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A new polymeric photosensitizer for dye-sensitized solar cell with porous TiO_2 from forest carbon resources

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Abstract

A series of new lignin derivatives (lignophenols) containing phenol, *p*-cresol, catechol, resorcinol and pyrogallol synthesized from Hinoki (*Chamaecyparis obtusa*) and Douglas fir (*Pseudotsuga menziessi*) as softwood and beech (*Fagas crenata*) as hardwood was investigated as sensitizers for a dye-sensitized solar cell (DSSCs) of porous TiO_2 under the irradiation of 150 W Xe lamp. For example, LPs–DSSCs of hinoki-ligno-*p*-cresol, directly derived from hinoki native lignin showed $V_{oc} = 0.34$ V, $I_{sc} = 0.65$ mA cm^{-2}, ff = 0.49 and $\eta = 0.11\%$ under AM 1.5 (100 W m^{-2}). The strong interactions between lignophenols and TiO_2 surface were estimated by UV-Vis and FT-IR spectra. The importance of interactions between phenolic hydroxyl groups and TiO_2 surface was discussed by FT-IR, solid UV-Vis spectra and ^{1}H NMR. The effects of chemical modifications were discussed using acethylated lignophenols (LPsOAc) or re-cycled lignophenols, treated by 0.5 M NaOH at 413 K (LPs–SF413) or 443 K (LPs–SF443). These results implied interactions between LPs and TiO_2 were consisted of anchors and stacking on TiO_2.

Keywords: Dye-sensitized solar cells; Lignin; Lignophenol; Forest carbon resources; Renewable resources

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention since the breakthrough on photochemical cells with porous nano-crystalline TiO_2 with the ruthenium complexes as photosensitizers by Grätzel and co-workers [1–3]. Because these cells showed high photoelectricity conversion efficiency with low cost, low production energy and low environmental pollution compared to silicon type, these cells have been expected to be next-generation solar cells [1–3]. Developments of dyes have highly contributed to achievement of high cell performance. Recently, several synthetic organic photosensitizers with high efficiency have been reported [4–7]. Moreover, a polymeric photosensitizer for solid-state cell also has been reported [8].

Recently biomass has also been watched with keen interest with apprehension for consumption of fossil resources. If natural organic materials could be utilized as photosensitizers like these synthetic ones for DSSCs, it was very interesting in the view of effective utilization of biomass. Although natural extractives, such as anthocyanins or poly-phenols, actually worked as photosensitizers for DSSCs [9], it is difficult to be collected and purified in large quantities because of small amounts in biomass.

Lignin is one of poly-phenols abundantly contained in biomass for 25–40%. Lignin is contained for 3×10^{11} t in the biosphere and is estimated to be re-produced annually by photosynthesis in the rate of 2×10^{10} t [10]. Although lignin is abundant in biomass, lignin has never been utilized sufficiently for industry because of difficulty in extraction from wood without destroying characteristics. For example, in pulping process, sensitive “native lignin”, which means natural lignin in wood, is changed into highly condensed “industrial lignins” by treatment with various chemicals and heat. It is difficult to utilize these industrial lignins as industrial materials because of complicated structures, random polymerizations and difficulty in dissolving into solvents.

Lignophenols (LPs), polymers with light-beige appearances, have been synthesized directly from native lignin by “phase-separation system”. This system is consisted of grafting phenols into native lignin by surface reaction by concentrated acid and phenols under 1 atm at room temperature (Scheme 1) [11–13]. LPs are more stable than native lignin because the benzyl positions, which are active sites, have been blocked by phenols. Moreover, LPs can be chemically designed because LPs have more simple structures than industrial lignins [12,13]. Therefore, these materials are

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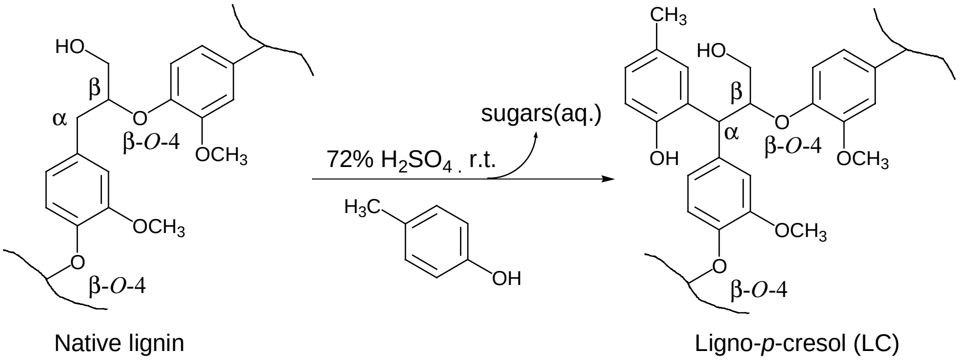


Scheme 1. A schematic model of "phase-separation system", which means a synthesis of LPs from native lignin. In this scheme only C_β-aryl ether linkages (β-O-4 structures) of native lignin and LPs which are the most frequent interunit linkages of lignin are showed in a case of a synthesis of ligno-*p*-cresol.

useful for industrial use instead of fossil carbon resources, petroleum and coal. LPs have been actually developed as recyclable materials, for example, composites with pulp, additives for plastics, etc. [12,13].

