Green synthesis of Pd@rGO nanocomposite using Piper (Piper nigrum) leaf extract and its catalytic activity towards alcohol oxidation in water at room temperature

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Abstract
A simple in situ methodology for the green synthesis of palladium decorated reduced graphene oxide (Pd@rGO) nanocomposite using green leaf extract of Piper plant (Piper nigrum) has been described. The one-pot synthetic method uses no external stabilizer. The obtained nanocomposite has very low Pd loading (0.012 mol % of Pd), and the size of the nanoparticles anchored in rGO sheets ranged between 6 to 20 nm. The as-synthesized nanocomposite was characterized by FT-IR, UV–vis, TGA, XRD, TEM, EDX, BET surface area measurement, and ICP-AES analysis. The Pd@rGO nanocomposite showed profound catalytic activity for the selective oxidation of primary as well as secondary alcohol in water at room temperature. It is worth noting that, under the optimal condition, it is equally useful for the oxidation of usually nonreactive alcohols like cyclohexanol, nonanol, furfuryl alcohol, etc. The catalyst showed excellent recyclability up to 5th cycles without significant loss of catalytic activity.

1. Introduction
Oxidation of alcohol is one of the most important and fundamental organic transformation frequently used in various organic syntheses involving the manufacture of several drugs, vitamins, fragrances, etc [1]. Traditionally, oxidation of alcohol is mostly based on the use of stoichiometric amount of oxidant such as K$_2$Cr$_2$O$_7$, KMnO$_4$, etc. which are toxic, expensive and produces copious amounts of metal waste [2]. Over the last few years in the quest of ‘going green’ continuous efforts are being made to replace these conventional methods in order to reduce their impact on the environment. A wide range of methods involving homogeneous as well as heterogeneous catalysts based on transition metal such as Pd, Pt, Ru, Rh [3–6], etc. are meaningfully developed for oxidation of alcohol. Although considerable advancements had been made however, most of these protocols suffered from critical disadvantages such as, long reaction time, either no or low recyclability, low separability, high reaction temperature, low product yield etc.

Transition metal nanoparticles also play an important role in catalysis. Due to their robust nature, high surface area and exceptional physiochemical properties transition metal nanoparticles become an attractive alternative to the traditional catalytic systems [7]. Oxidation of alcohol by catalysts containing nanomaterial has also received a staggering degree of attention. In recent years various methods involving transition metal nanoparticles as an effective catalyst for oxidation of alcohol have been reported [8–11]. Out of these, only few articles with Pd nanoparticles (PdNP) as active catalysts have been reported. Koresszegi et al [12], have reported a Pd/Al$_2$O$_3$ catalyst for oxidation of benzyl alcohol with cyclohexane as a solvent. A bio-reduced Pd nanocatalyst has been published by Hazarika et al [13], which shows excellent catalytic activity at a temperature of 70 °C. R B Nasirbaig et al [14], proposed the catalytic activity of a magnetically recoverable Pd-Fe nanocomposite which gives up to 99% selectivity at a temperature above 70 °C. However, most of them required high temperatures and organic solvents. Therefore, the development of new green, sustainable protocols that carry rapid and selective chemical transformation with implausible product yield is still demanding.
There are several traditional methods available for the synthesis of metal nanoparticles. But most of the methods encompass the use of chemical reducing and stabilizing agents which are not environmentally benign [15]. Therefore, the development of bio-inspired protocols for the synthesis of metal nanoparticles is highly attractive for greening chemical synthetic processes [16]. Biogenic synthesis not only reduces the consumption of noxious chemicals but also provides the nanoparticles a well-defined size and morphology. Moreover, the synthetic simplicity, cost-effectiveness, environmentally benign properties, bulk availability, and excellent biocompatibility give extra light to those methods [13]. In recent years, delving into the scalable synthesis of metal nanoparticle, several methods have been documented, which involve different plant extracts as environmentally benign and green alternatives to conventional reducing agents. Some examples include the use of Lotus (Nelumbo nucifera) [17], Aloe vera (Aloe vera) [18], Neem (Azadirachta indica) [19] etc. for the synthesis of metal nanoparticles.

