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공학석사학위논문

**Eumelanin supported palladium
nanoparticle as a heterogeneous
catalyst for Suzuki cross coupling
reaction in water**

유멜라닌 지지체를 이용한 불균일 팔라듐
나노입자 촉매 개발 및 물내에서 스즈키 교차
짝지음 반응에의 응용

2015년 2월

서울대학교 대학원

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유 재 명

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지도 교수 이 윤 식

이 논문을 공학석사학위논문으로 제출함

2015년 2월

서울대학교 대학원

화학생물공학부

유 재 명

유재명의 공학석사학위논문을 인준함

2014년 12월

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ABSTRACT

Eumelanin supported palladium nanoparticle as a heterogeneous catalyst for Suzuki cross coupling reaction in water

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Eumelanin, which is a biological pigment, is widely distributed in almost all living organism; animals, plants, human skins and hair. The pigment has many distinctive physical and chemical properties such as broad featureless absorption, antibiotic function and conducting property. Eumelanin contains various functional groups like hydroxyl and carboxylic acid groups which exhibit ability to capture metal ions. Thus, eumelanin could be a good candidate as a catalyst support. We have successfully prepared eumelanin supported palladium nanoparticle catalysts from L-DOPA (L-3,4-dihydroxyphenylalanine). As expected, the eumelanin supported palladium nanoparticle catalysts (Eum@Pd NP) exhibited a good catalytic activity in Suzuki cross coupling in water. Even with aryl chlorides, the catalyst gave high yield in water.

Keywords: Eumelanin, Palladium, Heterogeneous Catalyst, Suzuki-Miyaura Reaction, Water

Student number: 2013-20983

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| | |
|---------------------------------|---|
| CH ₃ COONa | sodium acetate |
| Cs ₂ CO ₃ | caesium carbonate |
| DHI | 5,6-dihydroxyindole |
| DHICA | 5,6-dihydroxyindole-2-carboxylic acid |
| FeCl ₃ | iron chloride |
| FT-IR | Fourier transform-infrared spectroscopy |
| GC-MS | gas chromatography/mass spectroscopy |
| HR-TEM | high resolution transmission electron microscopy |
| ICP-AES | inductively coupled plasma-atomic emission spectroscopy |
| K ₂ CO ₃ | potassium carbonate |
| K ₃ PO ₄ | potassium phosphate tribasic |
| KOH | potassium hydroxide |
| L-DOPA | L-3,4-dihydroxyphenylalanine |
| MOF | metal-organic frame |
| Na ₂ CO ₃ | sodium carbonate |
| Na ₃ PO ₄ | sodium phosphate tribasic |
| NaOH | sodium hydroxide |
| NP | nanoparticle |
| Pd | palladium |
| Pd/C | palladium on activated carbon |
| Eum@Pd NP | eumelanin supported palladium NP catalyst |
| TBAB | tertrabutyl ammonium bromide |
| TEA | triethylamine |
| TEM | transmission electron microscopy |
| UV | ultraviolet |
| Vis | visible |
| XPS | x-ray photoelectron spectroscopy |
| XRD | x-ray diffraction analysis |

**Eumelanin supported palladium
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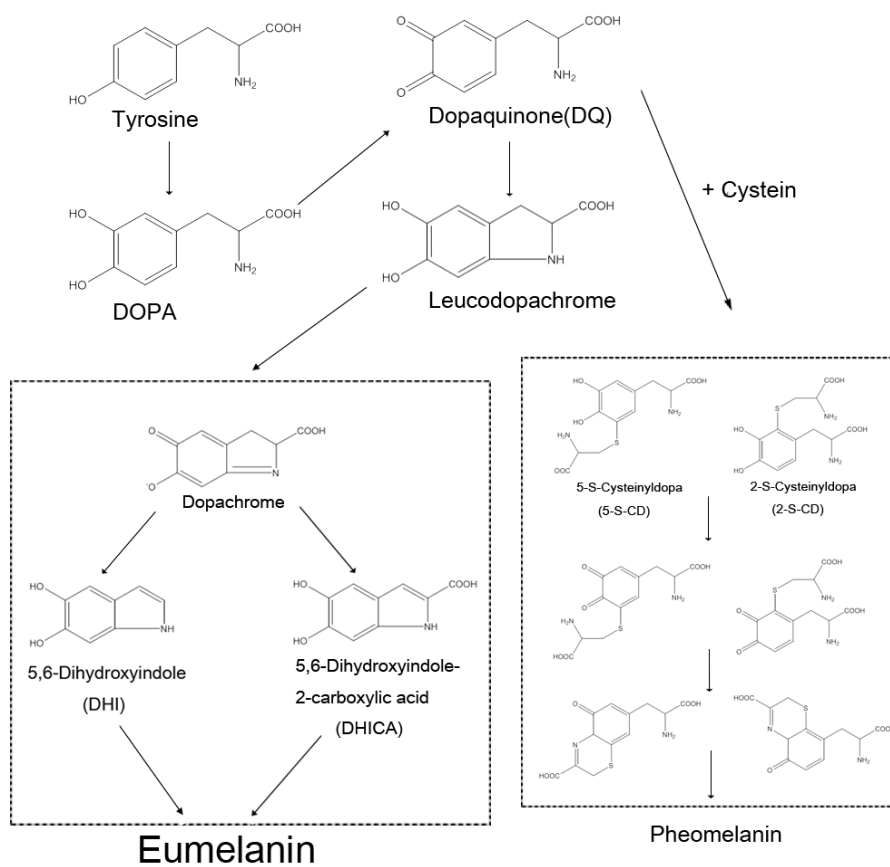
I. Introduction

I. 1. Eumelanin

Melanin is a fascinating biological pigment which can be easily found in nature such as human skin, eyes, animal fur, plants and even in microorganism like fungi.¹ In molecular biology, it is known that melanin is produced by the oxidation of tyrosine (Scheme 1).² The pigment has two distinctive pathways; depending on the participation of cysteine during the oxidation process, the pigment is divided into eumelanin and pheomelanin.³

Eumelanin, the most common type, is an oligomer composed of 3~4 indolic monomers, 5,6-dihydroxyindole (DHI), and 5,6-dihydroxyindole-2-carboxylic acid (DHICA).^{2 4} These chemical structures are important in determining the eumelanin's brown-black color depending on the size of the pigment granule. This implies that the combined effect of repeated absorption and scattering of light within the pigment granules leads to a diffusely reflected light.⁵ The unique properties of eumelain are derived from various functional groups and aggregate-level structure.⁶ These properties which include broad featureless absorption, amorphous organic semiconductor behavior and an ability to capture metal ions are defined by their

physical and chemical properties.^{2 7 8} Because of these unique functions, eumelanin has attracted much attention in various fields across biology, chemistry, and physics. For example, it has been reported that polydopamine thin film, which has similar superstructure to melanin, has electrical conductivities and highly stretchable properties which can be applied as flexible bio-electronic devices.⁹ Also, it has adhesive property that can be applied to surface modification of solid substrates.^{10 11}



Scheme 1. The synthetic pathway of melanin.

