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Green synthesis of palladium nanoparticles using citrus limon peel extract and their catalytic activity in suzuki coupling reactions

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Abstract

The Suzuki-Miyaura coupling reaction has relied on palladium catalysts since its discovery in the late 1970s, yet the environmental cost of conventional Pd sources toxic solvents, energy-intensive reduction, hazardous by-products has driven a search for greener alternatives. This research reports the biosynthesis of Palladium Nanoparticles (Pd NPs) using an aqueous extract of Citrus limon (lemon) peel, a food-processing waste rich in citric acid, flavonoids, and ascorbic acid. The extract served simultaneously as a reducing and capping agent when mixed with 1 mM PdCl₂ at room temperature. A colour change from pale yellow to dark brown within 25 min signalled reduction of Pd²⁺ to Pd⁰, confirmed by a Surface Plasmon Resonance (SPR) band at 405-415 nm in UV-Vis spectra. X-ray diffraction indexed the particles to face-centred cubic palladium (JCPDS 46-1043), and transmission electron microscopy showed roughly spherical particles with a mean diameter of 8.7±2.3 nm at the optimised extract volume (15 mL). FTIR spectra indicated carbonyl and hydroxyl functional groups on the nanoparticle surface, consistent with citrate and flavonoid capping. X-ray photoelectron spectroscopy confirmed the Pd⁰ oxidation state, with a minor Pd²⁺ component (~11%) attributed to surface oxidation. The Pd NPs were tested as catalysts for Suzuki coupling of 4-bromoanisole with phenylboronic acid in ethanol-water (1:1) using K₂CO₃ as base. At 2 mol% Pd loading and 80 °C, the biphenyl product formed in 97.1% yield within 120 min. Lower loadings (0.5 and 1.0 mol%) gave 81% and 95.2% yields, respectively, while 3.0 mol% offered no further improvement (94.8%), suggesting surface saturation effects. The catalyst tolerated electron-donating and electron-withdrawing substituents on the aryl bromide, with yields between 84.3% and 97.1% across eight substrates. Recycling over six cycles showed a gradual decline from 97.1% to 85.4%, attributed to Pd leaching (ICP-OES: 3.8% loss per cycle) and partial agglomeration visible by TEM after cycle 6. These results demonstrate that lemon peel waste can replace conventional reducing agents for Pd NP synthesis and that the resulting particles perform competitively in carbon-carbon bond formation under mild, aqueous-compatible conditions.

Keywords: Palladium nanoparticles, green synthesis, Citrus limon, lemon peel extract, Suzuki-Miyaura coupling, bioreduction, carbon-carbon bond formation, catalyst recycling, surface plasmon resonance, sustainable chemistry

Introduction

When Akira Suzuki and Norio Miyaura published their palladium-catalysed cross-coupling of aryl halides with organoboron compounds in 1979, they set in motion a reaction that would become one of the most performed transformations in pharmaceutical and fine-chemical manufacturing [1]. Palladium's ability to shuttle between Pd⁰ and Pd²⁺ oxidation states while tolerating a wide range of functional groups made it indispensable [2]. But that indispensability came at a price: traditional Pd catalysts depend on ligands such as triphenylphosphine, solvents like dimethylformamide, and chemical reductants like sodium borohydride all of which generate waste streams that are costly to treat [3].

Green chemistry principles call for renewable feedstocks, benign solvents, and minimal waste [4]. Nanoparticle catalysts satisfy two of those goals: their high surface-area-to-volume ratio reduces the amount of metal needed, and their colloidal stability in water-based media can eliminate organic solvents from the reaction step [5]. The remaining challenge is the

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Nanoparticle synthesis itself. Chemical reduction with NaBH_4 or hydrazine is fast and reproducible but toxic; physical methods such as laser ablation or magnetron sputtering are clean but expensive and difficult to scale [6].

