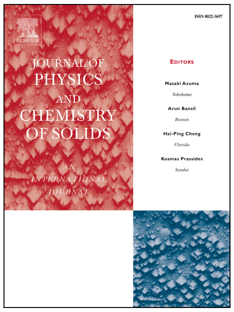

Green tea extract–modified silica gel decorated with palladium nanoparticles as a heterogeneous and recyclable nanocatalyst for Buchwald-Hartwig C–N cross-coupling reactions

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Graphical Abstract

Decorated palladium nanoparticles over *green tea* extract-modified silica gel as a heterogeneous and recyclable nanocatalyst for Buchwald-Hartwig C–N cross coupling reactions

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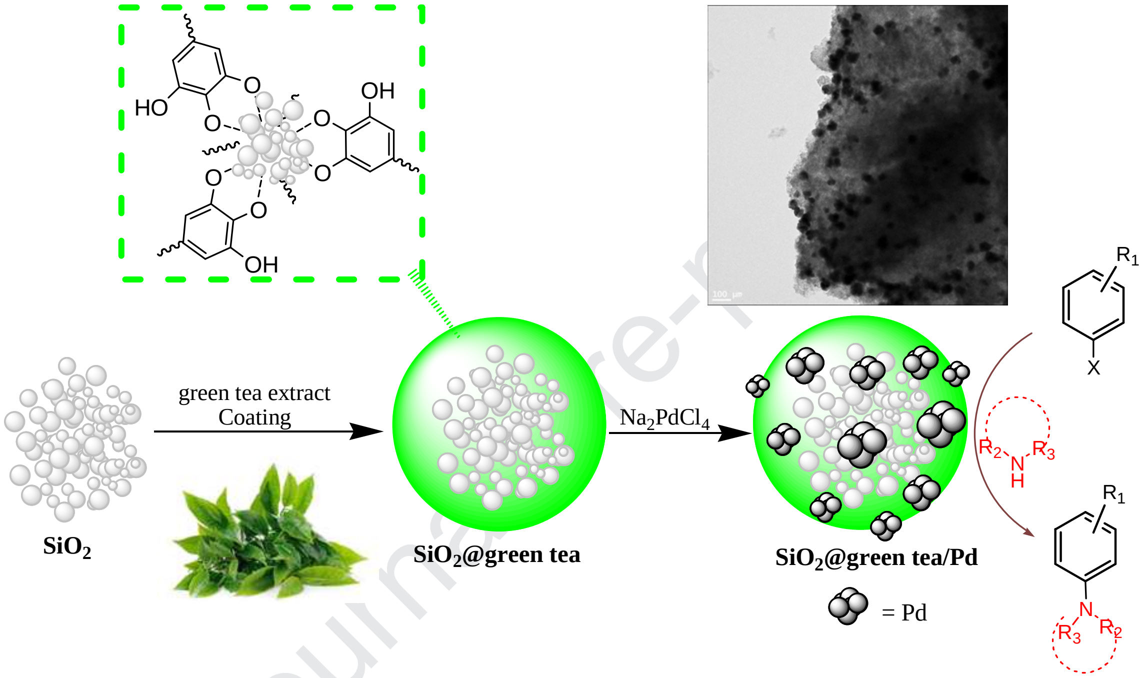

Green tea extract–modified silica gel decorated with palladium nanoparticles as a heterogeneous and recyclable nanocatalyst for Buchwald-Hartwig C–N cross-coupling reactions

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Abstract. A novel green tea extract–encapsulated silica gel decorated with in situ–generated Pd nanoparticles is reported as an efficient, green heterogeneous catalyst in the Buchwald-Hartwig C–N cross-coupling reaction. It was characterized by several analytical techniques. Thereafter, a wide range of aryl amines were synthesized in good to excellent yields by reaction of different substituted aryl halides and secondary amines over the catalyst. The material is sufficiently stable and could be used at least six times in a model Buchwald-Hartwig reaction without noticeable change in its catalytic activity. Heterogeneity of the catalyst was examined by a hot filtration test.

