectrochemical solar cells that contain an electrolyte, dyed TiO$_2$ electrode, a platinized counter electrode which have recently gained considerable academic and industrial interest because of high energy conversion efficiency, high-stability semiconductor and sensitizer, simple assembly technology and low manufacturing cost [1-3]. The adsorbed dye molecules become excited under the irradiation of visible light and inject electrons into the conduction band of the semiconductor. Then, the oxidized dye molecules are reduced by I⁻ ions. Electrolyte plays an important role in regeneration of the oxidized dye by reduction and oxidation reaction. The triiodide/iodide (I$_3^-$/I⁻) redox couple is by far the most frequently used in DSCs, although several alternatives have been developed, such as cobalt complexes [4, 5] and pseudohalogens [6, 7]. Apart from the redox role of electrolyte, cations and additives in electrolyte have been known to influence photovoltaic performance. Significant improvement of the solar cell performance can be obtained by the addition of certain compounds to the electrolyte. The most frequently used additive is 4-tert-butylpyridine (TBP) [8], guanidinium thiocyanate (GSCN) [9-11] and thiourea, which

has recently been used [12]. N-containing organic molecules such as TBP, pyrazole, imidazole, 1, 2, 4-triazole, pyridine, pyrimidine and pyrazine have been recently used as an additive in DSSC to improve the performance of DSSC [13, 14]. Kusama et al. [15] investigated the influence of some nitrogen containing compounds on the performance of DSSCs using a density functional theory method. They reported that a more efficient charge transfer between the nitrogen containing compounds and iodine molecules would occur when the V_{oc} value is increased. Carbon nanotubes (CNTs) have also been utilized as conductivity improving additives in the DSSC photoelectrodes in many different forms [16-18]. Several studies on the back reaction of injected electron were reported recently [19-21] and some methods to suppress recombination reaction have been suggested [22-25]. The additives could decrease the rate constants of triiodine reduction to suppress the dark current at the TiO_2/electrolyte interfaces, increase the electron, lifetime and decrease the conduction band of TiO_2, resulting in an increase of V_{oc} at a fixed photoinduced charge density [26].

The light-scattering layer has been shown to act as a photon-trapping system (Fig. 1). Cell efficiencies measured were 5% in dye sensitized solar cells using only the light-scattering TiO_2 layer. Losses of approximately 4% on the glass substrate due to reflection of incident light in DSC can be partially circumvented by adding an anti-reflecting film, which acts simultaneously as a 380 nm UV cut-off filter [27, 28]. Here initial we investigated the effect of thickness of TiO_2, light scattering and $TiCl_4$ on dye solar cell performance. Then we report novel hydroquinone derivatives (2-(3, 4-dihydroxy phenyl) benzothiazole (DHB) and Z)-4-(naphtalen-1-ylimino methyl) benzene-1, 2-diol, (NYB)) along with 1-((4-(benzo[d]thiazol-2-yl) phenyl)diazenyl)naphthalen-

2-ol (azo dye) (scheme 1) as additive in electrolyte. We tested these compounds and evaluated their effects on DSSC. In this work, hydroquinone derivatives, whose heterocyclic ring consisted of sulfur, nitrogen, and carbon, were examined as additives in an acetonitrile solution of an I^-/I_3^- redox electrolyte. The solar cell performance with hydroquinone was compared to that without an additive.
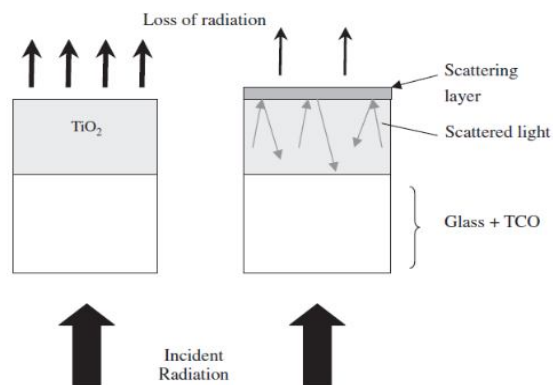
Fig. 1. Effect of light scattering layer in dye solar cell performance.

