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Solar energy assisted synthesis of palladium nanoplates and its application in 2-phenoxy-1,1′-biphenyls and *N*,*N*-dimethyl-[1,1′-biphenyl] derivatives synthesis

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ABSTRACT

Present work aims to develop a greener approach for the palladium nanoplates (PdNPs) synthesis and its catalytic applications. The protocol deals with solar energy assisted ionic palladium reduction in the presence of polyvinylpyrrolidone (PVP) and ethylene glycol (EG) with a good shape selectivity. Polyvinylpyrrolidone plays a duel role of capping agent and mild reductant; whereas, ethylene glycol acts as a reductant and solvent. The optimum sunlight concentration is a key factor to the anticipated nanoplate's synthesis. Results show that the most of nanoparticles are hexagonal and triangular nanoplates in the range of 20–50 nm. This is a first report which shows ∼70% selectivity to the nanoplates formation using sun light. The study also covers it's catalytic application, wherein; 2-phenoxy-1,1′-biphenyls and *N*,*N*-dimethyl-[1,1′-biphenyl] derivatives were synthesized by a simple, ligand free, faster, one pot, ecological and economic protocol in aqueous medium. The catalyst shows better performance than that of conventionally available 10% Pd/C catalyst. The prepared PdNPs showed excellent catalytic performance to the desired products with recyclability.

1. Introduction

Metal nanoparticle synthesis has been a current research theme as motivated by their widespread use in electronics, optoelectronics, optical sensing, biological labelling, imaging, catalysis, photography, photonics, plasmonics and information storage [1–10]. Size, shape, crystallinity, composition and structure of the metal nanoparticles determine their properties [11]. Palladium plays a central role and showing diverse industrial applications [12–17]. For example, it helps as a catalyst for low-temperature reduction of automobile pollutants as well as for organic reactions such as Heck and Suzuki coupling reactions. To enhance the performance, several efforts have been dedicated to the synthesis of Pd nanostructures in the presence of surfactants or polymers. Till date, Pd nanoparticles of various morphologies have been prepared such as cubes, cuboctahedrons, decahedrons, bars, single-crystal rods, icosahedrons, right bipyramids, fivefold twinned rods, and thin plates (triangular or hexagonal) using conventional methods under reflux condensations [18]. In earlier reports nanoparticle synthesis has been achieved by techniques like thermal, sonochemical, microwave, electrochemical and sonoelectrochemical routes. However, most of the protocols required harsh reaction conditions such as longer reaction time, high pressure, toxic reagents, harmful by-product formation, poisonous gas production and requirement of sophisticated equipments with tedious work up procedures. Hence, the development of non-conventional, environmental benign and inexpensive protocol for efficient synthesis of nanoparticles is still desirable.

Considering this issue, recent investigation focused towards available renewable energy sources for nanoparticles synthesis. Solar energy is one of the non-polluting, carbon free and easily available energy source. In earlier reports, metal nanoparticles are synthesized under normal sunlight [19,20]. Most of these reports relate to the silver and the gold nanoparticle synthesis which works in the temperature range of 30–50 °C. However, many other metal and metal oxide nanoparticles synthesis requires higher energy intensity, which is not possible under normal sunlight and hence the concept of concentrated solar energy has been developed [21–23].

Present study is focused on the palladium nanoplate's synthesis using solar energy. While working with this concept, we specifically expected at answering the following questions related to the synthesis of nanoplates: (a) the role of EG as a reducing agent and how it works for the synthesis of nanoplates? (b) How concentrated solar energy advantageous than that of conventional energy sources? While answering to these questions, it was observed that polyol reduction has long been known as a simple and versatile method

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for producing metal nanoparticles, wherein nanoplates synthesis using polyol method has been discussed [24]. Present study is a continuation of our previous works on multiple twinned particles (MTPs) synthesis, wherein, the reductant like citric acid was responsible to blocks the oxidative etching that results in the formation of MTPs. Hence to take the benefit of etching phenomena for the nanoplates synthesis herein, we used acetaldehyde derived from EG with PVP as a mild reductant.

The PdNPs synthesis is associated with the reduction of Pd (II) to Pd (0) which requires a higher driving force that is not achieved under the intensity of natural sunlight. The idea of 'Fresnel lens' assist to concentrate the solar radiation and to reduce the ionic palladium to metallic form was used. Though, concentrated solar energy helps in the reduction of ionic palladium, it may hurdle to nanoplates formation as nanoplates synthesis associated with slow reduction kinetics. Hence, the optimum driving force to the nanoplates formation from solar energy was obtained by adjusting the concentration ratio of sunlight. This above discussion helps to answer the second question. Hence, in continuation of previous work, present study deals with novel, etchant free, inexpensive and eco-friendly protocol for the synthesis of Pd nanoplates (triangular and Hexagonal) using a polyol process wherein PVP acts as a mild reducing agent and concentrated solar energy as an energy source for the reduction. The result reveals that the obtained nanoparticles are in the range of 20–50 nm having ~70% of triangular and hexagonal nanoplates contribution. Though the selectivity to the nanoplates formation is up to 70%; this is the first green approach wherein the concentration ratio of sunlight helps to the nanoplates synthesis in absence of organic etchants.

Along with the nanoplates synthesis, its application in the synthesis of 2-phenoxy-1,1′-biphenyl's and *N,N*-dimethyl-[1,1′-biphenyl] derivatives was also studied. In earlier works, such products were synthesized by different protocols linked with one or more drawbacks such as the use of complex ligands, multistep synthesis, organic reaction medium, and low yield. To overcome these limitations, herewith, we report simple one stroke, one pot, ligand free, heterogeneous, recyclable and fast approach with an excellent yield to the desired product. The synthesized Pd nanoplates showed excellent catalytic applications at lowest catalyst loading under mild reaction conditions. The nanoplates have shown better catalytic performance than that of conventionally available 10% Pd/C catalyst. The catalyst showing excellent performance up to three consecutive recycles without significant loss in catalytic activity. To the best of our knowledge, this is a first report wherein 2-phenoxy-1,1′-biphenyl's and *N,N*-dimethyl-[1,1′-biphenyl] derivatives are synthesized in one pot, one step, greener, faster protocol using Pd nanoplates as heterogeneous and recyclable catalyst in aqueous medium.