Keywords: Pd nanoparticles, Green tea extract, Heterogeneous nanocomposite, Buchwald-Hartwig reaction, C–N coupling

1. Introduction

Aromatic amines are ubiquitous in natural products and synthetic functional materials such as drugs and pharmaceuticals, agrochemicals, dyes, flavors, and perfumes [1, 2]. Consequently, the development of synthetic protocols for C–N bonds has achieved enormous importance in both industry and academia. The Buchwald-Hartwig reaction represents a transition metal–promoted versatile catalytic method for the formation of C–N bonds to obtained substituted aryl amines [3–5]. In the beginning, for these syntheses, aryl halides and organotin amides and amines were used as reactants for the cross-coupling in the presence of palladium-based catalysts [6–8]. Later, various research groups introduced aryl triflates, sulfamates, tosylates, esters, ethers, and carbamates as a substitute for aryl halides as the electrophilic counterpart [9–13]. Thereafter, the protocol was developed exceptionally by catalytic means in view of the broad range of accessible substrates. There are several reports of this reaction over Pd-complexed homogeneous catalysts [14–20]. However, the complexing ligands, such as phosphine and amine derivatives, are expensive and they make the catalysts moisture sensitive. Therefore, alternative means of heterogenization are necessary.

Heterogeneous catalysts has achieved precedence over homogeneous catalysts because of their easy handling, effortless isolation, and reusability [21, 22]. To increase the efficiency and stability of homogeneous catalysts, several approaches have been proposed following immobilization on different heterogeneous supports [23–25]. A number of Pd/heterogeneous supported catalysts have been reported for the Buchwald-Hartwig reaction by several research groups [26–29]. The catalytic protocol for the reaction was further developed when Pd nanoparticles were introduced. There are a few reports in literature on Pd nanoparticle catalysis in the Buchwald-Hartwig reaction [30–35]. Notably, different methods, such as chemical and electrochemical reduction, ion exchange, vapor deposition, thermal decomposition, and a polyol process, have been used in the synthesis of Pd nanoparticles. For stabilization, they usually require a capping agent.

In the modern trend for green chemistry, a bio-inspired method for metal nanoparticle synthesis is a landmark. The soft and mild biogenic synthesis, eco-friendliness of the procedure, use of water as a green solvent, absence of toxic chemicals, simple workup, and cost-effectiveness have attached attention in these approaches involving biomolecular surface functionalization [36, 37]. Furthermore, these unique strategies do not require high pressure, energy, and temperature [38]. However, despite having remarkable features and the advantages of biological plant extract–mediated green synthesis of nanoparticles, their applications are still very limited. This prompted us to use green tea extract, a biomolecule-rich floral medium that itself is a good reducing agent to reduce metal salts to produce nanoparticles and a stabilizer too. However, because of the nanometer size of the as-synthesized nanoparticles, isolation following standard procedures is difficult and therefore immobilization on silica gel, a heterogeneous support, was used, which favors their dispersion and stabilization [39, 40].

Green tea extract contains many phenolic group [41] and carbonyl [42] moieties, which in turn can be used in the surface modification of SiO_2 (Scheme 1). The feasibility of complexation of these organic oxo functionalities with polyvalent cations in aqueous solution improves the surface properties of the green tea extract–coated silica gel (SiO_2@green tea extract). Moreover, the nanobiocomposite (SiO_2@green tea) has the potential to act as both a reducing agent and a stabilizing agent for the in situ generation and immobilization of Pd nanoparticles.

Finally, in this manner, we demonstrate a procedure herein for the preparation of a nanocomposite of Pd nanoparticles stabilized and supported by green tea extract–coated silica gel (Scheme 1). The catalyst was used in the efficient synthesis of arylamines by C–N heterocoupling between aryl halides and different amines in the presence of Cs_2CO_3 as a base in dimethylformamide (DMF) following the Buchwald-Hartwig protocol (Scheme 1). The novel bio-inspired procedure, high surface area material, cheap and stable reagents, high yields and easy long-term reusability of catalyst are the key features of our protocol.