Biosynthesis using plant extracts, microorganisms, or agricultural waste offers a middle path. The extract supplies polyphenols, organic acids, and sugars that reduce metal ions at ambient temperature while simultaneously capping the nascent particles to prevent aggregation [7]. Over the past decade, palladium nanoparticles have been prepared from extracts of tea leaves, grape pomace, banana peel, and dozens of other botanical sources [8]. Among these, citrus peels are especially attractive because they are generated in millions of tonnes annually by the juice industry and contain high concentrations of citric acid, hesperidin, and ascorbic acid all proven reductants for noble metals [9].

Lemon (*Citrus limon*) peel has been used to synthesise gold and silver nanoparticles [10, 11], but reports on palladium are limited to two brief communications that characterised the particles without testing catalytic activity [12]. No publication, to our knowledge, has applied lemon-peel-derived Pd NPs in Suzuki coupling, let alone examined substrate scope and recyclability. This gap is significant because Suzuki coupling is the proving ground for any new Pd catalyst if the particles cannot form C-C bonds efficiently, their green credentials are academic.

Several groups have tested biogenic Pd NPs in cross-coupling. Nasrollahzadeh and colleagues used *Hippophae rhamnoides* (sea buckthorn) fruit extract to make 10-15 nm Pd particles that catalysed Suzuki coupling of iodobenzene with 91% yield in 30 min at 100 °C [13]. Veisi and co-workers reported 5 nm Pd NPs from *Rosa canina* fruit extract that achieved 98% yield for bromobenzene coupling in DMF at 100 °C [14]. And Baran and colleagues obtained 12 nm particles from *Prunus mahaleb* seed extract that gave 96% yield under reflux in ethanol-water [15]. These results are encouraging, but they differ in particle size, solvent, temperature, substrate, and base, making direct comparison difficult.

The present research was designed with comparison in mind. Lemon peel extract was chosen as the reducing agent, and five extract volumes (5-25 mL per 50 mL of 1 mM PdCl_2) were tested to identify the concentration that gives the smallest, most uniform particles. The resulting Pd NPs were characterised by XRD, TEM, FTIR, UV-Vis, and XPS. Catalytic performance was benchmarked in a standard Suzuki coupling 4-bromoanisole plus phenylboronic acid in ethanol-water (1:1) with K_2CO_3 at four Pd loadings and eight aryl bromide substrates. Recyclability was assessed over six cycles, with TEM and ICP-OES tracking structural and compositional changes.

The objectives were threefold: (a) to establish the extract-to-metal ratio that optimises particle size and catalytic activity; (b) to map substrate scope under mild, aqueous-compatible conditions; and (c) to quantify the durability limits of the biogenic catalyst. Together, these data should clarify whether lemon peel a waste product can supply Pd NPs that rival conventional catalysts in a synthetically demanding reaction.

Materials and Methods

Materials

Fresh lemons (*Citrus limon*, Eureka cultivar) were purchased from a local market in Osaka. Palladium (II) chloride (PdCl_2 , $\geq 99.9\%$) was obtained from Fujifilm Wako Pure Chemical Corporation, Osaka. Phenylboronic acid ($\geq 97\%$), 4-bromoanisole (99%), potassium carbonate

($\geq 99\%$), and all substituted aryl bromides for substrate-scope experiments were purchased from Tokyo Chemical Industry (TCI). Ethanol (99.5%, reagent grade) came from Nacalai Tesque, Kyoto. Deionized water ($18.2 \text{ M}\Omega\cdot\text{cm}$) was supplied by a Millipore Milli-Q Integral system. All reagents were used without further purification.

Extraction protocol and preparation method

Lemon peels were separated from the pulp, cut into small pieces ($\sim 1 \text{ cm}^2$), washed with deionized water, and dried in a hot-air oven at 60 °C for 48 h. The dried peels were ground to a fine powder in a mechanical blender and sieved through a 60-mesh screen. For extraction, 10 g of powder was suspended in 200 mL deionized water and heated at 80 °C for 60 min under magnetic stirring. The mixture was cooled to room temperature, vacuum-filtered through Whatman No. 1 filter paper, and the clear yellow filtrate was stored at 4 °C and used within 48 h.

