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Biosynthesis of supported Pd nanoparticles using *Poplar* leaf as a reducing agent and carrier: A green route to highly efficient and reusable Suzuki coupling reaction catalyst

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Abstract

A green process for the synthesis of supported Pd nanoparticles (NPs) using *Poplar* leaf extract (PLE) as a reducing agent and the extracted residue of *Poplar* leaf (RPL) as a carrier is reported. The Pd/RPL nanocomposites were characterized by XRD, TEM, SEM, EDS, XPS, FTIR and ICP-AES. The spherical PdNPs had a mean particle size of 3.1 nm and were evenly distributed on the RPL surface. More importantly, the Pd/RPL nanocomposites was used as a heterogeneous catalyst, which presented superior catalytic activity for the Suzuki coupling reaction. In addition, only a slight loss in the catalytic activity was observed after six recycles.

Keywords

Pd nanoparticles; Biosynthesis; Heterogeneous catalyst; Poplar leaf; Suzuki coupling reaction

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1. Introduction

The Suzuki coupling reaction is a powerful and popular reaction in the field of organic synthesis [1], because it is widely used to construct C-C bonds for synthesis biaryl compounds, which are often considered as partial structures in natural products [2, 3], pharmaceuticals [4] and advanced functional materials [5].

Traditionally, the coupling reactions are catalyzed by homogeneous Pd catalyst, which is coordinated with different ligands or other protective agents to produce water-soluble catalysts [6, 7] and can provide high reaction rate or high yield [8-10]. However, the main defect for this catalytic systems is the product separation and the catalyst reuse in consecutive reactions. In order to overcome these problems, heterogeneous Pd catalysts have got a considerable concern in recent years [11-13]. Numerous efforts have been made to immobilize Pd on a variety of solid supports, such as microporous polymers [14], nano-silica [15],TiO₂ [16] and carbon materials [17, 18], which made the catalyst easy to be separated from the reaction mixture by centrifugation.

The synthesis of Pd NPs were employed by chemical or physical methods, which requires high pressure, energy and toxic chemicals. From the 'green chemistry' point of view, the utilization of biological systems has been became a new method for the synthesis of metal NPs, because it is suitable to develop a low-cost, reliable and eco-friendly route for preparation nano materials [19, 20]. An amount of effort has been committed to green synthesis of metal NPs using bacteria [21-24], fungi [25-27], and plants [28-31]. Among the various biosynthetic methods, the synthesis of metal NPs using plants, which is a low-cost and renewable resources, has more

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benefits over microbes, which require high-cost to maintain microbial cultures and downstream processing.

Poplar is the *Salicaceae* family plant that widely distributed in the world. The main classes of secondary metabolites presented in this plant are alkaloids, terpenes, tannins, phenolic glycosides and flavonoid [32, 33]. Due to these potential antioxidant compounds exist in this plant. So it can serve as a good and green source for the reduction of Pd²⁺ to synthesize metal Pd NPs. Although the present study on biological methods for synthesis of Pd NPs was attracted widespread attention. There is no report on employing the extracted residue of plants as the carrier to synthesize supported Pd NPs.

In this work, we present a 'green' method for the synthesis of supported Pd NPs using *Poplar* leaf extract as the reducing agent and the extracted residue of *Poplar* leaf as the carrier. Surprisingly, the as-prepared Pd/RPL complexes could serve as a heterogeneous catalyst, which exhibited excellent catalytic activity for the Suzuki coupling reactions. In addition, only a slight loss in the catalytic activity was observed after six recycles.