I. 2. Heterogeneous Catalyst

Homogenous catalysts have been used in various organic reactions with high turnover number and selectivity.¹² For these reasons, many homogenous catalysts are exploited in industrial field. Despite their advantages, difficulty of its separation and contamination of ligand residue in the final product cause some limitation.¹³

To overcome these problems of homogeneous catalysis, various forms of heterogeneous catalysts have been developed; such as ligand-metal complex on a solid surface, metal-organic frame (MOF),¹⁴ morphology controlled metal nanoparticles (NPs) and metal NP-embedded solid support.^{13 15 16} These heterogeneous catalyst could be easily separated and re-used.^{13 16} Yet, there are still rooms to develop, specially in improving selectivity and performance of the catalyst, and ecofriendly reaction condition.¹⁶

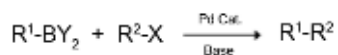
I. 3. Cross Coupling Reaction in Water

Cross coupling reaction is one of the powerful tools in organic chemistry especially in the synthesis of important bioactive molecules.

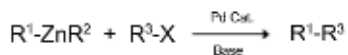
¹⁷ By transition metal catalyst, cross coupling reaction combines two molecular fragments and leads to the formation of new bonds such as C-C, C-N, and C-O. So far, many cross coupling reactions like Suzuki, Negishi, Stille, Heck, and Sonogashira reaction were reported, contributing great progress in organic chemistry. ¹⁶ Specially, Suzuki reaction, as a representative cross coupling reaction, has been reported frequently among these in the past decades. ^{18 19} A typical mechanism for Suzuki cross coupling reactions is summarized in Figure 1. As the reaction is running with zero valent state palladium metal catalysts, many researches studied to improve the performance of the catalysts under mild reaction condition. ^{13 20} As the cross-coupling reactions come with a heavy price to our environment and sustainability, developing non toxic condition and benign solvent system has become a challenge. ^{13 21} In other words, there have been many attempts to develop mild reaction condition like aqueous phase which is not compatible with organic synthesis. For example, various additives like

tertrabutylammonium bromide (TBAB) have been used as a solution for reaction in aqueous media.^{22 23} However, reactions in water without additive are still challenging.

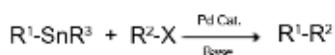
Suzuki reaction



Negishi reaction



Stille reaction



Heck reaction



Sonogashira reaction

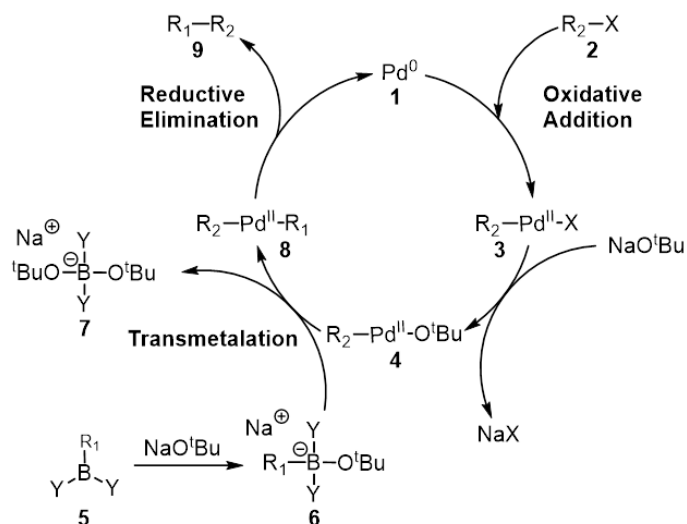
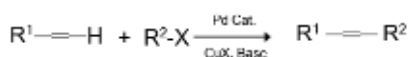


Figure 1. Examples of named cross coupling reaction and catalytic cycle of transition metal catalysed cross coupling reaction.

I. 4. Research Objectives

Eumelanin has metal capturing ability and good water compatibility.⁷⁻²⁴ Due to these properties, it has been used as a versatile coating material for arranging metal ions or nanoparticle (NP) on a target substrate.²⁵⁻²⁶ Through polydopamine coating, inorganic materials such as Au, Ag, Pt, and hydroxyapatite was uniformly aligned on organic or inorganic substrate; RGO, silica nanostructure, and polymer which could be utilized as biomaterials.^{25,27} However, to the best of our knowledge, eumelanin itself has never been used as a support for catalysts, especially, metal NPs. We chose eumelanin as a catalyst support because it can capture metal ions and afford good water compatibility due to its functional groups such as hydroxyl, carboxylic, and amino groups.¹⁻²⁴

Eumelanin supported palladium NP catalyst is prepared by simply adding Pd^{2+} ions with reducing agent into eumelanin solution (Figure 2). Uniform sized palladium NPs (ca. 3 nm in size) on the eumelanin support was successfully fabricated. It has been known that uniform distribution of palladium NPs around 1-10nm size is a key factor for exhibiting good catalytic effect.^{13,28} In addition, it is important to

control the pertinent loading level of metal NPs on the catalyst support, because too much NPs can reduce the surface area of NPs on which the catalytic reaction take places.¹⁵⁻²⁹ So, we controlled the amount of palladium NPs and found the most appropriated condition. Among the cross coupling reactions, Suzuki reaction has been selected as a model reaction for evaluating the eumelanin supported palladium NP catalyst (Eum@Pd NP). The Eum@Pd NP catalyst showed high yield of coupling products under aqueous solvent system.

