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## ARTICLE

# Biogenic Synthesis of Palladium Nanoparticles Using *Plucaria Glutinosa* Plant Extract and Their Catalytic Activity Towards Suzuki Coupling Reaction

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Green synthesis of nanomaterials finds the edge over chemical methods due to its environmental compatibility. Herein, we report a facile and eco-friendly method for the synthesis of palladium (Pd) nanoparticles (NPs) using an aqueous solution of *Pulicaria glutinosa*, a plant widely found in a large region of Saudi Arabia, as a bioreductant. The as-prepared Pd NPs were characterized using ultraviolet–visible (UV-vis) spectroscopy, powder X-ray diffraction (XRD), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), and Fourier-transform infrared spectroscopy (FT-IR). The hydroxyl groups of the plant extract (PE) molecules were found mainly responsible for the reduction and growth of Pd NPs. FT-IR analysis confirmed the dual role of the PE, both as a bioreductant as well as a capping ligand, which stabilizes the surface of Pd NPs. The crystalline nature of the Pd NPs was identified using XRD analysis which confirmed the formation of a face-centered cubic structure (JCPDS: 87-0641, space group: Fm3m (225)). Furthermore, the as-synthesized Pd NPs demonstrated excellent catalytic activity towards the Suzuki coupling reaction under aqueous and aerobic conditions. Kinetic studies of the catalytic reaction monitored using GC confirmed that the reaction complete in less than 5 minutes.

## Introduction

Recently, the green synthesis of metallic nanoparticles (NPs) has attracted tremendous attention in the scientific community, due to the growing environmental contamination caused by the conventional chemical methods.<sup>1-5</sup> Usually, NPs have been synthesized using various chemical and physical methods based on the availability and feasibility of protocols to achieve the required applications.<sup>6,7</sup> However, many of these methods either involve expensive equipment or hazardous chemicals which have harmful effects on environment as well as on human health.<sup>8</sup> Additionally, during the chemical synthesis, the residuals of some toxic chemicals may adsorb on the surfaces of the NPs, which prevents their application in biomedical equipment.<sup>9</sup> Therefore, there is strong immense interest in the development of environmentally friendly and sustainable methods for the preparation of NPs.<sup>10</sup>

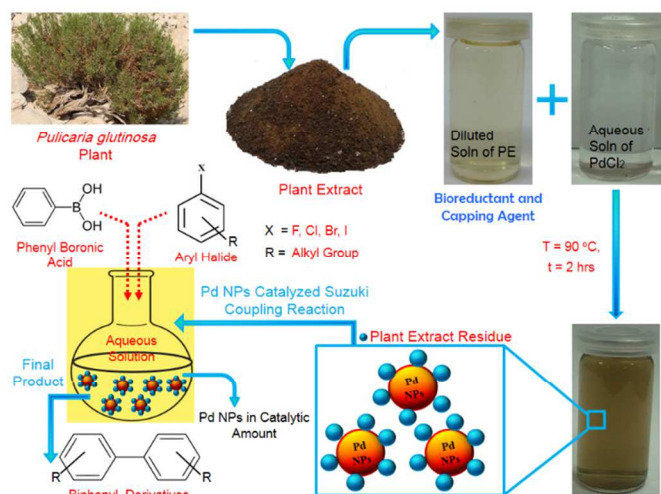
Several green methods have been applied for the preparation of NPs, including the applications of natural materials such as, microorganisms, marine organisms, biomolecules extracts and plant materials as bio-reductants or

mimicking the biochemical processes leading to the formation of complex biominerals.<sup>11-14</sup> However, among these methods plant extracts have attracted significant attention, due to easy and simple sampling, and cost effectiveness of this method facilitates the large scale biosynthesis of NPs.<sup>15-17</sup> Several metallic and bimetallic NPs, such as, Au, Ag, Pd, Pt, Cu, Ag/Au, Au/Pd and Cu/Au, having potential applications in various fields including optoelectronics, SERS based detection of small molecules analytes, biological labeling and catalysis, have been successfully synthesized using different kinds of plant materials.<sup>18-25</sup>

Among the metallic NPs, Pd has a variety of applications in the field of both homogeneous and heterogeneous catalysis.<sup>26-28</sup> Various catalytic reactions explored using Pd NPs includes hydrogenations, oxidations, carbon-carbon coupling as well as electrochemical reactions.<sup>29-32</sup> Especially, stable colloidal Pd NPs supported on a conventional and non-conventional supports have been exploited as catalysts for Suzuki cross coupling reactions.<sup>33-35</sup> In most of the cases the Pd NPs were synthesized by chemical, electrochemical or sonochemical

methods, using dendrimers, polymers, or metal-organic frameworks as stabilizers.<sup>36-38</sup>