Scheme 1. The structure of used additives: (A) DHB,
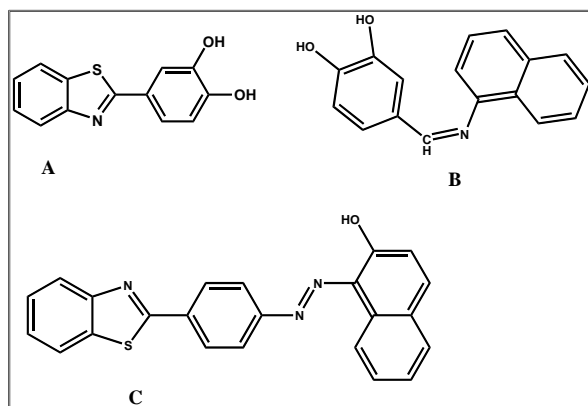
(B) NYB and (C) azo dye

2. Experimental procedure

2.1. Apparatus and chemicals

The dye solar cells performance was evaluated in AM 1.5 simulated lights (LuzchemSolar) using a potentiostat/galvanostat (IVIUM, Compactstat). X-ray diffraction measurement was carried out by using a Philips X'Pert Pro (Netherlands) in the 2θ angle range from 10 to 80°. FT-IR spectra were recorded as ATR on a Bruker, Eqinox55 spectrometer Perkin-Elmer 781 spectrophotometer. ^{1}H NMR spectra were recorded at 400 MHz, on a Bruker DXR-400 spectrometer using $CDCl_3$ as solvent and tetramethylsilane as internal standard. Digital micrometer Mitutoyo (japan) was used for measurement of thickness of Tio_2. Conductive glass (FTO glass, sheet resistance 8Ω sq^{-1} was purchased from South Korea) was used as a substrate for precipitating TiO_2 porous film. PEG (6000), anhydrous ethanol, iodine (I_2), MPII, hexachloroplatinic acid (H_2PtCl_6) and sensitizing dye were purchased from Merck and used without further purification. TiO_2 paste prepared based on S. Ito [28]. The TiO_2 nanoparticles were characterized by Scanning Electron Microscopy (SEM, Hitachi S-4160). $TiCl_4$ (Fluka) was diluted with water to 2 M at 0 °C to make a stock solution, which was kept in a freezer and freshly diluted to 40 mM with water for each $TiCl_4$ treatment of the FTO coated glass plates.

2.1. Fabrication of DSSC

To prepare the DSC working electrodes, the FTO glass used as current collector was first cleaned in a detergent solution using an ultrasonic bath for 15 min, and then rinsed with water and ethanol. The FTO glass plates were immersed into a 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min and washed with water and ethanol. The paste of TiO_2 nanoparticles with average diameter of 20-30 nm was deposited on the FTO glass by doctor

blade technique and then annealed at 130 °C for 30 min in electrical oven. Fig. 2 shows SEM (A) and XRD of TiO_2 nanoparticles (B). A second TiO_2 scattering layer (400 nm) was placed by doctor blade and the assembly dried 100 °C for 10 min on a hot plate, followed by sintering the film at 325 °C for 15 min, 375 °C for 5 min, 450 °C for 15 min, and 500 °C for 15 min in an electrical kiln under air atmosphere. The thickness of the TiO_2 films was controlled using transparent adhesive tape (Scotch, nominal thickness 40 μm) as a spacer. The thicknesses of first and second TiO_2 layers were estimated to be 5 and 10 μm, respectively. The TiO_2 "double-layer" film thus produced is once again treated with 40 mM $TiCl_4$ solution, as described previously, then rinsed with water and ethanol and sintered at 500 °C for 30 min.
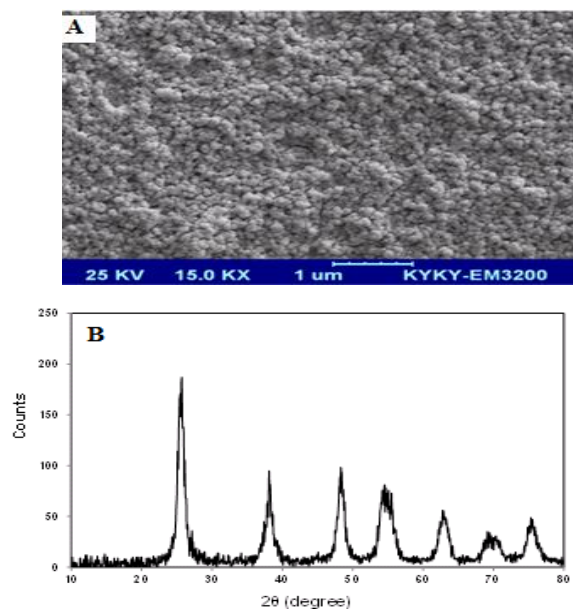
Fig. 2. SEM (A) and XRD of TiO_2 nanoparticles (B).