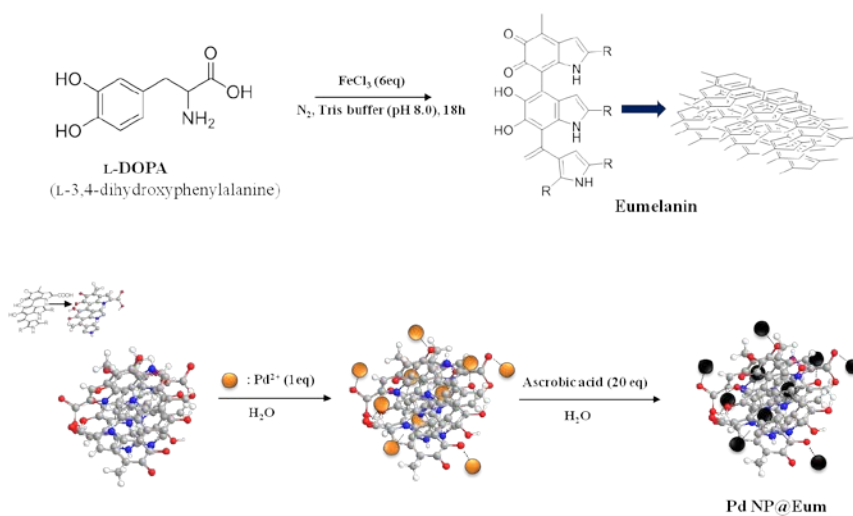


Figure 2. Preparation of eumelanin and Eum@Pd NP.

II. Experimental Section

II. 1. General

II. 1. 1. Materials

L-3,4-Dihydroxyphenylalanine (L-DOPA), iron chloride (FeCl_3), Palladium on activated carbon (10 wt% Pd/C), ascorbic acid, Tris buffer were purchased from Aldrich (St. Louis, MO, USA). Sodium tetrachloropalladate (II) hydrated (Na_2PdCl_4) was purchased from Aesar (USA).

II. 1. 2. Instrument

Eumelanin was characterized by fourier transform-infrared spectroscopy (FT-IR, Nicolet 6700, Thermo Scientific, USA) operating at ATR mode and ultra violet/visible spectrophotometry (OPTIZEN 2120UV, Mecasys, KOR). The loading of palladium on eumelanin was quantified by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPS-1000 IV, Shimadzu, Japan). Palladium 3d binding energy was investigated by X-ray photoelectron spectroscopy (XPS, SIGMA PROBE, ThermoVG, U.K) equipped with a full 180 degree

spherical sector analyzer. The crystal structure of eumelanin supported palladium nanoparticle (NP) was investigated by X-ray diffraction analysis (XRD, D8 Advance, Bruker, Germany). The morphologies of catalyst were investigated by transmission electron microscopy (TEM, JEM-1010, JEOL, Japan) operating at 80 kV and high resolution transmission electron microscopy (HR-TEM, JEM-3010, JEOL, Japan) operation at 300 kV, for which samples were deposited on a 300 mesh coated copper grid. The product yields of Suzuki coupling reactions were measured by gas chromatography/mass spectroscopy (GC-MS, Hewlett Packard).

II. 2. Preparation of Eumelanin Supported

Palladium Nanoparticle

II. 2. 1. Preparation of Eumelanin

L-DOPA (200 mg, 1 mmol) was dissolved in Tris buffer (40 ml, 20 mM). The buffer was previously degassed by bubbling with N₂ gas for 30 min. Iron (III) chloride (987 mg, 6 mmol) dissolved in Tris buffer was added to the L-DOPA. The reaction vessel was kept closed under N₂ condition and stirred vigorously for 18 h. The resulting black precipitate was washed with deionized water to remove any remaining iron salt and unreacted L-DOPA and dried on a freeze dryer. The prepared eumelanin was analyzed with FT-IR and UV/Vis spectroscopy.

II. 2. 2. Preparation of Eumelanin Supported Palladium Nanoparticle

Eumelanin (10 mg) was dissolved in deionized water (5.5 ml) and sodium tetrachloropalladate (II) (3.5 ml, 0.03 mmol) solution in water was added. Thus mixture was stirred for 30min. Finally, excess amount of ascorbic acid (103 mg, 1.36 mmol) as a reducing agent was added and the palladium ions are reduced to palladium NPs which were embedded on eumelanin. The product was washed with deionized water. The prepared catalyst was analyzed with TEM, XPS and XRD.

II. 3. Suzuki Coupling Reactions Catalyzed by Eumelanin Supported Palladium Nanoparticle

II. 3. 1. Optimization of Suzuki Coupling Reaction

Suzuki coupling reaction of chlorobenzene (0.35 mmol) with phenylboronic acid (0.42 mmol) was carried out using eumelanin supported palladium nanoparticle (0.05 mol% Pd) in aqueous solvent system (10 ml). The following bases (1.4 mmol) were examined; Cs_2CO_3 , K_2CO_3 , Na_2CO_3 , K_3PO_4 , Na_3PO_4 , KOH, NaOH, CH_3COONa , and TEA. The reaction mixture were stirred for 4 h at 80 °C in a reaction vessel. To identify the effect of the amount of palladium NP, 20, 30, 40, and 50 wt% palladium embedded eumelanin catalyst were prepared.

II. 3. 2. General Experimental Procedure for Suzuki Coupling

Aryl halide (0.4 mmol), phenylboronic acid (0.48 mmol, 1.2 eq), and a base (1.6mmol, 4 eq) dissolved in deionized water (10 ml) and Eum@Pd NP (0.05 mol% Pd) were added into a reaction vessel (20ml). The mixture was stirred at 80 °C for 4h. After the reaction, the organic products were extracted with diethyl ether (10 ml) and filterated through 0.45 μ m syringe filter. The filtered products were analyzed by gas chromatography/mass spectroscopy (GC-MS).

II. 3. 3. Reaction Profiled of Suzuki Coupling Reaction

Aryl halide (0.4 mmol), phenylboronic acid (0.48 mmol, 1.2 eq), and a base (1.6 mmol, 4 eq) dissolved in deionized water (10 ml) and Eum@Pd NP (0.05 mol% Pd) were added into a reaction vessel (20 ml). The mixture was stirred at 80 °C for a period of 10, 20, 30, 60, 120 minutes. Each reaction mixture was extracted with diethyl ether (10 ml) and filtered through a 0.45 μ m syringe filter. The filtered products were analyzed by GC-MS.

II. 3. 4. Reusability Test of Eumelanin Supported Palladium Nanoparticle

Aryl halide (0.4 mmol), phenylboronic acid (0.48 mmol, 1.2 eq), and a base (1.6 mmol, 4eq) dissolved in deionized water (10 ml) and Eum@Pd NP (0.05 mol% Pd) were added into a reaction vessel (20 ml). The mixture was stirred at 80 °C for 4 hours. After the reaction, the products were extracted with diethyl ether (10 ml) and filtered through a 0.45 µm syringe filter. The filtered products were analyzed by gas chromatography/mass spectroscopy (GC-MS). The catalyst was washed with deionized water and reused 5 times for the same reaction.