Piper is a medicinal plant available in various areas of India and China. The presence of flavonoids and phenolic acid such as gallic acid, protocatechuic acid, catechin, coumaric acid, etc. in the piper leaves and fruits have already been established [20]. These organic constituents of the plant extract having excellent antioxidant activity and stabilizing property are responsible for the formation of the Pd nanoparticles. The reduction of Na₂PdCl₄ and GO is done via a nucleation type electron transfer reaction by the OH group of catechin and gallic acid followed by adsorption [21]. Moreover, it is worthy to be noted that Pd nanoparticles also catalyze the reduction of GO to rGO, as GO was added to the reaction mixture after the formation of Pd nanoparticles [22].

Heterogeneous catalysis scores better compared to homogeneous one because of easy separation of product, retrievability, and high stability. Graphene Oxide (GO) is a unique sp² hybridized, honeycomb structured, carbon-based material having excellent thermal, electrical and mechanical properties. Due to exceptionally high specific surface area, reduced graphene oxide becomes an ideal carrier for nanoparticles [23]. The incorporation of nanoparticles on the sheets of reduced graphene oxide leads to the restacking of GO sheets through π–π interaction and reduces the chances of agglomeration of nanoparticles. Such hybrid nanomaterial is associated with the duel advantages of both GO and the other component which finds tremendous application in numerous fields. Therefore researchers are interested in functionalization of metal nanoparticles to GO or reduced graphene oxide (rGO) by tuning its interfacial properties.

Herein, we report an eco-friendly protocol for the synthesis of (Pd@rGO) nanocomposite using green leaf extract of Piper nigrum as a natural reducing agent. The catalytic efficiency of this nanocomposite has been investigated for oxidation of different primary and secondary alcohols in an aqueous medium, at room temperature.

2. Experimental

2.1. Materials and method

All the reagents used were of analytical grade and used without any prior treatment. The solvents used such as acetonitrile, DMSO, DCM, etc. and the oxidant H₂O₂ were purchased from Merck. PdCl₂ and alcohol substrates were purchased from Sigma Aldrich and TCI. FT-IR spectra of GO and Pd@rGO nanocomposite were recorded with a Shimadzu prestige 21 FTIR spectrophotometer (200–4000 cm⁻¹) as KBr disks. UV–vis spectra of the catalyst, PdCl₂ and the plant extract were recorded in aqueous phase with Shimadzu UV-1800 spectrophotometer. Thermogravimetric analysis (TGA) of GO and Pd@rGO were conducted on a Perkin Elmer STA-8000 analyzer with a heating rate of 10 °C per min under N₂ atmosphere. TEM images of Pd@rGO were obtained with a JEM/JEM-2100, operating at 200KV from SAIF, NEHU, Shillong. The powder x-ray diffraction pattern (PXRD) was obtained from, CSIC Dibrugarh University and recorded with a Rigaku Ultima-IV X-ray diffractometer (Japan) with Cu Kα radiation (λ = 1.54056 Å) at voltage-40KV. SEM-EDX spectrum of Pd@rGO was recorded at CSIC Dibrugarh University using a JEM, JSM IT-300 operating at 20KV. The specific surface area of GO, rGO, and Pd@rGO were determined using Quantachrome Autosorb-iQ analyzer, Bonton Beach, FL, USA following Brunauer–Emmett–Teller (BET) protocol. Inductively coupled plasma (ICP) analysis of the fresh, as well as recovered Pd@rGO were obtained from STIC, Kochi University, Kochi on Thermo electron IRIS INTREPID II XSP DUO. The 1H NMR spectra of the reaction products were recorded in CDCl₃ on a Bruker Avance-400 MHz at room temperature at SAIF, NEHU, Shillong.