2. Experimental

2.1. Materials and methods

Palladium chloride was purchased from M/s Parekh Platinum Ltd., Mumbai ($PdCl_2$, 99%); poly vinyl pyrrolidone (PVP, MW-40000) from M/s CDH and ethylene glycol was purchased from M/s s.d. Fine-Chem Ltd. The deionized water was distilled by water purification system (Milli-Q). All chemicals were of highest purity grade and used without further purification. Considering the low catalyst loading and highest accuracy the catalyst loading was done by using PdNPs stock solution, which prepared using 0.0106 g of PdNPs in 10 mL of DI water. In 2-phenoxy-1,1′-biphenyls synthesis optimized yields were calculated based on gas chromatography (GC) using external standard method.

2.2. Synthesis of Pd (0) nanoplates

In a typical synthesis, 0.017 g of $PdCl_2$ and 0.038 g of PVP (MW-40,000) were separately dissolved in 3 mL of EG at room temperature. Meanwhile, 7 mL of ethylene glycol was placed in a round bottom flask (equipped with air condenser) and heated under solar radiations concentrated by a 'Fresnel lens' for 10 min. The above solutions of Pd precursor with PVP were added in a reaction mixture slowly. The reaction mixture was continued with heating by solar energy for 3 h. Considering the aim of nanoplates synthesis the concentration ratio of sunlight has been adjusted in such a way that the temperature of reaction was in the range of $70 \pm 5\,^{\circ}C$. As the incident solar energy has a spatial and temporal variation, to minimize temperature variation all the experiments were conducted from 11 am to 2 pm in summer days. The Author's institute is located at Matunga, Mumbai (Geographical location: Greater Bombay, Maharashtra, India, Asia. Geographical Coordinates: 19°2′0″ North, 72°51′0″ East). The product was centrifuged at 18000 rpm for 20 min at 25 °C and washed with acetone followed by ethanol to remove additives.

2.3. Characterization of prepared palladium (0) nanoparticles

The obtained nanoplates were characterized using the UV spectrophotometer (Shimadzu 1650) to confirm reduction of Pd (II) to Pd (0). This was further confirmed by the X-ray Photoelectron spectroscopy (XPS) analysis using AXIS Ultra 'DLD' X-ray photoelectron spectrometer, Transmission electron microscopy (TEM) and selected area energy dispersion (SAED) was done by Philips model CM 200, Field Emission Gun-Scanning Electron Microscopy (FEG-SEM) and Energy dispersive X-ray Spectral analysis EDAX images were recorded with a JEOL JSM-7600 F.

2.4. Typical procedure for the synthesis of 2-phenoxy-1,1′-biphenyls and N,N-dimethyl-[1,1′-biphenyl] derivatives

In a typical synthesis, sealed tube of 10 mL capacity was charged with aryl halide (1.0 mmol), (2-phenoxyphenyl) boronic acid (1.2 mmol)/(3-(dimethylamino)phenyl) boronic acid, KOH (2.0 mmol), Pd nanoplates solution (50 μL, 0.0005 mmol) in aqueous medium. The reaction mixture was heated at 100 °C for 1 h and then allowed to cool at room temperature. Conversion of aryl halide and the formation of product were monitored by gas chromatography. The product was extracted with ethyl acetate (3 × 5 mL); died over Na_2SO_4 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 products are confirmed by GC–MS (Shimadzu GC-MS QP 2010). The representative products were characterized by ^{1}H NMR and ^{13}C NMR (Bruker UXNMR/XWIN-NMR (300 MHz) or Inova Varian VXR Unity (400, 500 MHz) instruments. Chemical shifts (δ) are reported in ppm downfield from an internal TMS standard. High resolution MS (HR-MS) data were recorded on a QSTAR XL Hybrid MS–MS mass spectrometer.

2.5. GC analysis

The reaction progress was analyzed by GC equipped with a flame ionization detector (FID) and a capillary column (Perkin–Elmer, Clarus 400, 30 m × 0.32 mm × 0.25 μm). The GC parameters were as follows: Initial temperature 80 °C; initial time 1 min; solvent delay 3 min; temperature ramp 10 °C/min; final temperature 250 °C;

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. Spectral data of 2-phenoxy-1,1′-biphenyls

(1) 2-phenoxy-1,1′-biphenyl (Table 2, entry 1)^{1}H NMR (400 MHz, $CDCl_3$): 7. 54 (2H, d, J = 10 Hz), 7.45 (1H, m), 7. 34 (2H, d, J = 10 Hz), 7.3–7.18 (5H, m), 7.02 (2H, t), 6.93 (2H, d, J = 10.4 Hz) ppm; GC–MS (EI) m/z (%): 246(100) $[M]^+$, 245(29.2), 231(11.8), 229(21.8), 228(12.1), 227(14.1), 217(11.4), 202(10.7), 152(37.0), 151(10.5), 115(13.3).

(2) 2′-phenoxy-[1,1′-biphenyl]-4-ol (Table 2, entry 2)GC–MS (EI) m/z (%): 263(18.7), 262(1 0 0) $[M]^+$, 185(5.7), 168(5.4), 157(5.7), 141(6.6), 139(9.3), 115(12.5), 89(5.7), 77(6.7), 45(13.4), 44(11.6).