Although, there are some reports on the green synthesis of Pd NPs using plant materials, e.g. extracts of Banana peel, leaf extracts of Soya bean and *Anacardium occidentale*, broth of *Cinnamomum camphora* leaf, bark of *Cinnamomum zeylanicum* and tuber of *Curcuma longa* as bioreductant, but they are not as extensive as published for gold and silver NPs.<sup>15,39-43</sup> Moreover, most of these methods resulted in agglomerated and non-homogenous nanoparticles. Therefore, it is important to explore other varieties of plants and plant based materials for the preparation of scalable, stable, homogenous and dispersible colloidal Pd NPs and to study the effect of these materials on the catalytic properties of the as-prepared NPs.



**Scheme 1** Schematic illustration of the green synthesis of palladium nanoparticles (Pd NPs) using aqueous extract of the *P. glutinosa* plant and their catalytic activity for Suzuki reaction.

In this report, we have tested the extract of the plant *Pulicaria glutinosa*, which has been collected from the local fields in Saudi Arabia, for the preparation of dispersible Pd NPs. The rich contents of polyphenolic and flavonoidic groups present in the *P. glutinosa* plant extract significantly enhance its reducing power and also serve as stabilizing agents.<sup>44</sup> These properties have already been exploited for the preparation of silver NPs in our previous study.<sup>45</sup> *Pulicaria* is a relatively large genus of plants belonging to the tribe *Inuleae*, a subtribe *Inulinaea* of the daisy family *Compositae*. It comprises of about 100 species distributed from Europe to North Africa and Asia, particularly around the Mediterranean.<sup>46</sup>

The Pd nanoparticles were synthesized using an aqueous extract of *P. glutinosa* plant (Scheme 1). The as-prepared Pd NPs were tested as a catalyst for the Suzuki coupling reaction in aqueous systems. During this study, a detailed kinetic analysis was performed on the product obtained from the catalytic coupling reaction. Pd NPs and the product of the catalytic reaction were characterized using various microscopic and analytical techniques including, gas chromatography (GC), XRD, FT-IR, UV-Vis and HRTEM.

## Experimental section

### Materials and Methods

PdCl<sub>2</sub> (99.9%), bromobenzene (99.5%), sodium dodecyl sulfate (98%), phenyl boronic acid (95%), tripotassium phosphate (98%) and other solvents were purchased from Sigma Aldrich and were used without any further purification.

The plant specimen of wild growing *P. glutinosa* was collected from the hilly area of Al-Hair in central Saudi Arabia during March 2011. The identity of the plant material was confirmed by a plant taxonomist from the Herbarium Division of the College of Science, King Saud University, Riyadh, Kingdom of Saudi Arabia. A voucher specimen was deposited in our laboratory as well as in the Herbarium Division of King Saud University with the voucher specimen number KSU-21598. The details of the preparation of plant extract were given in our previous study.<sup>45</sup> The solution of the plant extract used for the reduction of PdCl<sub>2</sub> was prepared using 0.1 gram of plant extract in 1 mL of solvent.

### Synthesis of palladium NPs

In a typical experiment, the reaction mixture was prepared by adding 5 mL of the plant extracts to 95 mL of 1 mM PdCl<sub>2</sub> (177.33 mg) solution in a 150 mL round bottom flask, which is mounted with cooling condenser and magnetic stir bar. The mixture was stirred for 2h at 90 °C (an immediate color change was observed from light yellow to dark brown. No further color change was observed even after two hours). After two hours the mixture was allowed to cool down followed by centrifugation (9000 rpm). After washing three times with distilled water, black powder was obtained which was dried overnight in an oven at 80 °C.

