

# A photochemical cell with nano-porous TiO<sub>2</sub> electrode sensitized by lignophenol under visible light irradiation

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## Abstract

A photochemical solar cell sensitized with a lignophenol, which has been directly synthesized from lignocellulosics through the phase-separation system, on a nano-porous TiO<sub>2</sub> film electrode was developed and improved by stirring, reflux and saturation in an acetone solution. Hinoki (*Chamaecyparis obtusa*)-lignophenol (*p*-cresol type, HKLC), Beech (*Fagus crenata*)-lignophenol (*p*-cresol type, BCLC), second derivatives-I of HKLC and BCLC (HKLC413, BCLC413) and second derivatives-II of HKLC and BCLC (HKLC443, BCLC443) were used as photo-sensitizers. The conversion of visible light from 150-W Xe lamp through a L41 UV cut filter into electricity was achieved with a sandwich-type cell consisted of FTO-glass-TiO<sub>2</sub> film-lignophenol-electrolytes-Pt coated FTO. The open circuit photovoltage ( $V_{oc}$ ), the short-circuit photocurrent density ( $I_{sc}$ ), the fill factor (FF) and the photo-electricity conversion efficiency ( $\eta$ ) for the cell with HKLC413 saturated on TiO<sub>2</sub> electrode were estimated under 85.0 mW cm<sup>-2</sup> visible light irradiation for 0.51 V, 10.23 mA cm<sup>-2</sup>, 0.59 and 3.61% respectively. On the other hand, the cell with HKLC saturated only on the surface of TiO<sub>2</sub> electrode was estimated for  $\eta = 0.81\%$ . Moreover, the amounts of HKLC413 and HKLC443 on the electrodes extracted by 1.0 M NaOH were larger than the amount of HKLC evaluated by UV-vis spectroscopy. After the extractions were carried out in NaOH, only both HKLC413 and HKLC443 were remained in electrodes with slight yellow appearances. These results indicated that lignophenols were adsorbed on the inner part of porous TiO<sub>2</sub> electrodes. Consequently, the performances of these cells were strongly influenced by the molecular sizes and the structures of lignophenols.

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**Keywords:** Photochemical cell; Lignophenol; Lignin; Nano-porous titanium dioxide

## 1. Introduction

Over past decades, a considerable number of studies have been conducted on dye-sensitized solar cells (DSCs) since Grätzel et al. achieved the breakthrough by using nano-porous titanium dioxide electrodes [1–17]. These photochemical cells showed high photo-electricity conversions by photo excitation of dyes. For example, the Ruthenium complex (N3 dye) showed  $\eta = 11.04\%$  [3]. Also natural photo sensitizers for DSCs have been discussed by using extractives of phytomass such as cyanidine [11], anthocyanin [12,13], santalline [14], tannins [15], chlorophyll derivatives [16] and polyphenols [17]. But generally these extractives are scarce materials, so it is difficult to obtain a large quantity at once. On the other hand, lignin deriva-

tives can be obtained more easily than the other extractives because lignin is abundant material. However, lignin is abundant carbon resources second to cellulose on the earth, it has never been utilized sufficiently as industrial materials because of their complicated structures produced by secondary random polymerization during the conventional separation processes. Therefore, generally industrial lignins or waste woods have been used as fuel for power generation. Funaoka et al. have reported the phase-separation system as a separation method for lignocellulosic compounds to sugars and lignin-based polymers (lignophenols) under room temperature [18–20]. Since lignophenols have switching properties for recycling, finally lignophenols are converted into phenols or carbohydrates like contents of petroleum.

