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Biosynthesis, Characterization and Application of Palladium Nanoparticles in Mizoroki-Heck Coupling

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ABSTRACT

Palladium nanoparticles (Pd NPs) have been successfully biosynthesized via biogenic production using starting materials of Palladium (II) chloride (PdCl₂) and bio-reductant Allium jesdianum leaf extract (A.J.L extract) as a green and straightforward technique in aqueous solution without any external agent. Leaf extracts are a rich source of phytochemicals such as polyols, polyphenols, sugars, flavonoids, and heterocyclic components, which function as capping, reducing, and stabilizing agents in the reductive process of Palladium (II) ions to Pd NPs under in-situ conditions. The as-synthesized palladium nanostructures were characterized by UV-visible spectroscopy, field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDS), and transmission electron microscopy (TEM) to confirm and study the morphological properties of the bio-produced palladium nanoparticles. FESEM and TEM analysis demonstrated the formation of spherically shaped Pd NPs with a diameter in the range of 10-59 nm. The Mizoroki-Heck cross-coupling reaction was used to investigate the catalytic activity of biosynthesized palladium nanoparticles. The reactions of various aryl halides with n-butyl acrylate were conducted under aerobic and solvent-free conditions, resulting in high yields of the desired products. The nanoparticles were isolated without requiring a complex or lengthy workup process. Furthermore, the nano-catalyst was easily recycled via simple filtration and reused successfully for six consecutive runs.

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1. Introduction

A key focus in nanotechnology research is the synthesis and characterization of metal nanoparticles (MNPs) of various sizes, chemical compositions, and morphologies. Recently, nanomaterials produced using biosynthesis have attracted considerable attention due to their non-toxic approaches. In the rapidly developing field of nanoscience, noble metal nanoparticles are at the forefront and exhibit unexpected chemical, physical, and biological properties that differ significantly from those in the bulk state [1, 2]. These compounds have widespread applications in various fields including medicine, sensing, catalysis and electronics [3-12].

There have been many metallic nanoparticles prepared with different morphologies. Additionally, their surface area, size, size distribution, and dispersion status could be used to tailor their chemical, physical and mechanical properties. Due to the unique chemical, physical, thermodynamic, and optical properties of Pd NPs, their production has attracted a lot of attention [13, 14]. As a result, Pd NPs have been widely used in the area of catalysis [15, 16] and drug delivery [17]. Chemical reduction of palladium (II) ions by alcohol [18], hydrazine [19], ascorbic acid [20] and dimethylamine-borane complex (21) are the most common ways for synthesis of Pd NPs. Nonetheless, the majority of these processes were carried out without any bio-stabilizers to synthesize and stable Pd NPs. In addition to routine physical and chemical methods, bio-fabrication of nanoparticles has gained popularity due to its environment-friendly process, mild experimental conditions, readily available, and affordable materials [22-25]. As an alternative procedure for the synthesis of biocompatible metal nanoparticles, it can be the use of microorganisms such as fungi, algae, bacteria, human cells, and plants as reducing/capping agents. In the last

decades, eco-friendly methods using live plants or plant extracts have emerged as a practical, simple and straightforward alternative to conventional procedures and have gained much attention [26-30]. Many antioxidants and plant metabolites such as alkaloids, terpenoids, flavonoids, vitamins, and phenolic compounds are presented in these stabilizing/reducing agents [31, 32]. The mentioned synthetic approach using plant extracts demonstrates the potential use of biomass for the bio-reduction of cations to zero-valent metal nanoparticles. It should be noted that many key parameters including crystal structure, size, stabilization, and controlled monodispersity influenced the catalytic activity of noble metal NPs. Transition metal nano-catalysts including copper, gold, palladium and their alloys are utilized extensively in carbon-carbon cross-coupling reactions and the formation of C-Het (N, S) bonds using a wide range of substrate, strong catalytic performance, and increased yields [33, 34]. Palladium nanoparticles are one of the most important noble metal NPs that is widely utilized as an effective catalyst for the degradation of organic contaminants [35], the decolorization of dyes [36], coupling reactions [16] and other applications. Nanoscience has played a pivotal role in catalysis, enhancing the desirable attributes and productivity of catalytic systems. The improvement in the efficiency of heterogeneous catalysts has been facilitated by the fabrication of uniformly sized nanoparticles. One of the most potent and extensively researched synthetic transformations is the formation of C-C bonds, particularly involving Cross-coupling reactions catalyzed by transition metals have become important in synthetic chemistry [37, 38]. Among transition metals, Pd catalysts have been widely utilized for carbon-carbon bond formation, including Hiyama, Stille, Negishi, Suzuki, Heck and Sonogashira reactions, which the last three coupling being the most

adaptable and widely used for the formation of single, double, and triple carbon-carbon bond, respectively [15, 39]. In this work, the *Allium jesdianum* plant was used to make the biomass extract for the synthesis of Pd NPs. To the best of our understanding, there aren't many research groups that have reported the green synthesis of nanomaterial using *Allium jesdianum* [40]. The chemical composition of this plant has been reported by Askari [41] including flavonoids and phenolic compounds as stabilizing/reducing agents. Also, it is used as an herbal medicine to treat kidney and hepatic failure, various cancers, and rheumatoid arthritis [42-44].

2. Materials and Methods

2.1. Chemical and Apparatus

All chemical reagents and solvents used in this research were purchased from the Merck chemical company without further purification. Deionized water (DW) was used to prepare all solutions. Figure 1 shows the *Allium jesdianum* plant. In the spring season, the fresh *Allium jesdianum* green leaves were harvested from the slope of Dena Mount (Zagros Mountains).