After cooling to 80 °C, the TiO_2 electrode was immersed into a 0.5 mM N-719 dye solution in a mixture of acetonitrile and tertbutyl alcohol (volume ratio, 1:1) and kept at room temperature

for 20–24 h to assure complete sensitizer uptake. The Pt-coated counter electrodes were prepared by spreading a drop of H_2PtCl_6 (2 mg Pt in 1 ml ethanol) on the FTO glass and heating it at 400 °C for 20 min under air ambient. The dye-covered TiO_2 electrode and Pt-counter electrode were assembled into a sandwich type cell. The size of the TiO_2 electrodes used was 0.25 cm^2 (i.e., 5 mm×5 mm).

2.2. Electrolyte

Electrolyte was composed of 0.7 M 1-methyl-3-propylimidazolium iodide (MPII), 0.05 M each additive and 0.05 M I_2 in a mixture of acetonitrile and valeronitrile (volume ratio, 85:15).

2.3. Additives

Synthesis of DHB:

A mixture of 2-aminothiophenol (1.2 mmol), 3,4-dihydroxybenzalaldehyde (1mmol) and $Al(HSO_4)_3$ (0.02 g) was heated at 80 °C for 10 minutes. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled and dissolved in ed in acetone followed by addition of water. The product was re-crystallized in hot ethanol. FT-IR (ATR, neat), ν=3478 (OH), 1470,1364,1264, 12000 1071,1055,765,721 cm^{-1}. ^{1}HNMR (400 MHz, Acetone-d6): δ: 6.98 (d, J=8.4 Hz, 1H), 7.38 (t, J=7.2 Hz, 1H), 7.51 (m, 2H), 7.67 (d, J=2 Hz, 1H), 7.96 (d, J=8.0 Hz, 1H), 8.02 (d, J=8.0 Hz, 1H), 8.50 (s, 1H), 8.69 (s, 1H). FT-IR frequency and NMR data is in Fig. 3.

Synthesis of azo dye:

In a mortar, a mixture of 0.14 g (2 mmol) of $NaNO_2$ and 0.2 g of $BF_3.SiO_2$ was grinded. Then, 2 mmol of aromatic amine was added and grinded.

Then, 1 mL of water was gradually added to this mixture and ground for 2 min for evolution of all obtained gas. After formation of diazonium salt, a solution containing 2 mmol sodium naphthoxide was added and sufficiently grinded. The obtained azo dye was dissolved in ethanol and filtered to isolation of catalyst. The ethanol solution of azo dye was concentrated. By addition of water to ethanol solution, the azo dye was separated in pure solid form.
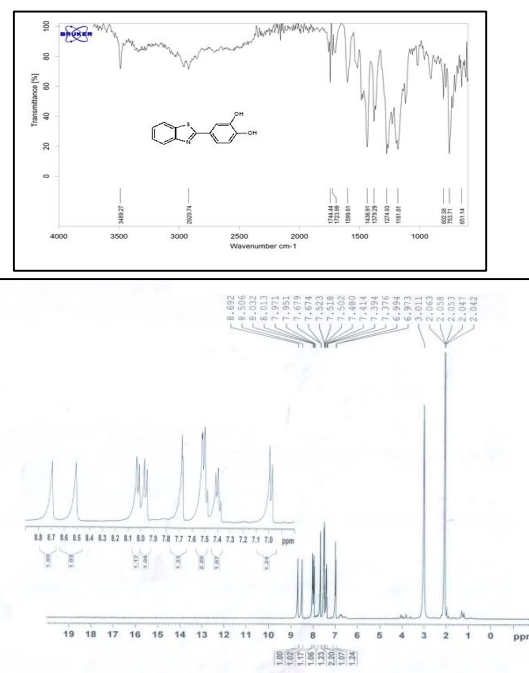