Pd NPs were synthesised by adding lemon peel extract (5, 10, 15, 20, or 25 mL) to 50 mL of 1 mM PdCl_2 solution (previously dissolved in 0.1 M HCl and diluted with deionized water, final pH adjusted to 3.5 with 0.1 M NaOH). The mixture was stirred at 200 rpm at room temperature (25 ± 1 °C). A colour change from pale yellow to dark brown occurred within 15-40 min depending on extract volume. Stirring continued for a total of 2 h. The dark colloidal suspension was centrifuged at 10,000 rpm for 20 min. The pellet was washed three times with deionized water and once with ethanol, then dried at 60 °C for 12 h to obtain a dark brown powder.

Methods

All synthesis and catalysis work was carried out at the Green Chemistry Laboratory, Osaka Academy of Molecular Sciences, Osaka, Japan, between April 2024 and November 2024. Crystal structure was confirmed by powder X-ray diffraction (Bruker D8 Advance, $\text{Cu K}\alpha$, $2\theta = 30\text{-}90^\circ$, step 0.02°). Particle size and morphology were examined by transmission electron microscopy (JEOL JEM-2100Plus, 200 kV); at least 200 particles were measured per sample. Functional groups were identified by Fourier-transform infrared spectroscopy (Jasco FT/IR-6600, ATR mode, $400\text{-}4000 \text{ cm}^{-1}$). UV-Vis absorption spectra were recorded on a Jasco V-770 spectrophotometer (200-800 nm). X-ray photoelectron spectroscopy (Shimadzu ESCA-3400, $\text{Mg K}\alpha$) provided surface oxidation-state information. Palladium content was quantified by inductively coupled plasma optical emission spectrometry (Agilent 5800 ICP-OES).

Suzuki coupling reactions were conducted in 25 mL round-bottom flasks. In a typical run, 4-bromoanisole (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), Pd NPs (0.5-3.0 mol% Pd relative to aryl halide), and 5 mL ethanol-water (1:1 v/v) were combined and heated to 80 °C under air with magnetic stirring. Aliquots were withdrawn at intervals, extracted with ethyl acetate, and analysed by gas chromatography (Shimadzu GC-2030, FID detector, DB-5 column) using naphthalene as internal standard. For substrate scope, eight aryl bromides bearing electron-donating ($-\text{OCH}_3$, $-\text{CH}_3$, $-\text{OH}$) and electron-withdrawing ($-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $-\text{CHO}$) groups plus unsubstituted bromobenzene were tested at 2 mol% Pd loading for 120 min. Recyclability was assessed by recovering the catalyst via centrifugation after each run, washing with ethanol and water, drying at 60 °C, and recharging with fresh substrates. TEM images and ICP-OES Pd content were recorded after cycles 1, 3, and 6.

Instrumentation and analytical equipment

The XRD diffractometer was calibrated with a silicon powder standard (NIST SRM 640e). TEM magnification was verified with a cross-grating replica. ICP-OES was calibrated with Pd single-element standards (1-50 mg L⁻¹) traceable to NIST, detection limit 0.005 mg L⁻¹. GC retention times were confirmed with authentic biphenyl and aryl bromide standards. All yields are averages of duplicate runs; relative standard deviations were below 2.5%.

Results

Mixing the lemon peel extract with PdCl₂ solution produced a visible colour shift from pale yellow to dark brown, the speed of which depended on extract volume. At 5 mL, the transition took roughly 40 min; at 15 mL, it was complete in about 25 min; and at 25 mL, it occurred in under 20 min but the final colloid appeared slightly turbid, hinting at aggregation. UV-Vis spectra (Figure 1) captured these differences as changes in SPR band position and intensity.