In general, the energy conversion of forest carbon resources has mainly depended on combustion of wood tips from woody industry or black liquor from pulping process. This energy conversion process has been paid much attention for electricity production by biomass. But combustion of biomass seems to be a short-cut to CO_2 because some biomass with slow rate of circulation in bio-systems such as lignin need 50–60 years to be decomposed into CO_2. In this viewpoint, light-electricity conversion system with LPs is conformed to rate of material flow of forest carbon resources in bio-systems.

In this work, DSSCs of porous TiO_2 sensitized by polymeric LPs (LPs–DSSCs) have been prepared and estimated. Various LPs have been investigated as new polymeric photosensitizers for DSSCs derived from natural materials out of limits of fossil carbon resources.

2. Experimental

2.1. Synthesis of LP

Synthesis of LP from wood was achieved by phase-separation system two-step method process-II by following the detail prescriptions in [11–13]. Three wood species of wood and five phenols were chosen as materials for LPs. Softwood were Hinoki (HK; *Chamaecyparis obtusa*) and Douglas fir (BM; *Pseudotsuga menziessi*). Hardwood was beech (BN; *Fagas crenata*). Phenols were phenol (P), *p*-cresol (C), catechol (Cat), resorcinol (Res) and pyrogallol (Pyr).

2.2. Characterization of LPs

FT-IR spectra (KBr disks) and emission spectra (in methanol) were determined on Shimadzu IR-470 spectrometers and Shimadzu RF-5300PC spectrofluorophotometers, respectively. Ultraviolet and Visible spectra (UV-Vis; in 1,4-dioxane or acetone) were determined on JASCO V560 spectrometers. UV-Vis spectra of solids were determined on integrating sphere attachment model ISV-469 (JASCO Co.) connected with JASCO V560 spectrometers. ^{1}H NMR spectra were estimated on JASCO ALPHA JNM-500 spectrometer (500 MHz). Molecular weight distributions of LPs were estimated on Shimadzu LC-10AD with UV detector. THF was used as the eluent.

2.3. Chemical modification of LP

2.3.1. Re-cycled LPs

LPs–SF413 and LPs–SF443, re-cycled LPs, were synthesized by treatments of 0.5 M aq. NaOH at 413 and 443 K, respectively, for 1 h (Scheme 2) following the prescription in [13].

2.3.2. Acethylation of LP

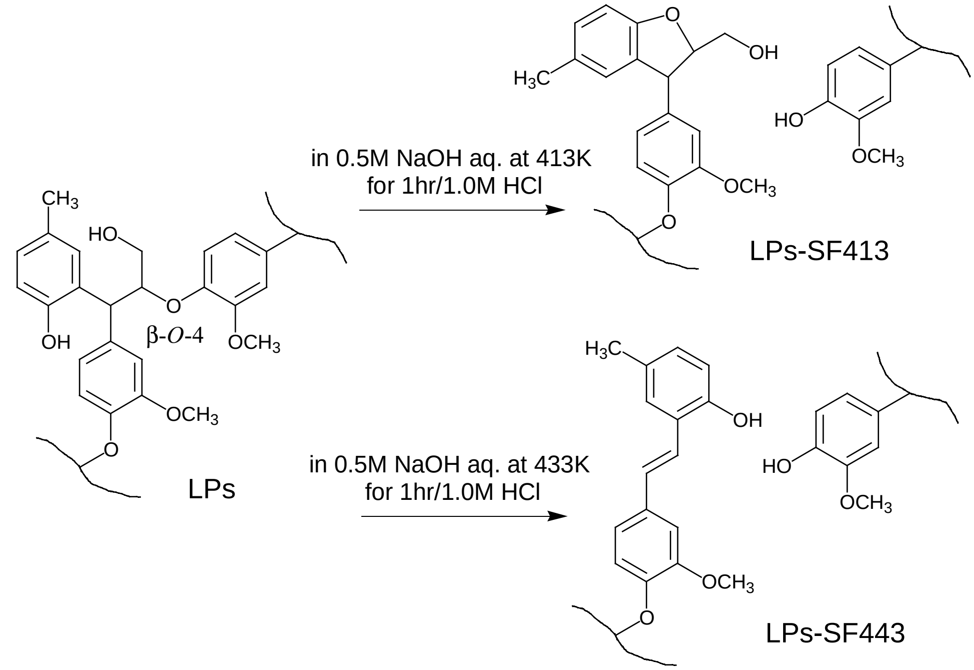
Acethylated LPs (LPsOAc) were synthesized as follows (Scheme 3). Acetic anhydride (1.0 cm^3, 10.6 mmol) was added into 1.0 cm^3 of a pyridine solution of LPs (0.1 mg cm^{-3}). After 48 h, the reaction mixture was poured into 200.0 cm^3 de-ionized water in ice bath under magnetic stirring. The light yellow precipitation was collected by centrifugation and dried over P_2O_5.

2.3.3. Composite of LP-TiO_2

When powders of TiO_2, ST-01 (>7 nm) and P-25 (>25 nm), were immersed into acetone solutions of LPs at room temperature. After 1–24 h, the solvent was evaporated a yellow or beige powder was estimated by FT-IR and UV-Vis spectrometers with integrating sphere.

2.4. Preparation of TiO_2 electrodes

Colloidal paste was prepared by mixing 1.0 g TiO_2 paste (PASOL-HPA-15R, Shokubai Kasei Co.) with 40 mg poly-ethyleneglycol (20 000 g mol^{-1}) and 100 mg P-25 TiO_2. The paste was well ground and applied on a glass



Scheme 2. Recycling processes of HKLC by cleavage of β-O-4 bonds in 0.5 M aq. NaOH at 413 and 443 K for 1 h. LPs, LPs–SF413 and LPs–SF443 are shown in this scheme.

