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FULL PAPER

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Application of biosynthesized palladium nanoparticles (Pd NPs) on *Rosa canina fruit* extract-modified graphene oxide as heterogeneous nanocatalyst for cyanation of aryl halides

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A green palladium (Pd)-based catalyst supported on *Rosa canina fruit* extract-modified graphene oxide [Pd nanoparticles (NPs)/reduced graphene oxide (RGO)-*Rosa canina*] hybrid materials has been used as a recoverable and heterogeneous nanocatalyst for cyanating aryl halides using $K_4[Fe\ (CN)_6]$ as the resource of cyanide. The nitriles were achieved in good to high yield, and the catalyst can be recovered and reused for up to seven cycles with no remarkable decrease in its catalytic activity.

KEYWORDS
cyanation, graphene oxide, nanocatalyst, palladium, plant extract

1 | INTRODUCTION

Aryl nitriles are one of the most adaptable organic building blocks. They are available in many natural products, and are utilized in agrochemicals, pharmacologicals and fragrances.[1–5] Additionally, the nitrile group can be changed to several functional groups like amides, carboxylic acids, aldehydes, ketones or amines. The production of these aryl nitriles needs a stoichiometric quantity of highly toxic cyanating reagents, such as copper cyanide,[6] potassium cyanide,[7] sodium cyanide,[8] zinc cyanide[1] or trimethylsilylcyanide.[9] Moreover, applying relatively less toxic cyanating reagents, such as phenyl cyanates,[10] acetone cyanohydrins[11] and benzyl thiocyanates,[12] is usually expensive and risky. Applying potassium hexacyanoferrate (II)

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trihydrate [$K_4Fe(CN)_6 \cdot 3H_2O$] as a cyanide resource in cyanation reactions by Schareina et al.[13,14] has attracted attention because it is less toxic, inexpensive and eco-friendly.[15,16] In $K_4Fe(CN)_6 \cdot 3H_2O$, cyanide ions are bound powerfully, slowing down releasing CN^- ions in the reaction environment, which in turn avoids fast deactivation of palladium (Pd) catalysts as a result of poisoning the palladium by CN^- ions.[17] There are studies on the application of palladium acetate,[18,19] palladium complex,[20] palladium on carbon[21] as catalysts for catalyzing cyanation reactions using $K_4Fe(CN)_6 \cdot 3H_2O$. The key disadvantage of these catalysts is the problem of recovering and recycling. Therefore, improvement of palladium-based catalysts,[22] which have a highly active and heterogeneous nature, is still a topic for studying as this can provide new benefits while taking into account both environmental and economical aspects.

Amongst the available catalytic approaches for synthesizing aryl nitriles, Pd-catalyzed cyanation of aryl halides has developed as one of the most commonly utilized processes.[22–26] Though homogeneous Pd complexes, frequently related with diverse phosphine ligands, are still the common studied catalysts in cyanation,[20,27–32] the application of heterogeneous systems is also explained. Simple Pd/C was used primarily,[1,33–37] followed by developing polymer-supported Pd (II) complexes that were confirmed to be effective cyanation catalysts in several cases.[14,16,38–45] In recent years, with the advent of nanoparticle (NP) catalysis, diverse Pd NP-based catalysts have been developed.[1,20,30–37] However, amongst supported/heterogeneous systems, they have not been comparatively studied.

In recent years, we have developed the production of Pd NPs supported on reduced graphene oxide (Pd NPs/RGO-*Rosa canina*) through reduction of the GO and Pd^{2+} ions with *Rosa canina* fruit extracts as a stabilizer and reductant agent.[38] The utilized approach synthesized well-dispersed Pd NPs on the graphene sheets used to degrade organic dyes in water in the existence of $NaBH_4$.[38] Herein, in continuing on our previous work utilizing nanocatalysts,[39] we applied Pd NPs/RGO-*Rosa canina* as an effective and heterogeneous nanocatalyst for cyanating aryl halides (X = I, Br, Cl) using low-cost and non-toxic $K_4[Fe(CN)_6]$ as a cyanation agent (Scheme 1).