Fig. 3. FT-IR frequency and NMR data of DHB

FT-IR (Neat)= ῡ (cm^{-1}): 3200-3600 (OH), 1602, 1554, 1480, 1452, 1434, 1313, 1253, 1227, 1207, 1149, 965, 835, 756. ^{1}H NMR (400 MHz, CDCl3), δ (ppm) = 16.4 (s, 1H, OH), 8.53 (d, J=7.2, 1H), 8.19 (d, J=8 Hz, 2H), 8.12 (d, J=8.4 Hz, 1H), 8.07 (d, J=7.6 Hz, 1H), 7.91 (d, J=7.2 Hz, 1H), 7.77 (d, J=8 Hz, 2H), 7.71 (d, J=9.6 Hz, 1H), 7.5-7.6 (m, 3H), 7.35-7.45 (m, 2H), 6.8 (d, J=9.2 Hz, 1H). FT-IR frequency and NMR data is in Fig. 4.
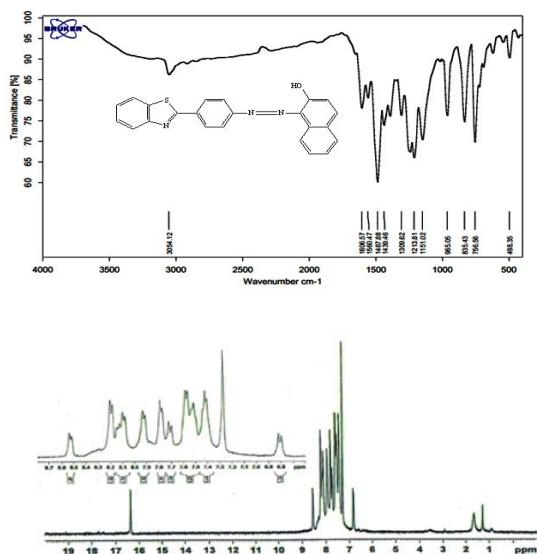
Fig. 4. FT-IR frequency and NMR data of AZO

Synthesis of NYB:

A mixture of 3, 4-dihydroxy benzaldehyde (1 mmol), α-naphthylamine (1 mmol), ethanol (5 mL) and 50% nano-TiCl$_4$.SiO$_2$ (0.1 g) was refluxed for appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and filtered to isolation of product and catalyst. The catalyst was separated from product by boiling ethanol. The crude solid product was purified by recrystallization procedure in ethanol:water.

FT-IR: ν (KBr) = 2500-3300 (OH), 1615 (C=N), 1509, 1460, 1335, 1263, 1201,827, 701 cm^{-1}. 1H-NMR (500 MHz, DMSO-d6): 7-8 (m, 9H, Ar-C-H), 8.4 (S, 1H, N= C-H), 6.8 (S, 1H, Ar-C-H), 3-4 (brs, 2H, OH) ppm. FT-IR frequency and NMR data is in Fig. 5.
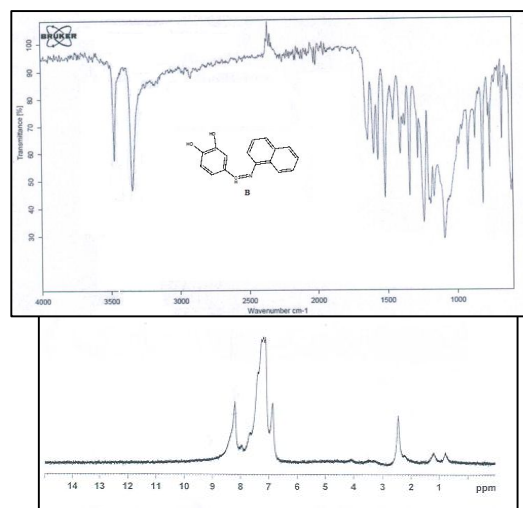