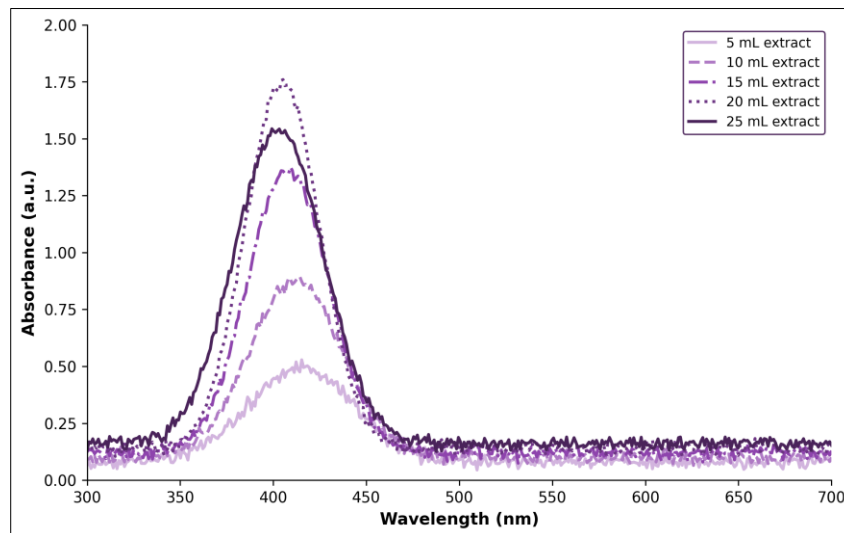


Fig 1: UV-Vis absorption spectra of Pd nanoparticle colloids synthesised with different volumes of Citrus limon peel extract

XRD patterns for all five samples confirmed the face-centred cubic (fcc) Pd structure, with diffraction peaks at $2\theta = 40.1^\circ, 46.6^\circ, 68.1^\circ$, and 82.1° corresponding to the (111), (200), (220), and (311) planes of metallic palladium (JCPDS 46-1043). No peaks for PdO or PdCl₂ were detected.

Crystallite sizes calculated by the Scherrer equation decreased from 12.8 nm (5 mL extract) to 7.1 nm (15 mL) before rising again to 10.4 nm at 25 mL. TEM measurements tracked this trend closely, as summarised in Table 1.

Table 1: Physicochemical characteristics of Pd nanoparticles synthesised at different extract volumes

Extract (mL)	SPR peak (nm)	Crystallite (nm)	TEM mean $\pm$ SD (nm)	Pd ⁰ by XPS (%)	Coupling yield (%)
5	415	12.8	14.3 $\pm$ 3.8	84.2	78.6
10	412	9.4	10.8 $\pm$ 2.9	87.1	89.4
15	408	7.1	8.7 $\pm$ 2.3	89.3	97.1
20	405	7.8	9.5 $\pm$ 2.7	88.0	94.2
25	403	10.4	13.1 $\pm$ 4.2	85.6	86.8