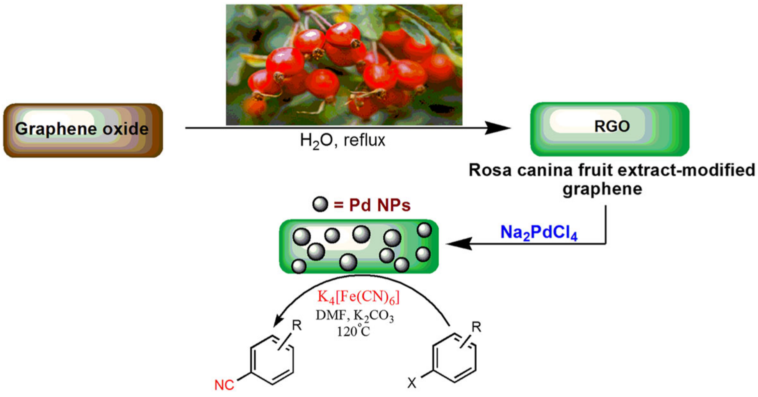
2 | EXPERIMENTAL

2.1 | *Rosa canina* fruit extract preparation

The fresh *Rosa canina* fruits were rinsed thoroughly with double-distilled water before using. Fruits (10 g) were added to deionized water (100 ml), and this mixture was boiled in a water bath for 15 min. Next, the mixture was passed through Whatman filter paper No. 1 to attain aqueous extract and cooled down. The filtered extract was kept in the refrigerator at a temperature of 4°C for the following experiments.

2.2 | The Pd NPs/RGO green synthesis using *Rosa canina* fruit extract

Lastly, the Pd NPs/RGO-*Rosa canina* was synthesized with *Rosa canina* fruits aqueous extract. In order to synthesize the Pd NPs/RGO-*Rosa canina*, the extract was mixed with the achieved GO from natural graphite powder by a modified Hummers method.[40] Next, 50 ml of 0.3 M Na_2PdCl_4 was dropwise poured into the mixture at 100°C under agitation for 12 hr. The obtained Pd NPs/RGO-*Rosa canina* was isolated from the reaction medium using centrifugation, rinsed using deionized water several times, and characterized. The palladium level in Pd NPs/RGO-*Rosa canina* determined using



SCHEME 1 Fabrication pathway of palladium nanoparticles (Pd NPs)/reduced graphene oxide (RGO)-*Rosa canina* and its application in the cyanation of aryl halides using $K_4[Fe (CN)_6]$

inductively coupled plasma-atomic emission spectrometry was 5.42 wt%.

2.3 | General procedure for cyanation reactions catalyzed by Pd NPs/RGO-*Rosa canina*

A solution of $K_4[Fe(CN)_6]$ (0.17 mmol), aryl halide (1.0 mmol), Na_2CO_3 (1.5 mmol), Pd NPs/RGO-*Rosa canina* (10 mg, 0.5 mol%) and DMF (5 ml) was prepared under stirring at a temperature of 120°C for the specified time. The reaction was followed using thin-layer chromatography. After completing the reaction, the achieved solution was cooled to room temperature and centrifuged, and the residue was washed with ethyl acetate (3 × 10 ml). In order to extract the ethyl acetate from the water phase (30 ml), it was combined with the organic phase. The organic phase was dried using Na_2SO_4. The products were obtained by evaporation of the organic solvent. In the case of requiring more purification, the products were passed through a short silica gel column using the eluent of *n*-hexane. All the products are known ingredients and were compared with real samples.

3 | RESULTS AND DISCUSSION

In the current study, Pd NPs/RGO-*Rosa canina* was synthesized over one step by reducing Pd (II) ions and GO with the extract of *Rosa canina* fruit as a stabilizer and reductant agent. In this study, it is assumed that the existence of phenols and acid compounds in the extract results in bioreduction and stabilization of Pd NPs without using toxic ingredients and toxic organic solvents.