2. Materials and Methods

2.1. Instruments and reagents

The *Poplar* leaves were collected from in and around Harbin, Heilongjiang, China. All chemicals were purchased from Tiajin Kermel and Sinopharm Chemical Reagent Co., Ltd. And all the chemicals were used without further purification. XRD analysis were recorded by a Bruker D8 advance diffractometer equipped with Cu Kα radiation. TEM was obtained on a

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JEM-2100FX-200kV. ICP-AES was detected by ICP-7510 (Shimadzu). SEM was performed on a JEOL IT300. FTIR spectra was recorded on Avatar Nicolet 6700 using pressed KBr pellets with a scanning range from 500 to 4000 cm⁻¹. X-ray photoelectron spectrometer (XPS) analysis was conducted on a Kratos AXIS ULTRA DLD spectrometer with Al X-ray source. 2.2. Preparation of PLE and RPL

The sundried *Poplar* leaves were milled. Then, 2 g of the milled powder was added into 100 ml deionized water and refluxed at 50°C for 30 min. The PLE obtained was centrifuged at 4000 rpm and filtered through Whatman No.1 filter paper. The filtrate was collected in an Erlenmeyer flask and stored at 4°C for further use. The filter residue was the RPL, which serves as the carrier for immobilization Pd NPs.

2.3. Synthesis of Pd/RPL catalysts

To synthesize the Pd/RPL nanocomposites with 5 wt% Pd, which denoted as $Pd_{0.05}/RPL$, RPL (0.2 g) was dispersed in the Na₂PdCl₄ solution (10 ml, 0.01 M) and impregnated for 12 h at room temperature. Then, the Pd²⁺ was adsorbed on the RPL surface. Subsequently, 10 ml of the PLE was added into this precursor mixture with stirring. The color of the mixture gradually changed from light yellow to deep black in 2 h at 80°C. It indicated that reduction of Pd²⁺ to Pd⁰ was completed around 2 h. For comparison, Pd_{0.01}/RPL, Pd_{0.03}/RPL and Pd_{0.10}/RPL nanocomposites were synthesized under the same experimental conditions.

2.4. Catalytic Suzuki Coupling Reactions

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Aryl halides (2.5 mmol), K₂CO₃ (5 mmol), EtOH (15 mL), H₂O (15 mL) and

Pd_{0.05}/RPL (0.1 mmol%) were uniformly mixed. Then, phenylboronic acid (3.75 mmol) was added into the mixture with vigorous stirring at 60°C. After the reaction, the product (5 ml) was added to NaOH (0.2 mol/L, 5 ml) and extracted with EtOAc (10 ml). Then, the product yields were determined by HPLC analysis.

2.5. Catalyst recyclability

After the reaction, the catalyst was collected by centrifugation step and washed several times with H_2O and EtOAc. In order to investigate the level of reusability and activity of the present catalyst. The recovered catalyst was reused for the coupling reaction of 4-bromotoluene with phenylboronic acid.

3. Results and discussion

3.1. Mechanism of synthesis of Pd/RPL

The RPL is mainly composed of hemicellulose and cellulose. These nature compounds come into being slight negative charge on the RPL surface, because of the hydroxyl ionization when dispersed in water [34]. Under the electrostatic interaction, the Pd²⁺ can be absorbed on the RPL surface. It can occur in mixing of RPL in Na₂PdCl₄ solution at the beginning of the process.

In addition, potential antioxidant compounds, such as alkaloids, terpenes, tannins, phenolic glycosides and flavonoid, in this plant extract will be supplied the required reducibility functional groups (-OH), which can be responsible for the reduction of Pd²⁺ to synthesize metal Pd NPs. The synthesis of Pd NPs supported on the RPL is schematically represented in Fig. 1.

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3.2. UV-vis Analysis

The reduction process of the Pd NPs was monitored by UV-visible spectroscopy at 240-800 nm. Fig. 2 shows the absorption spectra of palladium colloidal solution at 0.5 h intervals. The absorption bands appearing in the contrast spectrum of Na₂PdCl₄ solution were ascribed to the ligand-to-metal charge-transfer transition of the Pd (II) ions. The absence of absorption peak above 420 nm in all of the samples indicates that the initial Pd (II) species was adequately reduced to Pd (0). It was observed from Fig. 2 that the optimal time for the formation of Pd NPs was 2 h.