2.2. Synthesis of Piper (Piper nigrum) leaf extract

5 g of fresh piper leaf was collected and washed with de-ionized water. The wet leaves were crushed well in a mortar and boiled with 70 ml water for 1 h. The mixture was then allowed to cool to room temperature and centrifuged. The filtrate was collected and stored in a refrigerator for further use.
2.3. Synthesis of graphene oxide
Graphene oxide was prepared by modified Hummer’s method [24] using graphite. 2 g of graphite and 2 g of NaNO₃ were stirred with 120 ml of concentrated H₂SO₄ in an ice bath for 30 min, followed by the addition of 15 g of KMnO₄ with constant stirring by carefully maintaining the temperature below 20 °C. The ice bath was then removed and the mixture was left overnight at room temperature with constant agitation. The mixture progressively became pasty and the color changed to light brown. To this brown colored mixture 150 ml H₂O was added with constant stirring. The temperature of the reaction suddenly rose to 98 °C with effervescence and the color of the mixture became yellow. The resulting suspension was then stirred at 98 °C for one day, followed by the addition of 50 ml 30% H₂O₂. The mixture was centrifuged and rinsed repeatedly with 5% HCl and washed with de-ionized water. A grey solid was obtained by filtration which was dried under vacuum.

2.4. Synthesis of Pd@rGO nanocomposite
100 ml of Piper leaf extract was mixed with 60 ml 0.1 mM solution of Na₂PdCl₄ and stirred at 60 °C for 3 h, whereupon a black colored solution was observed, indicating the formation of Pd nanoparticles. After that, 0.05 g of graphene oxide was sonicated for 30 min and slowly added to the above solution followed by the addition of another 50 ml of the plant extract. The mixture was stirred at 80 °C for another 24 h. The resulting black colored solid mass was then centrifuged, filtered off and collected for characterization.

2.5. Typical procedure for catalytic reaction
In a typical reaction 1 mmol alcohol, 2 mmol H₂O₂ and 5 ml H₂O were taken in a round bottom flask followed by the addition of 10 mg catalyst. The mixture was then vigorously stirred at room temperature for the required time. The progress of the reaction was monitored by thin-layer chromatography. The reaction mixture was then allowed to cool to room temperature and the catalyst was removed by centrifugal precipitation. The organic content of the mixture was extracted by adding ethyl acetate (3 × 10 ml). The extracted organic portion was washed with brine and dried over Na₂SO₄. The mixture was filtered and the solvent (ethyl acetate) was removed by rotary evaporation. The crude products were purified by column chromatography on silica gel (60–120 mesh) using 40% ethyl acetate/hexane as eluent.

3. Results and discussion
3.1. Characterization of the catalyst
FT-IR spectra of GO and Pd@rGO are demonstrated in figure 1. The spectrum of GO shows a broad peak at 3300 cm⁻¹ corresponding to carboxylic acid O–H stretching vibration. The peaks at 1740, 1550 and 1240 cm⁻¹ could be attributed to carboxyl C=O, C=C and C–O alkoxy stretching vibrations, respectively. In the FT-IR spectrum of Pd@rGO a significant decrease of the intensity of these peaks clearly indicates reduction of GO.

In order to examine the formation of Pd nanoparticles, we have performed UV–vis analysis of PdCl₂ solution (0.1 M; H₂O:EtOH = 1:1), plant extract, and the colloidal nanoparticles solution (0.01 M). A moderate
peak at 320 nm demonstrated by PdCl₂ solution could be assigned to chloride to Pd (II) CT transition \[25\]. The absence of any peak above 300 nm in the spectrum of colloidal nanoparticle solution affirms the formation of Pd nanoparticles (figure 2) \[15\].