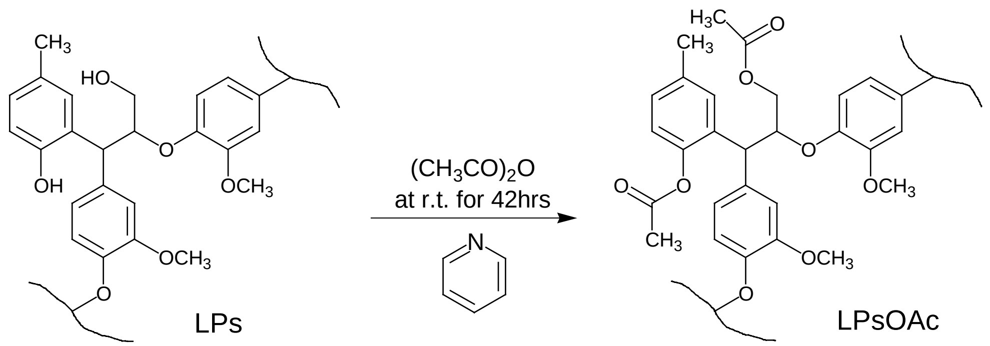
plate coated with transparent indium tin oxide (ITO-glass, $10\,\Omega\,\mathrm{sq}^{-1}$, Yasuda-Shoten Co.) by bar-coating with 63 μm-thickness mending tape as a spacer. After sintering at 723 K in a muffle furnace under an aerobic condition for 1 h, a TiO_2 thin film electrode was obtained.

2.5. Adsorption of LPs onto TiO_2 electrodes

The obtained electrode was immersed into an acetone or methanol solution of LPs ($2.0\,\mathrm{g\,dm^{-3}}$) and then kept at room temperature for 1–3 h.

2.6. Photovoltaic measurements of LPs–DSSCs

The LPs–DSSCs with two electrodes consisted of an LPs–TiO_2 electrode, a counter electrode and an organic electrolyte with a 126 μm spacer was used for photovoltaic measurements. The counter electrode was an Au–Pd (60/40, w/w) thin film with 16 nm thickness on an ITO-glass plate by ion-sputtering apparatus (Hitachi Co., E-1010). The electrolyte consisted of 0.5 M LiI and 0.05 M I_2 in propylenecarbonate. Concentrations of LiI and I_2 were decided by following the prescription in [14]. A 150 W Xe lamp (Hamamatsu Photonics Co.) was employed as a light source. Because irradiations were achieved without filter, performances of LPs–DSSCs were compared to non-treated TiO_2 electrodes. Intensity of lights was measured by FL250A thermopile head (Ophir Co.). The photovoltaic performance of LPs–DSSC was measured on Potentiostat/Garvanostat (HA-105, Hokuto Denko Co.). Moreover, measurements under AM 1.5 were achieved by 2400 Source Meter (KEITHLEY Co.) irradiation by Optical Module X (Ushio Co.) with AM 1.5 filter on Mie Prefectual Science and Technology Promotion Center.



Scheme 3. Acetylaton of LPs at room temperature for 48 h. LPs and LPsOAc are showed in this scheme.

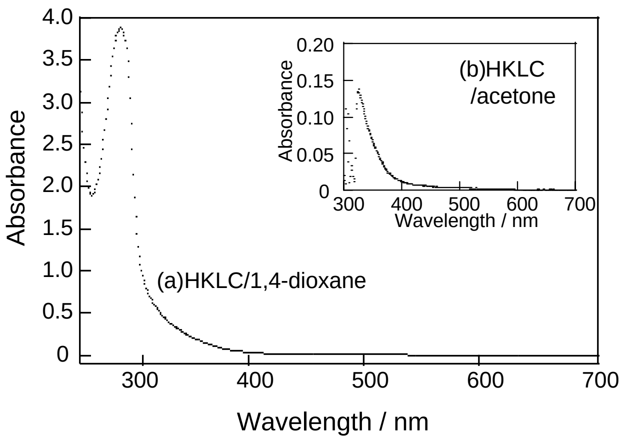


Fig. 1. UV-Vis spectra of (a) 8.0 mg dm^{-3} 1,4-dioxane solution with light brown and (b) 5.0 mg dm^{-3} acetone solution of HKLC with dark red brown (inset).

3. Results and discussion

3.1. UV-Vis spectra

3.1.1. UV-Vis spectra of LPs

Hinoki-ligno-*p*-cresol (HKLC) showed different broad peaks in 1,4-dioxane and acetone as shown in Fig. 1. Although LPs in an organic solvent showed few absorption in visible region, solid LPs showed broad peaks at λ = 350–800 nm. In fact, an acetone solution of HKLC showed more dark brown than 1,4-dioxane in spite of small ε in the visible region over 400 nm (Fig. 1). Only little difference in solid UV-Vis spectra was observed between HKLC and BNLC, softwood- and hardwood-LPs (Fig. 2(a) and (b)), respectively. This result implied that common structures in LPs, 1,1-bis(aryl)propanyl structures (Scheme 1), have never depended on wood species and probably never been effected on excited states of LPs.

