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Selective and efficient synthesis of decahedral palladium nanoparticles and its catalytic performance for Suzuki coupling reaction

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ABSTRACT

A convenient, mild and cost-effective synthesis of decahedral palladium nanoparticles by exposing aqueous PdCl₂ solution to the sunlight in the presence of citric acid as a reducing agent and PVP as a capping agent was reported. Natural solar energy which acts as a driving force for the generation of palladium nanoparticles makes the process attractive and economical. The obtained nanoparticles were thoroughly characterized by using techniques like TEM, SAED, FEG-SEM, XRD and EDAX. It was observed that up to 70% of the palladium nanoparticles have decahedron shape, while remaining 30% consists of all other different shapes. The citric acid helps in shapes selective synthesis, whereas concentrated solar energy supplies dual energy which helps to speed up the reduction process. The aqueous reaction mixture of palladium nanoparticles was directly employed for the Suzuki coupling reaction and hence centrifuging efforts and cost of reagents required for the isolation of nanoparticles were avoided. The synthesized nanoparticles demonstrated excellent catalytic activity in Suzuki coupling reaction of aryl halides with phenyl boronic acid under mild reaction conditions. The methodology is applicable to diverse substrates providing good to excellent yields of desired products. Notably, the obtained yields with lowest catalytic loading resulting in highest TOF (0.05 mol% catalyst loading and TOF of 1960 h⁻¹) were among the best ever reported for the Suzuki coupling reaction. In addition, the catalyst could be reused for three more consecutive recycles. The effectiveness of present new protocol for the PdNPs synthesis was also compared with PdNPs prepared using conventional heating method.

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1. Introduction

The synthesis of metal nanoparticles with a variety of geometries is an especially important issue because of their electronic, optical, magnetic and biomedical properties can be tuned by controlling their size and shape [1–4]. The activity of metal nanoparticles in chemical reaction depends on their surface properties which are influenced by the shape of synthesized nanoparticles [5]. Consequently, several face-centered cubic (fcc) structured noble metal nanoparticles have been synthesized, for example, shape selective synthesis has been achieved for a various metals such as Au, Ag, Pd, PT, Rh and Ir [6–11].

Particle having five fold twinning structure is considered as a decahedral particle which shows better optical electronic and catalytic applicability in organic synthesis. In this regards, various techniques have been developed for the decahedral nanoparticles synthesis such as reflux condensation [12], ICP [13], ultrasound-assisted membrane reduction [14], solvothermal method [15], reduction and annealing method [16]. Though above mentioned techniques have proven their application in the nanoparticles synthesis, most of these methods suffer from one or more drawbacks such as use of as higher temperature, higher pressure, longer reaction time, use of conventional energy source and sophisticated equipment setup. To overcome these drawbacks, the attention has been paid on free and greener energy sources like solar energy for the synthesis of nanoparticles. Recently, Chien et al. reported the synthesis of decahedral gold nanoparticles using solar energy, in which the reaction mixture was exposed to normal solar radiations where the temperature was up to $35 \,^{\circ}C$ [17]. Hence the development of newer, economic and eco-friendly techniques for the synthesis of nanoparticles is very much needed.

The metal nanoparticles, like PdNPs synthesis required higher driving force. The energy obtained by normal sunlight is not sufficient for the synthesis of PdNPs and to overcome this problem, we have recently reported concentrated solar energy concept for the synthesis of PdNPs [18]. The concentrated solar energy acts as a dual effect energy source (thermal and rotational) which helps to speed up the reaction, compared to the conventional methods like reflux. This new protocol uses naturally available solar

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energy, which is greener, non-polluting and cost effective energy source.

In literature Lim et al. reported decahedral palladium nanoparticles using citric acid as a reducing agent by reflux condensation method, in which author reported up to 90% decahedral PdNPs after 26 h [12]. In a continuation of our studies on the noble metallic nanoparticles herein we report shape selective synthesis of decahedral PdNPs (up to 70% yield) by the application of concentrated solar energy for 6h in the aqueous medium by overcoming the drawback of mixed morphology (triangular, octahedral, decahedral and icosahedra). An aqueous solution containing PdCl₂, citric acid and PVP (poly vinyl pyrrolidone) was exposed to sunlight from 10:00 am to 4:00 pm in the absence of any operations that required electricity, such as stirring the solution. We found that the existing reactant concentrations locked down the formation of a thermodynamically-favourable five fold twinning structure, whereas dual energy effect obtained by the concentrated solar energy is responsible to speed up the reaction. Present results were also compared with the results obtained by the conventional heating method showing the excellence of our new protocol.