The thermogravimetric analysis (TGA) of Pd@rGO and GO exhibited two major weight losses at two different temperature regions (figure 3). The GO showed a major weight loss of 36\% in the temperature range of 150 to 280 °C, attributed to the decomposition of oxygen-containing functional groups like epoxy, hydroxyl, carbonyl, and carboxyl, etc. It is noteworthy that the weight loss in this region significantly decreased to 8\% after the formation of Pd@rGO nanocomposite, showing the presence of lesser number of oxygen functionalities in the nanocomposite \[26\]. These results affirmed almost 90\% reduction of GO sheets. Another weight loss observed for both of GO and Pd@rGO above 500 °C could be assigned to the decomposition of hexagonal C-skeleton of the GO sheet \[27\].

The XRD pattern of GO (figure 4(a)) exhibits a sharp peak at 2θ value of 10.6° which is the characteristic peak for GO, indicative of insertion of oxygen rich functional groups within the graphite layers \[26\]. Another peak of weak intensity is observed at 42.3°, which corresponds to (100) plane indicates the presence of trace amount of graphite \[28\]. XRD pattern of Pd@rGO (figure 4(b)) nanocomposite shows prominent peaks at 2θ values of 40°, 46.6° and 68.04° which are assigned to (111), (200) and (220) crystallographic planes of fcc structured Pd nanoparticles, respectively (JCPDS card No-0021432). The disappearance of the peak at 10.6° corresponds to the
The reduction of GO to rGO. The figure 4(b) shows another broad peak between 20° and 30° which is an indication of (002) plane of rGO [29].

The distribution pattern, particle size and the surface morphology of Pd@rGO nanocomposite have been studied by transmission electron microscopy (figures 5(a)–(c)). The TEM micrograph (figure 5(a)) reveals that the Pd nanoparticles are randomly distributed over reduced GO sheets along with slight agglomeration. The particle size of the nanoparticles are in the range of 6–20 nm and as shown in the SAED pattern, lattice fringes and diffraction dots represent their crystallinity (figure 5(b)). The HRTEM image (figure 5(c)) shows the spacing between two lattice planes as 0.20 nm, which is consistent with the spacing between two (200) planes of Pd nanoparticle [15].

The BET surface area of GO, rGO, and Pd@rGO are shown in table 1. It has been observed that after the formation of rGO surface area dramatically raised up to 350 m² g⁻¹, indicative of porous nature of rGO. However, the decrease of surface area of Pd@rGO (280 m² g⁻¹) compared to rGO sheets clearly confirms the successful grafting of Pd nanoparticles on the rGO sheets.

The energy dispersive x-ray spectrum (figure 6) clearly indicates the presence of Pd on the surface of rGO sheets. From the ICP-AES analysis the amount of Pd in the composite was found to be 0.012 mol % per 20 mg of the Pd@rGO nanocomposite.

The above experimental analyses revealed that a well-dispersed Pd@rGO nanocomposite was formed by the treatment of Piper leaf extract (Piper nigrum) with GO and Na₂PdCl₄. It is also supported by the reported data [20, 30].

It is well established that due to the destruction of sp², the geometrically strained region of the GO sheet becomes much more reactive than the other part of the sheet and the electron density can be more easily transferred from the upper plane of the ring [31, 32]. Usually Pd²⁺ has a strong electrostatic interaction with the π-orbitals of alkenes. Thus under the effect of electrostatic interaction, the Pd²⁺ undergoes electrophilic...
substitution to the graphene sheet and gets anchored in it with gradual conversion into nanoparticles [33]. The polyphenols and flavonoids present in the plant extract stabilized the nanoparticles formed and thus prevent agglomeration of nanoparticles.