In the previous reports, a lignophenol and its derivatives acted as photosensitizers for photochemical solar cells based on nano-porous titanium dioxide electrodes. The cell sensitized by Hinoki-lignophenol (phenol type) achieved the

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best performance,  $V_{oc} = 0.48$  V,  $I_{sc} = 11.5$  mA cm<sup>-2</sup>, FF = 0.40 and  $\eta = 1.45\%$  under a 150-W Xe lamp direct irradiation (77 mW cm<sup>-2</sup>) [21]. But this result has been estimated under excess UV irradiation. Under only visible light irradiation, the cell sensitized by Hinoki-lignophenol(*p*-cresol type)-second derivative-I (HKLC413) has accomplished the best performance under visible light (135.0 mW cm<sup>-2</sup>),  $V_{oc} = 0.48$  V,  $I_{sc} = 4.03$  mA cm<sup>-2</sup>, FF = 0.54 and  $\eta = 0.77\%$  [22]. In this work, photo-electricity conversions of photochemical cells with nanoporous TiO<sub>2</sub> film electrodes sensitized by various lignophenol derivatives were tried to be improved by increase of adsorption. And the cells saturated with various LC derivatives were estimated under visible light irradiation.

## 2. Experimental

### 2.1. Synthesis of LC from lignocellulosics

Lignophenol (*p*-cresol type; LC) were directly synthesized from milled woods (>80 mesh pass) through the phase-separation system (Two-step process-II) composed of phenol derivatives and concentrated acid (72%) [18–20] (Scheme 1). *p*-Cresol (3.0 mol/C<sub>9</sub>, building units of native lignin with phenylpropane type structures) was added to extractives-free milled woods. Hinoki (*Chamaecyparis obtusa*) and Beech (*Fagus crenata*) were chosen as materials for softwood and hardwood, respectively. Sulfuric acid (72%) was added to the phenol-sorbed milled woods, and the mixture was stirred vigorously at room temperature for 1 h. The mixture was dropped into an excess amount of de-ionized water under stirring. The precipitates were washed by de-ionized water until the acid was removed. The resulting dry precipitates were extracted by acetone. Then the acetone solution was added dropwise to an excess amount of diethylether under stirring in an ice bath. The light-beige precipitate (diethylether insoluble LC) was collected by a centrifugation and dried over P<sub>2</sub>O<sub>5</sub> after evaporation of the solvent. Second derivative-I and II of LC (LC413 and LC443) were synthesized in 0.5 M NaOH solutions at 413 or 443 K for 0.5 h, respectively. When 1.0 M HCl added to adjust pH 2.0, precipitates were obtained. These precipitates of both HKLC413 and HKLC443 were washed by de-ionized water and then dried, the mixtures of derivatives were obtained [19,20,23,25]. These derivatives were identified by GPC profiles and FT-IR. The structures were determined by <sup>1</sup>H NMR, <sup>13</sup>C NMR and LC-MS analysis [23].

### 2.2. Structural analysis of LC

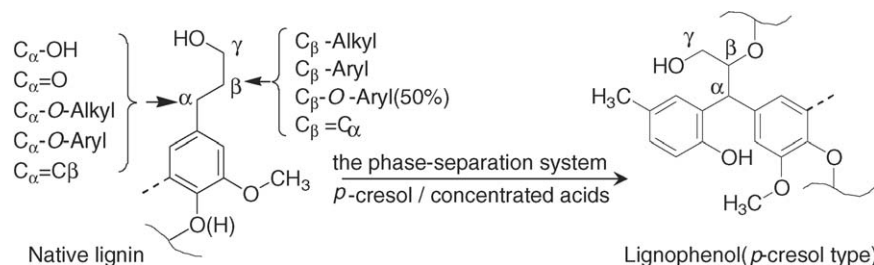
UV–vis absorption spectra were obtained by JASCO V560 spectrometer. FT-IR spectra were estimated by FT-IR Spectrum GX (Perkin Elmer Co.) with KBr disks. <sup>1</sup>H NMR spectra were measured by ALPHA JNM-500 (JOEL Co.) with *p*-nitrobenzaldehyde as the internal references. The average molecular weights were measured by LC-8A system (Shimadzu Co.) with four columns, connection of KF801, KF802, KF803 and KF804 columns (Shodex Co.) with polystyrene standards. Distilled tetrahydrofran was used as the eluent.