For the selective construction of carbon-carbon bonds, palladium-catalysed Suzuki reaction of arylboronic acids with aryl halides is one of the most influential and versatile method. It has been widely used in the synthesis of pharmaceuticals, herbicides, natural products, and advanced materials [19-22]. Till date various phosphine-based as well as phosphine-free palladium complexes were used as catalysts for these coupling reactions [23-25]. As we know phosphine ligands are very much toxic, expensive and moisture-sensitive this makes the 'ligand-free' palladium catalysts prominent tool for both the economic and environmental concerns [26]. Recently, several colloidal palladium nanoparticles are reported for the Suzuki-coupling reactions [27-30]. However, despite of their potential utility, they suffer from one or more drawbacks such as the use of hazardous organic solvents, use of expensive ligands, difficulties in isolation of nanoparticles, highest catalyst loading, longer reaction time and difficulties associated with catalyst-product separation thereby, limiting their general applications. Hence, development of an efficient, environmental benign, thermo-stable, the catalyst which will efficiently catalyse the Suzuki C-C coupling reaction under milder reaction condition is a subject of our current interests.

We herein first time reporting shape selective synthesis of decahedral PdNPs by concentrated solar energy and its catalytic activity for the Suzuki C–C coupling reaction. The catalyst exhibited a remarkable activity and the system tolerates a wide variety of substrates with good to excellent yields of desired products. As per our knowledge, the results show better yields with lowest catalyst loading (0.0005 mmol) and high TOF value (1960 h⁻¹) for Suzuki reaction.

2. Experimental

2.1. Materials and methods

Palladium (II) chloride (Parekh Platinum Ltd.), 99% citric acid (Polypharm), poly vinyl pyrrolidone (PVP, MW-40000) were sourced from CDH and used without further purification. Deionised water distilled by water purification system (Milli-Q). Glassware and Teflon coated magnetic stir bars were cleaned with acetone, followed by drying at $130 \,^{\circ}$ C in an oven.

2.2. Preparation of palladium (0) nanoparticles

The synthesis of palladium nanoparticles is carried out in the 25 mL round bottom flask fitted with a water condenser (Fig. 1). In



Scheme 1. Synthesis of palladium nanoparticles by using concentrated solar energy in aqueous medium.

a typical procedure for the synthesis of PdNPs, PVP (126 mg) and citric acid (161 mg) were added to palladium (II) chloride (31 mg) dissolved in deionized water (10 mL (Scheme 1). The obtained mixture was exposed for 6 h under solar radiations concentrated by 'Fresnel lens (1×1 ft)' at noon in summer (temperature range was 85–95 °C). As the solar energy effect is special and temporal, the experiment was carried out at a specific location at the time from 10:00 am to 4:00 pm. After completion of the reaction the nanoparticle solution was diluted up to 100 mL with deionized water and used as a stock solution for the Suzuki cross coupling reaction. The author's laboratory is located at Matunga, Mumbai (Geographical location: Greater Bombay, Maharashtra, India, Asia. Geographical Coordinates: 19°2'0'' North, 72°51'0'' East). The energy input for the reaction is measured by the pyranometer DWR 8101 which was recorded as $575 \text{ W} \text{ ft}^{-2}$.

2.3. Characterization of prepared palladium (0) nanoparticles

The Pd (0) nanoparticles were characterized by various analytical techniques. The X-ray crystallographic pattern was obtained by the XRD miniflex Rigaku model using Cu K α = 1.54 Å with a scanning rate of 2°/min from 0° to 80°. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) was recorded with a Philips model CM 200. Field emission gun-scanning electron microscopy (FEG-SEM) was done by JEOL JSM-7600F and Electron dispersive X-ray spectral (EDAX) analysis done by a JEOL-JFC 1600.