2. Experimental

2.1. Preparation of green tea extract

Leaves of *green tea* were collected in the hills of north Iran. The fresh *green tea* leaves were washed thoroughly three times with double-distilled water before use. Ten grams of the leaves was added to 100 mL of deionized water, and the mixture was boiled for 15 min in a water bath. The mixture was then cooled and filtered through Whatman filter paper no. 1 to obtain a clear aqueous extract. It was stored in refrigerator at 4 °C for further use.

2.2. Preparation of the SiO_2@green tea nanocomposite

Silica gel (230–400 mesh, 500 mg) was dispersed in 50 mL water and sonicated for 20 min. The green tea extract was then added to the mixture, and the resulting mixture was stirred for 24 h at room temperature. The precipitate so obtained was separated by centrifugation and washed several times with deionized water. Finally, it was dried in a vacuum oven at 40 °C for 12 h to produce the SiO_2@green tea nanocomposite.

2.3. Preparation of SiO_2@green tea/Pd

SiO_2@green tea (500 mg) was dispersed in deionized water (200 mL) in an ultrasonic bath for 30 min. Subsequently, a solution of Na_2PdCl_4 (50 mg) in 20 mL H_2O was added to the dispersion, and the mixture was stirred for 6 h at 100 °C to ensure complete reduction of Pd(II) ions in the precursor solution. The SiO_2@green tea/Pd nanocomposite was separated by centrifugation and washed with H_2O followed by acetone to remove the attached organic substrates. The final nanocomposite was dried in a vacuum at 40 °C.

2.4. General procedure for the Buchwald-Hartwig C–N cross-coupling reaction using the SiO_2@green tea/Pd nanocatalyst

A solution containing aryl halide (1.0 mmol), amine (1.1 mmol), and Cs_2CO_3 (2.0 mmol) in the presence of the SiO_2@green tea/Pd catalyst (0.020 g, 0.5 mol%) in 5 mL DMF was agitated for 12 h at 100 °C under a N_2 atmosphere. After completion of the reaction (checked by thin-layer chromatography), the catalyst was separated by simple filtration. To the filtrate, 10 mL water was added, followed by 10 mL ethyl acetate to extract organic compounds. Concentration of the organic layers and chromatographic purification afforded the products. All the products were known and confirmed by comparison with authentic samples.

3. Results and discussion

3.1. Catalyst characterization

As continuation of our studies on the synthesis, development, and application of functionalized nanomaterials [43], we report green tea extract–encapsulated silica gel supported with Pd(0) nanoparticles for use in the Buchwald-Hartwig reaction between aryl halides and secondary amines. After successful preparation of the nanocomposite material, it was well characterized by sophisticated analytical techniques, such as scanning electron microscopy (SEM), transmission electron microscopy, energy-dispersive X-ray spectroscopy, powder X-ray diffraction, X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Structural identity of the material was ascertained from the SEM image, as shown in Fig 1. It depicts a porous flake-like morphology. The surface of the flakes is somewhat homogeneous. It seems the material is partially agglomerated. However, the presence of Pd nanoparticles was not detected from the SEM image.

Transmission electron microscopy images are shown in Fig. 2. The green tea–fabricated silica gel moiety assumes a cotton-like morphology (Fig. 2a). Pd(0) nanoparticles decorating the matrix are evident from the image. The black dots signifying Pd(0) nanoparticles are well dispersed over the whole surface. A closer look at the Pd(0) nanoparticles (Fig. 2b) reveals their size is around 18–20 nm. The lattice planes inside the nanoparticles are clearly visible, which indicates high crystallinity. The elemental identity of the SiO_2@green tea/Pd nanocomposite was obtained from the energy-dispersive X-ray spectroscopy pattern (Fig. 3). The evolved peaks represent the Si, C, N, O, and Pd atoms. The presence of C, N, and O atoms confirmed the substituted polyphenolic attachment from green tea extract to the SiO_2 surface. The exact Pd content in the catalyst was found to be 0.25 mmol/g as determined from ICP-AES analysis.

The crystalline texture of the nanocomposite material was confirmed by an X-ray diffraction study (Fig. 4). There was no phase separation in the X-ray diffraction pattern, which indicates the formation of a firm nanocomposite. The broad peak at $2\theta = 24°$ is due to the amorphous state of typical silica. Two significant sharp reflection peaks, at $2\theta = 40°$ (111) and $2\theta = 47°$ (200), are attributed to crystalline Pd(0) nanoparticles.