The transmission electron microscopy and energy-dispersive X-ray (EDX) analyses were used to prove the nanostructure of Pd NPs/RGO-*Rosa canina* that was prepared again based on our earlier report with a little modification in the resource of palladium ions.[38] The image corresponding to nanocatalyst (Pd NPs/RGO-*Rosa canina*) at 100 nm indicated that the Pd NPs are well distributed on the surface of reduced GO. The results showed that *Rosa canina* fruit extract plays a key role in enhancing the dispersibility of Pd NPs (Figure 1). Most of these particles are in the range of 10–15 nm.

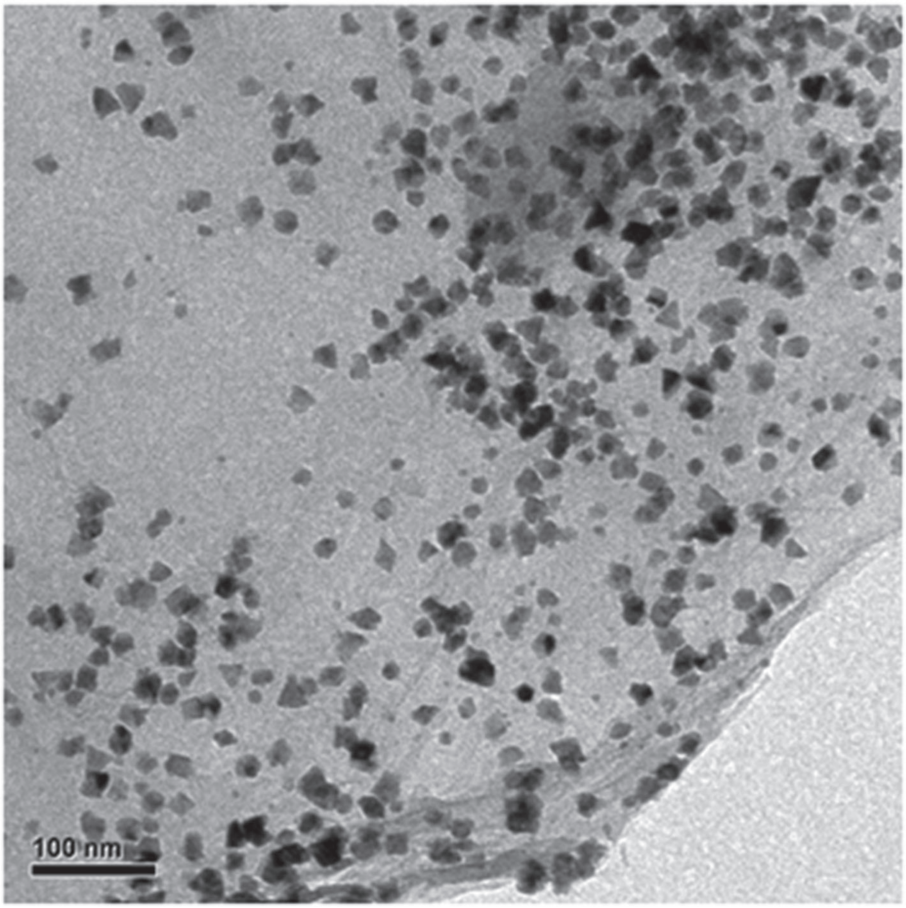


FIGURE 1 Transmission electron microscopy image of palladium nanoparticles (Pd NPs)/reduced graphene oxide (RGO)-*Rosa canina*