### 2.3. Preparation of electrodes

A nano-porous TiO<sub>2</sub> electrode was prepared as follows [21]. A FTO-glass (20 Ω sq<sup>-1</sup>) was used as a conductive glass. A paste of titanium dioxide was composed of 1.0 g of PASOL-HPA-15R paste (Shokubai Kasei Co.), 0.1 g of P25 (Nippon Aerosil Co.) and 0.04 g of polyethyleneglycol (*M* = 20,000, Wako Co.). The mixed paste was well-ground and applied on FTO glasses by bar coating with a 63 μm spacer. The electrode area was typically 0.40 cm<sup>2</sup>. After sintering was carried out at 723 K for 0.5 h in muffle furnace under aerobic condition, a titanium dioxide thin electrode was obtained. This electrode was immersed into acetone solution (5.0 g dm<sup>-3</sup>) of lignophenol under magnetic stirring for 24 h at room temperature or under reflux condition for 3 h at 323 K. A FTO-glass coated by Pt for 7 nm by ion sputtering was used as a counter electrode.

### 2.4. Photovoltaic measurements

A photochemical cell was prepared as combination of FTO-titanium dioxide film-lignophenol-electrolytes-Pt-FTO. The electrolyte was 0.5 M I<sub>2</sub> and 0.05 M LiI in acetonitrile. A 150-W Xe lamp through a L41 UV cut filter was employed as a light source. The light intensity on the surface of the cell was measured with a laser power meter model FL-250A head and NOVA (Ophir Optonics Inc.). The open circuit photovoltage ( $V_{oc}$ ), the short-circuit photocurrent density ( $I_{sc}$ ), the fill factor (FF) and the photo-electricity conversion efficiency ( $\eta$ ) for the cell were estimated on Potentiostat/Garvanostat HA-105 (Hokuto Denko Co.).



Scheme 1. Synthesis of lignophenol (*p*-cresol type) from native lignin in lignocellulosics through the phase-separation system under room temperature.

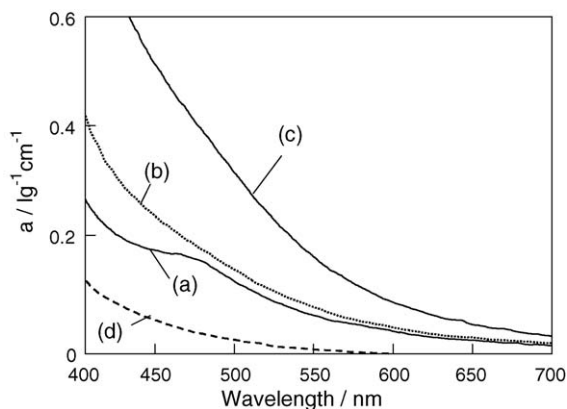


Fig. 1. Visible light absorption spectra of Hinoki-lignophenol (*p*-cresol type: HKLC) and HKLC derivatives obtained in  $2.5 \text{ g dm}^{-3}$  acetone solutions at room temperature. (a) HKLC, (b) HKLC413, (c) HKLC443 and (e) HKLC/OAc.

### 2.5. Estimation of adsorption

An amount of lignophenol on a  $\text{TiO}_2$  electrode was estimated by UV–vis spectrometer UV-560 (JASCO Co.) with a quartz cell ( $10 \text{ mm} \times 10 \text{ mm}$ ). The  $\text{TiO}_2$  electrode was immersed into a lignophenol acetone solution ( $5.0 \text{ g cm}^{-3}$ ) and stored at 293 K for 72 h. After an evaporation was carried out, the lignophenol was extracted from the  $\text{TiO}_2$  electrode in 1.0 M NaOH aqueous solution (3.0 cm) under stirring with an auto-shaker (110 rpm, 298 K). Absorbances at  $\lambda_{\text{max}} = 300, 294$  and 293 nm were evaluated for HKLC, HKLC413 and HKLC443, respectively. At these wavelengths Lambert–Beer's rule was stood up for each lignophenol in the NaOH solution between  $0.1$  and  $0.4 \text{ mg cm}^{-2}$ .