XPS was used to determine the chemical composition and chemical valence states of the components present on the surface of the nanocomposite (Fig. 5). The XPS survey spectrum of the SiO_2@green tea/Pd nanocomposite confirmed the presence of elemental Pd, Si, O, N, and C. The binding energy peaks observed at 335.8 and 341.2 eV are attributed to metallic Pd(0) and relate to the $3d_{5/2}$ and $3d_{3/2}$ states of Pd. This demonstrated that Pd was present in the metallic Pd(0) state, confirming the successful reduction of Pd(II).

3.2. Evaluation of catalytic activity

After the synthesis and meticulous characterization of the catalyst, its catalytic performance was investigated in classic Buchwald-Hartwig C–N coupling reactions. A very straightforward protocol was followed in the reaction. A mixture of substituted haloarenes, a base, and secondary amines was heated in a specified solvent over the catalyst. The progress of the reaction was checked by thin-layer chromatography, and after completion, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was concentrated and purified with use of a silica gel column. To determine the optimum conditions, the reaction between bromobenzene and morpholine was chosen as a model reaction in the presence of the

SiO_2@green tea/Pd catalyst. The effects of different factors, such as the solvent, base used, catalyst load, and temperature, on the outcome of the reaction were examined. The results are documented in Table 1. No product was found in the absence of the catalyst. There was only a trace of product in the absence of a base. The reaction was then screened for a range of solvents, such as toluene, EtOH, DMF, and H_2O in K_2CO_3 base, with use of 0.5 mol% Pd–loaded catalyst, and DMF gave the best result. With DMF as the best solvent, we varied the nature of the base. Among different bases, Cs_2CO_3 was the most productive for reaction at 100 °C. On increase of the temperature, no further increase in yield was observed. When the temperature and catalyst load were lowered, the yield decreased proportionally. Therefore, the reaction responded best in DMF at 100 °C with Cs_2CO_3 as a base in the presence of 0.5 mol% Pd–loaded catalyst.

After optimization of the reaction conditions, we studied substrate variants. A wide range of arylamine derivatives were prepared by the coupling of substituted aryl halides and secondary amines under stabilized conditions. Different substituent, such as CH_3, OCH_3, and CN, on bromoarenes and iodoarenes were very compatible with the procedure, indicating there was not any marked difference in the electron-withdrawing or electron-donating effects of the substituents. However, the chloroarenes were found to be less reactive than their bromo or iodo analogs, which was evident from their yields. The results are documented in Table 2. The isolated purified products were authenticated by comparison with standard samples.

3.3. Test of reusability and heterogeneity

In view of the green chemical implications of the protocol, a test of reusability of the catalyst is of utmost importance. The reaction of bromobenzene and morpholine was chosen as a model reaction with a larger batch size (2.0 mmol). After reaction the catalyst was separated by centrifugation, washed with ethanol, dried, and reused in the next run. It was used six successive times without any noticeable change in catalytic activity. The output is shown in Fig. 6. The ICP-AES analysis of the catalyst after the sixth run further confirmed that the Pd load of the catalyst (0.23 mmol/g) did not change considerably as there was no leaching of Pd, indicating its robustness.

To determine the heterogeneity of the catalyst, a hot filtration test was conducted for the same reaction under the optimized conditions. After a half time of the reaction, the catalyst was isolated from the reaction mixture by filtration and the reaction was allowed to continue. There was no further increase in the yield, verifying the heterogeneity of the catalyst.

4. Conclusion

In summary, a SiO_2@green tea/Pd composite nanomaterial was successfully prepared by in situ biogenetic reduction of metal salts immobilized on green tea extract–coated silica gel. Green tea extract functions as a natural reductant as well as a stabilizer of Pd(0) nanoparticles. The catalytic application of the material was investigated in Buchwald–Hartwig C–N coupling reactions by our reacting substituted aryl halides with different secondary amines. The green protocol is attractive in terms of its simplicity, cost-effectiveness, convenient operation, easy purification of products, reusability of the catalyst, and excellent yields.