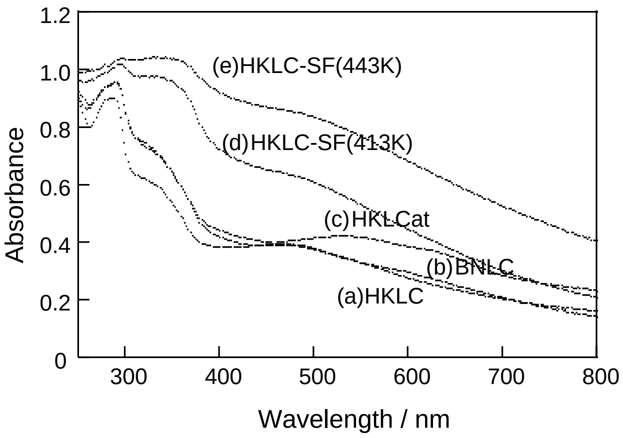


Fig. 2. UV-Vis spectra of solid LPs and derivatives were estimated by an integrating sphere: (a) HKLC; (b) BNLC; (c) HKLCat; (d) HKLC–SF413; (e) HKLC–SF443.

HKLCat, which is LPs consisted of poly-phenol, showed lager absorbance in the region of 500–800 nm than HKLC (Fig. 2(c)) because several neighboring hydroxyl groups of poly-phenols were partly condensed by 72% H_2SO_4. Actually, these LPs have more dark appearance than mono-phenol LPs. Moreover, chemically modified LPs also showed larger absorbance than LPs in the region of visible light (Fig. 2(d) and (e)) with increase of conjugations in the process of cleavages of main chains. These results implied that the absorbance of LPs would be improved by chemical modifications.

3.1.2. UV-Vis spectra of LPs–TiO_2 composites

A new broad peak was observed in UV-Vis spectrum of a composite of LP/TiO_2. When ST-01 were thrown into and suspended in a brown acetone solution of LPs, yellow participates were produced soon. Adsorption of 0.303 g of BMLC on 1.0 g ST-01 was estimated by UV-Vis spectroscopy with little desorption.

Fig. 3 showed UV-Vis spectra of TiO_2, HKLC and HKLC/TiO_2 composite. HKLC/ST-01 showed vivid yellow appearance by interactions between HKLC and ST-01 surface like santaline–Ti^{4+} complexes as Tennakone et al. reported [17,18]. Although ST-01 showed little absorbance at $\lambda > 400$ nm (Fig. 3(a)), HKLC/ST-01 showed twice lager absorbance than LPs at λ = 350–600 nm. Since HKLC/ST-01 (>7 nm) composite showed vivid yellow, HKLC/P-25 (>25 nm) had little yellow appearance (Fig. 3(c) and (d)). These results implied that the interactions between LPs and nano-structures of TiO_2 were produced. These adsorptions also achieved on surface of TiO_2 films on ITO glasses. Actually, TiO_2 electrodes quickly changed yellow appearances due to strong adsorptions when films were immersed into LPs solutions.

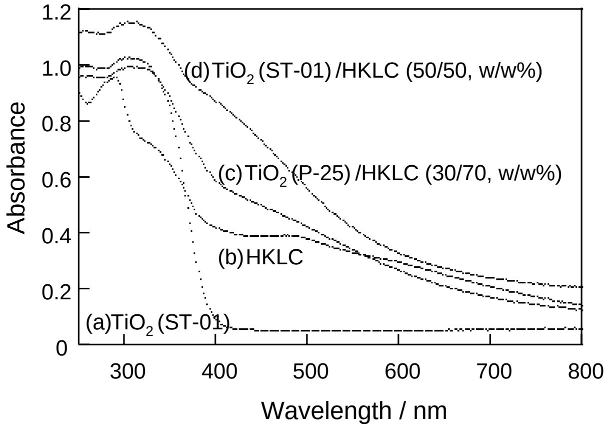


Fig. 3. UV-Vis spectra of HKLC, TiO_2 powders (ST-01 and P-25) and composites of HKLC/TiO_2 cast by acetone solution estimated with an integrating sphere: (a) ST-01; (b) HKLC, light beige powder; (c) 30/70 (w/w) HKLC/P-25 composites; (d) a 50/50 (w/w) HKLC/ST-01 composites.

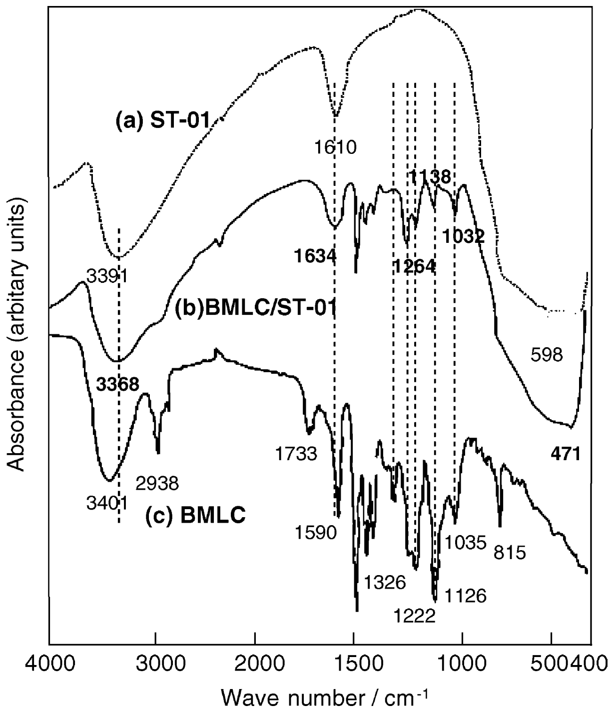


Fig. 4. FT-IR spectra of (a) ST-01, (b) BMLC/ST-01 (50/50%, w/w) cast from acetone solution and (c) BMLC by KBr method.