## 3. Results and discussions

### 3.1. Photophysical properties

Hinoki-lignophenol (*p*-cresol type) and its derivatives (LCs) were easily dissolved in organic solvents such as acetone, tetrahydrofuran (THF), dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP) and resulted in brown solutions. Fig. 1 showed UV–vis absorption spectra of LCs in acetone solutions. In this figure, HKLC443 (Fig. 2(c)) had three times larger absorptivity at 400–600 nm than the HKLC solution because

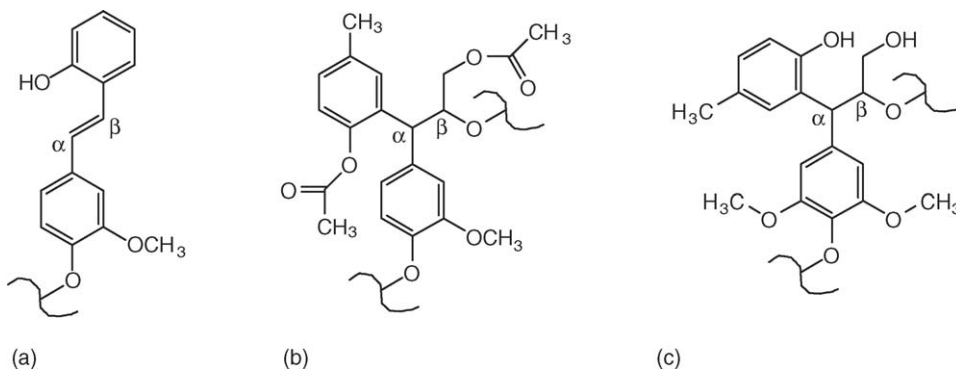


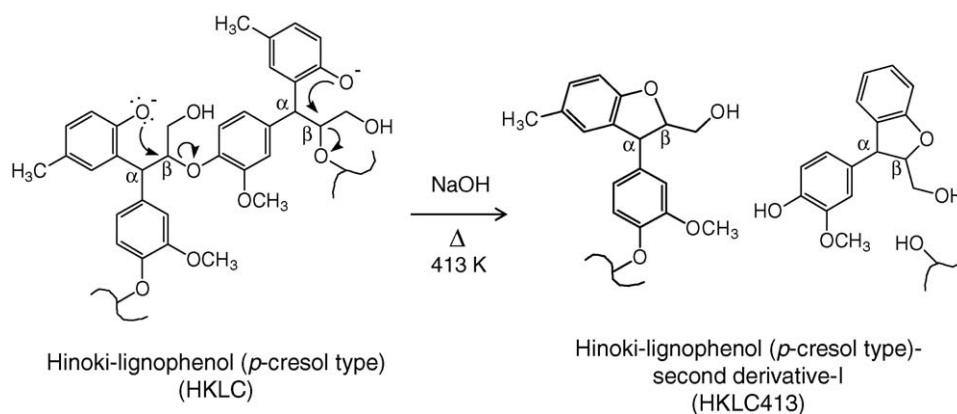
Fig. 2. Structures of various lignophenol: (a) Hinoki-lignophenol (*p*-cresol type)-2nd derivative-I (HKLC413), (b) acetylated HKLC and (c) Beech-lignophenol (*p*-cresol type).

HKLC443 involved stilbene type structures produced by cleavage of phenolic  $\text{C}_\beta$ -aryl ether linkages followed by aryl migration reactions [23–26]. As LCs have no carbonyl or carboxyl groups in the structures, this absorption resulted from  $\pi$ – $\pi^*$  transitions of 1,1-bis(aryl)propanyl structures. Moreover, these absorptions were influenced by inter- or intramolecular hydrogen bonds of both phenolic and aliphatic hydroxyl groups because LC has a lot of active hydroxyl groups. For example, HKLC has both 1.18 mol/C<sub>9</sub> of phenolic hydroxyl groups and 1.21 mol/C<sub>9</sub> of aliphatic hydroxyl groups. When hydroxyl groups of HKLC were blocked by acetyl groups (Fig. 2 (b)), the broad peak in 400–600 nm was decreased near to zero with a change in appearance brown to light yellow. Moreover, in the case of HKLC413, aryl coumaran type structures with five-member rings were produced in the end of main chains by nucleophilic attacks of phenoxide ions to  $\text{C}_\beta$ -carbon (Scheme 2) [21,23]. Thus the properties of LC were strongly influenced by interactions of hydroxyl groups.