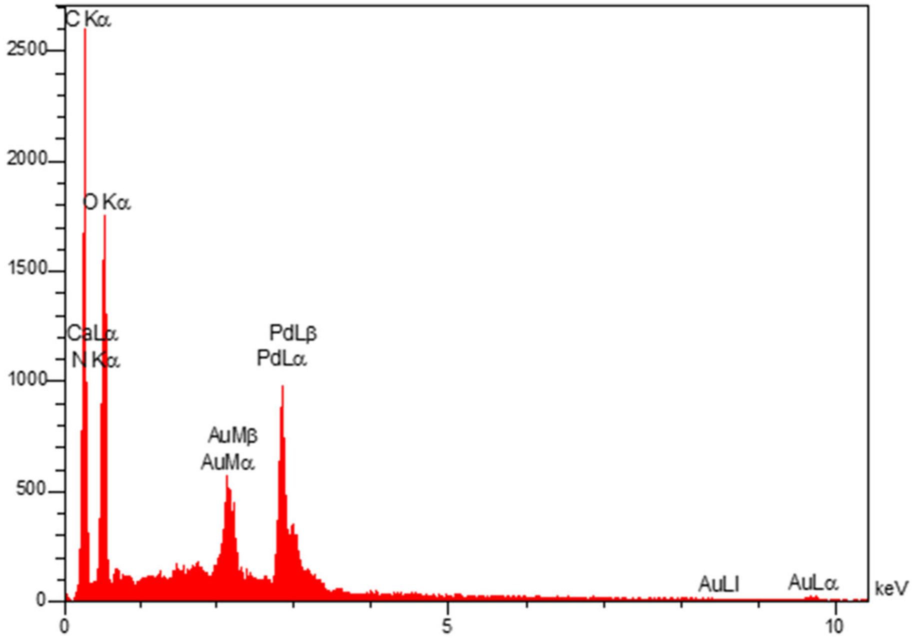


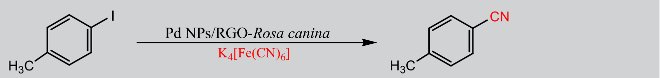
FIGURE 2 Energy-dispersive X-ray (EDX) spectrum of palladium nanoparticles (Pd NPs)/reduced graphene oxide (RGO)-*Rosa canina*

Furthermore, the presence of extract's biomolecules on the surface of graphene and Pd NPs was proved using EDX, which confirmed the existence of C, N, O and Pd, as shown in Figure 2.

After characterizing prepared Pd NPs/RGO-*Rosa canina*, its catalytic performance was evaluated on cyanation of aryl halides (Scheme 1). $K_4[Fe\ (CN)_6]$ was selected as the cyanide resource in aryl halide cyanation because it is low toxic, readily available and cost-effective. The cyanation of 4-iodotoluene was selected as the model reaction to optimize the reaction conditions. The effect of diverse reaction parameters, including solvent, base, temperature and amount of catalyst, were studied in detail (Table 1). The reaction did not proceed without using base and palladium resource (Table 1, entries 11 and 17). However, introduction of the catalyst to the reaction solution rapidly resulted in the product in high yields. In the case of solvent, DMF was found to be superior. Among the studied bases, Na_2CO_3 gave better outcomes over other bases. Moreover, the effect of catalyst loading was examined in the range of 0.4–0.7 mol% (Table 1, entries 9, 15 and 16). According to the outcomes, the highest performance can be obtained by 0.010 g (0.5 mol%) of the catalyst (Table 1, entry 9). Additionally, the optimum reaction temperature was obtained as 120°C (entry 9 vs. entries 12–14). Lower yield of the main product was studied at a reaction temperature of 25°C (Table 1, entry 14).

Table 2 demonstrates the results of investigating the substrate scope in aryl halide cyanation reaction using Pd NPs/RGO-*Rosa canina* under optimal conditions (Table 1, entry 9) for different aryl halides with

TABLE 1 The optimization of reaction parameters for cyanation of 4-iodotoluene using $K_4[Fe\ (CN)_6]$ catalyzed by Pd NPs/RGO-*Rosa canina*[a]

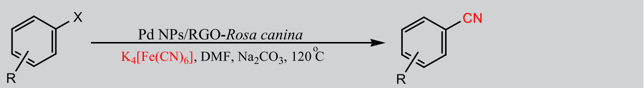


Entry	Pd (mol%)	Solvent	Base	T (°C)	Time (hr)	Yield (%)[b]
1	0.5	DMF	K_2CO_3	120	8	82
2	0.5	Toluene	K_2CO_3	120	12	40
3	0.5	EtOH	K_2CO_3	120	12	25
4	0.5	H_2O	K_2CO_3	120	24	25
5	0.5	CH_3CN	K_2CO_3	120	12	75
6	0.5	Xylene	K_2CO_3	120	12	50
7	0.5	DMF	NaOAc	120	12	45
8	0.5	DMF	Et_3N	120	12	25
9	0.5	DMF	Na_2CO_3	120	5	96
10	0.5	DMF	NaOH	120	24	30
11	0.5	DMF	No base	120	24	0
12	0.5	DMF	Na_2CO_3	100	12	75
13	0.5	DMF	Na_2CO_3	80	12	60
14	0.5	DMF	Na_2CO_3	25	24	20
15	0.4	DMF	Na_2CO_3	120	12	75
16	0.7	DMF	Na_2CO_3	120	5	96
17	0.0	DMF	Na_2CO_3	120	24	0