(3) 4′-methyl-2-phenoxy-1,1′-biphenyl (Table 2, entry 3)^{1}H NMR (400 MHz, $CDCl_3$): 7.43 (3H, d, J = 10.8 Hz), 7.3–7.2 (4H, m), 7.16 (2H, d, J = 10.8 Hz), 7.04–6.92 (4H, m), 2.34 (3H, s) ppm; GC–MS (EI) m/z (%): 260(1 0 0) $[M]^+$, 245(24.5), 244(7.5), 243(10.8), 217(8.7), 183(8.1), 168(9.8), 165(24.5), 152(21.7), 139(5.1), 115(7.9), 77(6.1).

(4) 4′-nitro-2-phenoxy-1,1′-biphenyl (Table 2, entry 4)^{1}H NMR (400 MHz, $CDCl_3$): 8.2 (2H, d, J = 11.6 Hz), 7.7 (2H, d, J = 11.6 Hz), 7.46 (1H, dd, J = 10), 7.38 (1H, dd, J = 10), 7.3–7.0 (5H, m), 6.9 (2H, d, J = 10.4 Hz) ppm; GC–MS (EI) m/z (%): 291(1 0 0) $[M]^+$, 245(9.1), 244(20.1), 228(10.0), 226(10.1), 218(11.7),215(17.6), 202(13.1), 168(8.9), 152(8.8), 151(10.0), 139(13.0) 77(11.9), 51(8.6).

(5) 2-methyl-2′-phenoxy-1,1′-biphenyl (Table 2, entry 5)GC–MS (EI) m/z (%): 260(1 0 0) $[M]^+$, 245(6.7), 182(14.9), 181(25.3), 165(57.8), 151(20.9), 149(33.4), 115(11.5), 91(61.4), 77(8.9), 51(8.0).

(6) 2-methoxy-2′-phenoxy-1,1′-biphenyl (Table 2, entry 6)^{1}H NMR (400 MHz, $CDCl_3$): 7. 36 (1H, dd, J = 5.2 Hz), 7.3–7.2 (5H, m), 7.17(1H, t, J = 5.2 Hz), 7–6.9 (5H, m), 6.87 (1H, d, J = 5.6), 3.6 (3H, s) ppm; GC–MS (EI) m/z (%): 276(1 0 0) $[M]^+$, 215(7.5), 183(7.5), 181(9.7), 169(7.8), 168(48.7), 152(5.0), 139(15.9), 115(4.1), 91(20.5), 77(5.5).

(7) 2′-phenoxy-[1,1′-biphenyl]-2-ol(Table 2, entry 7)GC–MS (EI) m/z (%): 262(1 0 0) $[M]^+$, 170(11.9), 169(95.0), 168(79.1), 141(20.3), 139(24.4), 115(18.5), 77(8.4), 51(8.2), 39(7.8).

(8) 2′-phenoxy-[1,1′-biphenyl]-2-amine (Table 2, entry 8)GC–MS (EI) m/z (%): 261(41.6) $[M]^+$, 169(10.0), 168(69.2), 167(100), 166(10.6), 139(8.2), 115(5.6), 89(9.1), 58(5.5), 45(24.0), 44(18.0), 43(7.6).

2.6.2. Spectral data of N,N-dimethyl-[1,1′-biphenyl] derivatives

(9) *N*,*N*-4′-trimethyl-[1,1′-biphenyl]-3-amine (Table 3, entry 1)^{1}H NMR (400 MHz, $CDCl_3$): 7.49 (d, J = 8.1 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 7.22 (d, J = 8.1 Hz, 2H), 6.94–6.91 (m, 2H), 6.73–6.71 (m, 1H), 2.99 (s, 6H), 2.38 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 150.90, 142.13, 139.33, 136.70, 129.30, 129.25, 127.10, 115.70, 111.40, 40.64, 21.04. GC–MS (EI) m/z (%): 211(1 0 0) [M]+, 195(8.1), 168(9.2), 165(11.4), 152(13.6), 105(18.2), 82(5.1), 63(2.7), 39(4.6). HRMS (ESI): m/z calcd. for $C_{15}H_{18}N[M+H]^+$ = 212.14338, found 212.14261.

(10) 2′-methoxy-*N*,*N*-dimethyl-[1,1′-biphenyl]-3-amine (Table 3, entry 2)^{1}H NMR (300 MHz, $CDCl_3$): 7.45–7.16 (m, 3H), 7.02–6.83 (m, 4H), 6.71 (d, J = 8.1 Hz, 1H), 3.77 (s, 3H), 2.94 (s, 6H) ppm. GC–MS (EI) m/z (%): 227(1 0 0) [M]+, 210(26.3), 196(13.3), 183(9.2), 181(9.0), 168(14.2), 152(5.6), 139(9.6), 113(8.1), 108(14.1), 98(10.8), 91(5.9), 78(5.8), 63(3.6), 39(4.8).

(11) *N*,*N*-dimethyl-4′-nitro-[1,1′-biphenyl]-3-amine (Table 3, entry 3)^{1}H NMR (300 MHz, $CDCl_3$): 8.26 (d, J = 8.7 Hz, 2H), 7.72 (d, J = 8.7 Hz, 2H), 7.35 (t, J = 7.9 Hz, 2H), 6.95–6.88 (m, 2H), 6.82–6.79 (m, 1H), 3.03 (s, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 150.96, 148.66, 146.88, 139.67, 129.71, 127.79, 123.81, 115.56, 112.88, 111.10, 40.45, 21.04. GC–MS (EI) m/z (%): 242(1 0 0) [M]+, 212(6.5), 196(19.2), 195(31.1), 152(23.2), 139(3.9), 98(4.7), 76(6.1), 63(4.4), 39(5.1). HRMS (ESI): m/z calcd. for $C_{14}H_{15}O_2N_2[M+H]^+$ = 243.11162, found 243.11280.