### 3.2. Interaction between lignophenol and $\text{TiO}_2$

LCs have produced stable composites with nano-sized  $\text{TiO}_2$  with vivid yellow appearances. The equilibrium of these composites was largely declined to composites because HKLC has never been desorbed into any organic solvents. Especially these compounds have been produced with nano-sized  $\text{TiO}_2$  such as ST-01 (Ishihara Sangyo Co.) or the surface of nano-porous  $\text{TiO}_2$  electrodes prepared. Although carboxyl groups of dyes were generally used as anchors on  $\text{TiO}_2$  [27–32], HKLC had few carboxyl or carbonyl groups in the structures as confirmed by FT-IR (data not shown). Therefore, hydroxyl groups were mainly anchored on the surfaces of  $\text{TiO}_2$ . However, the other mechanism of an electron injection has also been implicated because  $I_{\text{sc}}$  was observed by using acetylated HKLC (Fig. 2(b)) as showed in our previous report [21]. Though this mechanism has never been analyzed yet, the interactions with rich  $\pi$ -electrons or methoxyl groups on 1,1-bis(aryl)propanyl structures probably worked as anchors on  $\text{TiO}_2$ .

These compounds probably consisted of phenol– $\text{TiO}_2$  complexes because LC has rich hydroxyl groups. LCs produced complexes between  $\text{C}_\alpha$ -phenolic hydroxyl groups and Ti-ions on the  $\text{TiO}_2$  crystals as well as other phenols [33,34].



Scheme 2. Cleavage of  $\beta$ -O-4 arylether structures by the nucleophilic attacks of phenoxide ions to  $C_{\beta}$ -carbons in alkaline media at 413 K.

These phenolic complexes were produced new broad peaks at 400–600 nm in solid-state UV–vis spectra [21] as observed on other polyphenol–TiO<sub>2</sub> complexes with catechol skeletons [14,15,35,36]. Moreover, these complexes have been easily separated in dilute NaOH solutions under room temperature. HKLC solution showed dark brown appearances by phenoxide ions. In fact, almost 95% of HKLC were soon recovered from HKLC/ST-01 composites in 0.5 M NaOH solution at room temperature. This result indicated that HKLC and TiO<sub>2</sub> electrodes could be recovered from HKLC/TiO<sub>2</sub> electrodes after photo-electricity conversion.

### 3.3. Photovoltaic performance

Photochemical cells with various lignophenols showed stable photovoltaic performances under direct sunlight irradiation or a 150-W Xe lamp irradiation. The cell with Hinoki-lignophenol (phenol type) under the 150-W Xe lamp direct irradiation (177 mW cm<sup>-2</sup>) showed  $V_{oc} = 0.5$  V,  $I_{sc} = 11.5$  mA cm<sup>-2</sup>, FF=0.50 and  $\eta = 1.45\%$  [21]. As it was obvious that results under direct Xe lamp irradiation was strongly influenced of excess UV light, the photovoltaic performances of lignophenol cells were measured through L41 filter with cut of UV (<400 nm) for 99.95%. Under this condition (135.0 mW cm<sup>-2</sup>), the photochemical cell employing HKLC413 showed  $V_{oc} = 0.48$  V,  $I_{sc} = 4.03$  mA cm<sup>-2</sup>, FF=0.54 and  $\eta = 0.77\%$  [22]. As the performances of the cells employing HKLC413 were influenced by wood species like HKLC, softwood lignophenols such as HKLC were always superior to hardwood such as BCLC for 5–10% (Tables 1 and 2). Since only a hardwood lignophenol has 50% of dimethoxyl structures (syringyl units) in lignin core structures as shown in Fig. 2(c), these structures inhibit the interactions of 1,1-bis(aryl)propanyl units with TiO<sub>2</sub>. Furthermore, reflux at 333 K was effective to promote adsorption of HKLC413 (Table 1). Thus the increase of adsorption improved the performance of lignophenol cells.