### Suzuki reaction catalyzed by Pd NPs

A mixture of sodium dodecyl sulfate (144 mg, 0.5 mmol), tripotassium phosphate (K<sub>3</sub>PO<sub>4</sub>, 399 mg), phenylboronic acid (146 mg, 1.2 mmol) and deionized water (20 mL) was taken in a 100 mL round bottom flask. Bromobenzene (157.01 mg, 1.0 mmol) was added to this mixture under stirring, followed by the as-prepared Pd NPs (5 mol%, 5.32 mg). The mixture was stirred at 100 °C in an oil bath for 5 min and then extracted with ethyl acetate (3 × 20 mL). The combined organic extract was dried over anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), and the resulting mixture was analyzed by gas chromatography (GC). In order to identify the product obtained from the catalytic reaction, the as-obtained mixture was crystallized from ethanol. The resulting white powder was identified as biphenyl using <sup>1</sup>H and <sup>13</sup>C solution NMR and mass spectroscopy. <sup>1</sup>H NMR δ 8.25 (d, J=8.3 Hz, 4H, C-CH, next to ipso), 7.25-7.26 (m, 6H, remaining protons of phenyl ring); <sup>13</sup>C NMR δ 141.3 (2C, C-C, ipso), 128.8 (4C,CH-CH), 127.3 (2C,CH-CH, edge carbons), 127.2 (4C, C-CH, next to ipso); EIMS *m/z* 154 (M<sup>+</sup>).

### Characterization of the NPs

**UV-Vis Spectroscopy.** A Perkin Elmer lambda 35 (USA) UV-Vis spectrophotometer was used to conduct optical measurements. The analysis were performed in quartz cuvettes, using distilled water as a reference solvent. The samples for the UV measurements of crude mixture were prepared by diluting 1 ml of mixture (collected at the end of reaction) in 9 ml of water, sonicated for 15 min.

**X-RAY Diffraction.** Powder XRD patterns were collected on a Altima IV [Make: Regaku, Japan] X-ray powder diffractometer using Cu K $\alpha$  radiation ( $\lambda=1.5418$  Å).

**Transmission Electron Microscopy.** Transmission electron microscopy (TEM) was performed on a JEOL JEM 1101 (USA) transmission electron microscope. The samples for TEM were prepared by placing a drop of primary sample on a copper grid, which were dried for 6 hours at 80 °C in an oven.

**Fourier Transforms Infrared Spectrometer.** FT-IR spectra were measured on a Perkin- Elmer 1000 (USA) Fourier transforms infrared spectrometer. In order to remove any free biomass residue or unbound extract to the surfaces of NPs, Pd NPs were repeatedly washed with distilled water; subsequently the product was centrifuged at 9000 rpm for 30 min and dried. The purified Pd NPs were mixed with KBr powder and pressed into a pellet for measurement. Background correction was made using a reference blank KBr pellet.

**Gas Chromatography.** The conversion of the catalytic product was analysed using (GC, 7890A) Agilent Technologies Inc., equipped with a flame ionization detector (FID) and a 19019S-001 HP-PONA column.

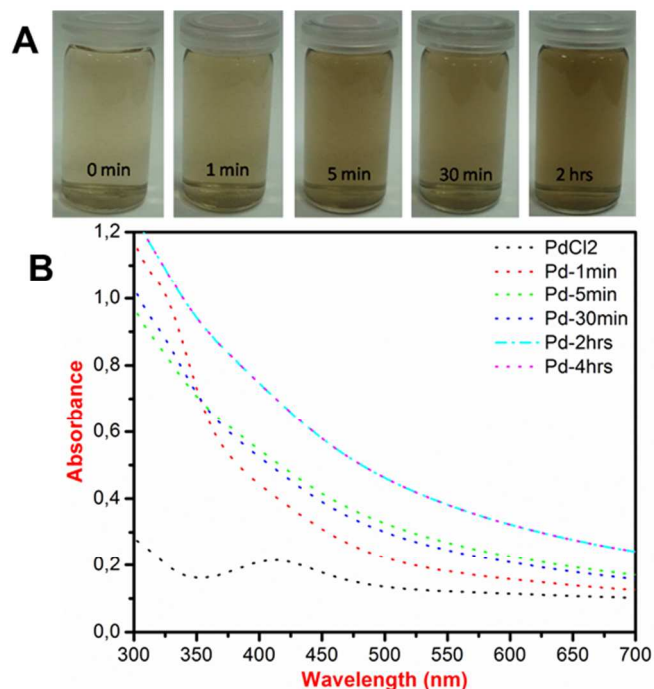
**Solution NMR and Mass.** Solution  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a JEOL ECP-400 spectrometer. The NMR samples were prepared in  $\text{CDCl}_3$  with tetramethylsilane (TMS) as an internal standard. Mass spectrum was recorded on an Agilent single quadrupole mass spectrometer with an inert mass selective detector (MSD-5975C detector, Agilent Technologies Inc., USA) coupled directly to an Agilent 7890A gas chromatograph. MS was acquired in EI mode (scan range  $m/z$  45–600, ionization energy 70 eV).