3.2. Catalytic activity of Pd@rGO towards oxidation of alcohol

After characterization we want to examine the activity of as-synthesized nanocomposite (Pd@rGO) as catalyst for oxidation of primary and secondary alcohols. To optimize the reaction conditions such as solvents, temperature, catalyst amount, etc. for excellent reaction performance, a number of runs were conducted using benzyl alcohol as model substrate (table 2). We have conducted the reaction in presence of a number of solvents like water, acetonitrile, DCM, DMF, DMSO etc. and our investigations showed that water is the best solvent in this case (table 2, entry 8). As per literature report water with a high polarity index facilitates the adsorption of the substrate on the active site of the catalyst by increasing the solubility of the organic substances. This is probably one of the reasons for the excellent reactivity in aqueous medium. A significant activity of the catalyst has also been observed when a mixture of solvent was used (table 2, entries 6 & 7) while in solvent-free condition the yield was very poor (table 2, entry-14). It has been observed that an increase in the amount of the catalyst does not accelerate the reaction (table 2, entry-11). Similarly, an increase in reaction temperature did not alter the product yield (table 2, entry-13). The reaction was also performed in presence of rGO and even in absence of catalyst (table 2, entry-15 & entry-16) but in both the cases only a trace amount of the product was formed, establishing a significant role of Pd@rGO nanocomposite in alcohol oxidation. It is quite interesting to note that while neat Pd nanoparticle (without support) was used as catalyst afforded 70% isolated yield (table 2, entry-12). This indicates that directly or indirectly GO also plays a role in the oxidation reaction. A 50% product yield was observed while air was used as an oxidant (table 2, entry-9). Variation of catalyst amount showed that 10 mg of the catalyst (0.006 mol% of Pd) is sufficient to carry out the transformation efficiently.

The optimization of reaction conditions for the oxidation of secondary alcohol was also carried out using Pd@rGO nanocomposite as catalyst by taking 1-phenylethanol as a model substrate (table 3). Our investigations revealed that 10 mg (0.006 mol% of Pd) of Pd@rGO as catalyst, 2 mmol of H₂O₂ as an oxidant at room temperature in aqueous medium is the best suitable condition to carry out the oxidation of primary as well as secondary alcohols.

After optimization, the catalytic activity of Pd@rGO was screened for various primary and secondary alcohols having electron-withdrawing as well as electron-donating group (table 4). It was observed that both

| Sl No | Material | Surface area (m² g⁻¹) |
|-------|----------|----------------------|
| 1     | GO       | 21                   |
| 2     | rGO      | 350                  |
| 3     | Pd@rGO   | 280                  |

Figure 6. SEM-EDX of Pd@rGO nanocomposite.
Table 3. Optimization of oxidation of 1-phenylethanol using Pd@rGO as catalyst

| Entry | Solvent (catalyst amount) | Time | Yield (%) |
|-------|---------------------------|------|-----------|
| 1     | DMF (0.006)               | 68   | 5         |
| 2     | DCM (0.006)               | 58   | 0         |
| 3     | Toluene (0.006)           | 68   | 0         |
| 4     | H2O:DMF (1:1) (0.006)    | 58   | 8         |
| 5     | Acetonitrile (0.006)      | 67   | 9         |
| 6     | H2O              | 68   | 5         |
| 7     | H2O:Acetonitrile (1:1) (0.006) | 58   | 8         |
| 8     | H2O (0.006)               | 58   | 8         |
| 9     | H2O (0.006)               | 58   | 8         |
| 10    | H2O (0.006)               | 58   | 8         |
| 11    | H2O (0.006)               | 58   | 8         |
| 12    | H2O (0.006)               | 58   | 8         |
| 13    | H2O (0.006)               | 58   | 8         |
| 14    | No solvent (0.006)        | 59   | 6         |
| 15    | H2O (0.006)               | 59   | 6         |
| 16    | H2O (0.006)               | 59   | 6         |

* Reaction conditions: 1-phenylethanol (1 mmol), H2O2 (2 mmol), Pd@rGO (10 mg, 0.006 mol% of Pd) at room temperature.  
* Isolated yield after column chromatography.  
* Air is used as oxidant.  
* Pd nanoparticles neat (without support) is used as catalyst.  
* 60 °C temperature is used.  
* Only rGO is used as catalyst.  
* No catalyst is used.

