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Facile and surfactant-free synthesis of Pd nanoparticles by extract of fruits of *piper longum* and their catalytic performance for Sonogashira coupling reaction in water under ligand- and copper-free conditions

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

This work reports a facile synthesis of palladium nanoparticles (Pd NPs) by extract of fruits of *piper longum* without any stabilizer or surfactant. The Pd NPs were found to be effective catalysts for ligand-, amine- and copper-free Songashira coupling reaction under aerobic conditions. The Pd NPs were characterized with UV-vis, FT-IR and TEM methods. This method has the advantages of high yields, simple methodology, and elimination of ligand, copper, organic solvent and homogeneous catalysts and easy work up. Water is used as the only solvent for the coupling reaction. More importantly, the catalyst was recovered and recycled by a simple decantation of the reaction solution and used for five consecutive trials without significant loss of its reactivity.

Introduction

The Sonogashira cross-coupling reaction has become one of the most important, powerful, and versatile tools in the formation of C(sp)-C(sp2) bonds over the past three decades, which plays an important role in the synthesis of a variety of compounds, including heterocycles, natural products, and pharmaceuticals.[1-3]

Generally, the Sonogashira reaction proceeds in the presence of toxic phosphine ligands with the combination of palladium and copper salts using a large excess of base in an organic solvent such as an amine, benzene, THF, or DMF under inert conditions, which were economically and environmentally malignant.[4,5]

However, each of these methods suffer from different drawbacks such as employing expensive phosphine ligands, use of hazardous and expensive organic solvents, harsh reaction conditions, tedious work-ups, long reaction times, low yields, inert atmosphere conditions, environmental pollution caused by formation of side products.[4,5] In Sonogashira coupling reaction, Glaser-type oxidative dimerization of the terminal alkynes cannot be avoided in copper-mediated reaction, in which side products (diyne) are generally difficult to separate from the desired products and copper acetylide is a potentially explosive reagent.[4,5] In addition, amines, such as triethylamine and piperidine, required in most Sonogashira reactions, have a bad smell and add to the environmental burden. Therefore, the development of convenient methods for Sonogashira reactions is an important objective.

The use of water, the most abundant and non-toxic solvent for reactions is reclaiming its importance due to pressing environmental, economical, and safety concerns. Moreover, the products can be isolated easily by extraction. Several examples of Pd-catalyzed Sonogashira reactions in aqueous medium have been reported; however, many of these reactions are carried out in an aqueous-organic medium and in some cases, specialized phosphine ligands and copper salts are required in order to achieve high reaction efficiency.[6-8] However, most of the above reactions were carried out homogeneously and, thus, had intrinsic problems such as difficulties in recovery, separation and recycling of the expensive, toxic catalysts and contamination of the ligand residue into the final product.[9] Therefore, development of mild, highly efficient and environmentally benign method for the ligand-, copper- and amine-free Sonogashira coupling reaction under heterogeneous conditions has been a major challenge in organic synthesis.

In recent years, there has been great interest in using nanoparticles (NPs) as catalysts in organic reactions.[10] Because of their easy preparation and being relatively stable in air, the nanoparticles of coinage metals were widely reported, and there are many excellent examples of their applications as catalysts.[11] Due to a higher available catalytic surface, heterogeneous catalysts are more and more used in the form of nanoparticles.[12] Additionally, nanocatalysis can make the products easily removable from the reaction mixtures and make the catalysts recyclable. Thus nanocatalysis is a promising alternative to the homogeneous catalysis to afford the same products with high reaction rates and high yields. However, these small-sized products require more complex production methods which often imply the use of toxic and expensive chemicals. Therefore, environmentally benign production methods of Pd nanocatalysts are very desirable.