2.4. Typical procedure for Suzuki cross coupling reaction

The reaction was carried out in a sealed tube with spin bar consisting phenylboronic acid (0.146 g, 1.2 mmol), potassium hydroxide (0.112 g, 2 mmol), iodobenzene (0.206 g, 1 mmol) and PdNPs solution (50 μ L, 0.0005 mmol) in aqueous medium at 100 °C for 1 h with constant stirring (Scheme 2). The progress of the reaction was monitored using GC analysis (Perkin-Elmer, Clarus 400). After completion of the reaction, the reaction mixture was cooled to room temperature and the reaction mixture was extracted with ethyl acetate for three times, dried over Na₂SO₄ and the solvent was evaporated under vacuum. The obtained crude product was then purified by column chromatography using silica gel, (100–200 mesh size) with petroleum ether/ethyl acetate (PE–EtOAc, 95:05) as eluent to give pure product. All the products are well known and were confirmed by GC–MS (Shimadzu GC–MS QP 2010).

For the recycling experiments, we have carried out the reaction of iodobenzene and phenyl boronic acid (4 mmol each). The PdNPs could be recycled and reused by separating them from the reaction mixture through centrifugation at 10,000 rpm at 25 °C for 15 min. Supernatant solution was removed and additional ethyl acetate was added to wash settled PdNPs. Again supernatant solution was removed and catalyst was taken for further recycle studies. The catalyst showed good performance up to three recycles.







Fig. 1. Schematic representation of reaction setup for the synthesis of PdNPs.

2.5. GC analysis

The reaction mixture was analysed by gas chromatography equipped with a flame ionization detector (FID) and a capillary column (Perkin-Elmer, Clarus 400, 30 m \times 0.32 mm \times 0.25 µm). The GC parameters were as follows: initial temperature 80 °C; initial time 1 min; solvent delay 3 min; temperature ramp 1 for 10 °C/min; final temperature 250 °C; final time 25 min; injector port temperature 250 °C; detector temperature 250 °C and injection volume 0.6 µL.

2.6. Spectral data of selected products

- 2.6.1. Characterization of biphenyls
- 1. 1,1'-Biphenyl (Table 2, entries 1, 12)
- GC-MS (EI) *m/z* (%)=154(100) [M]⁺, 153(38.3), 152(26.4), 77(8), 76(17.1).
- 2. 4-*Methyl*-1,1'-*biphenyl* (Table 2, entries 2, 9) GC-MS (EI) *m/z* (%)=168(100) [M]⁺, 167(65.6), 165(26), 153(17), 152(21.1), 83(10).
- 3. 4-Methoxy-1,1'-biphenyl (Table 2, entries 3, 10, 13) GC-MS (EI) *m/z* (%)=184(100) [M]⁺, 169(50.5), 141(39.7), 115(25.5).
- 4. 2-Methyl-1,1'-biphenyl (Table 2, entries 4, 11) GC-MS (EI) m/z (%)=168(100) [M]⁺, 167(85.9), 166(13.3), 165(39.3), 153(37.1), 152(26.6), 115(15.3), 83(16.8), 82(11.2).
- 5. 2-Methoxy-1,1'-biphenyl (Table 2, entry 5)

GC–MS (EI) *m/z* (%)=184(100) [M]⁺, 183(20.7), 169(52.3), 168(11.9), 141(34.8), 139(12.2), 115(31.7).

- 6. 1-([1,1'-Biphenyl]-4-yl)ethanone (Table 2, entry 6)
- GC-MS (EI) m/z (%)=196(59) [M]⁺, 181(100), 153(40.5), 152(51.7).
- 7. [1,1'-Biphenyl]-2-amine (Table 2, entry 7)

GC-MS (EI) m/z (%)=169(100) [M]⁺, 168(89.6), 167(42.8), 83(19.7).

- 8. 1-Phenylnaphthalene (Table 2, entry 8)
 - GC-MS (EI) m/z (%)=204(100) [M]⁺, 203(95), 202(58.5), 101(34.6).

3. Results and discussion

3.1. Preparation and characterization PdNPs

Reduction kinetics play a key role in controlling the nucleation and growth of nanoparticles. In this work, we have employed citric acid as a reducing agent. Citric acid works as a reducing agent in a manner similar to the mechanism of a conventional citrate-based synthesis of noble metal nanoparticles. Citric acid can effectively block oxidative etching by competing with oxygen adsorption onto the Pd surface or exhausting the adsorbed oxygen atoms [8,31,32].