3.2. FT-IR spectra

Fig. 4 shows the FT-IR spectra of ST-01, BMLC/ST-01 composite (30%, w/w) and BMLC. To the ST-01 and BMLC characteristic absorptions were found in Fig. 4(a) and (c), being in accordance with the results of lignins described in [15,16]. In Fig. 2(b) several shifts of peaks were observed. As peaks of 1032 and 3368 cm^{-1} were shifted toward low wave numbers, 1138, 1507 and 1610 cm^{-1} were shifted for large wave numbers. Especially an absorbance at 3368 cm^{-1} with blue shifts from 3401 cm^{-1} (BMLC) and 3391 cm^{-1} (ST-01) showed hydroxyl groups with hydrogen bonds or other interactions between BMLC and TiO_2.

As Tennakone et al. have reported productions of complexes between phenolic hydroxyl groups of santaline or tannins and Ti^{4+} on a surface of TiO_2 [17,18], these yellow compounds were probably LPs–Ti^{4+} complexes like santaline–Ti^{4+} complexes. As shown in Fig. 3, these complexes absorbed visible light. Recently various mechanisms of interactions between carboxyl groups and TiO_2 surface have mainly been discussed [19–23]. But interactions between phenolic hydroxyl groups and TiO_2 in photoelectricity conversion are especially significant for LPs because LPs have no carboxyl groups.

Because the other shifted peaks were belonged to core structures of LP, aromatic structures also interacted with TiO_2. Therefore, these two important interactions, phenolic hydroxyl groups and aromatics, worked on the surface of LPs–TiO_2 for photoelectricity conversion.

Table 1
Photovoltage and photocurrent of various LPs–DSSCs under 150 W Xe lamp direct irradiation (177 $\mathrm{W\,m^{-2}}$)

LPs	V_{oc} (V)	I_{sc} ($\mathrm{mA\,cm^{-2}}$)	ff
HKLC	0.35	2.42	0.42
BNLC	0.28	2.50	0.42
BMLC	0.54	3.84	0.42
HKLRes	0.42	2.70	0.28
HKLPyr	0.42	2.02	0.33
HKLCat	0.40	1.76	0.20
HKLP	0.47	4.32	0.26

LPs were adsorbed from acetone solution for 1 h at room temperature. Pt on an ITO-glass was used for counter electrode with 8 nm thickness.

3.3. Emission spectra

Weak continuous emission spectra of LPs in methanol were observed in a region of $\lambda = 580$–800 nm excited by $\lambda = 360$–520 nm light (data not shown). In addition, broad emission peaks with peak tops at 690 and 710 nm were observed by $\lambda = 520$–640 nm excited light. So LPs have singlet excited states and continuous energy levels.

3.4. Photovoltaic performance of LPs–DSSCs

Table 1 shows the photovoltaic performance of LPs–DSSCs under the 150 W Xe lamp direct irradiation. Almost all LPs–DSSCs showed low ff because of the series of resistant losses overall cell. For example, viscosity of propylene carbonate and difficulty on approaching to nano-porous TiO_2 film would effect on the low ff. So the V_{oc}, I_{sc} and ff value of LPs–DSSCs could be improved by optimizations. In fact, performances of LPs–DSSCs were improved by changing propylene carbonate into acetonitrile (Table 2).

Because of irradiations by 150 W Xe lamp without filters, excess UV or IR was probably involved compared to sun light. So results of LPs–DSSCs were compared to the performances of non-treated TiO_2 electrodes (Table 2). By UV irradiation, contributions of only TiO_2 at most 30% on

Table 2
Photovoltage and photocurrent of various LPs–DSSCs under 150 W Xe lamp direct irradiation (165.0 $\mathrm{W\,m^{-2}}$)

LPs	S ($\mathrm{cm^2}$)	V_{oc} (V)	I_{sc} (mA $\mathrm{cm^{-2}}$)	P_{max} (mW $\mathrm{cm^{-2}}$)	ff	η (%)
TiO_2/ITO[a]	1.45	0.34	0.34	0.05	0.40	0.03
BMLC	1.52	0.44	1.11	0.27	0.56	0.17
HKLP	1.19	0.51	2.88	0.68	0.46	0.41
HKLC	1.03	0.48	2.00	0.52	0.54	0.31
HKLC–SF413K	1.03	0.46	2.35	0.56	0.52	0.34
HKLC–SF443K	0.99	0.44	1.17	0.29	0.56	0.17
HKLRes	1.03	0.48	1.88	0.51	0.56	0.31
TiO_2/FTO[a]	1.75	0.03	0.45	0.01	0.44	0.01
HKLC/FTO	2.00	0.36	2.48	0.31	0.35	0.19

LP was adsorbed from acetone solution for 3 h at room temperature. Pt on an ITO-glass with 16 nm thickness was used for counter electrode. Electrolyte was 0.5 M LiI and 0.05 M I_2 in acetonitrile.

[a] Non-treated TiO_2 films.