3.3. TEM and ICP-AES Analysis

In Fig. 3, the TEM images are further investigated the size and morphology of the Pd NPs, which are supported on the RPL surface. With low palladium loads (1 wt% and 3 wt%), the spherical Pd NPs are quantitatively sparse dispersed on the RPL surface (Fig. 3a and b). At appropriate palladium loads (5 wt%), the spherical Pd NPs are more uniformly dispersed and well aligned on the RPL surface (Fig. 3c). According to the particle size distribution histograms the average particle size of the Pd_{0.05}/RPL is 3.12 nm (Fig. 3g), smaller than Pd_{0.01}/RPL (5.2 nm, Fig. 3e), Pd_{0.03}/RPL (5.0 nm, Fig. 3f) and commercial 5wt % Pd/C (5.7 nm, Fig. S1). The high-resolution transmission electron microscopy (HRTEM) pattern further indicated that the Pd crystal plane is 0.224 nm (Inset Fig. 3C), which is corresponded to the lattice spacing of the (111) plane of metallic Pd [35]. When the Pd loads increase to 10 wt%, which leads to the formation of non-spherical Pd NPs, such as triangular, cubic and rod structures (Fig. 3d). It may

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be due to the lack of biomolecules to act as capping agents, so that the most of non-spherical Pd NPs are formed and the average particle size increase to 10.5 nm (Fig. 3h). Apparently, it was found that the Pd/RPL complexes have been successfully synthesized with the small-sized Pd NPs highly distributed on the RPL in an appropriate Pd loads (5 wt%). The exact amounts of Pd in Pd_{0.05}/RPL are detected by ICP-AES and the content of Pd is 4.56 wt%.

3.4. XRD analysis

The X-ray diffraction was used to confirm the crystalline phase of the Pd/RPL complexes (Fig. 4). With the low Pd loading of 1wt% (Fig. 4a), the peak of Pd NPs are not obvious due to the relatively broad reflexes indicating that the quantitatively sparse or small size of Pd NPs are random dispersion on the RPL surface. The result showed that no the characteristics diffraction peak of Pd is observed by XRD up to a Pd loading of 3wt%. Only a broad (111) and a weak (200) peak of metallic Pd are observed (Fig. 4b). Up to a Pd loading of 5 wt% and 10 wt% (Fig. 4c and d), the peaks located at 40.1°, 46.1° and 67.9° are observed, which are indexed to the lattice planes of (111), (200) and (220), respectively. And this correspond to the Bragg reflections of face the centered cubic (fcc) structure of Pd (JPDS 87-0643) [36].

3.5. XPS Analysis

The XPS spectrum of the Pd 3d region for the $Pd_{0.05}/RPL$ complexes is shown in Fig. 5. The peak at 340.6 eV (3d_{3/2}) and 335.2 eV (3d_{5/2}) belong to Pd⁰, and the other peaks at 342.3 eV (3d_{3/2}) and 337.1 eV (3d_{5/2}) were assigned to Pd²⁺ [37]. On the basis of the peak areas analysis, the percent of zero-valent Pd in the Pd_{0.05}/RPL is 70%. A possible reason for the existence of Pd²⁺ is that the reduction of Pd²⁺ does not been proceed to completion during the fabrication.

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Another reason is that the exposed zero-valent Pd can be further oxidized into divalent Pd at ambient conditions.

3.6. SEM and EDS Analysis

The SEM image of $Pd_{0.05}$ /RPL catalyst is shown in Fig. 6a. It can be observed that the sample was consist of platelet-like sheets which consists of crushing plant cell walls. In Fig. 6b, the EDS spectrum of $Pd_{0.05}$ /RPL shows that the nanocomposite is consisted of C, O and Pd. And the Pd atomic ratio of the sample was 6.15%, approximately equal to the theoretical value.

3.7. FT-IR Analysis

As show in Fig. 7a, the FTIR absorbance peaks of PLE appear at 3400, 2923, 1728, 1600, 1396, 1265 and 1072, cm⁻¹ which are corresponding to O-H stretching vibration (3400 cm⁻¹), carbonyl group (C = O, 1728 and 1600 cm⁻¹), C-H bending vibration of alkane (2923 and 1265 cm⁻¹), C-OH (1396 cm⁻¹) and C-O-C (1072 cm⁻¹) stretching vibrations, respectively. Compere with PLE and Pd NPs revealed that the intensity of peaks at 1600, 1396 and 1072 cm⁻¹ decreased after the reaction. Based on the above analysis, we speculate that the water soluble heterocyclic compounds such as alkaloids, terpenes, tannins and phenolic glycosides can be acted as a reducing agent for the reduction Pd²⁺ to synthesize metal Pd NPs. And the protein compounds, with the (NH)-C = O groups, can serve as the stabilizing agent for protecting the Pd NPs.