In the recent time, several researchers have achieved success in the synthesis of metal nanoparticles with specific shape and size using various plants extracts, bacteria and fungus.[13,14] Greener synthesis helps to replace the hazardous chemicals that cause toxicity, minimizes harmful pollution to the environment when debris such as surfactants/dispersants released by the large scale industries and lead to an eco-friendly environment.[15-19]

Piper species, widely distributed in the tropical and subtropical regions of the world are used medicinally for presence of various phytochemicals. *Piper longum* or long piper belonging to the family *Piperaceae* is a slender aromatic climber with red fruits (Figure 1). These fruits turn grayish black with pungent smell

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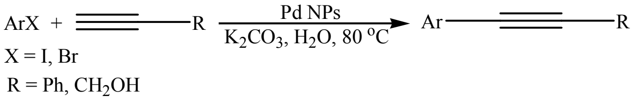
when dried. The primary active constituents namely piperine, piplartine, and piperlongumine are found to be present in the plant. Also *piper Longum* consists of polyphenolics such as glycoside flavonoids, alkaloids, lignans, steroids and organic acids.[20-23]

Figure 1. Image of *Piper longum* leaves and fruits.

Based on our continuous investigations on copper, palladium, iron and silver nanoparticles catalyzed reactions,[24] we wish to report herein an ecofriendly, clean, non-toxic, facile chemically preparative method for the synthesis of palladium NPs using extract of fruits of *piper longum* without any stabilizer or surfactant. The Pd NPs were characterized by TEM, FT-IR and UV-visible techniques. Also, the catalytic activity of Pd NPs for the ligand- and copper-free Sonogashira coupling reactions in water was studied under aerobic conditions (Scheme 1). To the best of our knowledge, no report has been issued on the biosynthesis of Pd NPs using extract of fruits of *piper longum*.



$$\mathrm{ArX} + \equiv\!-\mathrm{R} \xrightarrow[\mathrm{K_2CO_3,\ H_2O,\ 80\ ^oC}]{\mathrm{Pd\ NPs}} \mathrm{Ar}-\!\equiv\!-\mathrm{R}$$

X = I, Br
R = Ph, CH_2OH

Scheme 1. Sonogashira coupling reaction of aromatic aryl halides and terminal alkynes catalyzed by Pd NPs in water.

Result and Discussion

Plant extracts may act both as reducing agent and stabilizing agents in the synthesis of nanoparticles. This study was performed, to predict the plant based reducing agents that are involved in the reaction between extract of the fruits of the *piper longum* and $PdCl_2$. In this study we used the fruits of *piper longum* as a major part of the plant for presence of antioxidant glycoside flavonoids as potent reducing agents to green synthesize of palladium nano particles.

Characterization of extract of fruits of *piper longum*

To confirm the presence of reducing agents inside the extract and its ability to green synthesis of metallic nanoparticles, HPLC fingerprinting analysis and spectroscopic methods were used. The HPLC chromatogram demonstrates the presence of 11 constituents as Pipataline, Pellitorine, Sesamine, Brachystamide B, Guineensine, 5-Hydroxy-7,3',4'-Trimethoxyflavone, 5-Hydroxy-7,4'-dimethoxyflavone, 5,4'-Dihydroxy-7-methoxyflavone, Diaeudesmin, Piperine and Dihydropiperlonguminine, respectively (Figure 2).

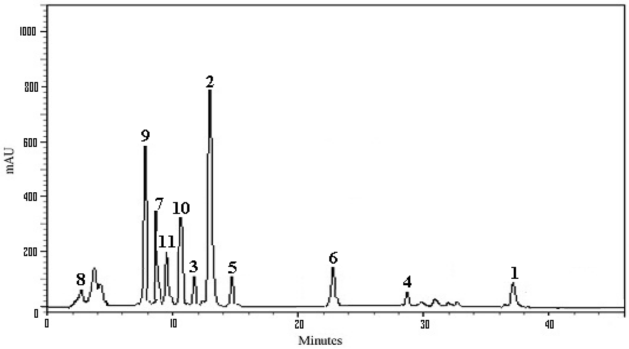


Figure 2. HPLC chromatogram of alcoholic extract of fruits of *Piper longum*; The characterized compounds according the peak numbers are **1-** Pipataline, **2-** Pellitorine, **3-** Sesamine, **4-** Brachystamide B, **5-** Guineensine, **6-** 5-Hydroxy-7,3',4'-Trimethoxyflavone, **7-** 5-Hydroxy-7,4'-dimethoxyflavone, **8-**5,4'-Dihydroxy-7-methoxyflavone, **9-** Diaeudesmin, **10-** Piperine, **11-** Dihydropiperlonguminine, respectively.