When LCs have been saturated on the TiO<sub>2</sub> electrodes, the photo-electricity conversion performances were improved drastically (Table 2). An electrode saturated with HKLC413, which has been stocked in 5.0 g dm<sup>-3</sup> acetone solution for four months

Table 1

Photo-electricity conversion performance of photochemical cells with nanoporous TiO<sub>2</sub> electrodes sensitized with lignophenols under visible light irradiation (95.8 mW cm<sup>-2</sup>)

Sample	Photovoltage $V_{oc}$ (V)	Photocurrent $I_{sc}$ (mA cm <sup>-2</sup> )	Fill factor	$\eta$ (%)
BCLC413 <sup>a</sup>	0.437	2.63	0.52	0.62
HKLC413 <sup>a</sup>	0.450	3.18	0.57	0.85
HKLC413 <sup>b</sup>	0.475	5.71	0.54	1.58

<sup>a</sup> Stirring for 24 h at room temperature.

<sup>b</sup> Reflux at 323 K for 3 h. Conditions: light source: 150-W Xe lamp with L41 UV cut filter, 95.8 mW cm<sup>-2</sup>.

at room temperature, showed the best performance under visible light irradiation (85.0 mW cm<sup>-2</sup>). This cell showed  $V_{oc} = 0.51$  V,  $I_{sc} = 10.23$  mA cm<sup>-2</sup>, FF=0.59 and  $\eta = 3.61\%$  as showed in Fig. 3. Generally under irradiation of an incident light with low intensity, a resistance of a solar cell comes down with a decrease of a photo-current, resulting in an increase of a fill factor. Therefore, the efficiency with HKLC413 is probably higher than an actual performance under the standard irradiation condition (AM1.5 condition, 100 mW cm<sup>-2</sup>). Considering this difference in the irradiation, the efficiency with HKLC413 showed probably higher performance than other natural extractives, such as polyphenols.

However HKLC was also saturated on a TiO<sub>2</sub> electrode, the performance (Table 1) was same as the result ( $\eta = 0.81\%$ ) of HKLC413 adsorbed for only 24 h [22]. This result indicated that

Table 2

Photo-electricity conversion performance of photochemical cells with nanoporous TiO<sub>2</sub> electrodes saturated with lignophenols under visible light irradiation (85.0 mW cm<sup>-2</sup>)

Sample	Photovoltage $V_{oc}$ (V)	Photocurrent $I_{sc}$ (mA cm <sup>-2</sup> )	Fill factor	$\eta$ (%)
HKLC	0.484	2.27	0.63	0.81
BCLC	0.458	2.91	0.49	0.76
HKLC413	0.508	10.23	0.59	3.61
HKLC443	0.478	8.11	0.57	2.57

Conditions: light source: 150-W Xe lamp with L41 UV cut filter, 85.0 mW cm<sup>-2</sup>.

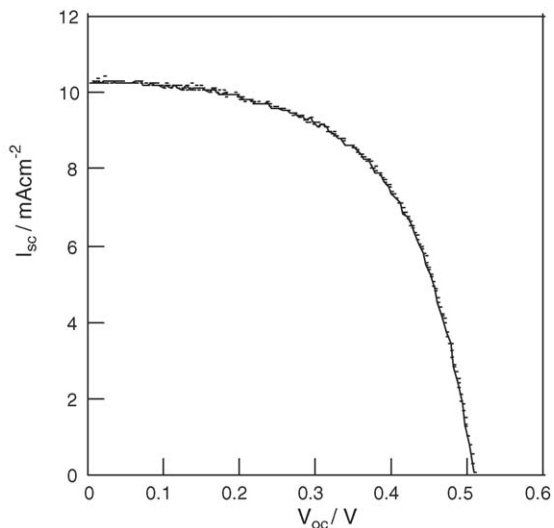


Fig. 3.  $I$ - $V$  curve for a photochemical cell with nano-porous  $\text{TiO}_2$  saturated with lignophenol (*p*-cresol type)-second derivative-I (HKLC413) under visible light irradiation ( $85.0 \text{ mW cm}^{-2}$ ).