Comparison between the FTIR spectrum of RPL and $Pd_{0.05}/RPL$ (Fig. 7b), the peaks at 1325 and 779 cm⁻¹ were distinct weakening after the reaction, which indicates that there is a covalently coupled interaction between the Pd NPs and the RPL in the Pd/RPL complexes.

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3.8. Catalytic Activity Evaluation

The Suzuki coupling reaction of 4-bromotoluene with phenylboronic acid (Scheme.1) was selected to compare the catalytic activity of the Pd/RPL complexes (1, 3, 5 or 10 wt%) and commercial 5 wt% Pd/C (denoted as $Pd_{0.05}/C$). The reaction was carried out in a rather mild condition using EtOH/H₂O (1:1) as solvent and K₂CO₃ as base with low amount of catalyst (0.1 mmol%) at 60°C.

Fig. 8 shows the yields of biphenyl at different intervals with various catalysts. In all of the catalysts, the $Pd_{0.05}$ /RPL exhibits the best and faster catalytic activity, the yield of 4-bromotoluene reached to 98.2% with 0.1 mmol% catalyst at 60°C for 30 min. Lower catalytic activity is obtained with the high Pd loads (10 wt%) and the low Pd londs (1 wt%), due to the increase of the particle size and reducing of the degree of dispersion, respectively. This result is also supported by TEM analysis. Therefore, the amount of dispersion and size uniformity are the key factors that determine the catalytic activity of catalysts. In addition, the Pd_{0.05}/RPL has a higher catalytic activity than the commercial 5wt % Pd/C (denoted as Pd_{0.05}/C). The excellent catalytic activity can be attributed to the close interaction between the Pd NPs and rich hydroxyl groups on the surface of RPL, which is beneficial to obtain the well-dispersed and small Pd nanoparticles.

In order to prove catalyst heterogeneity, the possible presence of dissolved palladium was investigated. After the coupling reaction had completed, the hot-filtered mother liquor was reacted with fresh substrates. No product was detected even after 30 min (Fig. 9). This result indicates that $Pd_{0.05}/RPL$ nanocomposite is indeed heterogeneous catalysts in the Suzuki

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coupling reaction. Furthermore, an ICP analysis of the hot-filtered mother liquor and the catalyst after the reaction indicated that less than 0.1% of the Pd leached from the $Pd_{0.05}/RPL$ during the reactions (Table S1).

In order to optimize the reaction conditions, we examined the effect of the solvents and base for the Suzuki coupling reaction, and the results are shown in Tables S2 and S3. According to the result of optimization and the principles of green chemistry, EtOH/H₂O (v/v = 1:1) and K₂CO₃ was selected as the optimal conditions.

As shown in Table 1, various aryl bromides containing either electron-donating or electron-withdrawing groups in the para position, the corresponding products were obtained in good to excellent yields (Table 1, entries 1-5). The m-substituted aryl bromide (Table 1, entry 8), gave the corresponding products in similar yields. The o-substituted aryl bromides (Table 1, entries 6 and 7), gave the corresponding products in poor yields due to the steric effects. Comparing with the commercial $Pd_{0.05}/C$, the yields of $Pd_{0.05}/RPL$ is higher than the commercial $Pd_{0.05}/C$ (Table 1, entries 2, 4 and 8).

From the economic point of view, the reusability of catalyst is crucial. As shown in Fig. 10, the $Pd_{0.05}/RPL$ catalyst could be recycled easily by centrifugation step. In addition, although the yield gradually reduced, a yield of 81% is still obtained in the sixth cycle. After six recycles, the amount of Pd in the $Pd_{0.05}/RPL$ detected by ICP-AES is 3.86 wt%.