3. Results and discussion

3.1. Preparation and characterization PdNPs

We initiated our investigation aiming at the synthesis of palladium nanoplates using the concept of solar energy. The seeds, crystallinity and the growth rates of different crystallographic facets are important in determining the shape of resultant nanostructures. In case of metal like palladium, synthesis of triangular or hexagonal nanoplates depends on the reduction kinetics. A shape evolution is observed during the growth mechanism: in the initial state the nanoplates have a circular cross section obtained by the combination of atoms; then it will evolve into hexagonal and then triangular shapes [25–27].

Cuboctahedrons and multiple twinned particles (MTPs) are the thermodynamically favourable shapes of Pd nanoparticles. At high reduction rate the final product will take the thermodynamically favoured shapes. When the reduction rate retarded, the nucleation as well as growth will be deviating into kinetic control and the final product can take a variety of shapes deviated from the thermodynamic ones. In previous studies, it was found that at elevated temperature $PdCl_4^{2-}$ was added to EG, the rapid reduction of $PdCl_4^{2-}$ takes place with EG and produced 10% MTPs and 90% Pd cubooctahedra of 8–10 nm in size [28].

As development of nanoplates is favourable at slow reduction process, the selective synthesis of Pd nanoplates has been attained by careful control of the reduction kinetics, mainly at the seeding stage. In earlier work, to achieve controlled synthesis of triangular and hexagonal nanoplates two different approaches have been reported to retard the reduction rate. In first approach, the reduction rate was substantially reduced through the introduction of etchants like Fe(III) species, which competed with the polyol reduction and altered the reduction kinetics helps to synthesis triangular or hexagonal nanoplates [29]. In the second approach, a mild reducing agent like PVP can be used to slow down the reduction [30]. The mild reducing power of such compound is anticipated for kinetically controlled synthesis of Pd nanoplates.

On the basis of the above discussion, herein concentrated solar energy protocol has been used for hexagonal and triangular nanoplates synthesis using a polyol synthesis protocol with PVP (MW = 40,000) as a stabilizer cum mild reductant. In case of Pd nanoparticle synthesis higher driving force is required for the reduction of ionic palladium species. Concentrated solar energy has combined effect of the thermal and radiational energy help to reduce ionic palladium to metallic palladium. Though, concentrated solar energy executes necessity of the ionic palladium reduction, the high intensity sunlight may create obstacle for nanoplate synthesis as it required slow reduction kinetics. Hence, essential energy requirement for nanoplates preparation was achieved by moving the 'Fresnel lens' towards the reactor (round bottom flask) which allows optimum sunlight concentration to the nanoplates formation. So here we can demonstrate that the concentrated solar energy not only helps for the reduction of ionic palladium but also it could be used for the selective nanoplate's formation too. Also, low molecular weight PVP act as a mild reductant to slow down the reduction process along with its capping effect [29,30]. In general, glycols can serve as the reductant source for the PdNPs synthesis [29,31]. In aqueous medium

Table 1
Effect of reaction parameters on synthesis of synthesis of 2-phenoxy-1,1′-biphenyls[a]

Entry	Catalyst amount (mmol)	Base	Temperature (°C)	Time (min)	Yield (%)[b]
Effect of catalyst loading					
1	0.001	KOH	100	60	98
2	0.0005	KOH	100	60	98
3	0.0002	KOH	100	60	61
4	0.0000	KOH	100	60	NR
Effect of temperature					
5	0.0005	KOH	60	60	71
6	0.0005	KOH	80	60	90
7	0.0005	KOH	100	60	98
8[c]	0.0005	KOH	27	1440	34
Effect of time					
9	0.0005	KOH	100	30	75
10	0.0005	KOH	100	45	92
11	0.0005	KOH	100	60	98

[a] Reaction conditions: iodobenzene (1 mmol), (2-phenoxyphenyl) boronic acid (1.2 mmol), water (4 mL). KOH (2 mmol).
[b] GC yield.
[c] Reaction time (24 h).

$$\mathrm{2CH_2OH\text{-}CH_2OH} \xrightarrow{\text{Solar energy}} \mathrm{2CH_3CHO} \qquad (1)$$

$$\mathrm{Pd(II)} \xrightarrow{\mathrm{2CH_3CHO}} \mathrm{Pd(0)} \qquad (2)$$

Scheme 1. Synthesis of palladium nanoparticles using ethylene glycol under solar irradiation.

glycols dehydrates to aldehyde, which can reduce metallic ions to elemental form. Herein, ethylene glycol initially acting as a solvent, and then it dehydrates to form acetaldehyde that results reduction of metallic ions [24]. The reaction was schematized as follows (Reaction Scheme 1):

'Fresnel lenses' often used as a solar concentrator helps here for the shape selective nanoplates (Fig. 1). Under the concentrated solar energy colour change from pale yellow to dark brown of reaction mixture was observed and that is a first point of evidence which indicates reduction of Pd (II) ions to Pd (0) (inset Fig. 1). The UV–Visible absorption spectrum of reaction mixture was taken before irradiation and after irradiation (Fig. 2). The results shows the palladium complex before irradiation shown absorption peak at 294 nm, which disappeared with irradiation time indicates reduction of ionic palladium and propagation towards the metallic palladium formation this gives another point to support the synthesis of PdNPs. The oxidation state of reduced material was further confirmed by the XPS analysis. The XPS of Pd 3d spectrum with the binding energies of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ lying at about 335.6 and 341.0 eV, respectively, suggest the presence of the Pd(0) species (Fig. 3). This result confirms metallic state of Pd and its stability in aqueous medium. The stable solution of synthesized PdNPs without any aggregation indicates the capping effect of PVP in synthesis. The TEM and FEG-SEM analysis were used for size and morphological investigation. The TEM image shows the maximum contribution of triangular and hexagonal nanoplates ranging from 20 to 50 nm (Fig. 4). The SAED pattern illustrates the crystalline nature of the product (Fig. 4 (inset)). In the synthesized material the nanoplate's contribution was observed up to 70%, which is calculated from TEM images at different locations and using manual calculation technique for 200 nanoparticles (Fig. 5). However, FEG-SEM gives three dimensional ideas about nanoplates structure (Fig. 6). The EDAX analysis shows the presence of elemental palladium along with Cu which is due to the use of Cu stub for the analysis (Fig. 7). Though the percentage of nanoplates is up to ~70%, this is the first example wherein the solar energy concept used for the shape selective