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Conflict of interest

The authors report no conflicts of interest in this work.

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Scheme 1. Green synthesis of the SiO_2@green tea/Pd nanocomposite and its catalytic application for Buchwald-Hartwig C–N coupling.

Fig. 1. Scanning electron microscopy image of the SiO_2@green tea/Pd nanocomposite.

Fig. 2. Transmission electron microscopy images of the SiO_2@green tea/Pd nanocomposite at different magnifications.

Fig. 3. Energy-dispersive X-ray spectroscopy pattern of the SiO_2@green tea/Pd nanocomposite.

Fig. 4. X-ray diffraction pattern of the SiO_2@green tea/Pd nanocomposite.

Fig. 5. X-ray photoelectron spectroscopy spectrum related to the elemental survey scan of the SiO_2@green tea/Pd nanocomposite and peaks in the Pd 3d region (inset).

Fig. 6. Recycling of the catalyst for the Buchwald-Hartwig reaction between bromobenzene and morpholine.

Table 1. Optimization of the reaction parameters for the Buchwald-Hartwig amination reaction between bromobenzene with morpholine over the SiO_2@green tea/Pd nanocomposite.

Pd (mol%)	Solvent	Base	*T* (°C)	Isolated yield (%)[b]
0.5	DMF	K_2CO_3	100	70
0.5	Toluene	K_2CO_3	100	30
0.5	EtOH	K_2CO_3	80	50
0.5	H_2O	K_2CO_3	100	30
0.5	DMF	NaOAc	100	65
0.5	DMF	Et_3N	100	65
0.5	DMF	Cs_2CO_3	100	95
0.5	DMF	NaOH	100	60
0.5	DMF	–	100	10
0.5	DMF	Cs_2CO_3	80	70
0.5	DMF	Cs_2CO_3	60	35
0.5	DMF	Cs_2CO_3	25	25
0.5	DMF	Cs_2CO_3	120	95
0.4	DMF	Cs_2CO_3	100	80
0.3	DMF	Cs_2CO_3	100	50
0.0	DMF	Cs_2CO_3	100	–

The reaction conditions were as follows: 1.0 mmol bromobenzene, 1.1 mmol morpholine, catalyst, 2 mmol base, and 3 mL solvent for 12 h.

DMF, dimethylformamide.

Table 2. N-arylation of aryl halides using the Buchwald-Hartwig reaction in the presence of the SiO_2@green tea/Pd nanocomposite.

Aryl halide	Amine	Isolated	Reference

		yield (%)	
C_6H_5I	Morpholine	96	[31]
C_6H_5Br	Morpholine	95	[31]
C_6H_5Cl	Morpholine	60	[31]
p-NCC_6H_4I	Morpholine	96	[30]
p-NCC_6H_4Br	Morpholine	90	[30]
p-NCC_6H_4Cl	Morpholine	60	[30]
p-$CH_3C_6H_4I$	Morpholine	96	[31]
p-$CH_3C_6H_4Br$	Morpholine	90	[31]
p-$CH_3OC_6H_4I$	Morpholine	90	[44]
p-$CH_3OC_6H_4Br$	Morpholine	85	[44]
C_6H_5I	Piperidine	96	[45]
C_6H_5Br	Piperidine	90	[45]
C_6H_5Cl	Piperidine	70	[45]
C_6H_5I	Imidazole	90	[46]
C_6H_5Br	Imidazole	80	[46]

The reaction conditions were as follows: 1.0 mmol aryl halide, 1.2 mmol amine, 0.5 mol% SiO_2@green tea/Pd catalyst, 2.0 mmol Cs_2CO_3, and 3.0 mL dimethylformamide at 100 °C for 12 h.

Table 3. Comparison of efficiency of SiO_2@green tea/Pd and some previously reported catalysts for the Buchwald□Hartwig amination reaction of bromobenzene and morpholine.