Fig. 5. FT-IR frequency and NMR data of NYB

3. Results and Discussion

3.1. Effect of TiO$_2$ thicknesses on photovoltaic performance

Variation in thickness of the nanocrystalline-TiO$_2$ layer is a crucial factor in optimizing photovoltaic performances of DSC. Precise measurements of the exact layer thickness are difficult to perform but it is very important. The obtained results are in Table 1. As this table shows the optimum film thickness to produce highly efficient DSC is 5 μm. With increasing of thickness rate of recombination increased and pathway for reaching of electron increased.

Table 1. J–V characterization of the dye-sensitized solar cells with different thicknesses

Number	V_{oc}	J_{sc}	FF	η (%)	Thickness
1	0.69	4.4	0.57	1.7	5
2	0.68	4.2	0.56	1.6	14
3	0.66	4	0.55	1.5	20

3.2. TiCl₄ treatment and effect of the light-scattering TiO₂ layer

Table 2 exhibits the photovoltaic improvements engendered by using the doub layer TiO₂ and TiCl₄ treatments followi screen printing of the mesoscopic (po film. As this table shows with a l layer and TiCl₄ treatment parameters measured wer V_{oc}=681 mV, FF=0.5 photovoltaic param light-scattering treatment h roughne parti

DHB. The adsorption of DHB on the surface of TiO_2 reduces the number of recombination centers and limits the charge losses, leading to higher R_{ct} values for cell DHB.
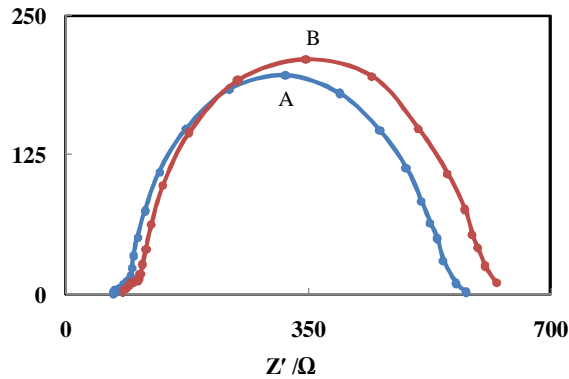
Fig. 7. Electrochemical impedance spectra of cell with DHB (A) and cell without DHB (B) measured in the dark.

The cell with azo dye showed the lowest J and V (Fig. 6, curve D). The decreased solar cell performance is due to the adsorption of AZO dye at the dye TiO_2 and dye free TiO_2 surfaces resulting in the suppression of light absorption from the N-719 TiO_2 surfaces.

4. Conclusions

New kinds of hydroquinone derivatives along with an azo dye were synthesized and their behavior as additives in the electrolyte of DSSCs was investigated. Cell with DHB showed more efficiency. Unlike the reported TBP and pyridine derivatives that leading to an increase in voltage and decrease or little change in photocurrent, addition of DHB in electrolyte was found to increase voltage and photocurrent of dye-sensitized solar cell. We suggest here that DHB is a useful additive since it shows dual effects of positive band edge shift, associated with high photocurrent, and suppression of recombination, associated with prevention of a large decrease in voltage. Also we can improve dye-

sensitized solar cell performance by changing in the structure DHB and introduction of more functional group. Table 3 shows the photovoltaic performances of DSSCs with different additives.

Table 3. photovoltaic performances of DSSCs with different additives

Additive	V_{oc}	J_{sc}	FF	η (%)	Ref
tributyl phosphate	0.82	6.38	0.58	3.03	32
[BuPyIm]Br	0.64	1.36	0.66	5.67	33
TiO_2 hollow pheres	0.73	15.48	0.64	7.25	34
MWCNT	0.47	3.82	0.47	0.85	35
DHB	0.68	12.8	0.56	4.8	This

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