## Results and discussion

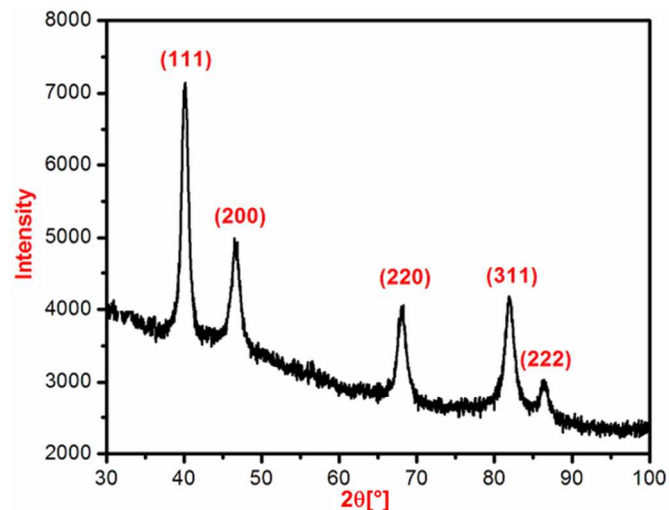
The *P. glutinosa* plant extract (PE) mediated synthesis of palladium (Pd) nanoparticles (NPs) was performed under facile conditions using an aqueous solution of  $\text{PdCl}_2$  and PE without addition of any other external reducing agent. The color of the aqueous solution of  $\text{PdCl}_2$  gradually changed from light yellow to dark brown upon addition of an aqueous solution of PE (Fig. 1A) and stirring for two hours, indicating the formation of Pd NPs.

Initially, the formation of the as-prepared Pd NPs was monitored via UV-Vis spectroscopy. Fig. 1B displays the UV-Vis spectra of  $\text{PdCl}_2$  and Pd NPs prepared at 90 °C after four hours. The spectrum of  $\text{PdCl}_2$  exhibits an absorption maximum at 415 nm due to the absorption of Pd (II) ions, which completely disappeared after reduction and replaced by a broad and continuous absorption, which clearly indicates the conversion of Pd (II) ions to Pd (0) NPs. As the reaction was performed at high temperature, the nucleation started very quickly, and most of the Pd (II) was already converted to Pd (0)

during the first five minutes of the reaction. This is clearly reflected by the UV-Vis spectra of solution where the absorption maximum at 415 nm disappeared during the initial measurements itself. However, it takes almost two hours to complete the growth of nanoparticles as evident by UV-vis spectra and color change observed visually.



**Fig. 1.** A) Digital micrograph taken at various time scale showing the colour change of the reaction mixture at 90°C. B) Ultraviolet–visible (UV-Vis) absorption spectra of the corresponding solution depicting the reduction of  $\text{PdCl}_2$  to Pd.

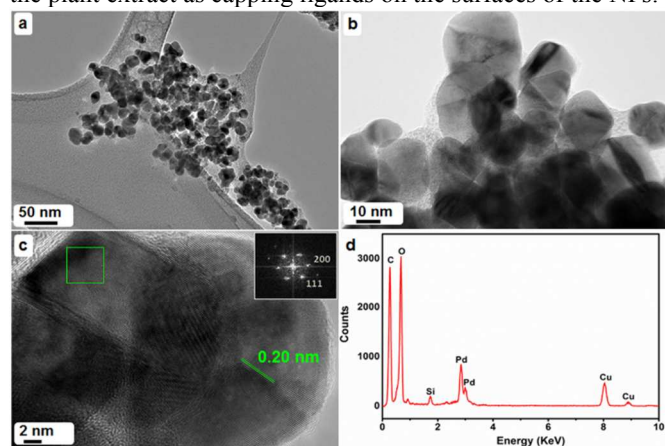


**Fig. 2.** XRD diffraction pattern of the as synthesized palladium nanoparticles.

The crystallinity of the as synthesized Pd NPs from *P. glutinosa* PE was confirmed via XRD analysis. As shown in Fig. 2, there are five distinct reflections in the diffractogram at 40.02° (111), 46.49° (200), 68.05° (220), 81.74° (311) and 86.24° (222).