Fig. 1. The fresh *Allium jesdianum* green leaves.

2.2. Synthesis of the *Allium jesdianum* extract

Allium jesdianum fresh leaves (biomass) were collected and properly washed, then dried in shade for five days with appropriate air conditioning and ground to a fine powder. 2.5 g of its powder was added to 50 mL of deionized water in round-bottom flasks of 100 ml capacity at 70 °C in the dark for 40 minutes and the mixture color changed to yellowish. To remove any impurities from the obtained extract,

it was filtered through Whatman filter paper No. 1 and centrifuged at 6000 rpm for 15 min.

2.3. Synthesis of Pd nanoparticles using the aqueous leaf extract of the *Allium jesdianum*

First, PdCl₂ salt (1.000 mmol) was dissolved by a few drops of HCl dilute solution with the aid of sonication. After that, the solution was diluted with DW to obtain a Pd (II) concentration as a stock solution (100 mL, 0.01 M). In the next step, 15 mL of freshly prepared extract was added dropwise to well-mixed aqueous PdCl₂ solution (25 mL, 1 mM) at 50 °C. The change in the color of the solution from yellowish to dark brown after 30 minutes indicates the complete formation of Pd nanoparticles [41, 45]. Moreover, the reaction progress was monitored by UV-vis spectroscopy at various times. Finally, the suspension was centrifuged at 5000 rpm for 15 min which gave rise to a Pd nanoparticle precipitate. The dark gray solid was washed with distilled water, dried and then kept under vacuum for 24 h.

2.4. Characterization of Palladium Nanostructures and the Heck Cross-Coupling Reaction Products

Ultraviolet-visible (UV-vis) spectroscopy analysis of the extract and the extract residue before and after bio-reduction respectively were performed on a HALO DB-20 spectrophotometer on wavelengths ranging from 200 to 600 nm. All experiments were examined at room temperature. The morphology of the sample and chemical analysis of produced nanoparticles were performed using TESCAN (MIRA III) SEM Transmission electron microscope (TEM) using a LEO 906E microscope operating at an accelerating voltage of 20 kV was carried out to identify the size and shape of Pd NPs. After purification of the Heck cross-coupling reaction products by Pd NPs catalyst, all NMR (¹H and ¹³C) spectra of them were recorded on a Bruker (¹H at 400.2 and ¹³C at 100.6 MHz) spectrometer in CDCl₃ using TMS as the internal standard at 25 °C.

2.5. Mizoroki–Heck coupling using biosynthesized Pd NPs

In a typical heterogeneous catalytic reaction, a mixture of aryl halide (1.0 mmol), n-butyl acrylate (1.5 mmol), Tripropylamine (Pr_3N , 1.5 mmol) and Pd NPs catalyst 0.1 g (containing 0.0048 mmol of Pd) was stirred under solvent-free conditions in an oil bath at 80 °C in the presence of air. The progress of the reaction was followed by TLC. Following the completion of the coupling, the reaction vessel was cooled down to ambient temperature, and 10 mL of ethyl acetate was added. The catalyst was separated by centrifugation and recovered. Water (3×15 mL) was added to the organic phase and it separated into two layers in the decanter. The organic phase was dried using anhydrous sodium sulphate. In the final step, the organic solvent was evaporated and the product was purified by column chromatography on silica gel using hexane/ethyl acetate as eluents. After complete drying, the catalyst was reused for the same reaction repeatedly for six runs.

3. Results and Discussion

3.1. UV-vis absorbance spectra of A.J.L extract, Pd^{2+} and biosynthesized Pd NPs

One of the basic techniques for characterizing nanoparticles in aqueous solutions/suspensions is UV-visible absorption spectroscopy [24]. The UV spectrum of the A.J.L extract in Fig. 2a reveals a maximum absorption peak at 253 nm which is related to phenolic compounds.

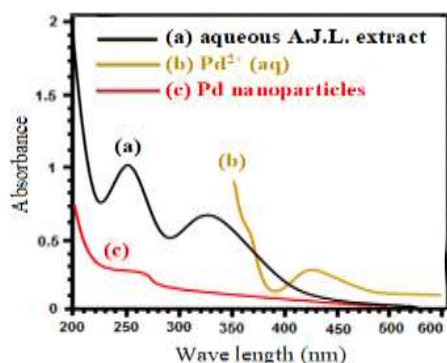


Fig. 2. The UV spectrum of a) the A.J.L extract, b) PdCl_2 aqueous solution, c) Pd NPs.

The intense peak centered at 335 nm is related to absorption of the ring system and $\pi \rightarrow \pi^*$ transitions on which this absorbent bond demonstrates the presence of flavonoid compounds [40, 46, 47]. The bio-reduction of the aqueous Pd (II) ions to zerovalent using A.J.L extract was studied based on the changes in the color of the solution during the formation of the product until attaining a fixed color indicating the end of the synthesis of Pd NPs completely and monitoring by UV-vis spectroscopy in the region of 200 - 600 nm.