III. Results and Discussion

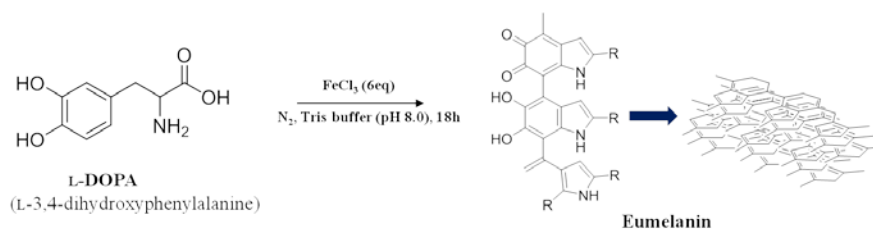
III. 1. Preparation and Characterization of Eumelanin Supported Palladium Nanoparticle

III. 1. 1. Preparation of Eumelanin

Tyrosine which is one of the natural amino acids is a precursor in biological melanin synthesis pathway. We mimicked the synthetic pathway and prepared eumelanin from L-DOPA (L-3,4-dihydroxyphenylalanine) and under a N₂ atmosphere (Scheme 2) to prevent oxidation by oxygen in the air. Iron chloride (Fe³⁺) dissolved in Tris buffer (20 mM) was added to the solution. The reaction vessel was kept closed and under N₂ condition. When Fe³⁺ solution was added to the mixture, the solution color turned green, which indicated that Fe³⁺ ion was coordinated with L-DOPA and the L-DOPA turned into primary oxidized structures; 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole-2-carboxylic acid (DHICA). As the reaction mixture was kept stirring for further oxidation, eumelanin was formed and the color became black.³⁰ The mixture was further stirred vigorously for 18 h. The resulting black precipitate was washed several times by deionized water to remove any remaining iron salt and unreacted L-DOPA. Finally, the black powder was dried by a freeze dryer and the structure was confirmed by UV-visible absorption and FT-IR analysis. As shown in Figure 3, the final product shows broad UV-visible absorption, which is one of the

unique properties of eumelanin. Before the oxidation, a peak at $\lambda \cong 280$ nm was observed, which was attributed to aromatic rings of L-DOPA. The peak was considerably reduced and broadened after the oxidative coupling. This is typical eumelanin's broad-band UV absorbance spectra.⁷

IR spectroscopy is an important tool for a better understanding of the structure of eumelanin. Figure 4 shows an overlay of the FTIR spectra of synthetic eumelanin and L-DOPA. Before oxidation, the absorption band at 3334 cm^{-1} represents the amide N-H groups. The peaks at 3000 , 2950 and, 1350 cm^{-1} represent C-H stretching bands. The band at 1500 cm^{-1} indicates aromatic C-C stretch and the bands from 1290 to 1190 cm^{-1} are attributed to carboxylic acid and aliphatic amine groups. Also, the bands from 860 to 680 cm^{-1} indicate aromatic C-H bending. After oxidation, eumelanin had identical absorption band at around 3200 cm^{-1} (O-H or N-H regions) and 1600 cm^{-1} (aromatic C-C stretch). The band from 1290 to 1200 cm^{-1} are attributed to the aromatic amines and carboxylic acids, which suggests that primary amines in L-DOPA became a secondary amine by a ring closure reaction³¹ and that eumelanin was successfully prepared from L-DOPA.



Scheme 2. Synthesis of eumelanin.

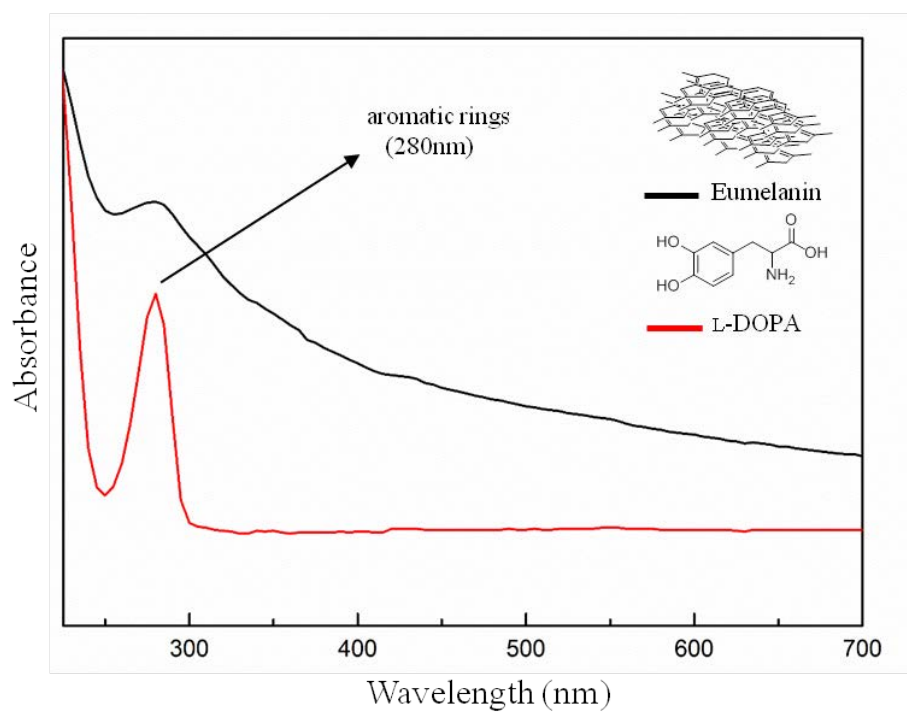


Figure 3. UV/vis absorption spectra of L-DOPA and Eumelanin.

