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A Photochemical Cell Sensitized with a Lignin-Based Polymer with High Recyclability

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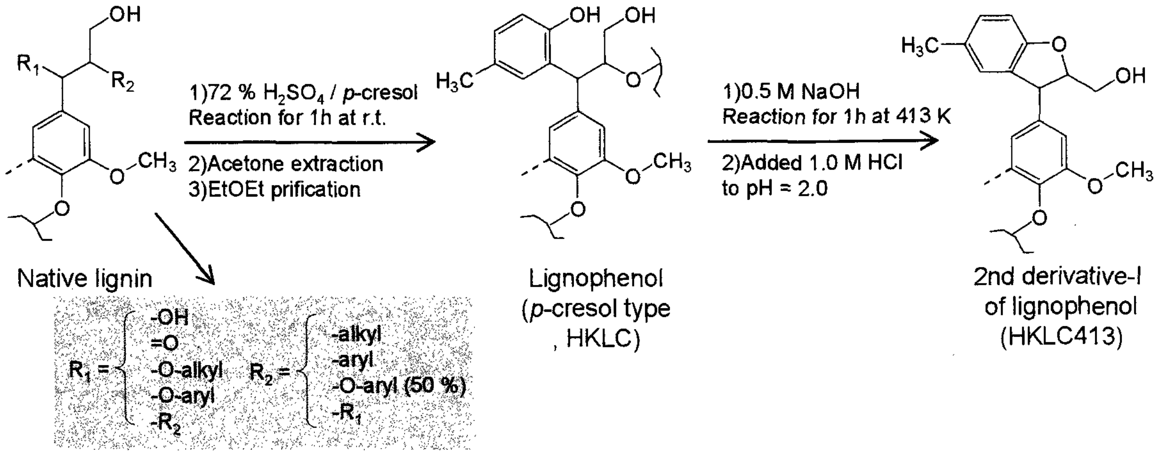
Lignophenols, which have been directly synthesized from lignocellulosics such as woods through the phase-separation system, were used as photosensitizers for nano-porous TiO_2 electrodes on FTO glasses. Photo-electricity conversions were measured under 100.3 $mWcm^{-2}$ of visible light irradiation. All lignophenols and their derivatives easily produced stable complexes with nano-porous TiO_2 electrodes in acetone solutions. Higher absorbance of lignophenol / TiO_2 electrodes in the region of λ = 400 - 600 nm tended to show higher photo-electricity conversions such as Hinoki-lignophenol (resorcinol type, HKLRes) and a second derivative-I of Hinoki-lignophenol (*p*-cresol type, HKLC413), which was synthesized from lignophenol in an alkaline medium. HKLRes showed V_{oc} = 0.47 V, I_{sc} = 1.64 $mAcm^{-2}$, FF = 0.45 and η = 0.42 %, and HKLC413 also showed V_{oc} = 0.43 V, I_{sc} = 2.06 $mAcm^{-2}$, FF = 0.54 and η = 0.48 %. Moreover the results were influenced by adsorption on inner electrodes. Thus these lignin-based polymers and their derivatives obtained in a recycle process were expected to be used as fine chemicals because both materials worked as photosensitizers for nano-porous TiO_2 electrodes.

Key words: lignophenol, lignin, photochemical cell, recycle

1. INTRODUCTION

Recently biomass such as forest carbon resources has been attracted as carbon resources instead of fossil carbon resources. Since it is difficult to separate natural components in biomass because of its complexity and high sensitivity for circumstance, biomass is often used as fuel for power generation rather than as a molecular material. In fact, for example, black liquors obtained in paper making processes were burned for a power generation. The conversion of biomass into power by burning reached about 1 % of all energy production in Japan in 2000. However biomass has been regarded as substitution of petroleum in these ways, all carbons have been converted into CO_2 through a short-cut route. To utilize biomass as sustainable materials, molecular deigns for sustainability are needed. In 1989, Funaoka has discovered a novel method to separate carbohydrates and lignin-based polymers from lignocellulosics quantitatively under a mild condition [1].



Scheme1 Synthesis of Hinoki-lignophenol (*p*-cresol type, HKLC) from native lignin in lignocellulosics through the phase-separation system composed of 72 % H_2SO_4 and *p*-cresol under r.t. for 1h. HKLC was extracted by acetone and then purified by an excess amount of EtOEt. A second dervative-I HKLC was synthesized from HKLC in 0.5 M NaOH solution at 413 K for 1.0 h.