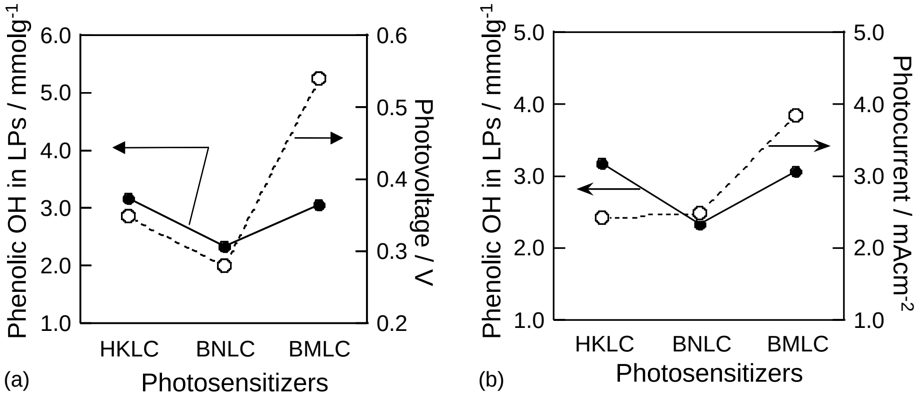


Fig. 5. Effects of phenolic hydroxyl groups in LPs for (a) V_{oc} and (b) I_{sc} under 150 W Xe lamp irradiation (177 W m^{-2}). Amounts of phenolic hydroxyl groups were estimated by ^{1}H NMR.

ITO glasses and 3% on FTO glasses were estimated to I_{sc} and η. Thus, LPs have been confirmed as photosensitizers for DSSCs.

3.5. Effects of phenolic hydroxyl groups

As shown in Fig. 5, the photovoltaic performance partially depended on amounts of phenolic hydroxyl groups in LPs estimated by ^{1}H NMR. These results supported important roles of phenolic hydroxyl groups in interactions between LPs and TiO_2 surface similar to other phenolic substrates [17,18]. As LPs of poly-phenols had been expected to show high performances with rich phenolic hydroxyl groups, the performances were low (Table 1, Fig. 6). Because neighboring hydroxyl groups partly were dehydrated by 72% H_2SO_4, performances were influenced on.

3.6. Effects of wood species

As shown in Table 1 and Fig. 7(b), photovoltaic performances of LPs–DSSCs based on softwood (HK and BM) were always higher than on hardwood (BN). In general, softwood native lignin is different from hardwood native lignin (Fig. 7(a)). Softwood lignin has only 2-methoxyl groups on propanyl phenyl units (guiacyl structures). On the other hand, hardwood lignin has 50% of guiacyl structures and

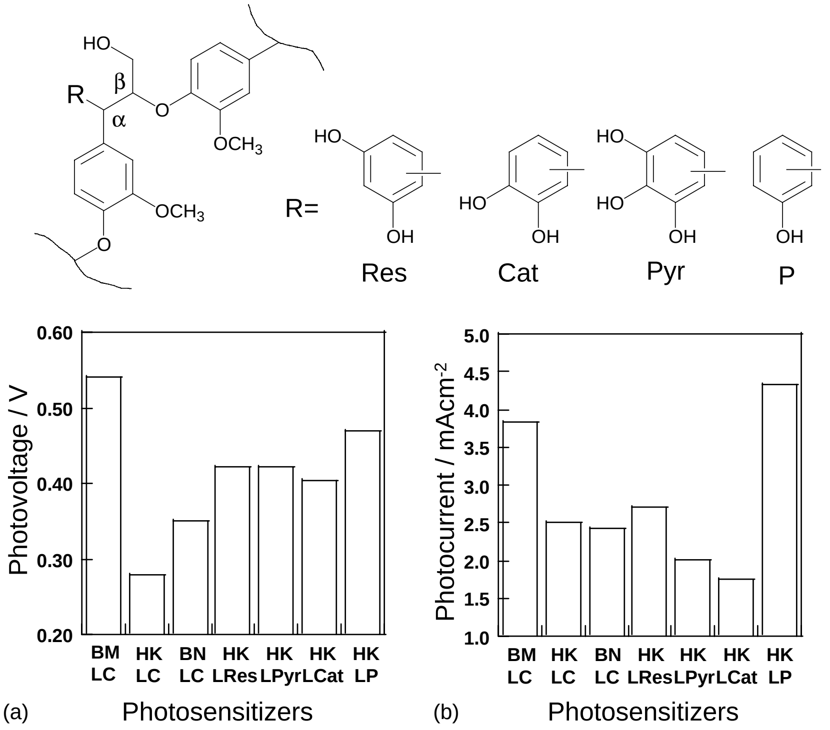
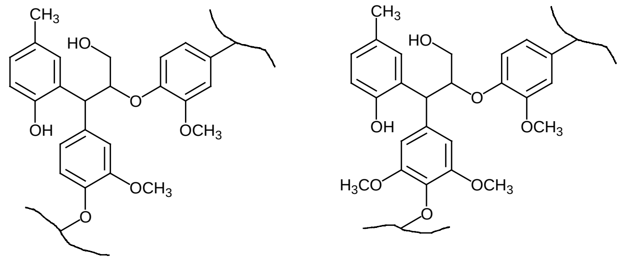


Fig. 6. Effects of grafted phenols for (a) V_{oc} and (b) I_{sc} under 150 W Xe lamp irradiation (177 W m^{-2}).