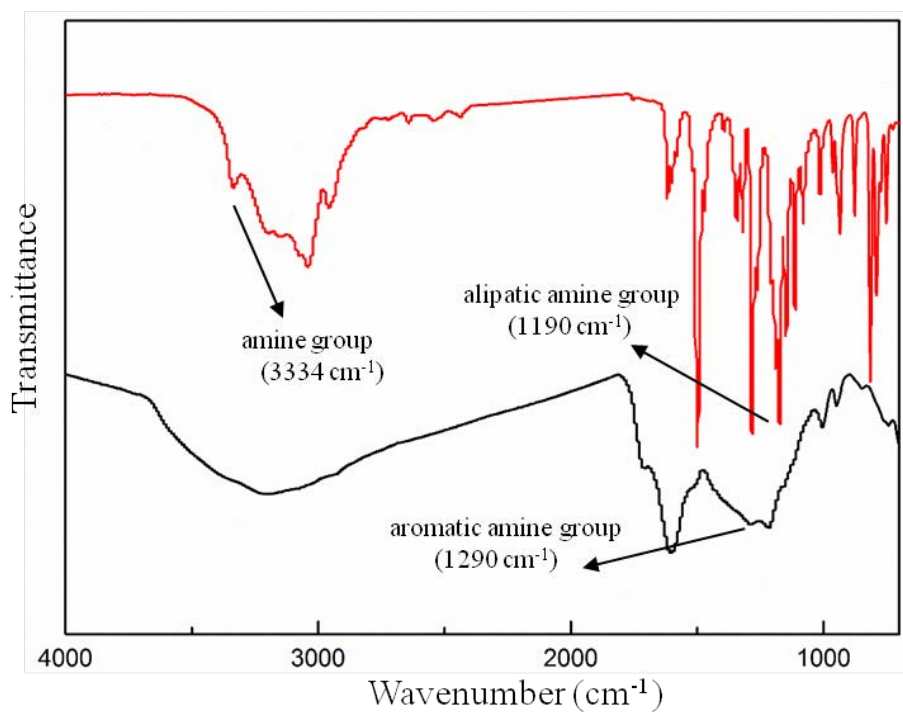


Figure 4. FT-IR spectra of L-DOPA and Eumelanin.

III. 1. 2. Characterization of Eumelanin Supported Palladium Nanoparticle

The catalyst's morphological changes and the embedded palladium nanoparticles was verified by the transmission electron microscopy (TEM) and X-ray diffraction (XRD). TEM images of Fig 5 shows that amorphous like eumelanin is prepared from L-DOPA. After introducing palladium NPs, the morphology of eumelanin was changed. As the palladium loading amount was increased, the eumelanin became more regularly shaped. Small size of palladium NPs (2-3 nm) was observed and its lattice spacing value is about 0.23nm, which indicates that {111} crystal plane spacing of palladium metal was formed (Figure 6). From XRD patterns and XPS of Eum@Pd NP catalyst, we could confirm more accurately about the state of palladium NPs. 2θ values of 40.1, 46.8, 68.1, 82.2, and 86.5 correspond to the {111}, {200}, {220}, {311}, and {222} reflections of face-centered cubic (fcc) palladium NP catalyst (Figure 7).^{32 33} Also Pd peak at 334.97 eV corresponds to Pd(0) species (Figure 8).³³
³⁴ These results confirm that palladium NPs were well-embedded on the eumelanin and Eum@Pd NP was successfully prepared.

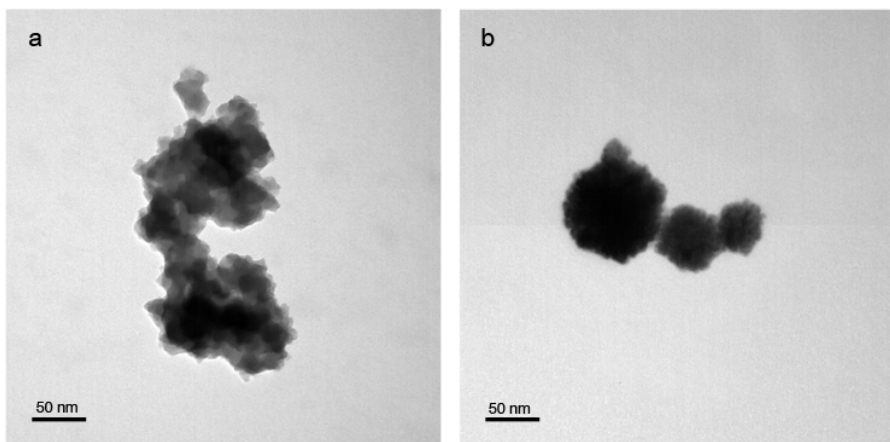


Figure 5. TEM images of (a) eumelanin, and (b) Eum@Pd NP.

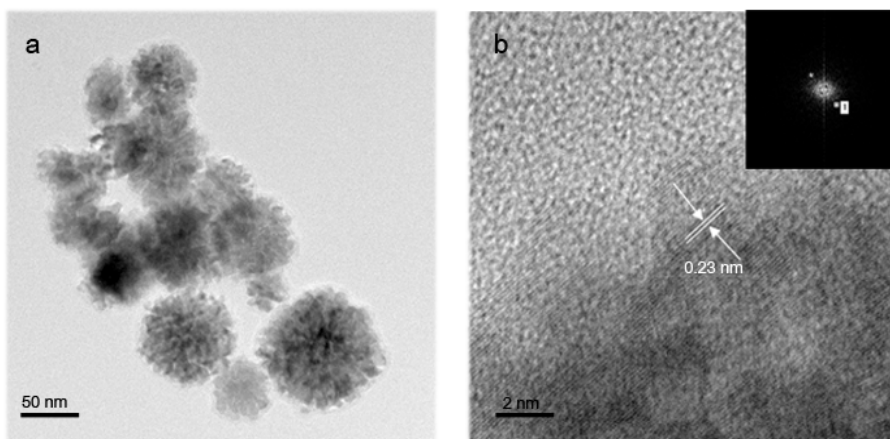


Figure 6. HR-TEM image of Eum@Pd NP.