Moreover, The UV spectrum of extract (Figure 3) shows bonds at λ_{max} 320 nm (bond I) due to the transition localized within the ring of cinnamoyl system; whereas the one centred at 241 nm (bond II) is for ring related to the benzoyl system. They are related to the $\pi \rightarrow \pi^*$ transitions and these absorbent bonds demonstrate the presence of polyphenolics.

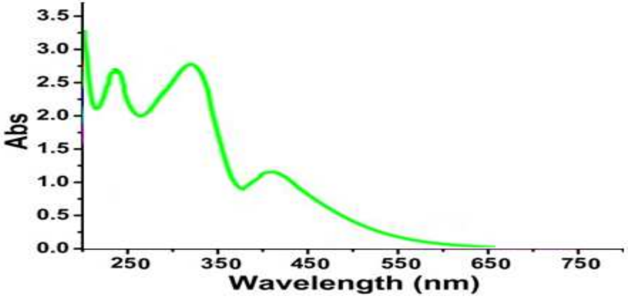


Figure 3. UV-vis spectrum of alcoholic extract of fruits of *piper longum*.

The FT-IR analysis was carried out to identify the possible biomolecules responsible for the reduction of $PdCl_2$ and capping of the bioreduced Pd NPs synthesized by extract of fruits of *piper longum*. The FT-IR spectrum of the crude extract, (Figure 4) depicted some peaks at 3500 to 3000, 1700 and 1650, 1522, 1396 and 1122 cm^{-1} which represent free OH in molecule and OH group forming hydrogen bonds, carbonyl group (C=O), stretching C=C aromatic ring and C-OH stretching vibrations, respectively. These peaks suggested the presence of flavonoid and other phenolics in the plant leaves extract. The presence of flavonoid and other phenolics in the extract could be responsible for the reduction of metal ions and formation of the corresponding metal nanoparticles.

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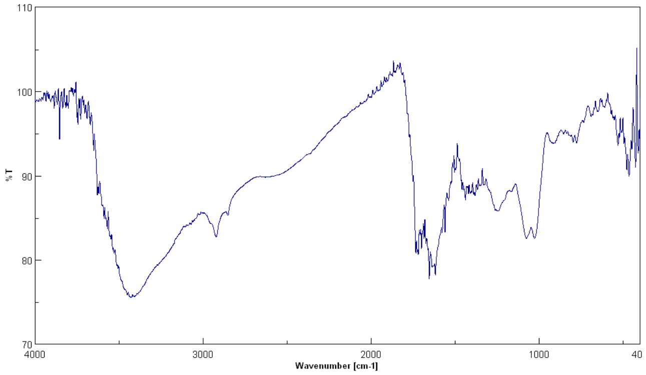

Figure 4. FT-IR spectrum of aqueous extract of fruits of *piper longum*.

Reduction of Pd^{II} to Pd^{o}

In this work, we have employed extract of fruits of *piper longum* as a reducing and stabilizing agent for the synthesis of Pd NPs. The mechanism for the formation of Pd NPs can be explained as shown in Scheme 2. On the basis of this mechanism, metal ions were reduced to nano zero valent (NZV) metallic particles using flavonoid (FlOH) contents of the plant as green (without any hazardous impact on the environment) chemicals (reducing agents) as an alternative to the commonly used hydride reducing agent, sodium borohydride.