After 12 hours, the color of the solution changed gradually from brownish yellow to dark brown, signifying the formation of Pd NPs. The absorption spectrum of PdCl_2 aqueous solution before bio-reduction is shown in figure 2b. The absorption peak at 430 nm is related to Pd (II) ions. The absorption spectrum of mixture after bio-reduction by A.J.L extract is shown in figure 2c. Figures 2b and 2c show that the disappearance of the absorption peak at 430 nm in the palladium colloidal suspension samples indicates that the initial Pd (II) ions have been completely reduced [48, 49]. These data indicate that the A.J.L extract serves as both a reducing agent and a stabilizing agent for Pd NPs. Also, the nanoparticles might be covered by a layer of phytochemicals, preventing the growth of nanoparticles and the formation of large particles; thus, phytochemicals stabilized the nanoparticles in the medium.

3.2. FESEM of biosynthesized Pd NPs.

FESEM was applied to study the size and surface morphology of the prepared Pd NPs. Figure 3 displays FESEM image of palladium nanoparticles acquired under the mentioned optimal conditions. FESEM analysis demonstrated the formation of nano-spherically shaped Pd NPs with a diameter in the range of 9-35 nm.

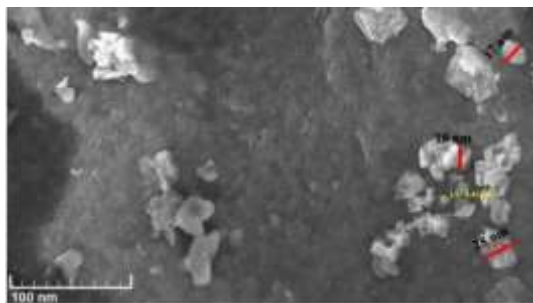


Fig. 3. FESEM image of palladium nanoparticles

Figure 4 displays the selected elemental mapping of the Pd nano-catalyst; it can be clearly seen that the elements Pd and O are uniformly distributed.

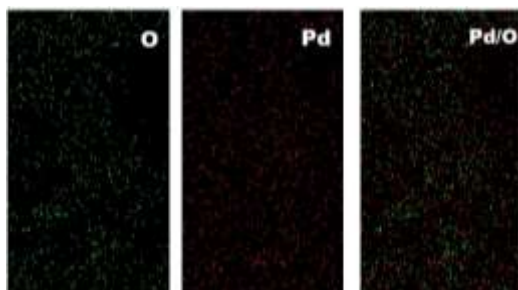


Fig. 4. The selected elemental mapping of Pd NPs

Figure 5 shows the elemental composition of the Pd NPs, determined using EDS analysis.

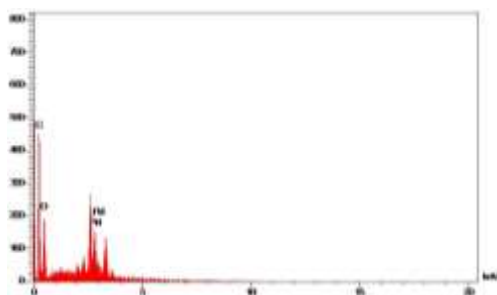


Fig. 5. The EDS analysis of the Pd NPs.

This elemental spectrum shows approximately strong signals of elemental Pd nanoparticles at about 3 keV and also, peaks of carbon and oxygen elements belonging extract were detected. The morphology, shape, and size of the green-synthesized Pd nano-catalyst in the colloidal

solutions were characterized by TEM image of palladium nanoparticles. Figure 6 shows TEM image of Pd NPs. According to transmission electron micrographs, Pd NPs are typically seen in spherical shapes and have relatively good monodispersity.

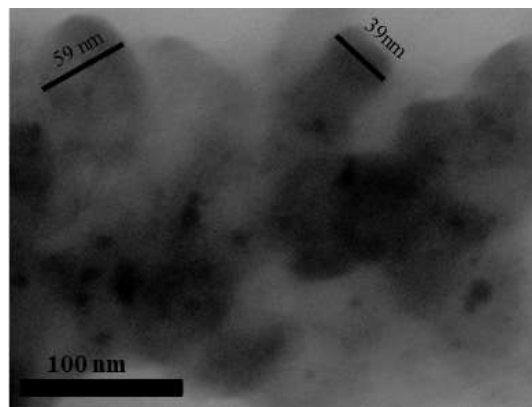
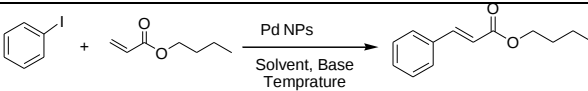


Fig. 6. TEM image of palladium nanoparticles.

3.3. Catalytic activity

To assess the activity of the nano-catalyst, it is used in the Heck reaction of iodobenzene which occurs easily at the temperature ranging from 80 to 140 °C. As a model reaction, the cross-coupling reaction of iodobenzene with *n*-butyl acrylate was utilized to assess the catalytic performance of the prepared heterogeneous nano-catalyst. To identify the optimal conditions for the Heck cross-coupling reaction, several parameters, including the amount of catalyst, type of base, solvent, and temperature, were investigated in the presence of Pd nanoparticles. The reaction of *n*-butyl acrylate (1 eq.) with iodobenzene (1 eq.) in the presence of tripropylamine (2 eq.) at 140 °C delivered a 93% product yield (Table 1, entry 11).