HKLC adsorbed only on the surface of the nano-porous  $\text{TiO}_2$  electrode because of a large size of molecules. Since a large average molecular weight of HKLC ( $M_w = 22\,773$ ,  $M_w/M_n = 5.0$ ) has been estimated by GPC, only small fragments could be adsorbed in the electrodes. On the other hand, HKLC413 and HKLC443 probably have been adsorbed on/in the  $\text{TiO}_2$  electrodes because these derivatives involved low molecular weight fractions such as dimers, trimers and oligomers with particular structures on the end of the polymers (Scheme 2), because HKLC413 showed  $M_w = 1\,100$ ,  $M_w/M_n = 2.2$  and HKLC443 showed  $M_w = 711$ ,  $M_w/M_n = 1.8$  estimated by GPC. In fact, an amount of HKLC ( $26.4 \mu\text{mol cm}^{-2}/C_9$ ) was smaller than both HKLC413 ( $50.2 \mu\text{mol cm}^{-2}/C_9$ ) and HKLC443 ( $76.3 \mu\text{mol cm}^{-2}/C_9$ ) on each electrode. Generally a large amount of a photo sensitizer on an electrode promotes a high photo-electricity conversion for a DSC. But the  $I_{sc}$  of HKLC413 was 5 times larger than HKLC, and 1.5 times larger than HKLC443 shown in Table 2. Nevertheless there were larger amounts of HKLC443 on the electrode, the performance was lower than HKLC 413 (Table 2) because 1,1-bis(aryl)propanyl structures were varied. These results indicated these differences in contribution for  $I_{sc}$  were influenced by not only amounts of lignophenol but structural properties. Moreover, both HKLC413 and HKLC443 remained in the electrodes with yellow appearances after NaOH extraction, but only HKLC was removed perfectly. Therefore, these results indicated that small molecules adsorbed on inner spaces but HKLC adsorbed only on the surfaces of electrodes. Furthermore, LCs have kept charge separations on  $\text{TiO}_2$  electrodes at least  $10^{-8}$  s until radical cations were reduced by  $\text{I}^-/\text{I}_3^-$  theoretically [10], because the photo-electricity conversion performances of lignophenol cells have been kept working for several hours. As this result showed LCs could produced stable charge separations on  $\text{TiO}_2$  for a time, lignophenols also can be applied for various electronics devices such as organic conductors or organic electronic luminescence.

#### 4. Conclusion

In this work the photochemical cells with  $\text{TiO}_2$  film electrode sensitized with LCs were investigated with improvement of adsorption by stirring, reflux and long-time adsorption. The effective improvements were both stirring and reflux for adsorption of lignophenols on  $\text{TiO}_2$ . Since HKLC413 has small molecular weight, HKLC413 could adsorb in/on  $\text{TiO}_2$  electrodes. On the other hand, HKLC with large molecular could adsorb only on the surface of  $\text{TiO}_2$  electrodes. The amount of adsorption on  $\text{TiO}_2$  electrode showed  $I_{sc}$  was influenced by not only an amount of lignophenol but also structural properties. Moreover, 1,1-bis(aryl)propanyl units were important structures for photo-electricity conversion because HKLC413 showed a larger photo-electricity conversion than HKLC443 because the aryl coumaran type structure was more effective. The cell with nano-porous  $\text{TiO}_2$  film electrode saturated with HKLC413 showed  $V_{oc} = 0.51 \text{ V}$ ,  $I_{sc} = 10.23 \text{ mA cm}^{-2}$ ,  $\text{FF} = 0.59$  and  $\eta = 3.61\%$  under visible light irradiation ( $85.0 \text{ mW cm}^{-2}$ ). Developments of these cells are expected as indoor small power supplies consisted of sustainable materials because high conversion efficiency was observed under only visible light. Moreover, low  $V_{oc}$  and FF implied this cell can be optimized by choosing combination of electrodes, electrolytes and lignophenols. As lignin is an abundant material that has never sufficiently utilized, these derivatives can be valuable for utilization of biomass as functional materials.

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