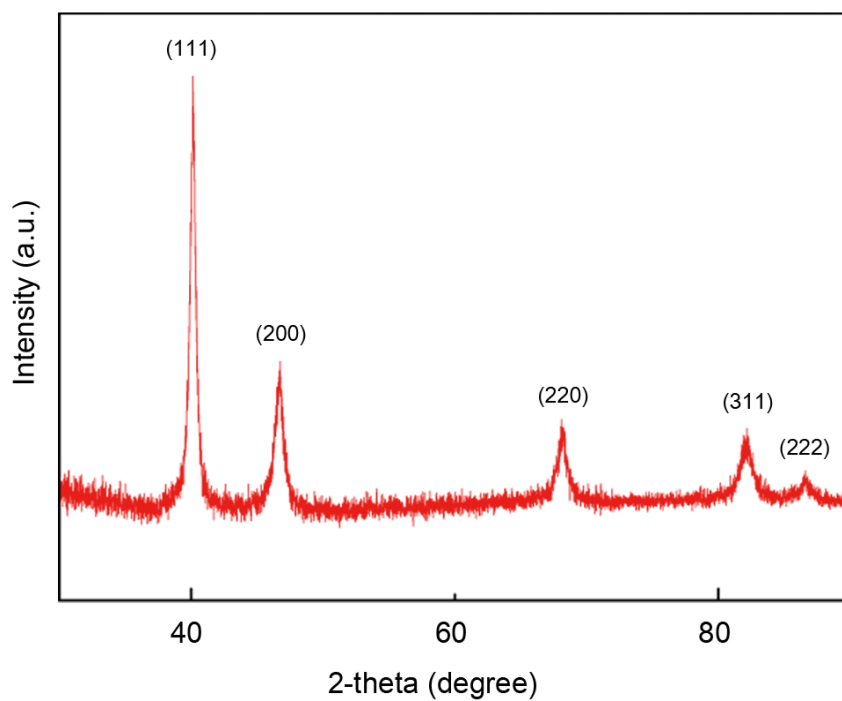


Figure 7. XRD data of Eum@Pd NP.

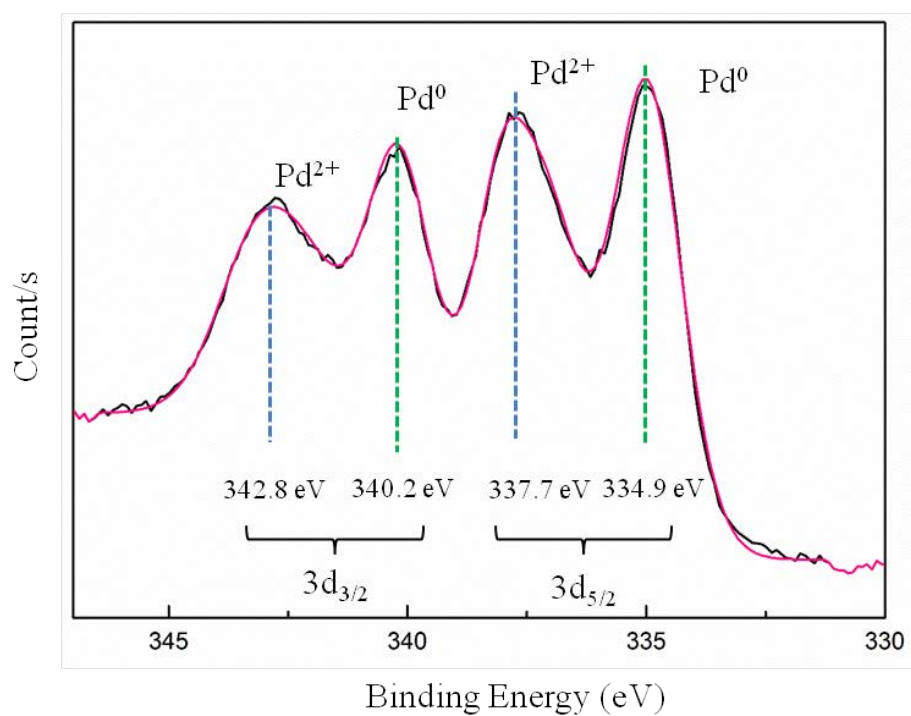


Figure 8. XPS Spectra of Eum@Pd NP.

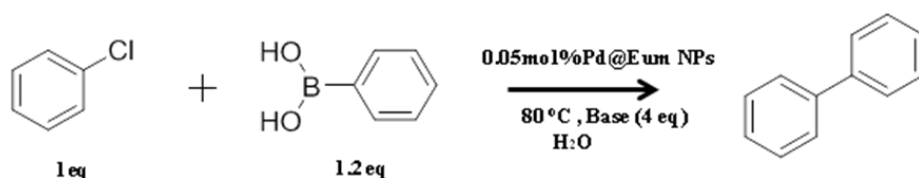
III. 2. Suzuki Coupling Reaction Catalyzed by Eumelanin Supported Palladium Nanoparticle

III. 2. 1. Effects of Bases and Palladium NPs Suzuki Coupling Reaction.

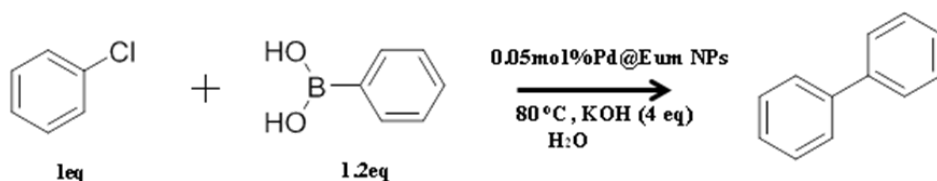
A model reaction of Suzuki coupling reaction of chlorobenzene with phenylboronic acid was carried out to optimize the reaction condition using the Eum@Pd NP as a catalyst. First, Suzuki coupling reactions were carried out with the following bases; Cs_2CO_3 , K_2CO_3 , Na_2CO_3 , K_3PO_4 , Na_3PO_4 , KOH , NaOH , CH_3COONa , and TEA , using 20 wt% eumelanin supported palladium NP as a catalysts (0.05 mol% Pd) (Table 1). TEA which is an organic base, turned out to be not suitable in aqueous solvent system. The results with Cs_2CO_3 , Na_2CO_3 , K_3PO_4 , and CH_3COONa were about the same, and KOH and NaOH showed the best yield. Thus KOH was used in the following Suzuki coupling reactions.

The amount of palladium ions added during the catalysts preparation process determined the contents of palladium NP embedded on the eumelanin. For good catalytic effect, we need to find out the most appropriate quantity of palladium ions which can give uniform distributions of palladium NPs around 1-10 nm size. To compare the activities of the catalysts, Suzuki reaction was performed

(Table 2), using KOH as a base. While catalysts 1-4 gave the coupling product with 99, 96, 98 and 99 % conversion in 2 h, and only 4 showed better activity (28 %) in 1 h reaction time, exhibited a good catalytic activity with a turnover number (TON) of 1980 and turnover frequency (TOF) of 990 h⁻¹.



Scheme 3. Effect of various bases in Suzuki coupling reaction of chlorobenzene with phenyl boronic acid in water.