Table 1. The effect of various parameters on the reaction of iodobenzene with *n*-butyl acrylate^a


Entry	Base	Solvent	T / °C	Time	Isolated Yield (%) ^b
1	<i>n</i> -Pr ₃ N	DMF	130	25 min	91 (100)
2	<i>n</i> -Pr ₃ N	DMSO	130	25 min	90 (100)
3	<i>n</i> -Pr ₃ N	H ₂ O	Reflux	18 h	36 (60)
4	<i>n</i> -Pr ₃ N	EtOH	Reflux	18 h	27 (32)
5	<i>n</i> -Pr ₃ N	THF	Reflux	18 h	2 (5)
6	<i>n</i> -Pr ₃ N	Toluene	Reflux	18 h	3 (8)
7	<i>n</i> -Pr ₃ N	None	80	12 h	4 (10)
8	<i>n</i> -Pr ₃ N	None	100	12 h	75 (80)
9	<i>n</i> -Pr ₃ N	None	120	2 h	86 (100)
10	<i>n</i> -Pr ₃ N	None	130	55 min	91 (100)
11	<i>n</i> -Pr ₃ N	None	140	7 min	93 (100)
12	NaOH	None	140	18 h	70 (77)
13	KOAc	None	140	18 h	80 (86)
14	K ₂ CO ₃	None	140	18 h	84 (89)
15	DABCO	None	140	1.5 min	91 (97)

^aReaction conditions: iodobenzene (1 mmol), *n*-butyl acrylate (1.5 mmol) and base (1.5 mmol) in the presence of Pd NPs (0.1 g containing 0.0048 mmol of Pd).

^bThe data shown in the parentheses refer to the iodobenzene conversion.

These reaction conditions were selected for additional experiments. In solvent-free conditions, we investigated different bases. It was observed that the used base had an important effect on the reaction, and the best result was related to tripropylamine with a shorter reaction time and the highest yield (Table 1, entry 11). Therefore, in the presence of tripropylamine, the efficiency of the catalyst in the reaction of *n*-butyl acrylate (1 eq.) with other aryl halides was investigated. As the temperature rose, the reaction proceeded more efficiently. When the reaction was performed under solvent-free conditions at 120-140 °C, the conversion of iodobenzene was complete. (Table 1, entries 9-11). The best results were obtained with iodobenzene (1.0 mmol) and *n*-butyl acrylate (1.5 mmol) under solvent-free conditions at 140 °C, which gave the high-efficiency products. After that, the efficacy of the palladium nanoparticles with aryl halides including both electron-donating and electron-withdrawing groups was examined (Table 2).

According to the published research in recent [50], it has been verified that reactivity order of different

aryl halides in heck reaction is R-Cl < R-Br < R-I.

As seen in table 2, the aryl Iodide (Table 2, entries 1, 2, 5, 6, 8 and 11) reacted in less time than bromide ones (Table 2, entries 3, 7, 9 and 12) and for the aryl Bromide (Table 2, entries 3, 7, 9 and 12) reacted in less time than chloride ones (Table 2, entries 4 and 10). Also, the electron-withdrawing groups such as -NO₂ on the aromatic ring increases the reactivity of the corresponding aryl halide in the Heck reaction (Table 2, entries 11 and 12), whereas electron-donating groups such as -Me (Table 2, entries 5- 7) or -OMe (Table 2, entries 8- 10) have opposite effect. As indicated in Table 2, it is clear that our method is logically general and applicable to a variety of aryl halide types. Additionally, the product yield of deactivated aryl halides was unaffected by the steric hindrance of substituents. It can be claimed that this procedure consistently provided the desired products with desirable yields.

3.4. Spectral data of some products

Product 2b: ¹HNMR (CDCl₃, 400.2 MHz): δ (ppm): 1.04 (t, 3 H, J= 7.2 Hz), 1.52 (sex, 2 H, J= 7.6), 1.78 (quint, 2 H, J= 6.8), 4.31 (t, 2 H, J= 6.8

Hz), 6.58 (d, 1 H, $J = 15.6$ Hz), 7.49-7.62 (m, 3 H), 7.78 (d, 1 H, $J = 7.2$ Hz), 7.91 (t, 2 H, $J = 6$ Hz), 8.23 (d, 1 H, $J = 8.4$ Hz), 8.57 (d, 1 H, $J = 15.6$ Hz). ^{13}C NMR (CDCl_3 , 100.6 MHz): δ (ppm): 13.84, 19.30, 30.87, 64.57, 120.97, 123.42, 125.02, 125.48, 126.24, 126.87, 128.76, 130.49, 131.44, 131.85, 133.71, 141.61, 167.02.

Product 2e: ^1H NMR (CDCl_3 , 400.2 MHz): δ (ppm): 1.00 (t, 3 H, $J = 7.6$ Hz), 1.47 (sex, 2 H, $J = 7.2$ Hz), 1.72 (quint, 2 H, $J = 6.4$ Hz), 2.39 (s, 3 H), 4.23 (t, 2 H, $J = 6.4$ Hz), 6.42 (d, 1 H, $J = 15.6$ Hz), 7.21 (d, 2 H, $J = 8$ Hz), 7.45 (d, 2 H, $J = 8$ Hz), 7.69 (d, 1 H, $J = 16$ Hz). ^{13}C NMR (CDCl_3 , 100.6 MHz): δ (ppm): 13.79, 19.24, 21.47, 30.83, 64.35, 117.20, 128.07, 129.62, 131.77, 140.61, 144.57, 167.31.

Product 2i: ^1H NMR (CDCl_3 , 400.2 MHz): δ (ppm): 0.97 (t, 3 H, $J = 7.2$ Hz), 1.45 (sex, 2 H, $J = 7.6$ Hz), 1.69 (quint, 2 H, $J = 6.8$ Hz), 3.83 (s, 3 H), 4.21 (t, 2 H, $J = 6.8$), 6.32 (d, 1 H, $J = 16$ Hz), 6.90 (d, 2 H, $J = 8.8$ Hz), 7.48 (d, 2 H, $J = 8.8$ Hz), 7.65 (d, 1 H, $J = 16$ Hz). ^{13}C NMR (CDCl_3 , 100.6 MHz): δ (ppm): 13.77, 19.23, 30.84, 55.32, 64.24, 114.30, 115.76, 127.2, 129.68, 144.20, 161.34, 167.4.