Through this process, the phase-separation system composed of a concentrated acid and a phenol, both aqueous carbohydrates and 1,1-bis(aryl)propane-2-*O*-arylether type polymers (lignophenols) were directly obtained from lignocellulosics under room temperature and 1 atm (Scheme 1). These lignin-based phenolic polymers differed from conventional industrial lignins such as kraft lignin. Lignophenols showed high solubility for various organic solvents, thermal plasticity, light beige appearance and high recyclabilty by neibouring group participation [2]. Since a main chain of a lignophenol was cleft, an arylcoumaran type structure was produced in the end of the molecule through this nucleophillic reaction (Scheme 1). Therefore a control of particular functionality and molecular weight of lignophenols are realized in order to meet the requirements. These recyclable materials were expected to utilize as substitutions of chemical substances such as electron donors from petroleum.

Recently dye-sensitized solar cells have been paid a lot of attentions since Grätzel accomplished the breakthrough on the photo-electricity conversion (η = 10.2 %) with Ruthenium-complexes and nano-porous TiO_2 electrodes in 1991 [3]. In our previous work, lignophenols have acted as photosensitizers for nano-porous TiO_2 electrodes [4]. Moreover, this type photochemical cell sensitized by a second derivative-I of Hinoki-lignophenol (*p*-cresol type, HKLC413) showed V_{oc} = 0.51 V, I_{sc} = 10.21 mAcm^{-2}, FF = 0.59 and η = 3.61 % under 85.0 mWcm^{-2} of visible light irradiation [5]. In the present work, both photochemical properties and performance of lignophenols with different grafted phenols as photosensitizers were investigated.

2. EXPERIMENTAL

2.1 Synthesis of lignophenols

Lignophenol has been directly synthesized from extractive-free milled woods (< 80 mesh) through the phase-separation system composed of 72 % H_2SO_4 and phenol derivatives such as *p*-cresol under 300 K and 1 atm [2]. Using polyphenols such as catechol, resorsinol and pyrogallol, 95 % H_3PO_4 was used as a hydorophillic reagent in order to avoid a random rearrangement. Hinoki (*Chaemeaus obtusa*) was used as a woody material. Phenols were added in 3 mol for an amount of phenylpropane (C_9) units of a native lignin determined by Klason method. The resulting lignophenol was purified by EtOEt from the acetone solution. The properties of lignophenol were estimated by UV-vis, ^{1}H-NMR, FT-IR, GPC, TMA and fluorescence spectroscopy. Solid-state UV-vis spectrum was measured by quartz sphere ISV-469 (JASCO Co.).

2.2 Preparation of nano-porous TiO_2 electrode

A nano-porous TiO_2 electrode on FTO was obtained by sintering at 723 K under an aerobic condition. A well-ground TiO_2 paste was composed with HPA-15R TiO_2 paste (Shokubai Kasei Co.), P25 (Nippon Aerogel Co.) and PEG20 000 (=100/10/4, w/w/w). The lignophenol was adsorbed on this electrode in 5.0 gdm^{-3} (25.0 mmolC$_9$dm^{-3}) of a dry acetone solution at 293 K for 24 h [4]. An amount of lignophenol adsorbed on the electrode was estimated by UV-vis spectroscopy after extraction by 1.0 M NaOH.

2.3 Measurement of photo-electricity conversion

A photochemical cell was composed of FTO (20 Ohmsq^{-1})-TiO_2-lignophenol-electrolyte-Pt-FTO [4]. The electrolyte was 0.5 M LiI, 0.05 M I_2 in acetonitlile. A photo-electricity conversion performance was measured by Potentiostat HA-105 (Hokuto Denko Co.) under visible light irradiation through L41 UV cut filter from 150-W Xe lamp.

3. RESULTS AND DISCUSSION

3.1 Basic properties of lignophenols

Conventional industrial lignins have complicated network structures due to random rearrangement in the separation process under high pressure and high temperature, complicated conjugated systems spread on the network structures. On the other hand, lignophenol has light beige appearance in bulk without random condensation. Because almost all conjugation systems of lignophenol were cut by sp^3-carbons on C_2-positions (Scheme1), properties of lignophenols such as high solubility and thermal plasticity were produced. Since Hinoki-lignophenol (*p*-cresol type, HKLC) was plasticized at 443 K, various manufactures such as molding or mixing with other materials can be easily carried out.