Earlier, Xiong et al. have shown the influence of temperature on the morphology of nanoparticle formation [33]. The shape and size of the product depended on temperature in three different ways. First, slow reduction at low temperatures greatly reduced the level of super saturation and hence the number of seeds formed in the nucleation step. At the same concentration of Pd precursor, a decrease in the number of seeds resulted in the formation of Pd nanoparticles with larger sizes. Second, the reduction rate, depending on the temperature, was critical to the control of reduction kinetics and hence the formation of triangular nanoplates. As temperature was increased, the yield of nanoplates decreased distinctly. Third, oxidative etching of twinned particles could be partially eliminated at low temperatures. In general, the morphology of nanoparticles is strongly dependent on temperature, due to the influence of temperature on both reduction kinetic and oxidative etching of multiple twinned species.

Similarly, Lim et al. obtained decahedral PdNPs using citric acid, by 26 h reflux condition [12], it clears that thermal effect helps in the synthesis of decahedral PdNPs along with citric acid; but it will take longer time; whereas the concentrated solar energy because of dual energy effect works in a same way in shorter reaction time. It helps to speed up the reduction and hence gradually increases the level of super saturation which results the nanoparticles of lower size. As mentioned above the yield of nanoplates formation is decreased whereas decahedral nanoparticle formation is increased due to the higher temperature effect obtained by dual energy source. The dual energy effect also helps to speed up the oxidative etching process, helps in the decahedral nanoparticle formation, which is less at low temperature. 'Fresnel lens' is often used as solar concentrator. The reaction rate increased sharply with temperature, as indicated by a quick change in colour for the solution (from yellow-brown to dark brown). In the PdNPs synthesis, this dual energy source is responsible to speed up the synthesis process and decreases the time required for synthesis.

Herein, continue with our previous work we focus on shape controlled palladium (0) nanoparticles synthesis and their application in the C—C bond formation. The PdNPs were synthesized by PdCl₂ using citric acid as reducing and PVP as a capping agent under the concentrated solar radiations in aqueous media. We observed that the prepared PdNPs solution was steady for several months without any agglomeration signifying that PVP serve as very efficient capping agent, along with the citric acid acting as a reducing agent.

The synthesized Pd nanoparticles are characterized by using techniques like TEM, FEG-SEM and XRD. The Transmission electron microscopy (TEM) image demonstrated that the obtained product is in the nano region with uniform size ranging from 30 nm to 45 nm containing higher (up to 70%) concentration of decahedral particles (Fig. 2). The SAED pattern shows the crystalline nature of obtained palladium nanoparticles and the three diffused rings indicating (111), (200), and (220) reflections of fcc palladium (Fig. 3). This result was supported by the FEG-SEM image which gave an idea about three dimensional structures (Fig. 4). The XRD pattern of the PdNPs in which peaks observed at 2θ of 40, 47 and 69, which readily assigned to the (111), (200) and (220) replicate the fcc phase of metallic palladium (JCPDS card no. 5-681) appreciate the crystalline nature of the nanoclusters (Fig. 5). The 100% metallic palladium was shown by the EDAX pattern (Fig. 6). To show the effectiveness of our methodology we carried out the same PdNPs synthesis under same reaction parameters on a hot plate for 6 h, wherein we obtained PdNPs of various morphologies (decahedral nanoparticles where up to 15% (Fig. 7)). Fig. 8 gives the clear idea about the PdNPs synthesised under concentrated solar energy and under normal heating condition.

3.2. Catalytic activity of PdNPs in the Suzuki cross-coupling reactions

To optimize the reaction conditions, a series of experiments under varied conditions in terms of catalyst loading, base, solvent,



Fig. 2. TEM image of PdNPs synthesized by solar irradiation after 6 h.



Fig. 3. SAED pattern of PdNPs synthesized by solar irradiation after 6 h.

reaction temperature and time for a model coupling reaction of iodobenzene with phenylboronic acid were carried out as illustrated in Table 1. Initial studies were conducted using the mixture of PVP stabilized PdNPs which was directly employed as a catalyst for Suzuki cross coupling reactions of iodobenzene



Fig. 4. FEG-SEM image of PdNPs synthesized by solar irradiation after 6 h.