The ^1H NMR spectrum of the product 2a is provided as a sample in Figure 7.

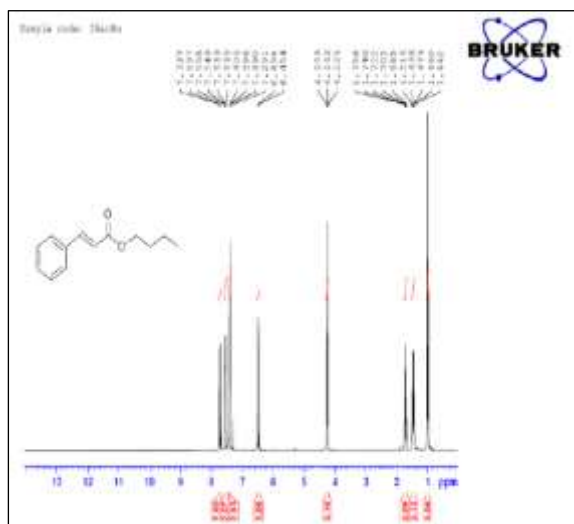


Fig. 7. ^1H NMR spectrum of the product 2a (CDCl_3 , 400.2 MHz: δ (ppm)).

In order to learn the catalytic activity of Pd@ *Allium jesdianum*, we compared our results with different

reported catalysts used in the cross-coupling reaction of iodobenzene and butyl acrylate. The results illustrate the high activity of the catalyst developed in the current work (Table 3).

3.5. Catalyst recyclability

The recyclability of the catalyst is an important issue in the Heck coupling reaction and was examined through a series of experiments via a used catalyst with n-butyl acrylate under optimized reaction conditions. The reusability of the catalyst was confirmed using iodobenzene with n-butyl acrylate as model substrates (Table 1, entry 11) by carrying out a set of consecutive experiments in which the used catalyst was filtered, washed with fresh deionized water, dried at 70 °C and used for the next reaction. The reaction time of the six successive runs revealed the good recyclability of the used Pd catalyst (Table 4). The results showed that after six trials, there was no appreciable decrease in the activity of the catalyst. Also, the TEM analysis of the recovered Pd nanoparticles in Figure 7 revealed that their size distribution and morphology remained significantly unchanged compared to the TEM image of the fresh nano-catalyst.

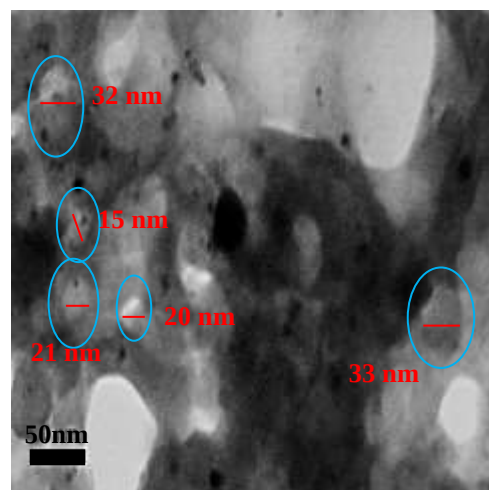


Fig. 7. TEM images of palladium nanoparticles.

Table 2. Mizoroki-Heck reaction of n-butyl acrylate and various aryl halides using the Pd NPs^a

Entry	Aryl Halide	Product	Time (min)	Yield (%)	TON/TOF (min ⁻¹)
1	1a	2a	7	93	193/27.5
2	1b	2b	30	91	189/6.3
3	1c	2c	720	63	131/0.18
4	1d	2d	1080	74	154/0.14
5	1e	2e	18	91	189/10.5
6	1f	2f	25	90	187/7.5
7	1g	2g	1080	60	125/0.1
8	1h	2h	25	93	193/7.7
9	1i	2i	1320	62	129/0.1
10	1j	2j	1080	50	104/0.1
11	1k	2k	35	90	187/5.3
12	1l	2l	90	89	185/2

^aReaction conditions: **1** (1 mmol), **2** (1.5 mmol), Pr₃N (1.5 mmol), Pd NPs (0.1 g containing 0.0048 mmol of Pd), solvent free.

^bIsolated yields.

Table 3. Comparison of the prepared catalyst with other catalysts for Heck reactions from iodobenzene with butyl acrylate.

Entry	Catalyst	Condition	Time (min)	Yield (%)	Reference
1	Pd@Agarose	Solvent-free, 100 °C	120	90	[51]
2	Pd/SDPP	Solvent-free, 130 °C	60	99	[52]
3	Fe ₃ O ₄ @CQD@Si@PNIPAM-NH ₂ /Pd	DMF, 95 °C	60	95	[53]
4	Pd@Chitosan-PAAS	DMAc, 110 °C	180	95	[54]
5	Pd@NHC@ZIF-8	DMF/H ₂ O, 110 °C	45	90	[55]
6	Pd(0)-SMTU-boehmite	PEG, 80° C	25	99	[56]
7	Fe ₃ O ₄ @triazole-Schiff-basePd	PEG-400, 120 °C	25	98	[57]
8	Pd@Allium jesdianum	Solvent-free, 140 °C	7	93	This work

Table 4. Recyclability of nano-catalyst in Mizoroki-Heck cross-coupling reaction^a

Run	1	2	3	4	5	6
Time (min) ^b	7	9	13	17	20	25

^aReaction conditions: 140 °C, solvent-free, iodobenzene (1 mmol), n-butyl acrylate (1.5 mmol), Pr3N (1.5 mmol) and Pd NPs.