These characteristic reflections can be indexed to the of face centered cubic (fcc) structure of Pd (JCPDS: 87-0641, space group: Fm3m (225)).<sup>40</sup> The intense reflection at (111), in comparison to the other four, may indicate the preferred growth direction of the nanocrystals.<sup>45</sup> On the basis of the half width of the (111) reflection, the average crystallite size ( $\sim 20$  nm) of the Pd NPs was determined using the Scherrer equation.<sup>47</sup>

Morphology and size of the as synthesized Pd NPs was investigated using high resolution transmission electron microscopy (HRTEM) (Fig. 3). The overview image in Fig. 3a shows the morphology and size distribution of the as synthesized Pd NPs with diameters of  $\sim 20$ –25 nm. A magnified overview image (Fig. 3b) reveals the presence of an organic layer (light contrast) around the nanoparticles. The HRTEM image (Fig. 3c) of one of the nanoparticles measured along the [01-1] zone axis displays well-resolved, continuous fringes with a lattice spacing of 2.0 Å, which can be indexed as {200} of face-centered cubic Pd. The Fourier transform patterns (insets of Fig. 3c) show the spots which could be indexed to the cubic structure with space group Fm-3m. The elemental composition of the as synthesized NPs was also determined via EDX, which is shown in Fig. 3d. The presence of Pd is clearly indicated in the spectrum, together with other elements including, carbon and oxygen. This also indicates the presence of residual phytomolecules of the plant extract as capping ligands on the surfaces of the NPs.

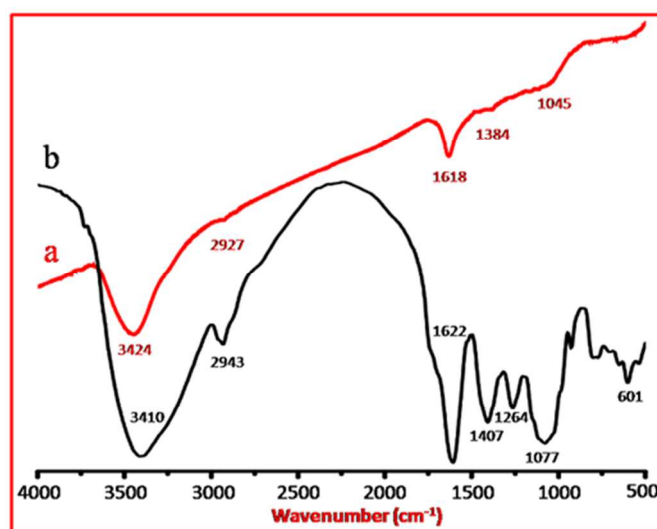


**Fig. 3.** Transmission electron microscope (TEM) and high resolution (HRTEM) images of the Pd NPs a) overview, b) magnified HRTEM image, c) HRTEM image with labelled *d*-spacing and FFT (as an inset on top right corner) taken from the place marked as green box. d) Energy dispersive X-ray spectrum (EDX) of as synthesized Pd NPs confirming the composition of product.

In order to further confirm the dual role of the plant extract as a bioreductant and capping agent FT-IR spectra of both as synthesized Pd NPs as well as the PE were measured (Fig.4). To exclude the presence of any unbound ligands on the surfaces of the Pd NPs, freshly prepared Pd NPs were re-dispersed in distilled water via sonication and centrifuged at a speed of 9000 rpm for 30 min; subsequently this process was repeated twice to isolate pure Pd NPs. The FT-IR spectra of as synthesized Pd NPs in comparison to plant extract shows the presence of PE on the surface of nanoparticles.

Detailed analysis of the PE spectrum strongly suggested the presence of flavonoids and polyphenols, apart from other phytochemicals, which were mainly responsible for the