3.2 Properties of lignophenol solutions

Solutions of lignophenols had brown appearances in aprotic solvents such as acetone, EtOH, MeOH, ethyleneglycol, THF, 1,4-dioxane, NMP, DMF and DMSO. The peak positions in the visible region shifted slightly with ε_s of solvents toward 470 nm. The differences of peak positions were observed with different grafted phenols (Fig.1). Hinoki-lignophenol (*p*-cresol type, HKLC) had strong absorbance at UV region and a broad peak in a visible region. In contrast, both Hinoki-lignophenol (resorcinol type, HKLRes) and Hinoki-lignophenol (catechol type, HKLCat) had stronger absorbance than HKLC at visible region. Especially HKLCat strongly absorbed from 400 nm to 600 nm. Two shoulder peaks were observed at 460 nm and 490 nm for these lignophenols. However there were only slight differences in peak positions, similar photochemical behaviors were observed in the same solvents in spite of difference of phenols. These results showed the absorption of lignophenol was influenced on 1,1-bis(aryl)propane type structures, which are major structural units in lignophenols.

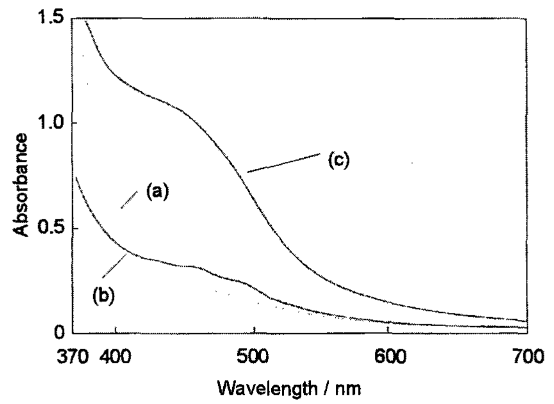


Fig.1 UV-vis spectra of lignophenols in DMF (0.25 gdm^{-3}). (a) Hinoki-lignophenol(p-cresol), (b) Hinoki-lignophenol(resorcinol type) and (c)Hinoki-lignophenol(catechol type).

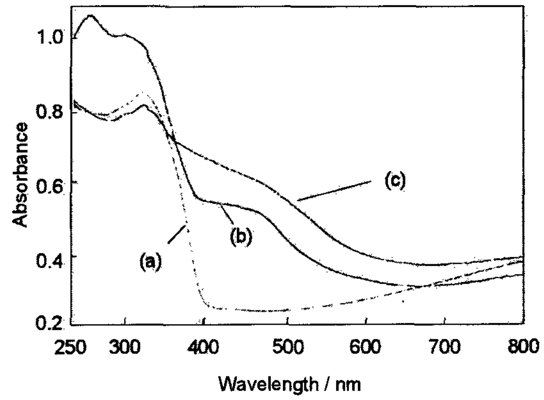


Fig.2 Solid-state UV-vis spectra for lignophenol / nano porous TiO_2 electrodes on FTO glasses. (a) TiO_2 electrode, (b) Hinoki-lignophenol (*p*-cresol type, HKLC) and (c)second derivative-I of HKLC (HKLC413).

These absorbance depended on only π–π^* transitions, because no carbonyl or carboxyl groups existed in the molecules as confirmed by FT-IR [4] and only small sovatochromism was observed. Moreover lignophenols showed fluorescence in these solutions at various excitation wavelengths from UV to visible region

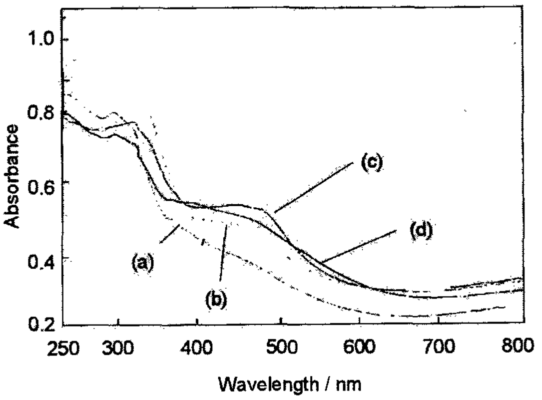


Fig.3 Solid-state UV-vis spectra of lignophenol-nano-porous TiO_2 electrodes on FTO glasses. (a) Hinoki-lignophenol (catechol type, HKLCat), (b) Hinoki-lignophenol (*p*-cresol type, HKLC), (c)Hinoki-lignophenol (resorcinol type) and (d) Hinoki-lignophenol (pyrogallol type).