Scheme 4. Effect of the amount of Pd NPs in Suzuki coupling reaction of chlorobenzene with phenyl boronic acid in water.

Table 1. Effect of various bases in Suzuki coupling reaction of chlorobenzen with phenyl boronic acid^a

| Entry | Base | Yield (%) ^b |
|-------|---------------------------------|------------------------|
| 1 | Cs ₂ CO ₃ | 26 |
| 2 | K ₂ CO ₃ | 9 |
| 3 | Na ₂ CO ₃ | 35 |
| 4 | K ₃ PO ₄ | 50 |
| 5 | Na ₃ PO ₄ | 9 |
| 6 | KOH | >99 |
| 7 | NaOH | >99 |
| 8 | CH ₃ COONa, | 43 |
| 9 | TEA | 17 |

^aReaction conditions: Chlorobenzene (0.4 mmol, 1eq), phenylboronic acid (0.48 mmol, 1.2eq), Eum@Pd NP catalyst (0.05 mol%) in H₂O (10 ml) at 80 °C for 2 hours. ^bDetermined by GC analysis.

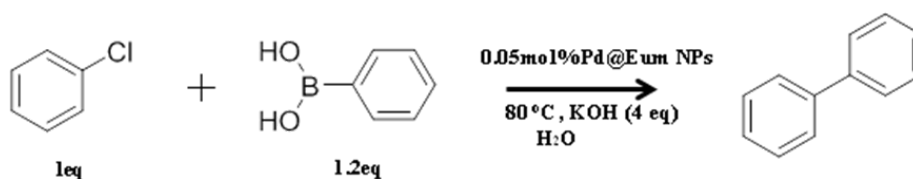
Table 2. Effect of the amount of Pd NPs in Suzuki coupling reaction of chlorobenzen with phenyl boronic acid^a.

| Entry | Time (h) | Yield (%) |
|-------|----------|-----------|
| 1 | 1 | 7 |
| | 2 | >99 |
| 2 | 1 | 12 |
| | 2 | >99 |
| 3 | 1 | 12 |
| | 2 | >98 |
| 4 | 1 | 28 |
| | 2 | >99 |

^aReaction conditions: Chlorobenzene (0.4 mmol, 1eq), phenylboronic acid (0.48 mmol, 1.2eq), KOH (1.6 mmol, 4eq), Eum@Pd NP catalyst (0.05 mol%) in H₂O (10 ml) at 80 °C for 2 hours. ^bDetermined by GC analysis.

III. 2. 2. Reaction Profile of Suzuki Coupling Reaction

To establish proper reaction time, Suzuki reaction of chlorobenzene with phenylboronic acid were performed in 10, 20, 30, 60, and 120 minutes intervals. From the results, we found out that the induction period was around 10 minutes and the activity of the catalyst reached its maximum in 120 minutes (Figure 9). Thus, 120 minute reaction time was used in the following Suzuki coupling reactions.



Scheme 5. Reaction profiles of the Suzuki coupling reaction of chlorobenzene with phenylboronic acid in water.

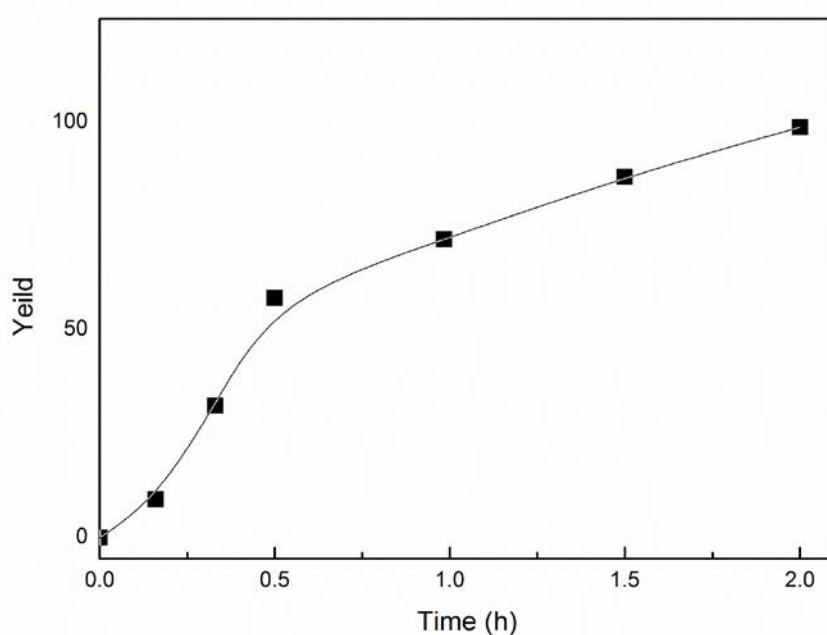
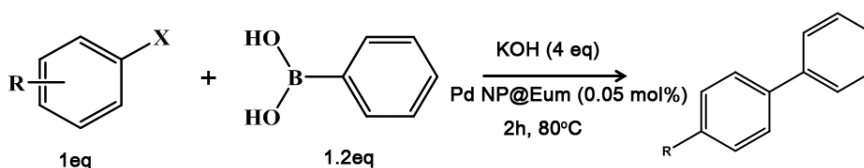


Figure 9. Reaction profiles of the Suzuki coupling reaction of chlorobenzene with phenylboronic acid.


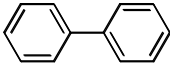

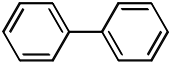

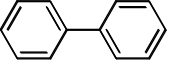

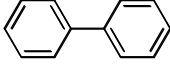

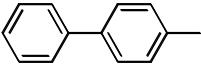

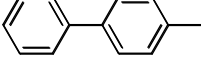

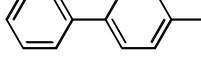

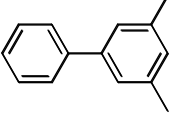

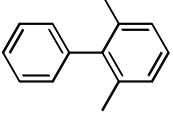

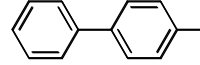
III. 2. 3. Suzuki Coupling Reaction of Various Aryl Halides with Phenylboronic Acid in Water

Suzuki coupling reaction of various aryl halides with phenyl boronic acid was performed in water. Almost all the aryl halide were converted to the biaryls in excellent yields in water. Deactivated aryl bromide as well as aryl chlorides were also converted to the corresponding biaryl compounds (Table 3). To compare the effect of catalytic activity, palladium on activated carbon (10 wt% Pd/C) was tested as a control, which showed low activity in Suzuki reaction (entry 17). Unfortunately, 2-bromo-1,3-dimethylbenzene did not give satisfactory yields due to the existence of steric hindrance (entry 9 in Table 3). Also due to strong electron donating group, 2-chloroanisole and 4-chloroanisole gave low yields (entry 14 and 15 in Table 3).