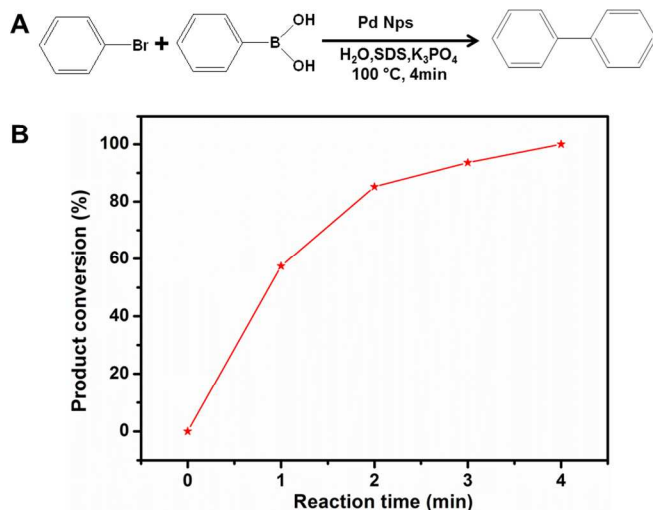
formation of the Pd NPs. As reported in our previous study, hydroxyl groups belonging to the phytomolecules of the PE could be responsible for the formation of silver NPs.<sup>45</sup> The spectrum of the PE shows the broad absorption peaks centered at  $3410\text{ cm}^{-1}$  corresponding to the hydrogen-bonded hydroxyl (OH) and the peak at  $2943\text{ cm}^{-1}$  indicates the presence of C–H. The absorption peaks present around  $1753$ ,  $1622$ , and  $1407\text{ cm}^{-1}$  are the characteristic peaks for the C–H, C–C, and C–O stretching, respectively, of the aromatics. The bands at  $1264$  and  $1077\text{ cm}^{-1}$  indicate the presence of C–O stretching of alcohols, carboxylic acids, and ester and ether groups.



**Fig. 4.** Fourier-transform infrared spectra of pure green synthesized palladium nanoparticles (Pd NPs) (red line (a)) and *P. glutinosa* PE (black line (b)).

In order to explore the possible applications of Pd nanoparticles, the catalytic activity of as synthesized Pd NPs was tested in the Suzuki reaction of bromobenzene with phenylboronic acid (Fig. 5). Commonly, the biaryl carbon-carbon coupling reactions, including Suzuki reactions are carried out in a mixture of an organic solvent and an aqueous inorganic base, under inert conditions.<sup>48</sup> However, some of the Suzuki reactions have also been carried out under aqueous conditions, which usually require activation by phosphine ligands.<sup>49</sup> In this study, we followed a reported method for the Suzuki reaction which does not required any pre-activation.<sup>34,50</sup> The Pd NPs obtained from the *Pulicaria glutinosa* extract catalyzed the reaction of bromobenzene with phenylboronic acid in water containing SDS (sodium dodecyl sulfate) and  $\text{K}_3\text{PO}_4$  under aerobic conditions to obtain biphenyl. Furthermore, the kinetic studies were also performed for the Suzuki reaction using 5 mol% of the Pd NPs from the *Pulicaria glutinosa* extract as catalyst. The results were analysed using gas chromatography (GC–FID) equipped with a capillary column (HP-PONA). The temperature profile for GC was as follows. The starting column temperature was  $120^\circ\text{C}$ , which was increased to  $180^\circ\text{C}$  at a ramp rate of  $10^\circ\text{C}/\text{min}$  and maintained at this temperature for 5 min. The samples were collected every minute and quenched immediately. The GC results clearly indicated that the reaction was complete within 4

minutes, as shown in the graphical representation of the kinetics of the reaction in Fig. 5b. It is clear from the Fig. 5 that ~60 % of the reaction was already completed within the first minute of reaction. After this induction period, the conversion was about 85% in the 2<sup>nd</sup> minute, and eventually total conversion (100%) was achieved after 4 min. Similar reaction which has been reported earlier has taken longer than 5 min. under different conditions.<sup>51,52</sup>



**Fig. 5.** A) Schematic representation of Suzuki reaction of bromobenzene with phenylboronic acid under aqueous conditions. B) Time dependent conversion efficiency of Suzuki reaction of bromobenzene with phenylboronic acid under aqueous and aerobic conditions determined by GC analysis.

## Conclusions

We have demonstrated a green approach for the synthesis of Pd NPs using *P. glutinosa* PE as a bioreductant. Applying this method, highly crystalline, spherical-shaped Pd NPs were prepared without using any harmful reducing or capping agents. The phytochemicals of the PE were not only responsible for the reduction of PdCl<sub>2</sub> but also function as capping ligands to the surfaces of the Pd NPs, as confirmed by FT-IR spectroscopy. The as-prepared Pd NPs exhibited excellent catalytic activity towards Suzuki coupling reaction carried out in water under aerobic conditions. The kinetic studies of the reaction monitored by GC confirmed the complete conversion of bromobenzene to biphenyl in a very short time (<5 min). Therefore, the eco-friendly protocol presented here can easily be exploited for the large-scale synthesis of efficient and low-cost Pd NPs catalysts, which can be potentially applied for the green synthesis of many organic compounds including biaryls.