Catalyst	Conditions	Time (h)	Yield (%)	Reference
Pd-PFMN	K_2CO_3, 120 °C	24	94	[35]
RD Pd NCs	1,4-Dioxane, *t*-BuOK, 100 °C	24	92	[44]
PNP-SSS	K_2CO_3, DMF, 120°°C	12	89	[30]
[Pd(pp3S4)(dba)]	2-Propanol, Cs_2CO_3, 80 °C	24	80	[47]

Pd(II) thiosemicarbazone complex	2-BuOH, K_2CO_3, 100 °C	24	89.2	[45]
PFG-Pd	*t*-BuONa, 110 °C	12	88	[48]
GO-Chit-Pd	*t*-BuOK, DMF,	12	90	[31]
SiO_2@green tea/Pd	Cs_2CO_3, DMF, 100 °C	12	95	This work

DMF, dimethylformamide.

PFMN, phosphine-functionalized magnetic nanoparticles.

RD Pd NCs, rhombic dodecahedra palladium nano clusters.

PNP-SSS, Pd nanoparticles on silica-starch substrate.

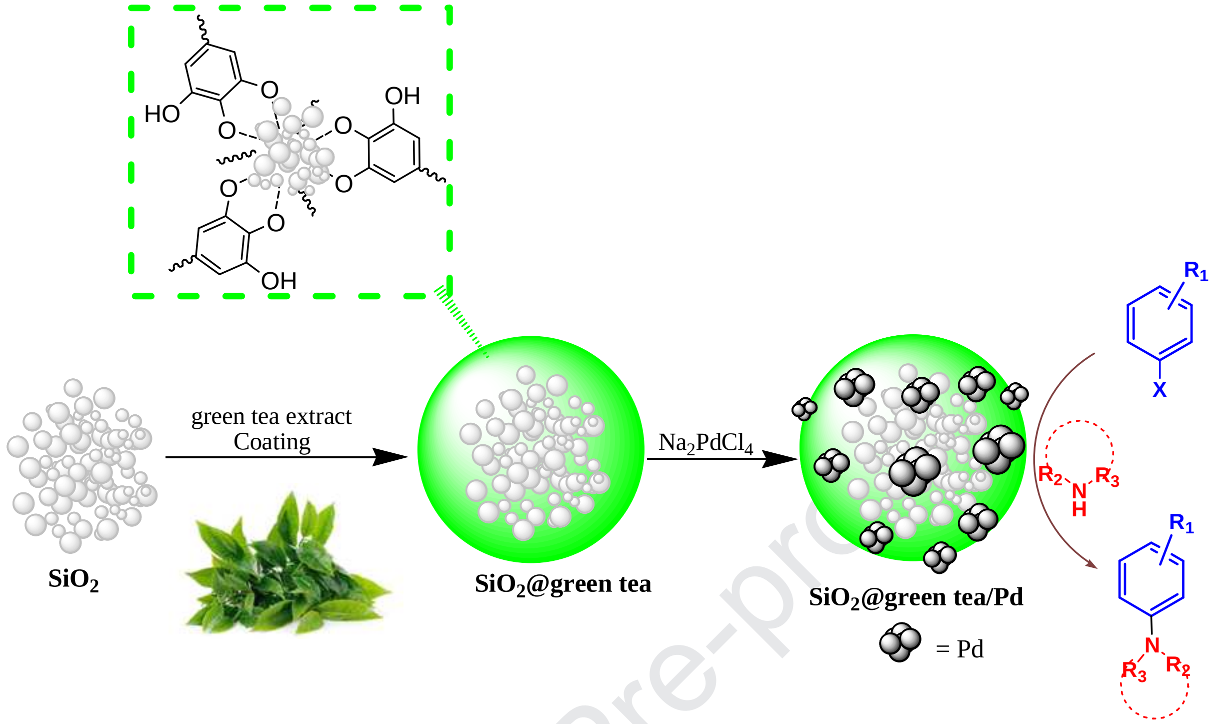
[Pd(pp3S4)(dba)], pp3S4is tris[2-(diphenylphosphino)ethyl]phosphine tetrasulfide and dba is dibenzylideneacetone.

PFG, phosphine-functionalized graphene.

GO-Chit, Graphene-Chitosan.

t-BuOK, Potassium tert-butoxide.

t-BuONa, Sodium t-Butoxide.