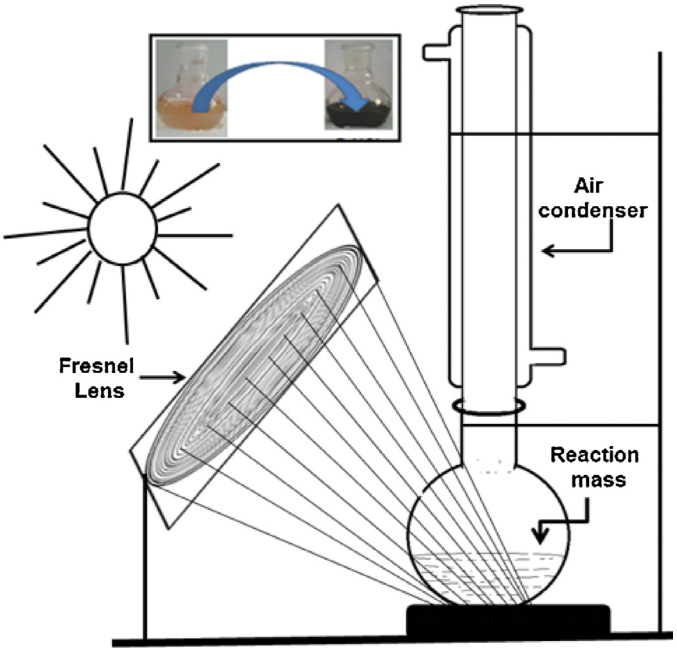


Fig. 1. Schematic representation of reaction setup with reaction progress observed by colour change (inset).

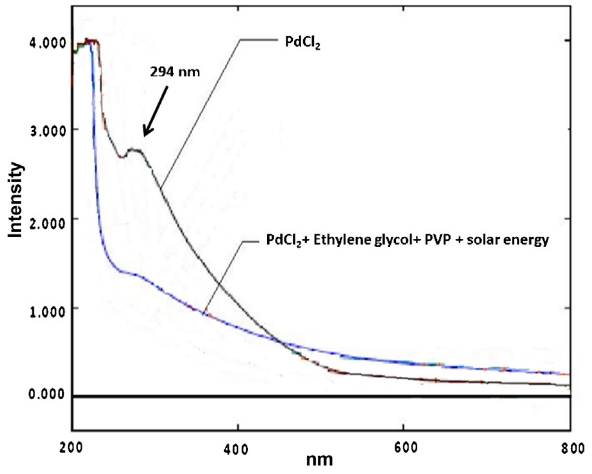
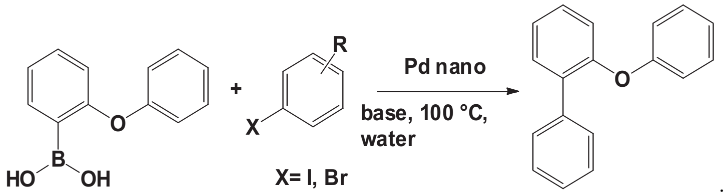
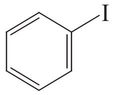
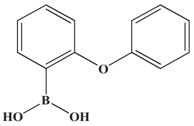
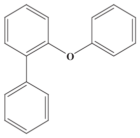
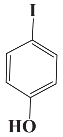
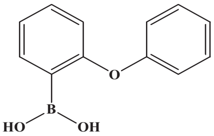
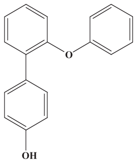
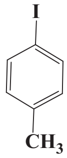
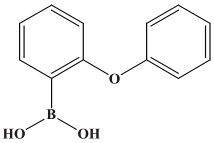
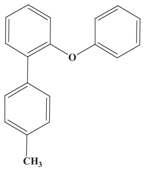
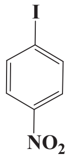
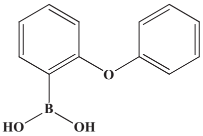
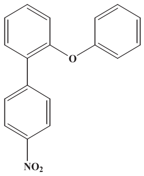
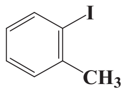
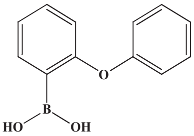
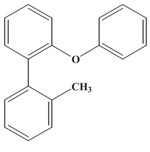
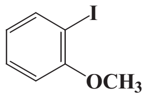
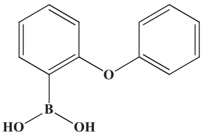
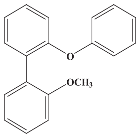
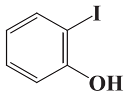
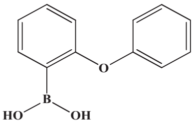
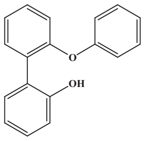
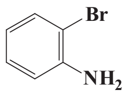
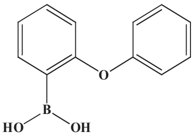
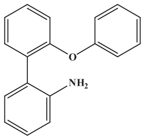


Fig. 2. UV–vis spectrum showing reaction progress.