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## Notes and references

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- 1 S. Irvani, *Green Chem*, 2011, **13**, 2638.
- 2 H. Zhu, M. L. Du, M. Zou, C. Xu and Y. Q. Fu, *Dalton Trans.* 2012, **41**, 10465.
- 3 P. Raveendran, J. Fu and S. L. Wallen, *J. Am. Chem. Soc.* 2003, **125**, 13940.
- 4 S. B. Kalidindi and B. R. Jagirdar, *Chem. Sus. Chem.*, 2012, **5**, 65.
- 5 R. S. Varma, *Curr. Opin. Chem. Engin.* 2012, **1**, 123.
- 6 B. Nakhjavan, M. N. Tahir, F. Natalio, H. Gao, K. Schneider, T. Schladt, I. Ament, R. Branscheid, S. Weber, U. Kolb, C. Sönichsen, L. M. Schreiber, W. Tremel, *J. Mater. Chem.* 2011, **21**, 8605.
- 7 M. N. Tahir, F. Natalio, M. A. Cambaz, M. Panthöfer, R. Branscheid, U. Kolb, and W. Tremel, *Nanoscale*, 2013, **5**, 9944.
- 8 J. R. Peralta-Videa, L. Zhao, M. L. Lopez-Moreno, G. Rosa, J. Hong and J. L. Gardea-Torresdey, *J. Hazard. Mater.* 2011, **186**, 1.
- 9 K. Byrappa, S. Ohara and T. Adschiri, *Adv. Drug Delivery Rev.* 2008, **60**, 299.
- 10 J. M. Campelo, D. Luna, R. Luque, J. M. Marinás and A. A. Romero, *Chem. Sus. Chem.*, 2009, **2**, 18.
- 11 S. V. Otari, R. M. Patil, S. R. Waghmare, S. J. Ghosha and S. H. Pawar, *Dalton Trans.*, 2013, **42**, 9966.
- 12 T. Hennebel, S. D. Corte, W. Verstraete and N. Boon, *Curr. Opin. Biotechnol.* 2012, **23**, 555.
- 13 M. N. Tahir, F. Natalio, H. A. Therese, A. Yella, N. Mets, M. R. Shah, E. Mugnaioli, R. Berger, P. Theato, H. C. Schroeder, W. E. G. Mueller, W. Tremel, *Adv. Funct. Mater.* 2009, **19**, 285.
- 14 M. N. Tahir, P. Theato, W. E. G. Müller, H. C. Schröder, A. Boreijko, S. Faiß, A. Janshoff, J. Huth, W. Tremel, *Chem. Commun.* 2005, **28**, 5533.
- 15 M. S. Akhtar, J. Panwar, and Y. S. Yun, *ACS Sustainable Chem. Eng.*, 2013, **1**, 591.
- 16 A. K. Mittal, Y. Chisti and U. C. Banerjee, *Biotechnol. Adv.*, 2013, **31**, 346.
- 17 P. P. Gan and S. F. Y. Li, *Rev. Environm. Sci. Biotechnol.* 2012, **11**, 169.
- 18 F. Coccia, L. Tonucci, D. Bosco, M. Bressan and N. d'Alessandro, *Green Chem.*, 2012, **14**, 1073.
- 19 F. Cheng, J. W. Betts, S. M. Kelly, J. Schaller and T. Heinze, *Green Chem.*, 2013, **15**, 989.
- 20 K. M. Kumar, B. K. Mandal, and S. K. Tammina, *RSC Adv.*, 2013, **3**, 4033.
- 21 G. Zhang, M. Du, Q. Li, X. Li, J. Huang, X. Jiang and D. Sun, *RSC Adv.*, 2013, **3**, 1878.
- 22 H. J. Lee, J. Y. Song and B. S. Kim, *J. Chemical Technol. Biotechnol.* 2013, **88**, 1971.
- 23 P. Dauthal and M. Mukhopadhyay, *Ind. Eng. Chem. Res.*, 2012, **51**, 13014.
- 24 B. Xia, F. He and L. Li, *Langmuir*, 2013, **29**, 4901.
- 25 K. D. Arunachalam, S. K. Annamalai and S. Hari, *Inter. J. Nanomed.* 2013, **8**, 1307.
- 26 F. Zaera, *Chem. Soc. Rev.*, 2013, **42**, 2746.
- 27 G. C. Fortman and S. P. Nolan, *Chem. Soc. Rev.*, 2011, **40**, 5151.
- 28 A. J. Hickman and M. S. Sanford, *Nature*, 2012, **484**, 177.
- 29 M. Zhu, Y. Wang, C. Wang, W. Li and G. Diao, *Catal. Sci. Technol.*, 2013, **3**, 952.
- 30 Y. Lu, H. Zhu, W. Li, B. Hu and S. Yu, *J. Mater. Chem. A*, 2013, **1**, 3783.
- 31 S. Santra, P. Ranjan, P. Bera, P. Ghosh and S. K. Mandal, *RSC Adv.*, 2012, **2**, 7523.
- 32 S. Deng, J. Lei, Y. Huang, X. Yao, L. Ding and H. Ju, *Chem. Commun.*, 2012, **48**, 9159.
- 33 H. Itoh, H. Maeda, S. Yamada and Y. Hori, *Chem. Cat. Chem.*, 2012, **4**, 1737.