Table 1

Effect of reaction parameters on Suzuki coupling reaction of iodobenzene with phenyl boronic acid.^a

Entry	Catalyst Conc. (mmol)	Base	Temperature (°C)	Time (min)	Yield (%) ^b				
Effect of catalyst loading									
1	0.001	КОН	100	60	98				
2	0.0005	КОН	100	60	97				
3	0.0002	КОН	100	60	46				
4	0.0001	КОН	100	60	20				
5	0.0000	КОН	100	60	NR				
Effect of base									
6	0.0005	NaOH	100	60	95				
7	0.0005	K ₂ CO ₃	100	60	88				
8	0.0005	Na ₂ CO ₃	100	60	86				
Effect of temperature									
9	0.0005	КОН	60	60	75				
10	0.0005	КОН	80	60	94				
11	0.0005	КОН	100	60	97				
12	0.0005	КОН	120	60	97				
13 ^c	0.0005	КОН	27	1440	34				
Effect of time									
14	0.0005	КОН	100	30	64				
15	0.0005	КОН	100	45	90				
16	0.0005	КОН	100	120	98				

^a Reaction conditions: iodobenzene (1 mmol), phenyl boronic acid (1.2 mmol), base (2 mmol), water (4 mL).

^b GC yield.

^c Reaction time (24 h).



Fig. 5. X-ray diffraction pattern of PdNPs synthesized by solar irradiation after 6 h.



Fig. 6. EDAX pattern of PdNPs synthesized by solar irradiation after 6 h.



Fig. 7. FEG-SEM image of PdNPs synthesized by heating at 90 °C for 6 h.



Fig. 8. Percentage decahedral PdNPs synthesized under conventional heating and concentrated solar energy.

Table 2

Pd nanoparticles-catalysed Suzuki cross coupling reaction of aryl halides and phenyl boronic acida



Table 2 (Continued)



^a Reaction conditions: aryl halide (1 mmol), arylboronic acid (1.2 mmol), Pd (0) nanoparticles (0.0005 mmol), KOH (2 mmol), water (4 mL), 100 °C, 60 min. ^b GC yield.

with phenylboronic acid under aqueous medium. The obtained results proved that synthesized PdNPs are a highly active catalyst in comparatively mild reaction conditions. The probable reason for high catalytic activity is might be due to the nanoparticles having better numbers of decahedral particles. A decahedral particle having a number of sharp and smooth faces which accountable to increase the available surface area in the reaction. Along with this, well dispersion and stability of PdNPs in aqueous medium may contribute to the better performance for Suzuki reaction.

In transition metal catalysed reactions, the amount of catalyst employed proves to be an important aspect, considering which efforts were made to determine the optimum concentration of the catalyst (Table 1, entries 1-4). Initially the reaction was carried out by 0.001 mmol catalyst loading where we obtained 98% vield, then the catalyst loading was decreased to half (0.0005 mmol) and it was observed that reaction gave yield (97%). A further decrease in the catalyst loading (0.0002 and 0.0001 mmol), we observed the product yield of 46% and 20%, respectively. To check the necessitate of PdNPs in Suzuki cross coupling reaction the control experiment was carried out in the absence of catalyst keeping other reaction parameters constant however no yield of the desired product was obtained even after completion of 24 h (Table 1, entry 5) signifying that PdNPs was responsible for the respective transformation.

Considering the importance of neutralizing base in the reaction, we screened a variety of inorganic bases (Table 1, entries 6–8) among those screened inorganic bases such as KOH, NaOH, Na₂CO₃ and K₂CO₃ we found that KOH gave an excellent yield (97%) of the desired product. Accordingly further studies were carried out with KOH as a base.

In order to examine the effect of temperature on reaction outcome, different temperature conditions ranging from 60°C to 120 °C (Table 1, entries 9–13) were studied addressing 100 °C as a best temperature condition (Table 1, entry 11). In addition to this 34% product yield was observed at room temperature even after 24 h. To optimize the time we carried out the model reaction for different time intervals in the range of 30-120 min (Table 1, entries 14-16), and it was observed that desired product could be achieved with highest yield in 60 min. The Final optimized parameters for the Suzuki C–C coupling reaction are iodobenzene (1 mmol), phenyl boronic acid (1.2 mmol), PVP stabilized decahedral PdNPs (0.0005 mmol), KOH (2 mmol), at 100 °C for 1 h in aqueous medium (Table 1, entry 2). Herein we also focused on the catalytic activity of PdNPs synthesized by the conventional heating method (90 °C for 6 h); wherein we obtained 93% conversion under optimized conditions.