To determine the reason of the decrease catalytic performance, the TEM image of $Pd_{0.05}$ /RPL catalyst after six times is shown in Fig. 11. Compering with the TEM of fresh catalyst

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(Fig. 3c), we can find that the Pd NPs have obvious agglomeration on the surface of the carrier (Fig. 11a). According to the particle size distribution histograms the average particle size of the $Pd_{0.05}/RPL$ is 16.5 nm (Fig. 11b). As shown in Table S1, less than 0.1% of leaching Pd was observed in the catalyst recycled once. After recycled six times, the amount of palladium remained at 3.86 wt%, indicating that the Pd leached from the $Pd_{0.05}/RPL$ during the reactions. The most important conclusion drawn from these results is that the reduced catalytic activity was due to the Pd leaching and agglomerating.

Conclusions

In conclusion, a highly efficient and reusable supported Pd NPs catalyst was successfully prepared by using *Poplar* leaf extract as the reducing agent and the extracted residue of *Poplar* leaf as the carrier. The spherical Pd NPs with small-size and highly-dispersed were successfully prepared at appropriate Pd loads. And the $Pd_{0.05}/RPL$ catalyst demonstrated excellent catalytic performance for the Suzuki coupling reaction and could be reused at least six times without significant loss of activity. This method provides a simple and eco-friendly route for synthesis supported Pd NPs, which will find potential application in other nano metal materials.

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Table 1	The Suzuki	coupling rea	action of v	various aryl	halides and	l phenylbor	onic acid."
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			Yield ^b /%		
Entry	Aryl halide	Time/h			
			Pd _{0.05} /RPL	Pd _{0.05} /C	
1	H ₃ C-Br	0.5	98.2	96.5	
2	O ₂ N-Br	0.5	95.6	55.0	
3	H ₃ COCBr	0.5	97.5	95.4	
4	NC	0.5	96.3	69.8	
5	H ₃ CO-Br	0.5	97.5	97.3	
6	OCH ₃ Br	0.5	33.1	26.9	
7	CH ₃ Br	0.5	82.4	70.9	
8	O ₂ N Br	0.5	93.5	72.6	

^aReaction conditions: aryl halide (2.5 mmol), phenylboronic acid (3.75 mmol), Pd_{0.05}/RPL (0.1 mmol%), K₂CO₃ (5 mmol), EtOH/H₂O (15 mL/15 mL) at 60°C.

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^b Isolated yields.

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Fig. 1. Schematic of biosynthesis of Pd NPs on RPL: Pd nanoparticles supported on (a) cellulose

and (b) hemicellulose.

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Fig. 2. UV-vis spectrum of Pd NPs prepared with different time.

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Fig. 3. (a) TEM image and (e) size distribution of Pd_{0.01}/RPL, (b) TEM image and (f) size distribution of Pd_{0.03}/RPL, (c) TEM image, HRTEM (Inset c) and (g) size distribution of Pd_{0.05}/RPL, (d) TEM image and (h) size distribution of Pd_{0.10}/RPL.

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Fig. 4. XRD patterns of (a) Pd_{0.01}/RPL, (b) Pd_{0.03}/RPL, (c) Pd_{0.05}/RPL and (d) Pd_{0.10}/RPL.

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Fig. 5. Pd 3d spectrum of the $Pd_{0.05}/RPL$.

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Fig. 6. (a) SEM image and (b) EDS spectrum of Pd_{0.05}/RPL catalyst.

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Fig. 7. FTIR spectra of (a) PLE and Pd NPs, (b) RPL and Pd_{0.05}/RPL.

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Fig. 8. Yields of biphenyl at different intervals with various catalysts.

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Fig. 9. Suzuki coupling reaction in the presence of the hot-filtered mother liquor.

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Fig. 10. Reuse of $Pd_{0.05}$ /RPL catalyst for Suzuki coupling reaction.

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Fig. 11. (a) TEM image and (b) size distribution of $Pd_{0.05}/RPL$ catalyst after six times.

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Scheme. 1 Suzuki coupling reaction.

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