- 34 S. Cacchi, E. Caponetti, M. A. Casadei, A. D. Giulio, G. Fabrizi, G. Forte, A. Goggiamani, S. Moreno, P. Paolicelli, F. Petrucci, A. Prastaro and M. L. Saladino, *Green Chem.*, 2012, **14**, 317.
- 35 M. P. Lorenzo, *J. Phys. Chem. Lett.*, 2012, **3**, 167.
- 36 J. Cookson, *Platinum Metals Rev.*, 2012, **56**, 83.
- 37 L. Liang, A. K. Diallo, L. Salmon, J. Ruiz and D. Astruc, *Eur. J. Inorg. Chem.* 2012, **2012**, 2950.
- 38 D. J. Gavia and Y. S. Shon, *Langmuir*, 2012, **28**, 14502.
- 39 A. Bankar, B. Joshi, A. R. Kumar and S. Zinjarde, *Mater. Lett.* 2010, **64**, 1951.
- 40 S. S. Shankar, A. Rai, B. Ankamwar, A. Singh, A. Ahmad and M. Sastry, *Nature Mater.*, 2004, **3**, 482.
- 41 D.S. Shenoy, D. Philip and J. Mathew, *Spectrochimica Acta Part A*, 2012, **91**, 35.
- 42 X. Yang, Q. Li, H. Wang, J. Huang, L. Lin, W. Wang, D. Sun, Y. Su, J. B. Opiyo, L. Hong, Y. Wang, N. He and L. Jia, *J. Nanopart Res.*, 2010, **12**, 1589.
- 43 M. Sathishkumar, K. Sneha, I. S. Kwak, J. Mao, S. J. Tripathy and Y. S. Yun, *J. Hazard. Mater.* 2009, **171**, 400.
- 44 C. A. Williams, J. B. Harborne, J. R. Greenham, R. J. Grayer, G. C. Kite and J. Eagles, *Phytochemistry*, 2003, **64**, 275.
- 45 M. Khan, M. Khan, S. F. Adil, M. N. Tahir, W. Tremel, H. Z. Alkhatlan, A. Al-Warthan and M. R. H Siddiqui, *Int. J. Nanomed.* 2013, **8**, 1507.
- 46 M. Stavri, K. T. Mathew, A. Gordon, S. D. Shnyder, R. A. Falconer and S. Gibbons, *Phytochem.* 2008, **69**, 1915.
- 47 P. Scherrer, *Göttinger Nachrichten Gesell.*, 1918, **2**, 98.
- 48 A. F. Littke, C. Dai and G. C. Fu, *J. Am. Chem. Soc.*, 2000, **122**, 4020.
- 49 L. J. Gooßen and K. Ghosh, *Angew. Chem. Int. Ed.*, 2001, **40**, 3458.
- 50 Y. Li, X. Fan, J. Qi, J. Ji, S. Wang, G. Zhang and F. Zhang, *Nano Res.*, 2010, **3**, 429.
51. M. Cao, J. Lin, H. Yang, R. Cao, *Chem. Commun.*, 2010, 46, 5088.
52. M. Cano, A. Benito, W. K. Maser, and E. P. Urriolabeitia, *Carbon* 2011, 49, 652.

## Biogenic Synthesis of Palladium Nanoparticles Using *Plucaria Glutinosa* Plant Extract and Their Catalytic Activity Towards Suzuki Coupling Reaction

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A Green approach allowed for the synthesis of highly crystalline Pd nanoparticles using *P. glutinosa* extracts. They display good catalytic activity towards Suzuki coupling reaction under aerobic conditions.