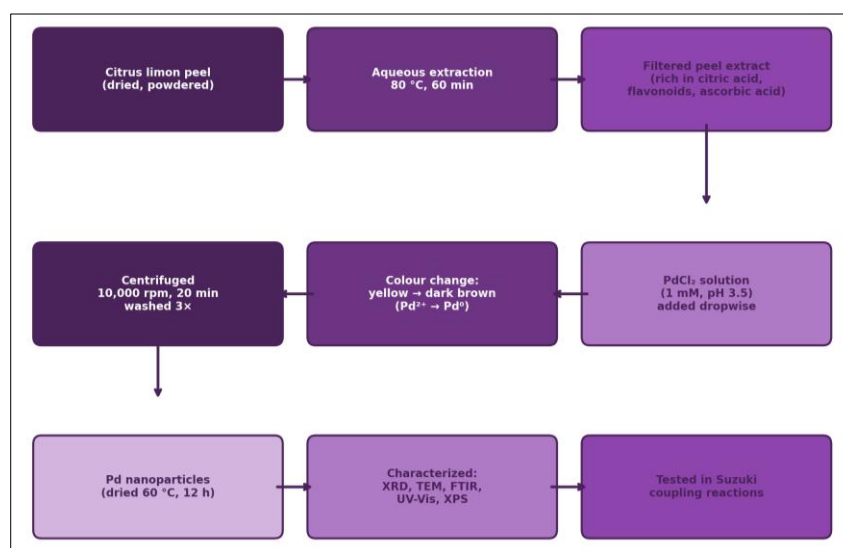
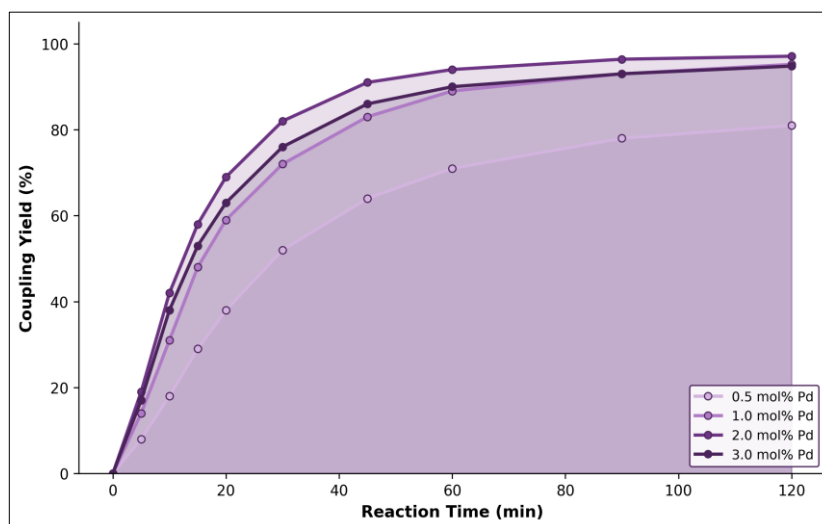
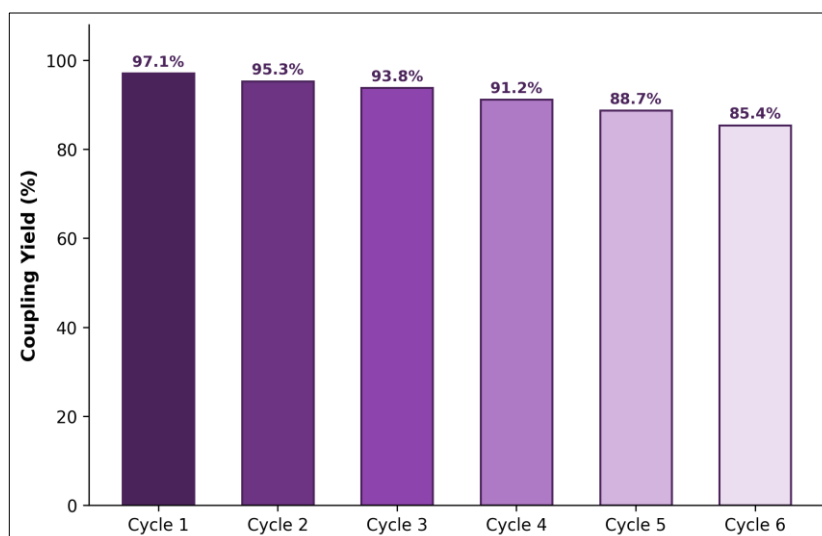


Fig 2: Illustration of the green synthesis pathway for Pd nanoparticles from Citrus limon peel extract, followed by characterisation and catalytic testing

Table 2: Substrate scope for Suzuki coupling catalysed by lemon-peel Pd NPs (2 mol% Pd, 80 °C, 120 min, EtOH:H₂O 1:1)