Scheme 1. Green metric synthesis SiO$_2$@*green tea*/Pd nanocomposite and its catalytic application for Buchwald-Hartwig C–N coupling.

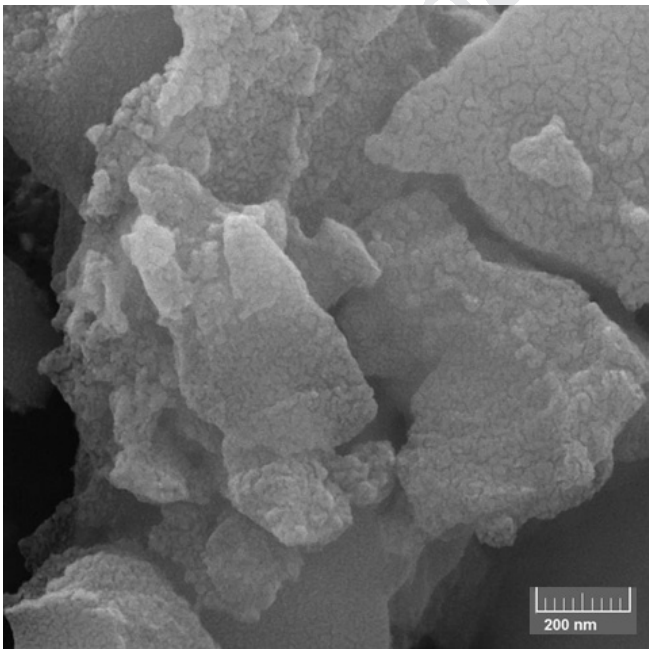


Fig. 1. SEM image of the SiO$_2$@*green tea*/Pd nanocomposite

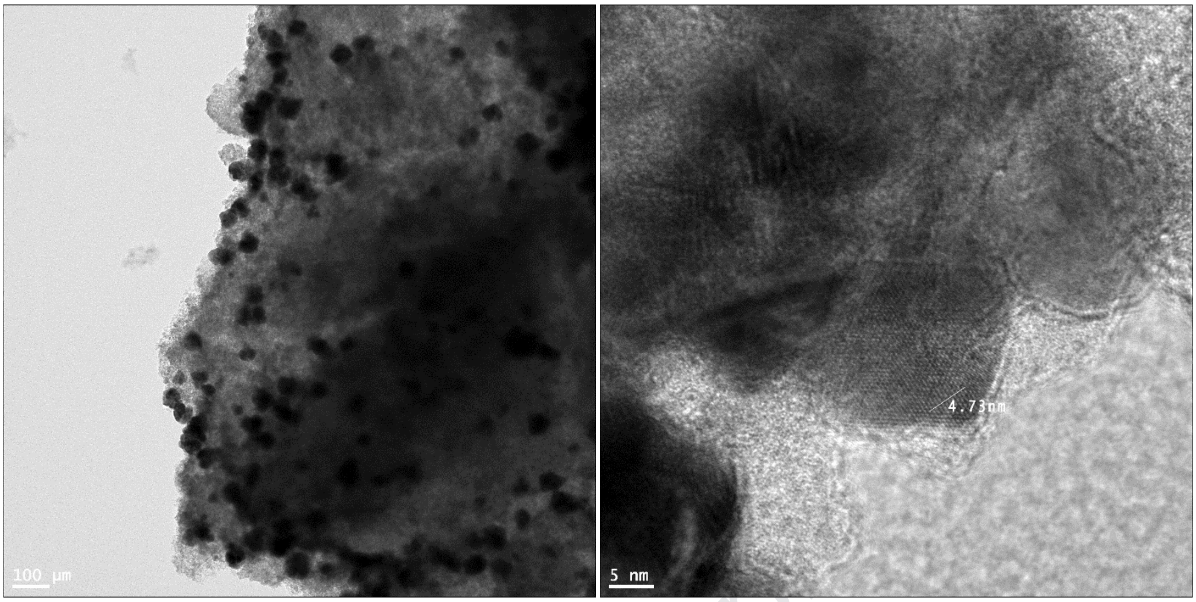


Fig. 2. a) TEM images of the SiO_2@*green tea*/Pd nanocomposite at different magnifications.