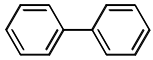

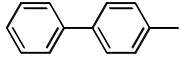

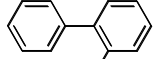

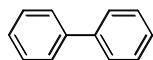

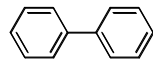

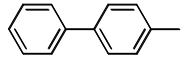

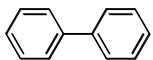
Scheme 6. Suzuki coupling reaction of various aryl halides with phenyl boronic acid in water.

Table 3. Suzuki coupling reaction of various aryl halides with phenylboronic acid^a

| Entry | Time | Substrate | Product | Yield |
|-------|------|---|--|-------|
| 1 | 2 |  |  | >99 |
| 2 | 2 |  |  | >99 |
| 3 | 2 |  |  | >99 |
| 4 | 2 |  |  | 85 |
| 5 | 2 |  |  | 92 |
| 6 | 2 |  |  | 90 |
| 7 | 2 |  |  | 82 |
| 8 | 2 |  |  | 49 |
| 9 | 2 |  |  | 18 |
| 10 | 2 |  |  | 90 |

^aReaction conditions: Aryl bromide (0.4 mmol, 1 eq), phenylboronic acid (0.48 mmol, 1.2 eq), KOH (1.6 mmol, 4 eq), Eum@Pd NP catalyst (0.05 mol%) in H₂O (10 ml) at 80 °C for 2 hours. ^bDetermined by GC analysis.

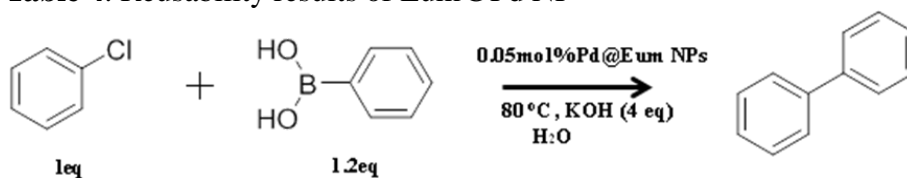
Table 3. Suzuki coupling reaction of various aryl halides with phenylboronic acid^a (continued)

| Entry | Time | Substrate | Product | Yield(%) |
|-------|------|---|---|----------------|
| 11 | 2 |  |  | >99 |
| 12 | 2 |  |  | >99 |
| 13 | 2 |  |  | 91 |
| 14 | 2 |  |  | 36 |
| 15 | 2 |  |  | 38 |
| 16 | 2 |  |  | >99 |
| 17 | 2 |  |  | 0 ^c |

^aReaction conditions: Aryl chloride (0.4 mmol, 1 eq), phenylboronic acid (0.48 mmol, 1.2 eq), KOH (1.6 mmol, 4 eq), Eum@Pd NP catalyst (0.05 mol%) in H₂O (10 ml) at 80 °C for 2 hours. ^bDetermined by GC analysis. ^cPd/C was used as a catalyst.

III. 2. 4. Reusability Test of Eumelanin Supported Palladium Nanoparticle for Suzuki Coupling Reaction

To evaluate the reusability of the catalysts which is one of the major advantage of heterogeneous catalyst, recycling test was proceeded in Suzuki coupling reaction with chlorobenzene at 80 °C (Table 4). After each reaction, the product was recovered by diethyl ether extraction and analyzed by gas chromatography. As shown in Table 4, the reaction yielded biphenyl in high yield in the first cycle, affording good catalytic activity. However the conversion yield was decreased, probably due to the palladium NPs leaching. We supposed that the hydroxyl groups in eumelanin were deprotonated under basic condition and then weaken the structure of palladium NPs on eumelanin.³⁵

Table 4. Reusability results of Eum@Pd NP^a

| | 1 st | 2 st | 3 st | 4 st | 5 st |
|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Yield (%) | 99 | 74 | 6 | - | - |

^aReaction conditions: Chlorobenzene (0.4 mmol, 1 eq), phenylboronic acid (0.48 mmol, 1.2 eq), KOH (1.6 mmol, 4 eq), Eum@Pd NP catalyst (0.05 mol%) in H₂O (10 ml) at 80 °C for 2 hours. ^bDetermined by GC analysis.

IV. Conclusions

Eumelanin supported Pd NP catalyst was developed and tested as a heterogeneous catalyst for Suzuki coupling reaction in water. With small amount of the catalyst (0.05 mol%), eumelanin supported palladium NP exhibited a good catalytic activity. Even aryl chlorides could be activated with the catalysts. Although there are still more issues to be addressed such as chemical stability under basic condition, our results afforded a remarkable advancement which opens a new avenue in developing heterogeneous catalysts.

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요 약

본 연구에서는 탄소-탄소 결합 반응을 촉진시키기 위해 유멜라닌 지지체를 이용한 불균일상 Pd 나노입자를 개발 하였다. 먼저 L-도파를 염화 철을 이용하여 수용액 상에서 산화시켜 유멜라닌을 합성하였고 이렇게 얻어진 유멜라닌은 비결정성 구조를 가졌으며, 이는 TEM, UV/vis 및 IR 분광법을 통해서 분석 하였다. 물에 잘 분산되는 유멜라닌은 수용액 상에서 Pd^{+2} 이온과 잘 섞였고 아스코빅산을 이용하여 환원시켜 Pd 나노입자를 합성 하였다. 이 불균이상 나노입자 촉매의 구조는 ICP-AES, TEM, XRD 및 XPS 분석을 통해 규명 할 수 있었다. 이렇게 만들어진 촉매는 수용액 상에서 탄소-탄소 결합 반응인 Suzuki 반응에서 2시간에 90%이상의 수율을 보이는 우수한 촉매 활성을 보였다. 특히 반응에 참여하기 어렵다고 알려진 알릴 클로라이드 화합물도 성공적으로 반응에 참여하였다. 비록 염기 환경에서 유멜라닌의 화학 안정성이 좋지않아 촉매 회수에 어려움이 있었으나 가교결합 같은 추가적인 반응을 활용한다면 재활용 실험에서 좋은 결과를 보일 것으로 기대된다.