^bCompletion time for the reaction.

4. Conclusion

In the present work, we reported a rapid, simple, and economical biosynthesis procedure to synthesize Pd nanoparticles using a reducing agent of A.J.L. extract. TEM, SEM, and EDS analysis results confirmed the successful synthesis of stable Pd nanoparticles exhibiting a spherical morphology and a small diameter. Pd NPs synthesized by A.J.L. extract were stable and efficient catalyst in the Mizoroki–Heck cross-coupling reaction with high yields and chemoselectivity in acceptable reaction time. The polyols, polyphenols, flavonoids, sugar, and heterocyclic components were responsible for the capping and reduction of Pd (II) ions and then the stabilization of palladium nanoparticles.

The reactions are carried out in the open air, indicating that the Pd nano-catalyst is highly stable and not oxygen-sensitive. The catalytic system is applicable to various aryl halides (chloride, bromide and iodide), and can be easily separated from the

products and reused without considerable loss of efficiency.

Acknowledgments

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Conflicts of Interest

The authors declare that there is no conflict of interests regarding the publication of this manuscript. In addition, the authors have entirely observed the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy.

5. References

- [1] Minhas FT, Arslan G, Gubbuk IH, Akkoz C, Ozturk BY, Asikkutlu B, et al. (2018). Evaluation of antibacterial properties on polysulfone composite membranes using synthesized biogenic silver nanoparticles with *Ulva compressa* (L.) Kütz. and *Cladophora glomerata* (L.) Kütz. extracts. *International journal of biological macromolecules*. 107:157-65.
- [2] Bhattacharya R, Mukherjee P. (2008). Biological properties of “naked” metal nanoparticles. *Advanced Drug Delivery Reviews*. 60(11):1289-306.

- [3] Hosseinzadeh H, Hassanpour A, Alihosseini M, Safardoust H, Mirzaei M. (2024). Synthesis and Characterization of NiO/ZnO Nanocomposite and its Application in Ibuprofen Drug Delivery. *Applied Chemistry Today*. 19:69-80.
- [4] Keypour H, Noroozi M. (2015). Hydrogenation of benzene in gasoline fuel over nanoparticles (Ni, Pt, Pd, Ru and Rh) supported fullerene: Comparison study. *Journal of Applied Chemistry*. 10(37):31-42.
- [5] Khazaei A, Rahmati S, Ghaderi A, Roshani L. (2014) Palladium nanoparticles supported on gum arabic as a reusable catalyst for solvent-free Mizoroki-Heck reaction. *Journal Iranian Chemical Society*. 11:263–269.
- [6] Proniewicz E. (2023). Metallic nanoparticles as effective sensors of biomolecules. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 288:122207.
- [7] Fatolahi L. (2025). Synthesis and combination of SrFe_2O_4 nano-spinel on CuO for photocatalytic removal: a kinetic study. *Applied Chemistry Today*. 20(74) 265-80.
- [8] Rahmati S, Arabi A, Khazaei A, Khazaei M. (2017). In situ stabilization of Pd(0) nanoparticles into a mixture of natural carbohydrate beads: A novel and highly efficient heterogeneous catalyst system for Heck coupling reactions. *Applied Organometallic Chemistry* 31, 4:e3588.
- [9] Taghavi Larmaei A, Zanganeh AR. (2024). The use of covalent organic framework nanoparticles as a sensing material for the fabrication of Silver voltammetric sensor: optimization of experimental conditions with the half fraction central composite design. *Applied Chemistry Today*. 19:127-50.
- [10] Gautam A, Komal P, Gautam P, Sharma A, Kumar N, Jung JP. (2021). Recent trends in noble metal nanoparticles for colorimetric chemical sensing and micro-electronic packaging applications. *Metals*. 11(2):329.
- [11] Khazaei A, Khazaei M, Rahmati S. (2015). A green method for the synthesis of gelatin/pectin stabilized palladium nanoparticles as efficient heterogeneous catalyst for solvent-free Mizoroki–Heck reaction. *Journal of Molecular Catalysis A: Chemical*. 398:241-7.
- [12] Farahmand Malekabadi Z, Alizadeh R, Seyfi S, Amani V. (2023). Synthesis of Nanoparticles of Pd(II) Complexes Containing Triazole and Tetrazole Derivative Ligands and Corresponding Metal-nano Oxides by Sonochemical Method. *Journal of Applied Chemistry*. 18 (66):63-78.
- [13] Watanabe K, Menzel D, Nilius N, Freund H-J. (2006). Photochemistry on Metal Nanoparticles. *Chemical Reviews*. 106(10):4301-20.
- [14] Jamkhande PG, Ghule NW, Bamer AH, Kalaskar MG. (2019). Metal nanoparticles synthesis: An overview on methods of preparation, advantages and disadvantages, and applications. *Journal of drug delivery science and technology*. 53:101174.
- [15] Trzeciak A, Augustyniak A. (2019). The role of palladium nanoparticles in catalytic C–C cross-coupling reactions. *Coordination Chemistry Reviews*. 384:1-20.
- [16] Bej A, Ghosh K, Sarkar A, Knight DW. (2016). Palladium nanoparticles in the catalysis

of coupling reactions. RSC advances. 6(14):11446-53.