[4]. These results showed there were complicated excitation and relaxation processes of singlet states. These excited electrons were probably separated from lignophenols on TiO_2 electrodes under irradiation in the photochemical cells. Therefore it is possible 1,1-bis(aryl)propane type structures act as antennas, anchors, electron injection sites on the TiO_2 electrodes.

3.3 Lignophenol-TiO_2 electrodes

Since lignophenols were dissolved in solvents, it was also easy to mix with other materials such as metal oxides. When nano-suructured TiO_2 were immersed into any solution, yellow complexes were easily obtained. These complexes were also obtained on the nano-structured TiO_2 electrodes. Visible light absorbance of TiO_2 was increased with lignophenols from 400 nm to 700 nm as shown in Fig.2. Moreover HKLC413 with aryl coumaran type structures improved absorption in a wider region than HKLC.

Appearance of a lignophenol / TiO_2 composite was varied with different grafted phenols (Fig.3). Since generally neighboring hydroxyl groups of polyphenols with catechol skeletons were likely to combine with metal ions with quinone type structures observed in natural polyphenols [5], both HKLCat and HKLPyr also produced stable conjugated structures such as quinones. Therefore lignophenol-TiO_2 complexes absorbed more visible light than HKLC (Fig.3). These complexes improved visible light absorption from λ = 400 nm to 600 nm compared to TiO_2 electrodes. Since HKLC and HKLRes showed similar behavior in Fig.3, adsorption on TiO_2 occurred by only one phenolic hydroxyl group.

3.4 Photo-electricity conversion

As shown in Table I, HKLC413 showed best performance under visible light irradiation. HKLC413 on a TiO_2 electrode strongly absorbed more visible light from 400 nm to 600 nm as shown in Fig.1. Moreover HKLRes showed high performance. However HKLPyr on TiO_2 electrode absorbed much visible light between 400 nm and 600 nm, the photo-electricity conversion was lower. Because of rich hydroxyl groups in HKLPyr, adsorption was occurred on only the surface of the electrode. In fact, an amount of HKLC413 on the electrodes was twice larger than HKLC [5]. Moreover yellow appearance remained in the electrode after NaOH extraction. Therefore V_{oc} of HKLC, HKLCat and HKLPyr were low because electrons with high energy in excited states have not efficiently been transferred from lignophenols to charge band of TiO_2. These results implied the interactions between a lignophenol and TiO_2 mainly occurred on phenolic hydroxyl groups. Thus lignophenols with different grafted-phenols acted as photosensitizers for nano-porous TiO_2 electrodes under visible light irradiation. Lignin-based polymers and their derivatives were expected to be used as fine chemicals because both materials worked as photosensitizers for nano-porous TiO_2 electrodes. More investigations for these interactions are needed to improve the performance of photo-electricity conversion.

Table I Photovoltage and photocurrent of dye-sensitized solar cells sensitized with lignophenols (LPs) under 150W Xe lamp irradiation through L41 filter (101.35 $mWcm^{-2}$) with a 63μm spacer. Second derivative-I of Hinoki-lignophenol (*p*-cresol type) was adsorbed on a TiO_2 electrode on a FTO glass in 5.0 gdm^{-3} dry acetone solution for 72 hrs. at r.t.. Pt was used for counter electrode. Electrolyte was 0.5M LiI and 0.05M I_2 in acetonitrile.

Lignophenols[1)]	Photovoltage V_{oc}/V	Photocurrent I_{sc}/$mAcm^{-2}$	Fill factor	η / %
HKLC	0.315	2.06	0.42	0.27
HKLC413	0.433	2.06	0.54	0.48
HKLCat	0.399	0.80	0.43	0.14
HKLRes	0.469	1.64	0.45	0.42
HKLPyr	0.375	0.40	0.45	0.07

1)HKLC: Hinoki-lignophenol (*p*-cresol type), HKLC413:second derivative-I of HKLC synthesized at 413 K in 0.5 M NaOH solution ,HKLCat: catechol type, HKLRes: resorcinol type and HKLPyr: pyrogallol type.

5. REFFERENCES

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