$$\mathrm{nFlOH + Pd^{+2} \longrightarrow nFlO\ (radical) + nPd^{0}}$$

$$\mathrm{nFlO\ (Radical) + Pd^{+2} \longrightarrow nFlOX + nPd^{0}\ (Nucleation)}$$

$$\mathrm{nPd^{0} + Pd^{+2} \longrightarrow Pd_{n}^{+2}\ (Growth)}$$

$$\mathrm{Pd_{n}^{+2} + Pd_{n}^{+2} \longrightarrow Pd_{2n}^{+2n}}$$

$$\mathrm{(Pd_{2n}^{+2n})_{n} + (FlOH)_{n} \longrightarrow Palladium\ NZV}$$

Scheme 2. Reducing ability of antioxidant phenolics to produce Pd NPs where FlOH and NZV are flavonoid and nano zero valent, respectively.

Characterization of Pd NPs

The stable Pd NPs obtained were fully characterized by UV-Vis, TEM and FT-IR.

The formation of Pd NP was monitored with the help of UV-vis spectrometry. The UV-vis spectrum of green synthesized Pd NPs using *piper longum* fruits extract (Figure 5) showed the significant changes in the absorbance maxima due to surface plasmon resonance demonstrating the formation of Pd NPs. Also, the progression of the reaction, formation and stability of palladium nanoparticles were controlled by UV-vis spectroscopy. The yellow color of the Pd^{II} solution (λ_{max} 415 nm) immediately changed dark brown (λ_{max} 270-330 nm) indicating reduction of Pd^{II} to Pd^{o} and formation of Pd NPs as characterized by UV-vis spectrum. The synthesized palladium nanoparticles by this method are quite stable and no obvious variance in the shape, position and symmetry of the absorption peak is observed even after one month indicating the stability of Pd NPs.

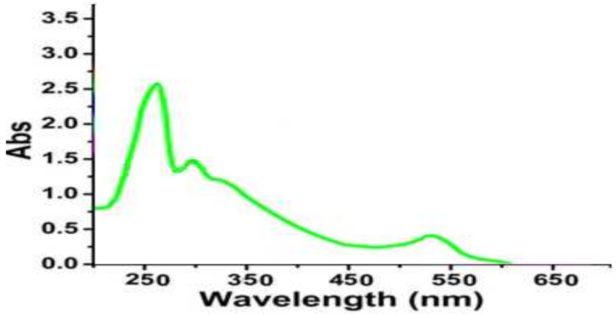

Figure 5. UV-vis spectrum of green synthesized Pd NPs using extract of fruits of *Piper longum*.

Furthermore, the FT-IR of extract after adding $PdCl_2$ while formation of Pd NPs shows demonstrative differences in the shape and location of signals indicating the interaction between $PdCl_2$ and involved sites of phytochemicals for production of nanoparticles (Figure 6). Changing the location of peaks at 3500 to 3200, 1695, 1452, 1381 and 1074 cm^{-1} represent the OH functional groups, carbonyl group (C=O), stretching C=C aromatic ring and C-OH stretching vibrations, respectively. Polyphenolics could be adsorbed on the surface of metal nanoparticles, possibly by interaction through π-electrons interaction in the absence of other strong ligating agents. In fact the π-electrons of carbonyl group (C=O) from C ring of flavonoids in a Red/Ox system can transfer to the free orbital of metal ion and convert that to the free metal.

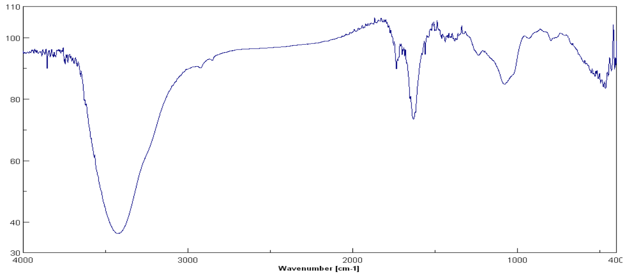

Figure 6. FT-IR spectrum of aqueous extract of fruits of *piper longum*.