(a) LPs with guaiacylstructure LPs with syringylstructure

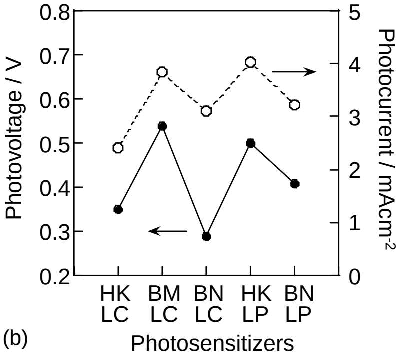


Fig. 7. (a) Models of LPs with 4-methoxyl (guiacyl) and 2,4-dimethoxyl (silingyl) structures. Only hardwood lignin has both guaiacyl and silingyl structures, (b) effects of wood species for V_{oc} and I_{sc} under 150 W Xe lamp irradiation (177 W m^{-2}).

50% of 2,6-dimethoxyl groups on propanyl phenyl units (syringyl structures). As 1,1-bis(aryl)propanyl structures probably were related with interactions between LPs and TiO_2 surface, these results implied that methoxyl groups in LPs inhibit interactions between LPs and TiO_2.

3.7. Effects of chemical modification

Various chemical modified LPs (Schemes 2 and 3) showed better photovoltaic performance than LPs. Especially HKLC–SF413 showed 0.51 V and 5.12 mA cm^{-2} (Fig. 8), because of high density on TiO_2 surface with small molecular. While HKLC–SF443 showed large I_{sc} (4.6 mA cm^{-2}) like HKLC–SF413, V_{oc} (0.32 V) was lower than LPs. Although regions of absorbance became wide with increasing conjugations (Fig. 2(e)), it was difficult to approach TiO_2 surface with increasing rigid stilbene structures.

Moreover, both HKLCOAc and BNLCOAc, acethylated HKLC and BNLC, also showed $V_{oc} = 0.43$ V, $I_{sc} = 2.82$ mA cm^{-2} and $V_{oc} = 0.37$ V, $I_{sc} = 3.41$ mA cm^{-2}, respectively (Fig. 8). Although phenolic hydroxyl groups were blocked by acethyl groups, photovoltaic performances were estimated. Probably acethyl groups and aromatic rings of 1,1-bis(aryl)propanyl structures stacked on TiO_2 surfaces without production of complexes because of no change of colors. These results implied that LPs have two other interactions with TiO_2 surface. These results also implied that chemical modifications of LPs are effective for improvements of photovoltaic performance of LPs–DSSCs.

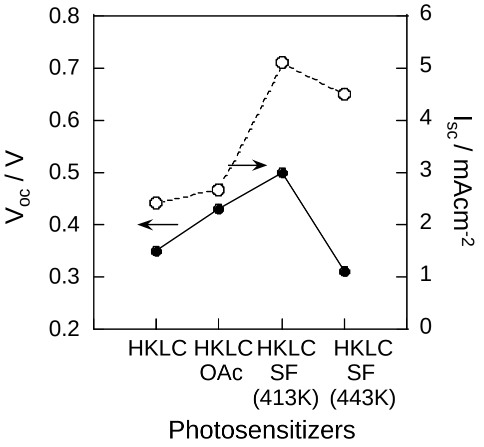


Fig. 8. Photovoltaic performances for various LPs–DSSCs under 150 W Xe lamp irradiation (177 W m^{-2}).

3.8. The best performance of LPs–DSSCs under 150 W Xe lamp irradiation

Fig. 9 shows I–V curves of the best photovoltaic performances of LPs–DSSCs under 150 W Xe lamp direct irradiation (177 W m^{-2}). HKLP (0.48 cm^2) showed $V_{oc} = 0.48$ V, $I_{sc} = 11.5$ mA cm^{-2}, ff = 0.40 and $\eta = 1.45\%$. Moreover, BMLC (0.76 cm^2) showed $V_{oc} = 0.53$ V, $I_{sc} = 9.5$ mA cm^{-2}, ff = 0.42 and $\eta = 1.40\%$.

Moreover, under AM 1.5 condition (100 W m^{-2}), HKLC and HKLP showed $V_{oc} = 0.34$ V, $I_{sc} = 0.65$ mA cm^{-2} and ff = 0.49, $\eta = 0.11\%$, and $V_{oc} = 0.39$ V, $I_{sc} = 0.34$ mA cm^{-2} and ff = 0.46, $\eta = 0.06\%$, respectively.

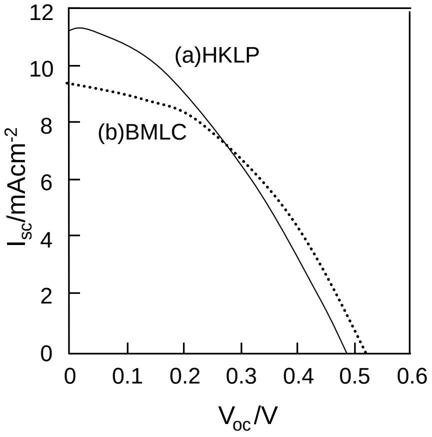


Fig. 9. Photovoltaic performances of LPs–DSSCs of HKLP and BMLC under 150 W Xe lamp irradiation (177 W m^{-2}). Counter electrode was Pt on an ITO-glass with 16 nm thickness. Electrolyte was 0.5 M LiI and 0.05 M I_2 in acetonitrile: (a) HKLP: $S = 0.48$ cm^2, $V_{oc} = 0.48$ V, $I_{sc} = 11.5$ mA cm^{-2}, ff = 0.40, $\eta = 1.45\%$; (b) BMLC (dotted line): $S = 0.76$ cm^2, $V_{oc} = 0.53$ V, $I_{sc} = 9.5$ mA cm^{-2}, ff = 0.42, $\eta = 1.40\%$.