Table 2

Pd nanoplates-catalyzed reaction of (2-phenoxyphenyl) boronic acid and aryl iodides and bromide[a]



Entry	Aryl iodide	Aryl boronic acid	Product	Yield (%)[b]
1				97
2				96
3				91
4				93
5				91
6				90
7				96
8				12

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[a] Reaction conditions: aryl halide (1 mmol), (2-phenoxyphenyl) boronic acid (1.2 mmol), Pd(0) nanoplates (0.0005 mmol), KOH (2 mmol), water 4 mL, 100 °C, 60 min.

[b] GC yield.

nanoplates synthesis, which could be a greater opportunity for the further research.

3.2. Catalytic activity of Pd nanoplates for the 2-phenoxy-1,1′-biphenyls synthesis

The nanomaterial applications in catalysis overcome variety of problems that associated with homogeneous catalysis by offering a bridge between homogeneous and heterogeneous catalysis. In addition to the nanoplates synthesis this study also associated with simple and heterogeneous protocol with economic and ecological views for the synthesis of 2-phenoxy-1,1′-biphenyls (Reaction Scheme 2). In earlier work, such products were synthesized by different groups and their protocols have limitations due to multistep synthesis, catalyst separation and reusability, harsh reaction conditions like high catalyst loading, toxic solvents, expensive and

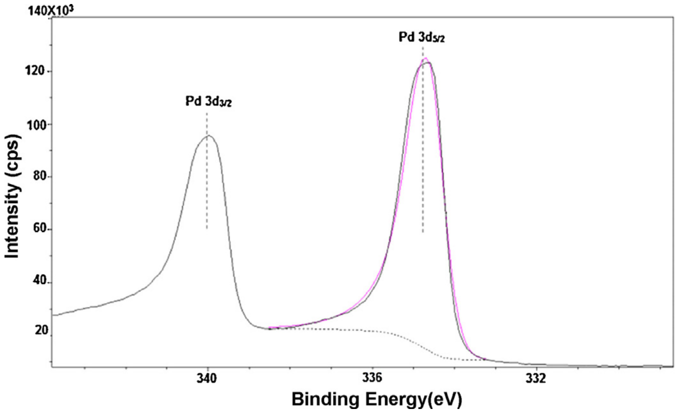


Fig. 3. XPS spectra of Pd 3d spectrum recorded at 160 eV pass energy and 600 W X-ray power.

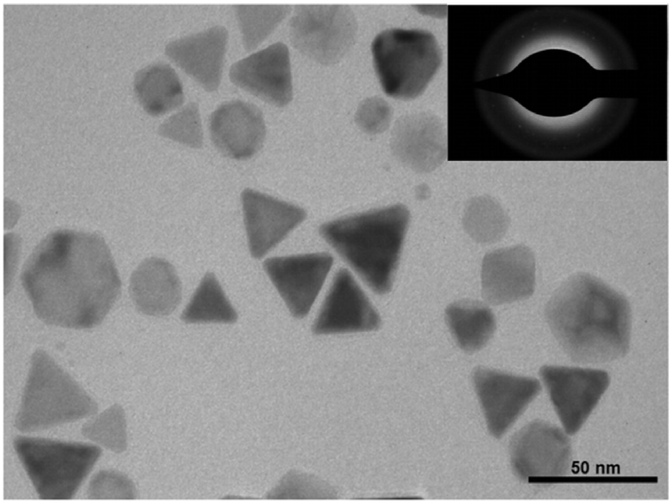


Fig. 4. TEM image of palladium nanoplates with SAED pattern (inset).

toxic ligands. Hosseinzadeh et al. reported copper-catalyzed arylation of 1,1′-biphenyl-2-ol with aryl iodides using KF/Al_2O_3 as a suitable base and CuI and 1,3 diphenyl-1,3 propandione as the catalyst wherein the catalyst and substrate loading is quite high [32]. Niu et al. reported similar arylation technique by copper (I)–bipyridyl complex catalyst [33]. Considering the above discussed issue herein, we are reporting a simple approach of Suzuki coupling reaction for the synthesis of 2-phenoxy-1,1′-biphenyl and derivatives using Pd nanoplates.

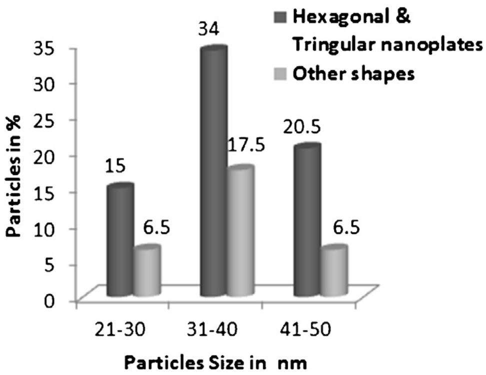


Fig. 5. Particle size distribution of 2 0 0 nanoparticles using TEM images.

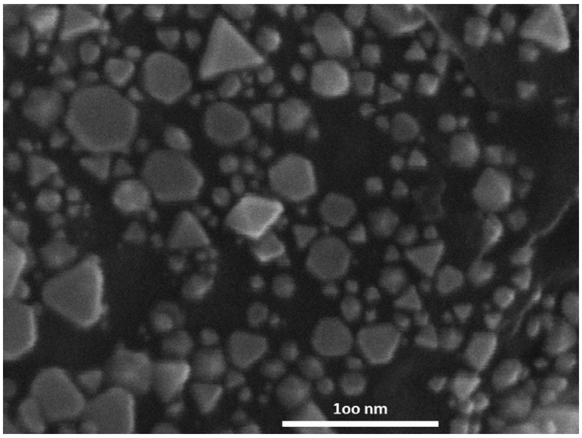


Fig. 6. FEG-SEM image of palladium nanoplates.