Particles morphology and size of Pd NPs were studied by TEM. Figure 7 shows TEM image of typical nanoparticles synthesized from extract of fruits of *piper longum* as both reducing and stabilizing agent. Particle sizes ranged from 5 to 40 nm and most were near spherical. The methanolic plant extract was involved as capping and stabilizing the size of the Pd NPs.

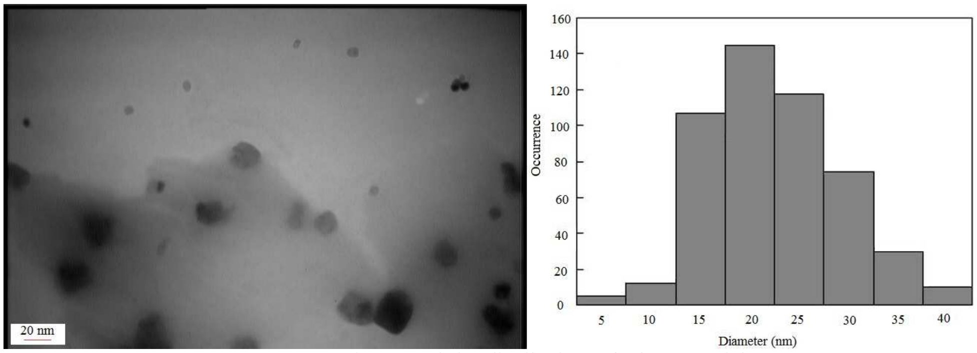

Figure 7. TEM image and size distributions of Pd nanoparticles.

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DOI: 10.1039/C4RA12875C

Catalytic ability and application of the synthesized Pd NPs for the Sonogashira coupling reaction

After characterization of the Pd NPs, their catalytic activities were examined in the Sonogashira coupling reaction. In order to test the catalytic ability and application of synthesized Pd NPs, we first investigated their catalytic effects for ligand-, amine- and copper-free Sonogashira coupling between *p*-iodoanisole and phenylacetylene under aerobic conditions. As shown in Table 1, no product was obtained in the absence of the base (Table 1, entry 1). We examined different bases, such as, KOH, Na_2CO_3, DMAP, K_3PO_4, NaOH, Et_3N and K_2CO_3. The results revealed that the inorganic bases used were more effective than organic bases like DMAP or Et_3N and hence the economically cheaper K_2CO_3 was chosen as a base for these coupling reactions. The effect of the amount of the catalyst was determined for Sonogashira coupling reaction. It can be seen that with an increase in the amount of catalyst from 1.0 mol% to 3.0 mol%, a considerable increase in the yield was observed (Table 1, entries 2 and 3). No significant improvement on the yield was observed using higher amounts of the catalyst (Table 1, entry 11). Thus, the quantity of 3.0 mol% was found to be the best weight of catalyst for the condensation of *p*-iodoanisole (1.0 mmol) with phenylacetylene (1.2 mmol) in H_2O (4.0 mL) at 80 °C (Table 1, entry 3). No surfactant, ligand or organic co-solvent was required. Since no copper salt used, the undesired formation of Glaser-type oxidative homocoupling product, a diyne, was also avoided.

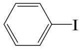
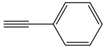
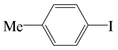
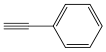
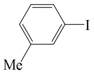
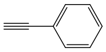
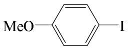
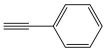
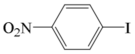
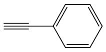
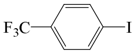
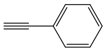
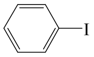
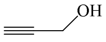
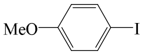
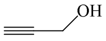
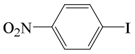
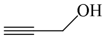
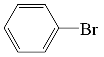
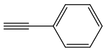
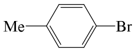
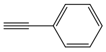
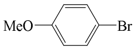
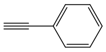
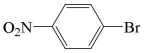
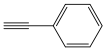
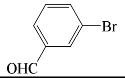
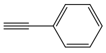
Table 1. Palladium nanoparticles catalyzed coupling reaction of *p*-iodoanisole and phenylacetylene.[a]