[17] Shanthi K, Vimala K, Gopi D, Kannan S. (2015). Fabrication of a pH responsive DOX conjugated PEGylated palladium nanoparticle mediated drug delivery system: an in vitro and in vivo evaluation. Rsc Advances. 5(56):44998-5014.

[18] Johnston EV, Verho O, Kärkäs MD, Shakeri M, Tai CW, Palmgren P, et al. (2012). Highly dispersed palladium nanoparticles on mesocellular foam: an efficient and recyclable heterogeneous catalyst for alcohol oxidation. Chemistry–A European Journal. 18(39):12202-6.

[19] Yonezawa T, Imamura K, Kimizuka N. (2001). Direct preparation and size control of palladium nanoparticle hydrosols by water-soluble isocyanide ligands. Langmuir. 17(16):4701-3.

[20] Sun Y, Zhang L, Zhou H, Zhu Y, Sutter E, Ji Y, et al. (2007). Seedless and templateless synthesis of rectangular palladium nanoparticles. Chemistry of Materials. 19(8):2065-70.

[21] Kameo A, Yoshimura T, Esumi K. (2003). Preparation of noble metal nanoparticles in supercritical carbon dioxide. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 215(1-3):181-9.

[22] Alqahtani MA, Al Othman MR, Mohammed AE. (2020). Bio fabrication of silver nanoparticles with antibacterial and cytotoxic abilities using lichens. Scientific Reports. 10(1):16781.

[23] Shrivastava V, Chauhan PS, Tomar RS. Bio-Fabrication of metal nanoparticles: (2018).

A review. International Journal of Current Research in Life Sciences. 7(04):1927-32.

[24] Wang W, Zhang B, Liu Q, Du P, Liu W, He Z. (2018). Biosynthesis of palladium nanoparticles using *Shewanella loihica* PV-4 for excellent catalytic reduction of chromium (VI). Environmental Science: Nano. 5(3):730-9.

[25] Singh P, Kim Y-J, Zhang D, Yang D-C. (2016). Biological synthesis of nanoparticles from plants and microorganisms. Trends in biotechnology. 34(7):588-99.

[26] Pantidos N, Horsfall LE. (2014). Biological synthesis of metallic nanoparticles by bacteria, fungi and plants. Journal of Nanomedicine & Nanotechnology. 5(5):1.

[27] Sayadi MH, Salmani N, Heidari A, Rezaei MR. (2018). Bio-synthesis of palladium nanoparticle using *Spirulina platensis* alga extract and its application as adsorbent. Surfaces and Interfaces. 10:136-43.

[28] Gulbagca F, Aygün A, Gülcan M, Ozdemir S, Gonca S, Şen F. (2021). Green synthesis of palladium nanoparticles: Preparation, characterization, and investigation of antioxidant, antimicrobial, anticancer, and DNA cleavage activities. Applied Organometallic Chemistry. 35(8):e6272.

[29] Mojaddami A, Koolivand Z, Panahimehr M, Chamkouri N. (2023). Green synthesis, phytochemical analysis, characterization and cytotoxic evaluation of gold–zinc oxide nanocomposites using Russian *Artemisia* leaf extract. Nano-Structures & Nano-Objects. 34:100979.

[30] Mojaddami A, Koolivand Z, Panahimehr M, Chamkouri N. (2023). Biosynthesis,

characterization, and biological evaluation of cellulose nanofibers@ l-lysine@ silicon dioxide nanoparticles using Russian Artemisia extract. *Inorganic Chemistry Communications*. 148:110354.

[31] Qazi F, Hussain Z, Tahir MN. (2016). Advances in biogenic synthesis of palladium nanoparticles. *RSC Advances*. 6(65):60277-86.

[32] Kasote DM, Katyare SS, Hegde MV, Bae H. (2015). Significance of Antioxidant Potential of Plants and its Relevance to Therapeutic Applications. *International Journal of Biological Sciences*. 11(8):982-91.

[33] Ashraf M, Ahmad MS, Inomata Y, Ullah N, Tahir MN, Kida T. (2023). Transition metal nanoparticles as nanocatalysts for Suzuki, Heck and Sonogashira cross-coupling reactions. *Coordination Chemistry Reviews*. 476:214928.

[34] Ganesh M, Ramakrishna J. (2020). Synthetic Organic Transformations of Transition-Metal Nanoparticles as Propitious Catalysts: A Review. *Asian Journal of Organic Chemistry*. 9(10):1341-76.

[35] Gong Z, Ma T, Liang F. (2021). Syntheses of magnetic blackberry-like Ni@ Cu@ Pd nanoparticles for efficient catalytic reduction of organic pollutants. *Journal of Alloys and Compounds*. 873:159802.

[36] Li G, Li Y, Wang Z, Liu H. (2017). Green synthesis of palladium nanoparticles with carboxymethyl cellulose for degradation of azo-dyes. *Materials Chemistry and Physics*. 187:133-40.

[37] Moreno-Manas M, Pleixats R. (2003). Formation of carbon– carbon bonds under catalysis by transition-metal nanoparticles. *Accounts of chemical research*. 36(8):638-43.

[38] Dey D, Bhattacharya T, Majumdar B, Mandani S, Sharma B, Sarma TK. (2013). Carbon dot reduced palladium nanoparticles as active catalysts for carbon–carbon bond formation. *Dalton Transactions*. 42(38):13821-5.