Table 2. Optimization of oxidation of benzyl alcohol using Pd@rGO as catalyst

| Entry | Solvent (catalyst amount) | Time | Yield (%) |
|-------|---------------------------|------|-----------|
| 1     | Acetonitrile (0.006)      | 4    | 75        |
| 2     | DCM (0.006)               | 5    | 80        |
| 3     | DMF (0.006)               | 6    | 83        |
| 4     | DMSO (0.006)              | 6    | 79        |
| 5     | Toluene (0.006)           | 5    | 72        |
| 6     | H2O:Acetonitrile (1:1) (0.006) | 5 | 85        |
| 7     | H2O:DMF (1:1) (0.006)     | 5    | 85        |
| 8     | H2O (0.006)               | 5    | 96        |
| 9     | H2O (0.006)               | 24   | 50        |
| 10    | H2O (0.006)               | 7    | 75        |
| 11    | H2O (0.012)               | 5    | 96        |
| 12    | H2O (0.006)               | 6    | 70        |
| 13    | H2O (0.006)               | 5    | 96        |
| 14    | No solvent (0.006)        | 12   | 40        |
| 15    | H2O (0.006)               | 24   | Trace     |
| 16    | H2O (0.006)               | 24   | Trace     |

* Reaction conditions: Benzyl alcohol (1 mmol), H2O2 (2 mmol), Pd@rGO (10 mg, 0.006 mol% of Pd) at room temperature.  
* Isolated yield after column chromatography.  
* Air is used as oxidant.  
* Pd nanoparticles neat (without support) is used as catalyst.  
* 60 °C temperature is used.  
* Only rGO is used as catalyst.  
* No catalyst is used.
Table 4. Oxidation of various primary and secondary alcohols using Pd@rGO as catalyst.

| Entry | Substrate | Product | Time (h) | Yield (%) | TON |
|-------|-----------|---------|----------|-----------|-----|
| 1     | \( \text{Ph} \text{CH(OH)} \) | \( \text{Ph} \text{CH(O)} \) | 4        | 97        | 16166 |
| 2     | \( \text{Ph} \text{CH(OH)} \) | \( \text{Ph} \text{CH(O)} \) | 4        | 92        | 13333 |
| 3     | \( \text{Ph} \text{CH(OH)} \) | \( \text{Ph} \text{CH(O)} \) | 5        | 93        | 15500 |
| 4     | \( \text{Ph} \text{CH(OH)} \) | \( \text{Ph} \text{CH(O)} \) | 5        | 91        | 15166 |
| 5     | \( \text{Ph} \text{CH(OH)} \) | \( \text{Ph} \text{CH(O)} \) | 4.5      | 94        | 15666 |
Table 4. (Continued.)

| Entry | Substrate | Product | Time (h) | Yield (%) | TON  |
|-------|-----------|---------|----------|-----------|------|
| 6     |           |         | 5        | 85        | 14166|
| 7     |           |         | 3.5      | 95        | 15833|
| 8     |           |         | 4        | 93        | 15500|
| 9     |           |         | 4        | 89        | 14833|
Table 4. (Continued.)

| Entry | Substrate | Product | Time (h) | Yield (%) | TON |
|-------|-----------|---------|----------|-----------|-----|
| 10    | ![OH](image1.png) | ![O](image2.png) | 5        | 88        | 14666 |
| 11    | ![O](image3.png) | ![O](image4.png) | 6        | 86        | 14333 |
| 12    | ![OH](image5.png) | ![O](image6.png) | 9        | 60        | 10000 |
| 13    | ![OH](image7.png) | ![O](image8.png) | 8        | 67        | 11166 |

Pd@rGO nanocomposite-10mg (0.006 mol%) H$_2$O$_2$ (2 mmol), H$_2$O, RT
Table 4. (Continued.)