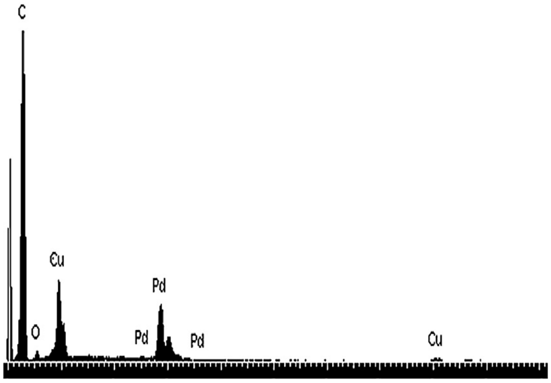
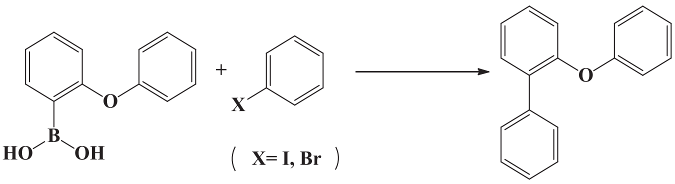


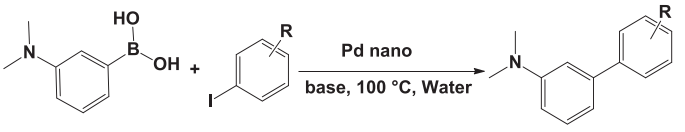
Fig. 7. EDAX pattern of synthesized palladium nanoparticles.

The optimum reaction parameter selection was started with catalyst screening wherein, catalyst concentration was varied from 0.001 to 0.0002 mmol (Table 1, entries 1–4). Initially, 0.001 mmol catalyst loading shows 98% yield however, at half concentration (0.0005 mmol) it gave same yield 98%. A further decrease in the loading (0.0002) showing 61% of the desired product. The blank experiment without catalyst displaying no product formation indicates the necessity of PdNPs for the synthesis. The reaction was carried at various temperatures ranging from 60 to 120 °C (Table 1, entries 5–8) and 100 °C was found to be the optimum temperature. Followed to this study reaction time was optimized and for this various reactions in the range of 30–120 min were performed (Table 1, entries 9–11). It showed that 60 min is the optimum reaction time. In combine, optimized parameters for the synthesis are: iodobenzene (1 mmol), (2-phenoxyphenyl) boronic acid (1.2 mmol), Pd nanoplates (0.0005 mmol), KOH (2 mmol), at 100 °C for 1 h in aqueous medium.

These optimized conditions were applied for the synthesis of various derivatives of 2-phenoxy-1,1′-biphenyls. The screening of various electron donating and withdrawing groups like —CH_3,



Scheme 2. Pd nanoparticles-catalyzed synthesis of 2-phenoxy-1,1′-biphenyls using (2-phenoxyphenyl) boronic acid and aryl halides.



Scheme 3. Pd nanoplates-catalyzed synthesis of *N*,*N*-dimethyl-[1,1′-biphenyl] using (3(dimethylamino) phenyl) boronic acid and aryl iodides.

—OCH_3, —OH, NH_2 and —NO_2 on aryl iodide (I, Br) smoothly undergoes Suzuki coupling reaction with (2-phenoxyphenyl) boronic acid providing desired products in the presence PdNPs in aqueous medium (Table 2, entry 1–9).

3.3. *Catalytic activity of Pd nanoplates for the N,N-dimethyl-[1,1′-biphenyl] and derivatives synthesis*

Followed to the above discussion and applications the catalytic activity of the Pd nanoplates was explored for the synthesis of *N*,*N*-dimethyl-[1,1′-biphenyl] derivatives (Reaction Scheme 3). In literature, only two reports are available for the synthesis of such compounds. In 2006, Solodenko et al. reported PVP supported palladium catalyst in the presence of tetra-n-butylammonium bromide (TBAB), at 0.25 mmol catalyst loading under 130 °C microwave heating for 3 h [34]. In 2007, Fleckenstein and Plenio reported the synthesis of *N*,*N*-dimethyl-[1,1′-biphenyl], but the reaction conditions were harsh and it requires the use of fluorenyl-based phosphine ligand and high catalyst loading [35]. In comparison to the previous reports, herein, we are reporting a simple, one step, faster, green protocol for the synthesis of the *N*,*N*-dimethyl-[1,1′-biphenyl] in aqueous medium. The synthesis was carried out under optimized reaction conditions using 1 mmol of aryl halide and 1.2 mmol of (3-(dimethylamino)phenyl) boronic acid at 0.0005 mmol catalyst loading (Pd (0) nanoplates) and it gives excellent yield of the desired product. The catalyst showing excellent activity for the both electron donating and electrons withdrawing moieties (Table 3 entries 1–3).

In addition to the above applications to the organic transformations we compare the catalyst activity with the commercially available 10% Pd/C catalyst. This comparison study was done by carrying representative experiments from both the reactions under the same optimized conditions by using 10% Pd/C (0.0005 mmol Pd) (Table 4).Table 4 showing comparative data between catalytic performance of PdNPs and 10% Pd/C for the above mentioned reaction. The TOF values of obtained results were compared and it is noticed that the Pd nanoparticles shown better performance than that of Pd/C. The TOF values obtained using PdNPs are 1940 and 1860 h^{-1} (Table 4, entries 1 and 3) whereas, the same reactions using Pd/C shown 1680 and 1500 h^{-1} respectively (Table 4, entries 2 and 4). The better performance of PdNPs is credited to the well dispersion and smaller size of the nanoparticles.