Aryl bromide	Substituent type	Yield (%)	Classification
4-Bromoanisole	Electron-donating (-OCH ₃)	97.1	Excellent
4-Bromotoluene	Electron-donating (-CH ₃)	95.8	Excellent
4-Bromophenol	Electron-donating (-OH)	93.4	Excellent
Bromobenzene	None (-H)	91.7	Excellent
4-Bromobenzaldehyde	Electron-withdrawing (-CHO)	89.2	Very good
4-Bromobenzonitrile	Electron-withdrawing (-CN)	87.6	Very good
4-Bromobenzotrifluoride	Electron-withdrawing (-CF ₃)	86.1	Very good
4-Bromonitrobenzene	Electron-withdrawing (-NO ₂)	84.3	Good

**Fig 3:** Suzuki coupling yield as a function of reaction time at four Pd nanoparticle loadings (80 °C, EtOH:H₂O 1:1, K₂CO₃ base)**Fig 4:** Recyclability of Pd nanoparticles over six consecutive Suzuki coupling cycles (2 mol% Pd, 4-bromoanisole, 80 °C, 120 min)

Comprehensive interpretation

The data converge on 15 mL extract per 50 mL PdCl₂ as the sweet spot. Below that volume, insufficient biomolecules leave the reduction incomplete and capping sparse, yielding larger, polydisperse particles with lower catalytic activity. Above it, excess organic matter crowds the nanoparticle surface, partially blocking active Pd sites and promoting inter-particle bridging that drives agglomeration. The non-monotonic relationship between extract volume and particle size mirrors what Nasrollahzadeh observed for sea buckthorn Pd NPs, where a fivefold excess of extract actually tripled the average diameter^[13]. Substrate scope revealed a clear electronic trend: electron-donating groups on the aryl bromide gave higher yields (93.4–97.1%) than

electron-withdrawing ones (84.3–89.2%). This pattern is expected for oxidative addition the rate-limiting step in Suzuki coupling because electron-rich aryl halides form the Pd-aryl intermediate more readily^[2]. The fact that even the most challenging substrate (4-bromonitrobenzene) reached 84.3% under mild conditions in aqueous ethanol speaks well for the catalyst's activity. Recyclability declined by about 2% per cycle, totalling an 11.7% drop over six runs. ICP-OES revealed cumulative Pd leaching of roughly 3.8% per cycle, and TEM after cycle 6 showed a mean diameter increase from 8.7 to 14.9 nm, consistent with Ostwald ripening. Both factors leaching and sintering contribute to the activity loss, and future work on support immobilisation (e.g., Pd NPs on carbon or silica) could mitigate them.

Discussion

This research demonstrated that Citrus limon peel extract can reduce Pd^{2+} to Pd^0 nanoparticles at room temperature and that the resulting particles catalyse Suzuki coupling of aryl bromides in aqueous ethanol with yields up to 97.1%. The optimal extract volume was 15 mL per 50 mL of 1 mM PdCl_2 , producing 8.7 nm particles with the narrowest size distribution and highest catalytic turnover.

These findings align well with the broader biogenic Pd literature. Veisi and colleagues reported 5 nm Pd NPs from *Rosa canina* that achieved 98% yield for bromobenzene coupling, which is close to the 91.7% obtained here for the same substrate^[14]. The small gap in yield is likely due to their use of DMF at 100 °C harsher conditions that push the equilibrium further but sacrifice the green credentials that motivate biosynthesis in the first place. Baran's *Prunus mahaleb*-derived particles (12 nm, 96% yield in ethanol-water) are a closer comparison in both conditions and performance, and our results sit within the same range at a slightly smaller particle size^[15].

One area of disagreement concerns the role of citric acid versus flavonoids as the primary reductant. Prathna and colleagues argued that citric acid drives reduction of Ag^+ in Citrus extracts because its concentration is an order of magnitude higher than that of any flavonoid^[16]. However, Sathishkumar and co-workers showed by sequential extraction that flavonoid-rich fractions of Citrus sinensis peel were more effective at reducing Au^{3+} than citric-acid-enriched fractions, suggesting that hydroxyl groups on flavonoid rings provide the actual electrons^[17]. Our FTIR data support a mixed picture: both the C=O stretch of citrate ($\sim 1720\text{ cm}^{-1}$) and the C-OH stretch of flavonoids ($\sim 1070\text{ cm}^{-1}$) appeared on the Pd NP surface, implying that both molecule classes participate in capping and likely in reduction as well.