| Entry | Substrate | Product | Time (h) | Yield (%) | TON |
|-------|-----------|---------|----------|-----------|-----|
| 14    | R<sub>1</sub>OH -> R<sub>1</sub>CO<sub>2</sub>R<sub>2</sub> | Pd@rGO nanocomposite-10mg (0.006 mol%) | 7 | 50 | 8333 |

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* Reaction conditions: Alcohol (1 mmol), H<sub>2</sub>O<sub>2</sub> (2 mmol), Pd@rGO (10 mg, 0.006 mol % of Pd) at room temperature.

* Isolated yield.
primary and secondary alcohols having electron-withdrawing and electron-donating groups were converted to their corresponding carbonyl compounds with excellent yields. Contrastingly, aliphatic and heterocyclic aromatic alcohols exhibited moderate activity to this protocol.

3.3. Reusability test
The scope of recyclability is the main attractiveness of heterogeneous catalysis. Therefore, we have checked the recyclability of our catalyst for oxidation of benzyl alcohol. For this purpose, 1 mmol of benzyl alcohol, 2 mmol H₂O₂ and 10 mg (0.006 mol % of Pd) of the catalyst was taken in a round bottom flask and stirred at room temperature required time. After the completion of the reaction (monitored with GC), the catalyst was recovered from the reaction mixture by vigorous centrifugal precipitation. It is then washed with ethyl acetate and dried overnight in an oven at 110°C and then reused for subsequent runs. Identical reaction conditions were maintained during the subsequent runs. To our delight, the catalyst has retained its efficiency even after 5th cycle.

To know any physical changes of the catalyst that may occur during the course of the reaction, we recorded XRD pattern of the reused catalyst after 5th cycle (figure 7(b)). Interestingly the recovered catalyst after 5th run showed almost similar XRD pattern to that of the fresh catalyst.

3.4. Heterogeneity test
The heterogeneity of the catalyst was checked by performing a hot filtration test (figure 9), taking benzyl alcohol as model substrate. For this purpose 1 mmol of benzyl alcohol, 2 mmol H₂O₂ and 10 mg (0.006 mol % of Pd) catalyst was mixed in a round bottom flask and stirred at room temperature. After 2 h the reaction was stopped and the solid catalyst was removed through centrifugal precipitation (35% yield found from GCMS). The filtrate was stirred for another 2 h without catalyst, but no increase in the product yield had been observed. However, another reaction without hot filtration of the catalyst was carried out simultaneously which showed 96%
conversion as detected by GC-MS analysis, which clearly indicates insignificant leaching of the catalyst. Moreover, to examine any catalyst leaching we have carried out ICP-AES analysis of the filtrate but only a negligible amount of Pd was detected, which further establishes the heterogeneous nature of the catalyst.

In order to check the superiority of Pd@rGO catalyst, we have performed a comparative study. It has been observed that most of the reported protocols are associated with the drawback of high temperature requirement. The results are summarized in Table 5.

**4. Conclusion**

A very simple time efficient green procedure has been applied for the one pot synthesis of Pd@rGO nanocomposite using Piper leaf extract (Piper nigrum). The organic constituents of the green leaf like gallic acid, protocatechuic acid, coumaric acid, etc. are probably responsible for the reduction of PdCl₂ and also for the stabilizing action. The Pd@rGO nanocomposite demonstrated an excellent catalytic activity for the oxidation of both primary and secondary alcohols in water with excellent product yield. The most important feature of the present protocol is that under the optimized condition it is moderately useful for the oxidation of usually nonreactive alcohol like cyclohexanol, nonanol, furfuryl alcohol, etc. The catalyst can retain its catalytic activity up to 5th cycle without profound loss in activity. The excellent reusability, absolute heterogeneity, use of green reaction conditions, short time requirement and most importantly low Pd loading (0.012 mol% per 20 mg) gave an extra light to the new catalyst.

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