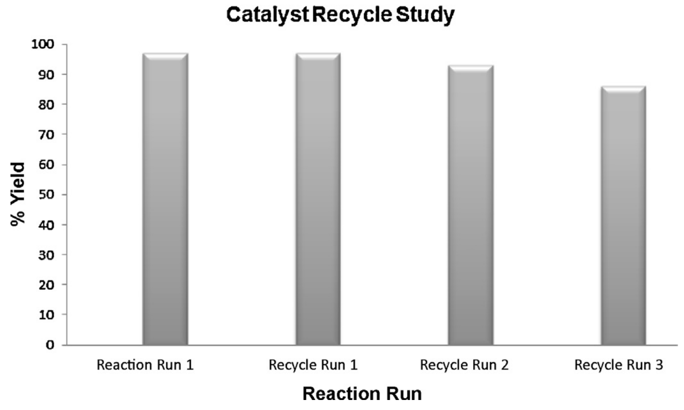
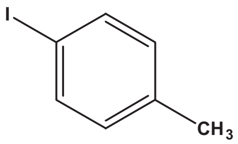
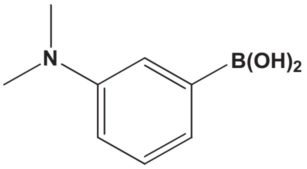
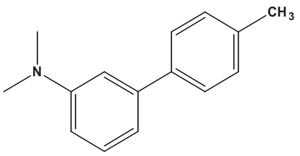
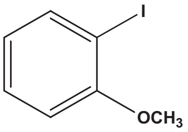
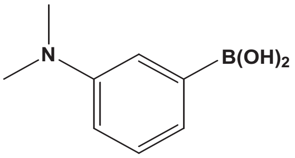
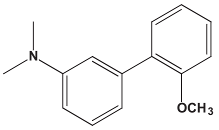
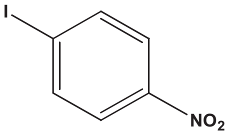
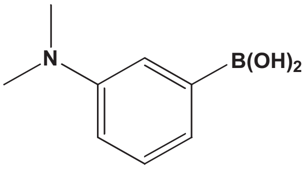
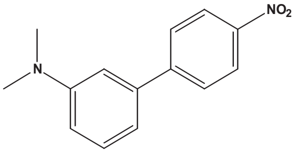


Fig. 8. Recyclability of Pd nanoplates for Suzuki coupling reaction.

3.4. *Catalyst recyclability*

Considering economic and ecological issues reusability of catalyst is a very important aspect. The catalyst recycles study was done by scale up of model reaction to 4 mmol wherein, Pd nanoplates shows excellent performance up to three consecutive recycles to the reaction of iodobenzene with (2-phenoxyphenyl) boronic acid (Fig. 8). The nanoparticles was separated and reused by centrifugation at 18000 rpm at 25 °C for 20 min with frequent wash with water followed by ethyl acetate. The reduction of % yield (88%) after third recycle is may be due to the handling loss of catalyst.

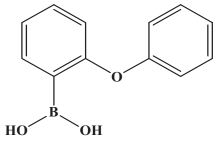
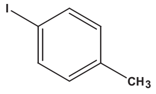
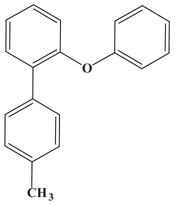
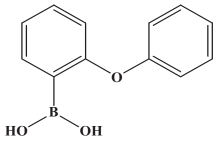
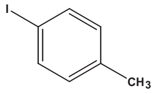
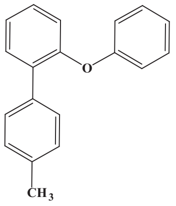
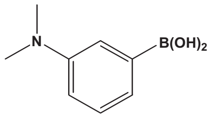
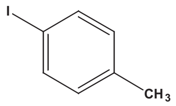
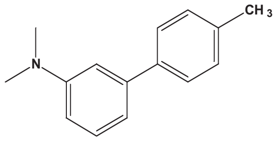
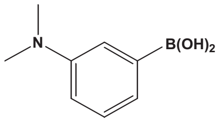
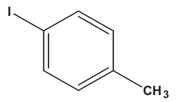
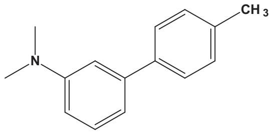
Table 3
Pd nanoplates-catalyzed synthesis of *N*,*N*-dimethyl-[1,1′-biphenyl] derivatives.[a]

Entry	Aryl iodide	(3(dimethylamino) phenyl) boronic acid	Product	Yield (%)[b]
1				93
2				96
3				88

[a] Reaction conditions: aryl halide (1 mmol), (3(dimethylamino) phenyl) boronic acid (1.2 mmol), Pd(0) nanoplates (0.0005 mmol), KOH (2 mmol), water 4 mL, 100 °C, 60 min.

[b] GC yield.

Table 4
Activities of Pd [0] nanoparticles catalyst and 10% Pd/C catalyst in terms of TOF values[a]

Entry	Catalyst	Boronic acid derivative	Aryl iodide	Product	Yield[b] (%)	TOF (h^{-1})
1	PdNPs				97	1940
2	10% Pd/C				84	1680
3	PdNPs				93	1860
4	10% Pd/C				75	1500

[a] Reaction conditions: aryl halide (1 mmol), boronic acid derivative (1.2 mmol), Pd catalyst (0.0005 mmol Pd content), KOH (2 mmol), 100 °C, 60 min.
[b] GC yield.

4. Conclusions

In conclusion, we have developed a novel, green and simple method for the synthesis of well dispersed palladium nanoparticles with a maximum contribution of nanoplates using ethylene glycol as a reducing agent and concentrated solar radiations as a renewable energy source. The optimum reaction condition for nanoplate's formation was attained by adjusting the concentration ratio of sunlight in presence of PVP as a mild reductant. The obtained nanoplates showing greater catalytic applicability in the novel and greener protocol for synthesis of 2-phenoxy-1,1′-biphenyls and *N*,*N*-dimethyl-[1,1′-biphenyl] derivatives at mild reaction condition. The catalyst could be reused for three more consecutive cycles.

Acknowledgments

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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.2013.07.012.

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