These optimized conditions were applied to the C–C coupling of various aryl halides with phenyl boronic acids and its derivatives, the results are summarized in Table 2. Various electron donating and withdrawing groups like -- CH₃, -- OCH₃, -- COCH₃, -- NH₂ on both aryl iodide and boronic acid smoothly undergoes Suzuki coupling reaction providing desired diaryls (Table 2) and show high TOF values in the presence of PVP stabilized palladium (0) nanoclusters in water. It is clearly seen from Table 2 that the Suzuki coupling reaction of phenyl boronic acid and its derivatives with aryl halides bearing either electron donating or electron withdrawing substituent were afforded the corresponding biaryls in excellent yields (Table 2, entries 1-11). The reaction was also studied for aryl bromides in which the reaction of bromobenzene with phenyl boronic acid and o-methoxy bromobenzene with phenyl boronic acid gave a good yield of the desired product under the optimized reaction conditions (Table 2, entries 12 and 13).

Table 3

Activities of various Pd (0) nanoparticles catalyst in terms of TOF values have been tested for Suzuki cross-coupling of aryl bromides or iodides and phenylboronic acid for same amount of reactants in water (1.0 mmol aryl bromide and 1.2 mmol phenylboronic acid)



Entry	—R	Х	Catalyst	Temp. (°C)	Time	Yield (%)	$TOF(h^{-1})$	Ref.
1	-OCH ₃	Br	Pd-PVP (MTPs)	100	60 min	84	1680	This study
2	-OCH ₃	Br	PSSA-co-MA-Pd ⁰	100	10 min	96	576	[34]
3	—OCH ₃	Br	Pd-SDS	100	5 min	95	456	[35]
4	—OCH ₃	Br	Pd-PEG	25	120 min	98	490	[36]
5	—OCH ₃	Br	Pd-1/FSG	100	12 h	86	72	[37]
6	—OCH ₃	Br	Fe ₃ O ₄ -Pd	50	12 h	90	12	[38]
7	—OCH ₃	Br	pEVPBr-Pd	90	9 h	68	38	[39]
8	—OCH ₃	Br	Pd-polystyrene	100	5 h	99	10	[40]
9	—OCH ₃	Ι	Pd-PVP (MTPs)	100	60 min	98	1960	This study
10	—OCH ₃	Ι	Pd-CD	100	120 min	95	48	[41]
11	-OCH ₃	Ι	Pd-PS-PEO	50	4 h	86	22	[42]



Fig. 9. Recyclability of PdNPs for Suzuki coupling reaction.

Table 3 shows the comparative data between various catalyst systems where the PVP stabilized decahedral palladium (0) nanoparticles synthesized by this method shows superb catalytic activity in coupling of aryl bromides with phenylboronic acid under the optimized reaction conditions. TOF values 1680 and $1960 h^{-1}$ (Table 3, entries 1 and 9) for Suzuki coupling reactions of 4-methoxy bromobenzene and 4-methoxy iodobenzene with phenylboronic acid catalysed by PVP stabilized palladium (0) nanoclusters in water, respectively, are one of the highest values ever reported.

3.3. Catalyst reusability

The recycling potential of PdNPs catalyst was studied by 4 mmol model Suzuki coupling reaction for iodobenzene with phenyl boronic acid in three consecutive cycles. The PdNPs could be recycled and reused by separating them from the reaction mixture through centrifugation at 10,000 rpm at 25 °C for 15 min and frequent washing with ethyl acetate. The results show that the yield of product after three runs was only slightly reduced (Fig. 9). This decrease in the percentage yield is might be due to the loss of catalyst while handling.

4. Conclusion

In summary, herein we demonstrated a simple, rapid and high yielding synthetic route to prepare decahedral palladium nanoparticles by concentrated solar energy using PVP as a capping agent and citric acid as reducing agent. The aqueous solution of PdNPs was directly employed in the Suzuki coupling reaction, and hence save time and cost of isolation. To the best of our knowledge, the prepared nanoparticles demonstrated excellent catalytic activity in C–C coupling reaction with lowest catalyst loading ever reported. The significant advantages of this protocol are simple operation and being an environmentally gracious process in excellent yields with the highest TOF values for the Suzuki coupling reaction catalysed by palladium nanoparticles. The new PdNPs synthesis methodology showed excellent performance compared to the conventional heating method. The catalyst showed best performance up to three recycles.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2012.08.023.

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