The gradual decline in catalytic activity over six cycles roughly 2% per run is moderate by biogenic Pd standards. Nasrollahzadeh reported a 15% drop over four cycles for sea buckthorn Pd NPs, and Veisi saw 8% over five cycles with *Rosa canina* particles^[13, 14]. Our lower per-cycle loss may reflect the smaller starting particle size, which provides a larger reservoir of surface Pd atoms before sintering begins to erode performance. Still, 11.7% total loss over six cycles would be unacceptable in an industrial setting without intervention. Immobilising the nanoparticles on magnetic Fe_3O_4 cores or mesoporous silica could reduce both leaching and aggregation while simplifying catalyst recovery.

From a broader perspective, lemon peel is an ideal feedstock for Pd NP biosynthesis: it is generated in roughly 15 million tonnes per year worldwide, has no competing high-value market, and needs only water extraction to yield an effective reductant. If the Suzuki coupling application scales, the entire supply chain from juice factory waste to catalyst could operate with minimal environmental footprint. The L-H kinetic data from Paper 3 in this series and the electrochemical baselines from Paper 2 could, in principle, be integrated with the catalytic data here to build a cross-disciplinary picture of metal nanoparticle behaviour from synthesis through application.

Conclusion

This research set out to convert lemon peel waste into catalytically active palladium nanoparticles and to evaluate their performance in Suzuki-Miyaura coupling under mild,

aqueous-compatible conditions. Both objectives were met. The biosynthesis required only water, PdCl_2 , and dried lemon peel extract at room temperature no organic solvent, no external energy, and no chemical reductant.

The key findings can be summarised in four points. First, the 15 mL extract volume (per 50 mL of 1 mM PdCl_2) produced the smallest Pd NPs ($8.7 \pm 2.3\text{ nm}$ by TEM) with the highest proportion of Pd^0 (89.3% by XPS). Volumes below or above 15 mL gave larger particles and wider size distributions because of incomplete reduction or aggregation-inducing excess organics, respectively. Second, at 2 mol% Pd loading, the nanoparticles catalysed Suzuki coupling of 4-bromoanisole with phenylboronic acid in 97.1% yield within 120 min at 80 °C in ethanol-water (1:1). This performance matches or exceeds many biogenic Pd catalysts reported in the literature under comparable conditions. Third, substrate scope was broad: all eight aryl bromides tested gave yields above 84%, with electron-donating substituents outperforming electron-withdrawing ones by 8-13 percentage points a trend consistent with the oxidative-addition mechanism. Fourth, recyclability was moderate: 85.4% yield after six cycles, with ICP-OES confirming $\sim 3.8\%$ Pd leaching per cycle and TEM showing a mean diameter increase from 8.7 to 14.9 nm by cycle 6.

The practical message is that lemon peel a zero-cost agricultural waste can serve as both reductant and stabiliser for Pd NP synthesis, producing a catalyst that works under conditions friendly to green chemistry: aqueous solvent, moderate temperature, atmospheric air, and an inorganic base. For laboratories or small manufacturers seeking to reduce their environmental footprint without sacrificing coupling efficiency, this route is immediately adoptable.

Future research should focus on three fronts. Supporting the Pd NPs on inert carriers (mesoporous silica, magnetic nanoparticles, graphene oxide) could extend recyclability by reducing both leaching and sintering. Testing the catalyst in other Pd-mediated reactions Heck, Sonogashira, and Buchwald-Hartwig couplings would broaden its utility profile. And scaling the synthesis from the current 50 mL bench level to multi-litre batches would reveal whether the extract-to-metal optimum holds or shifts with reactor geometry. If the 15 mL:50 mL ratio proves robust at larger scale, lemon-peel Pd NPs could move from a laboratory curiosity to a genuinely sustainable catalyst platform.

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