Entry	Pd NPs (mol%)	Base	Yield (%)[b]
1	1.0	-	0.0
2	1.0	K_2CO_3	56
3	3.0	K_2CO_3	93
4	3.0	DMAP	0.0
5	3.0	Na_2CO_3	80
6	3.0	NaOH	18
7	3.0	KOH	20
8	3.0	K_3PO_4	75
9	3.0	KOAc	Trace
10	3.0	Et_3N	Trace
	5.0	K_2CO_3	93

[a] Reaction conditions: *p*-iodoanisole (1.0 mmol), phenylacetylene (1.2 mmol), Pd NPs (3.0 mol%), base (2.0 mmol), water (4.0 mL), 80 °C, 4 h.
[b] Isolated Yield.

Sonogashira reactions of different aryl halides and terminal alkynes with 3.0 mol% of Pd NPs as catalyst were investigated. Reactions were carried out in H_2O at 80 °C and different times. The results are listed in Table 2. It can be seen from Table 2 that most of the aryl halides with electron-donating or electron-withdrawing substituents resulted in excellent yields.

Table 2. Sonogashira coupling reaction of aromatic aryl halides and terminal alkynes catalyzed by Pd NPs.[a]

Entry	Aryl halide	Alkyne	Time (h)	Yield ^{b} (%)
1			4	91
2			4	92
3			4	91
4			4	93
5			3	96
6			3	92
7			4	90
			4	89
8			3	93
9			6	84
10			6	92
11			6	94
12			5	95
13			8	93

[a] Reaction conditions: aryl halide (1.0 mmol), terminal alkyne (1.2 mmol), Pd NPs (3.0 mol%), K_2CO_3 (2.0 mmol), water (4.0 mL), 80 °C.
[b] Isolated yield.

Catalyst recyclability

One of the advantages of heterogeneous catalysts is their easy separation from the reaction mixture. After each cycle, the Pd NPs catalyst could be separated and recovered conveniently by centrifugation from the reaction mixture and washed with ethanol and dried in an oven, and then, new substrates and K_2CO_3 were added to set up a new reaction. Before being employed in the next run, the recovered catalysts were washed with ethanol and distilled water several times respectively. As shown in Figure 8, recovered catalyst was recycled five times for the coupling reaction of *p*-iodonitrobenzene and phenylacetylene. This reusability demonstrates the high stability and turnover of catalyst under operating conditions.

To check the heterogeneity of this catalyst, which is an important factor, the filtrate of each cycle was analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) technique. Very low palladium contamination was observed during the course of a reaction. According to the ICP analysis, less than 0.2% of the initial amount of palladium was detected.

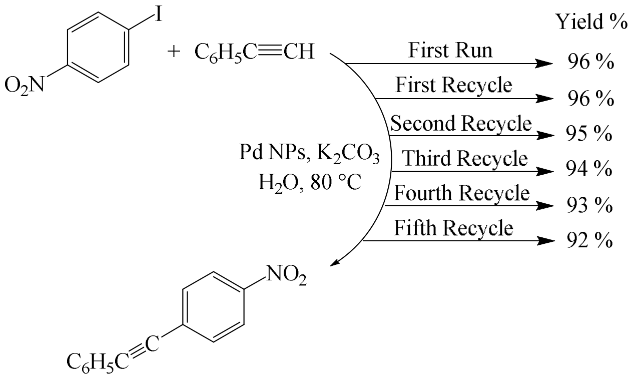


Figure 8. Pd NPs reusability for Sonogashira coupling reaction.