[a] Reaction conditions: 4-iodotoluene (1.0 mmol), $K_4[Fe\ (CN)_6]$ (0.17 mmol), catalyst, base (1.5 mmol) and solvent (5 ml).

[b] Isolated yield.

TABLE 2 Pd NPs/RGO-*Rosa canina*-catalyzed cyanation of aryl halides using $K_4[Fe(CN)_6]$[a]



Entry	Aryl halide	Time (hr)	Yield (%)[b]	Ref[c]
1	C_6H_5I	2	96	[41]
2	C_6H_5Br	4	90	[41]
3	C_6H_5Cl	7	60	[41]
4	*p*-NCC_6H_4I	5	95	[16]
5	*p*-NCC_6H_4Br	8	90	[16]
6	*p*-NCC_6H_4Cl	10	50	[16]
7	*p*-$CH_3C_6H_4I$	5	96	[14]
8	*p*-$CH_3C_6H_4Br$	6	85	[14]
9	*p*-$CH_3OC_6H_4I$	4	90	[14]
10	*p*-$CH_3OC_6H_4Br$	6	90	[14]
11	*p*-$NO_2C_6H_4I$	5	96	[16]
12	*p*- $NO_2C_6H_4Br$	6	95	[16]
13	*o*-$CH_3OC_6H_4I$	8	90	[42]
14	*o*-$CH_3OC_6H_4Br$	12	85	[42]

[a] Reaction conditions: arylhalide (1.0 mmol), $K_4[Fe(CN)_6]$ (0.2 mmol), Na_2CO_3 (1.5 mmol), Pd NPs/RGO (0.5 mol%) were stirred in DMF (5.0 ml) at 120°C.

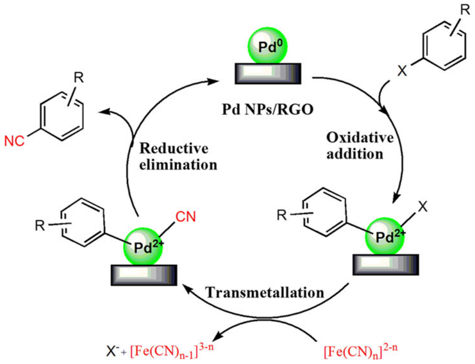
[b] Isolated yield.

[c] Earlier reference of the corresponding product.

electron-withdrawing and electron-donating groups. Aryl halides with both electron-withdrawing and electron-donating groups have good tolerance and result in good to high yields by adjusting the reaction time. Both aryl iodides and aryl bromides underwent the cyanation reaction acceptably and their yields were comparatively similar. However, converting aryl chlorides to cyanated products was less compared with their iodide and bromide counterparts.

Recyclability is a key parameter to judge the adaptability and importance of the catalyst. Thus, recyclability of Pd NPs/RGO-*Rosa canina* catalyst was studied over the cyanation of 4-iodotoluene with $K_4[Fe(CN)_6]$. At the end of each cycle, the catalyst can be successfully retained from the reaction solution through centrifugation, and is rinsed with ethanol and water and dried. The retained catalyst can be reused up to seven times with no decrease in its performance (Figure 3).