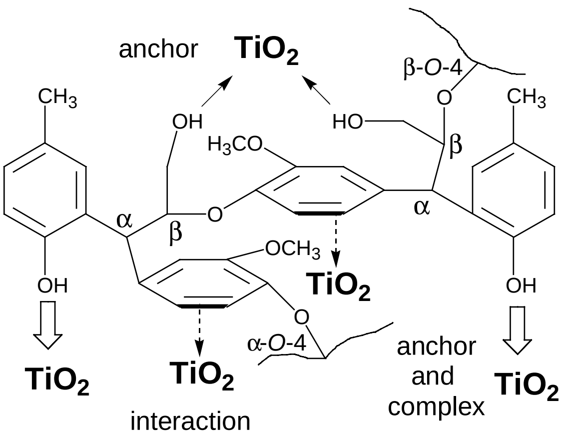


Fig. 10. A proposal model of interaction between LPs and TiO_2.

Since LPs–TiO_2 composites have little absorbance of visible light, as shown in Fig. 3, effective photoelectricity conversion have never occurred sufficiently. Therefore, LPs need to be improved of absorbance in the region of visible light.

4. Conclusion

In conclusion, LPs and LPs-derivatives were available for photosensitizers of dye-sensitized solar cells composed of nano-porous TiO_2. Probably, the phenolic hydroxyl groups were important anchors on TiO_2 surface with production of complexes. But results of LPsOAc implied not only hydroxyl groups but other interactions existed between LPs and TiO_2 surface as shown in Fig. 10. After anchors produced on TiO_2 surface, 1,1-bis(aryl)propanyl structures also approached to TiO_2 surface. The stacking is one of the most important interactions between LPs and TiO_2 surface.

Photovoltaic performances of LPs–DSSCs were under the influences of species of wood, phenols and chemical modifications. In various combinations, LPs with mono-phenol derived from softwood showed the best performance. Nevertheless LPs need to be optimized in combinations of wood species, phenols, and chemical modified, it is notable that these new polymers directly derived from abundant forest carbon resources could be utilized for photosensitizers of DSSCs.

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References

[1] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, O. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. 115 (1993) 6382.
[2] B. O'Regan, M. Grätzel, Nature 353 (1993) 737.
[3] A. Hagfeldt, M. Grätzel, Chem. Rev. 95 (1995) 49.
[4] K. Hara, K. Sayama, Y. Ohga, A. Shinpo, S. Suga, H. Arakawa, Chem. Commun. (2001) 569.
[5] K. Hara, Y. Tachibana, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, H. Arakawa, Solar Energy Mater. Solar Cells 77 (2003) 89.
[6] K. Sayama, K. Hara, N. Mori, M. Suzuki, S.Suga, S. Tsukagoshi, Y. Abe, H. Sugihara, H. Arakawa, Chem. Commun. (2000) 1173.
[7] W. Tai, K. Inoue, Mater. Lett. 57 (2003) 1508.
[8] P.M. Sirimanne, T. Shirata, L. Domodare, Y. Hayashi, T. Toga, T. Jimbo, Solar Energy Mater. Solar Cells 77 (2003) 15.
[9] G.P. Smestad, Solar Energy Mater. Solar Cells 55 (1998) 157.
[10] H. Sadermann, D. Scheel, T. Van der Trenck, J. Appl. Polym. Sci. 37 (1983) 407.
[11] M. Funaoka, I. Abe, Tappi J. 72 (1989) 145.
[12] M. Funaoka, S. Fukatsu, Holzforshung 50 (1996) 245.
[13] M. Funaoka, Polym. Int. 47 (3) (1998) 277.
[14] K. Hara, T. Horiguchi, T. Kinoshita, K. Sayama, H. Arakawa, Solar Energy Mater. Solar Cells 70 (2001) 151.
[15] A.M.A. Nada, M. El-Sakhawy, S.M. Kamel, Polym. Degrad. Stab. 60 (1998) 247.
[16] A.M.A. Nada, M. El-Sakhawy, S.M. Kamel, Polym. Degrad. Stab. 62 (1998) 157.
[17] K. Tennakone, G.R.R.A. Kumara, I.R.M. Kottegoda, V.P.S. Perera, P.S.R.S. Weerasundara, J. Photochem. Photobiol. A 117 (1998) 137.
[18] K. Tennakone, G.R.R.A. Kumara, A.R. Kumarasinghe, P.M. Sirmanne, K.G.U. Wijiyantha, J. Photochem. Photobiol. A 94 (1996) 217.
[19] T. Ma, K. Inoue, H. Noma, K. Yao, E. Abe, J. Photochem. Photobiol. A 152 (2002) 207.
[20] A. Ehret, L. Stuhl, M.T. Spitler, Electrochim. Acta 45 (2000) 4553.
[21] K.S. Finnie, J.R. Bartlett, J.L. Woolfrey, Langmuir 14 (1998) 2744.
[22] T. Ma, K. Inoue, K. Yao, H. Noma, T. Shuji, E. Abe, J. Yu, X. Wang, B. Zhang, J. Electroanal. Chem. 537 (2002) 31.
[23] P. Falaras, Solar Energy Mater. Solar Cells 53 (1998) 163.