Conclusion

We have successfully synthesized Pd NPs via the reduction of aqueous Pd^{2+} ions using extract of fruits of *piper longum* without any stabilizer or surfactant. The flavonoids present in extract of fruits of *piper longum* act as both reducing and capping/stabilizing agents. The nanoparticles have been characterized by UV-vis, FT-IR and TEM. In addition, the synthesized Pd NPs capped by biomolecules showed potent catalytic application for the ligand- and copper-free Sonogashira coupling reaction in aqueous medium. The present method has the advantages of readily available starting materials, straightforward and simple work-up procedures, elimination of ligand, high yields, tolerance for a wide variety of functionality, and excellent reusability of the catalyst. It is also observed that the catalyst was recycled five times without any significant loss of catalytic activity. The described strategy for Pd NPs is straightforward, robust, environmentally friendly, and cost-effective, and shows considerable great potential. The synthesized Pd NPs by this method are quite stable and can be kept under inert atmosphere for several months.

Experimental

High-purity chemical reagents were purchased from the Merck and Aldrich chemical companies. All materials were of commercial reagent grade. Melting points were deter-mined in open capillaries using a BUCHI 510 melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DRX-400 spectrometer at 400 and 100 MHz, respectively. FT-IR spectra were recorded on a Nicolet 370 FT/IR spectrometer (Thermo Nicolet, USA) using pressed KBr pellets. The element analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer carried out on Perkin-Elmer 240c analyzer. TLC was performed on silica gel polygram SIL G/UV 254 plates. Transmission electron microscopy (TEM) was recorded on a Zeiss-EM10C-80 KV. UV-visible spectral analysis was recorded on a double-beam spectrophotometer (Hitachi, U-2900) to ensure the formation of nanoparticles. The RP-HPLC-DAD instrument consisted of auto injector, sample cooler, pumps, and column oven and diode array detector. An ODS 5μ (3) column (250 x 4.60 mm, particle size 5 μm) was applied. The mobile phase containing methanol: water was filtered through 0.2 μ membrane filter before use. Flow rate of the effluent was 1 mL/min, the detector wavelengths 270 nm and 370 nm and the volume of injection 10 μL. Identification was based on co-injections of reference compounds and comparisons of absorption spectra. All solvents were HPLC-grade and chemicals were analytical grade.

Preparation of extract of fruits of *piper longum*

50 g of dried fruits powdered of *piper longum* was added to 300 mL 30% methanolic solution in 500 mL flask and well mixed. The preparation of extract was done by using magnetic heating stirrer at 70 °C for 30 min. The extract obtained was centrifuged in 6500 rpm then filtered and filtrate was kept at refrigerator to use further.

Preparation of sample for HPLC analysis

The 30% methanolic extract of fruits of *Piper longum* was prepared by soaking in for 24 h. The extract was centrifuged at 5000 rpm and filtered through 0.2 μ membrane filter using high-pressure vacuum pump and the clear solutions were used for HPLC fingerprint analysis.

Preparation of palladium nanoparticles

In a typical synthesis of Pd NPs, 15 mL extract of the plant fruits was added dropwise to 50 mL of 0.003 M aqueous solution of $PdCl_2$ with constant stirring at 80 °C. Reduction of palladium ions (Pd^{II}) to palladium (Pd^o) was completed around 30 min, using monitoring by UV-vis and FT-IR spectra of the solution. The color of the reaction mixtures gradually changed in 30 min at 80 °C indicated the formation of palladium nanoparticles. Then the colored solution of palladium nanoparticles was centrifuged at 7000 rpm for 45 min to absolute precipitation of Pd NPs.

General procedure for Sonogashira coupling reaction

An aryl halide (1.0 mmol), a terminal alkyne (1.2 mmol) and K_2CO_3 (2.0 mmol) were added to a freshly prepared solution of palladium in water (3.0 mol%) in a glass flask under vigorous stirring. The mixture was stirred at 80 °C for the appropriate time under aerobic conditions. After completion of the reaction (monitored by TLC or GC), the reaction mixture was cooled and the organic layer was extracted with EtOAc, washed with water, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was subjected to column chromatography to afford the pure product. The desired pure products were characterized by NMR, FT-IR and from their melting points. All the products are known and the spectroscopic data and melting points were consistent with those reported in the literature.[1,6-9]

Acknowledgement

We gratefully acknowledge the Iranian Nano Council and University of Qom for the support of this work.

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