[39] Molnár Á. (2011). Efficient, selective, and recyclable palladium catalysts in carbon–carbon coupling reactions. *Chemical reviews*. 111(3):2251-320.

[40] Sheikh-Mohseni MH, Sedaghat S, Derakhshi P, Safekordi A. (2020). Green bio-synthesis of Ni/montmorillonite nanocomposite using extract of *Allium jesdianum* as the nano-catalyst for electrocatalytic oxidation of methanol. *Chinese Journal of Chemical Engineering*. 28(10):2555-65.

[41] Askari Y. (2022). Composition of essential oil of *Dorema aucheri* Boiss. and *Allium Jesdianum* Boiss. medicinal plants. *International Journal of Advanced Biological and Biomedical Research*. 10(1):72-83.

[42] Sohrabinezhad Z, Dastan D, Asl SS, Nili-Ahmadabadi A. (2019). *Allium jesdianum* extract improve acetaminophen-induced hepatic failure through inhibition of oxidative/nitrosative stress. *Journal of Pharmacopuncture*. 22(4):239.

[43] Hosseini A, Shafiee-Nick R, Ghorbani A. (2015). Pancreatic beta cell protection/regeneration with phytotherapy. *Brazilian Journal of Pharmaceutical Sciences*. 51:1-16.

[44] Asemani Y, Zamani N, Bayat M, Amirghofran Z. (2019). *Allium* vegetables for

possible future of cancer treatment. *Phytotherapy Research*. 33(12):3019-39.

[45] Banu R, Reddy GB, Ayodhya D, Ramakrishna D, Kotu GM. (2023). Biogenic Pd-nanoparticles from *Lantana trifolia* seeds extract: Synthesis, characterization, and catalytic reduction of textile dyes. *Results in Chemistry*. 5:100737.

[46] Moradi M-T, Karimi A, Alidadi S, Hashemi L. (2018). In vitro anti-herpes simplex virus activity, antioxidant potential and total phenolic compounds of selected Iranian medicinal plant extracts.

[47] Arora S, Itankar P. (2018). Extraction, isolation and identification of flavonoid from *Chenopodium album* aerial parts. *Journal of traditional and complementary medicine*. 8(4):476-82.

[48] Liu D, Wu F. (2017). Biosynthesis of Pd nanoparticle using onion extract for electrochemical determination of carbendazim. *International Journal of Electrochemical Science*. 12(3):2125-34.

[49] Luo C, Zhang Y, Wang Y. (2005). Palladium nanoparticles in poly (ethyleneglycol): the efficient and recyclable catalyst for Heck reaction. *Journal of Molecular Catalysis A: Chemical*. 229(1-2):7-12.

[50] Khazaei A, Rahmati S, Hekmatian Z, Saeednia S. (2013). A green approach for the synthesis of palladium nanoparticles supported on pectin: Application as a catalyst for solvent-free Mizoroki–Heck reaction. *Journal of Molecular Catalysis A: Chemical*. 372:160-6.

[51] Firouzabadi H, Iranpoor N, Kazemi F, Gholinejad M. (2012). Palladium nanoparticles supported on agarose as efficient

catalyst and bioorganic ligand for C C bond formation via solventless Mizoroki–Heck reaction and Sonogashira-Hagihara reaction in polyethylene glycol (PEG 400). *Journal of Molecular Catalysis A: Chemical*. 357:154-61.

[52] Iranpoor N, Firouzabadi H, Motevalli S, Talebi M. (2012). Palladium nanoparticles supported on silicadiphenyl phosphinite (SDPP) as efficient catalyst for Mizoroki-Heck and Suzuki-Miyaura coupling reactions. *Journal of Organometallic Chemistry*. 708-709:118-24.

[53] Ghasemi S, Badri F, Rahbar KH. (2024). Pd catalyst supported thermo-responsive modified poly (N-isopropylacrylamide) grafted $\text{Fe}_3\text{O}_4@\text{CQD}@\text{Si}$ in heck coupling reaction. 2024. *Asian Journal of Green Chemistry*. 8:39-56.

[54] Du Y, Wei S, Tang M, Ye M, Tao H, Qi C, et al. (2020). Palladium nanoparticles stabilized by chitosan/PAAS nanofibers: A highly stable catalyst for Heck reaction. *Applied Organometallic Chemistry*. 34(5):5619.

[55] Azad M, Rostamizadeh S, Estiri H, Nouri F. (2019). Ultra-small and highly dispersed Pd nanoparticles inside the pores of ZIF-8: Sustainable approach to waste-minimized Mizoroki–Heck cross-coupling reaction based on reusable heterogeneous catalyst. *Applied Organometallic Chemistry*. 33(7):4952.

[56] Hajighasemi Z, Nahipour A, Ghorbani-Choghamarani A, Taherinia Z. (2023). Efficient and biocompatible new palladium-supported boehmite nanoparticles: synthesis, characterization and application in Suzuki-Miura and Mizoroki-Heck coupling reactions. *Nanoscale Advances*. 5(18):4925-33.

[57] Mehdar YT, Alshamsan FM, Nashawi AA, Eledum H, Alshammari AM, Almutairi JA. (2025). A nanomagnetic triazole-based Schiff-base complex of palladium (0) as an efficient heterogeneous catalyst for the Mizoroki-Heck C-C cross-coupling reaction under green conditions. *Nanoscale Advances*. 10:1039.