Leaching of palladium ions is a major issue for supported palladium catalysts, and avoids separating and recovering catalyst. Consequently, leaching investigation was accomplished from separating the Pd NPs/RGO-*Rosa canina* catalyst following 30 min of reaction time for the model reaction, and the similar reaction was also performed for more than 3 hr and the separation yield obtained was about 55%. This proves that leaching of palladium from the Pd NPs/RGO-*Rosa canina* catalyst was not taking place,



SCHEME 2 Proposed mechanism for palladium nanoparticles (Pd NPs)/reduced graphene oxide (RGO)-*Rosa canina*-catalyzed cyanation of aryl halides

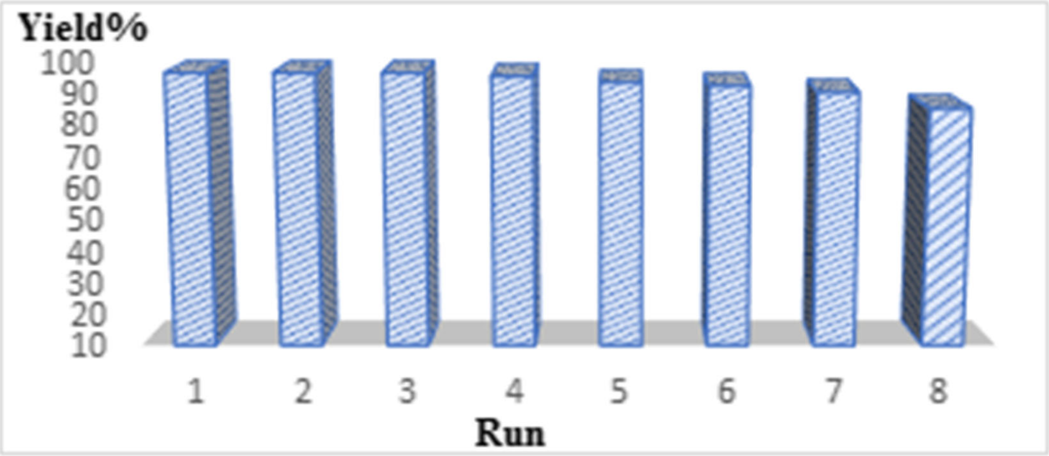


FIGURE 3 The recycling of the palladium nanoparticles (Pd NPs)/reduced graphene oxide (RGO)-*Rosa canina*

TABLE 3 Comparison efficiency of Pd NPs/RGO-*Rosa canina* with some reported catalysts for the cyanation of 4-bromonitrobenzene using $K_4[Fe\ (CN)]_6$ as cyanide source

Entry	Reaction conditions	Time (hr)	Yield%	Ref.
1	$Pd@CC_1{}^r/Pd@CC_2{}^r$, DMF, 140°C	15	99	[44]
2	Pd-Zeolite, DMF, 130°C	10	90	[45]
3	$PdNCs/C@Fe_3O_4$, DMF, 120°C	18	96	[46]
4[a]	Pd/C, PEG4000-H_2O, 140°C	2	75	[21]
5[a]	Palladacycle-1, DMF, 130°C	7	92	[47]
6	Pd/PPy, NMP, 120°C	8	87	[48]
7	Pd NPs/RGO-*Rosa canina*, DMF, 120°C	6	95	This work

[a]Under microwave irradiation.

perhaps owing to the particular nature of the prepared Pd NPs/RGO-*Rosa canina* catalyst.

A likely mechanism for the Pd NPs/RGO-*Rosa canina*-catalyzed cyanation reaction is a well-known mechanism relating to cyanation of aryl halides, which occurs on the catalyst surface (Scheme 2).[14,43] The reaction progressed by the oxidative addition of aryl halide over catalyst and continued via moving cyanide anion from $K_4[Fe\ (CN)]_6$, and finally the reductive removal phase resulted in the aryl cyanide product.

In order to prove the application of Pd NPs/RGO-*Rosa canina* catalyst in cyanation of 4-bromonitrobenzene using $K_4[Fe\ (CN)]_6$ as cyanide source, this catalyst was compared with several other proposed palladium catalysts (Table 3). As presented in Table 3, our catalyst system is comparable with the proposed homogeneous and heterogeneous catalysts in terms of efficiency.

4 | CONCLUSION

In conclusion, Pd NPs/RGO-*Rosa canina* can be applied as an effective and recyclable heterogeneous nanocatalyst for cyanating aryl halides with $K_4[Fe\ (CN)_6]$ as the cyanation agent. The nitriles were produced in good to high yield, and the catalyst can be recovered and reused for up to seven cycles without considerably changing its catalytic behavior.

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