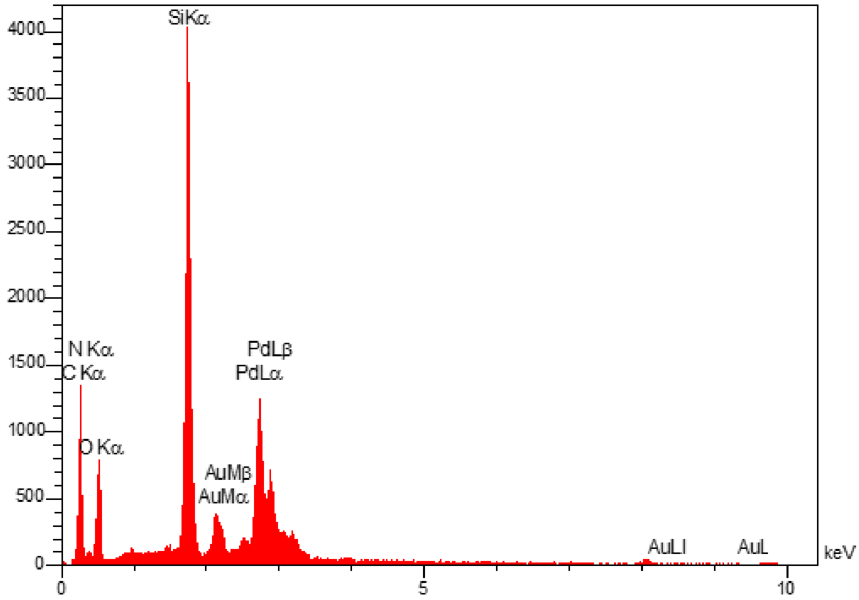


Fig. 3. EDX pattern of SiO_2@*green tea*/Pd nanocomposite.

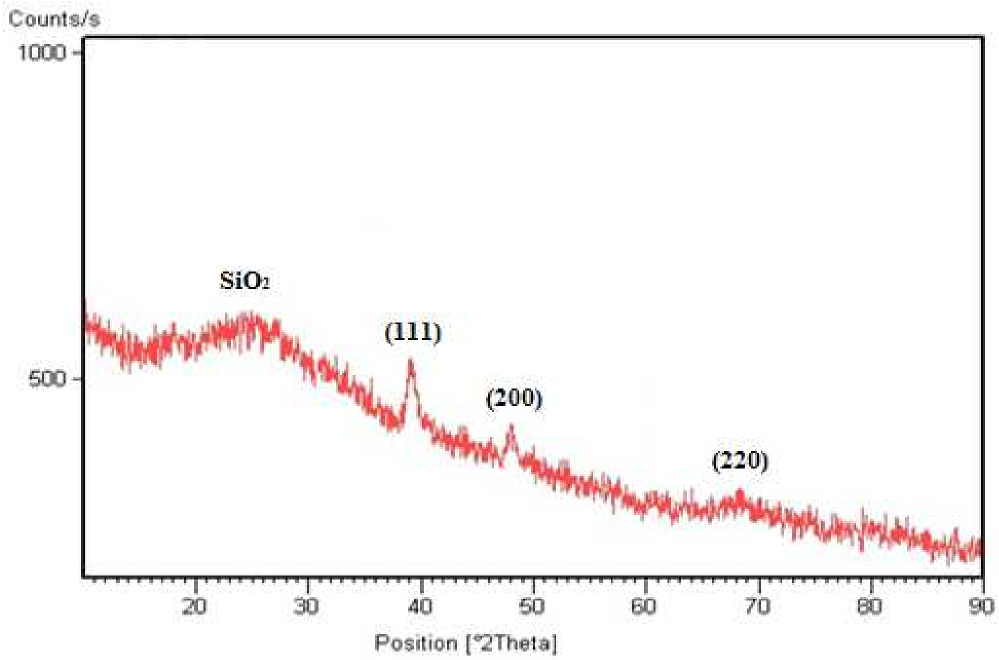


Fig. 4. X-ray diffraction study of the SiO_2@*green tea*/Pd nanocomposite

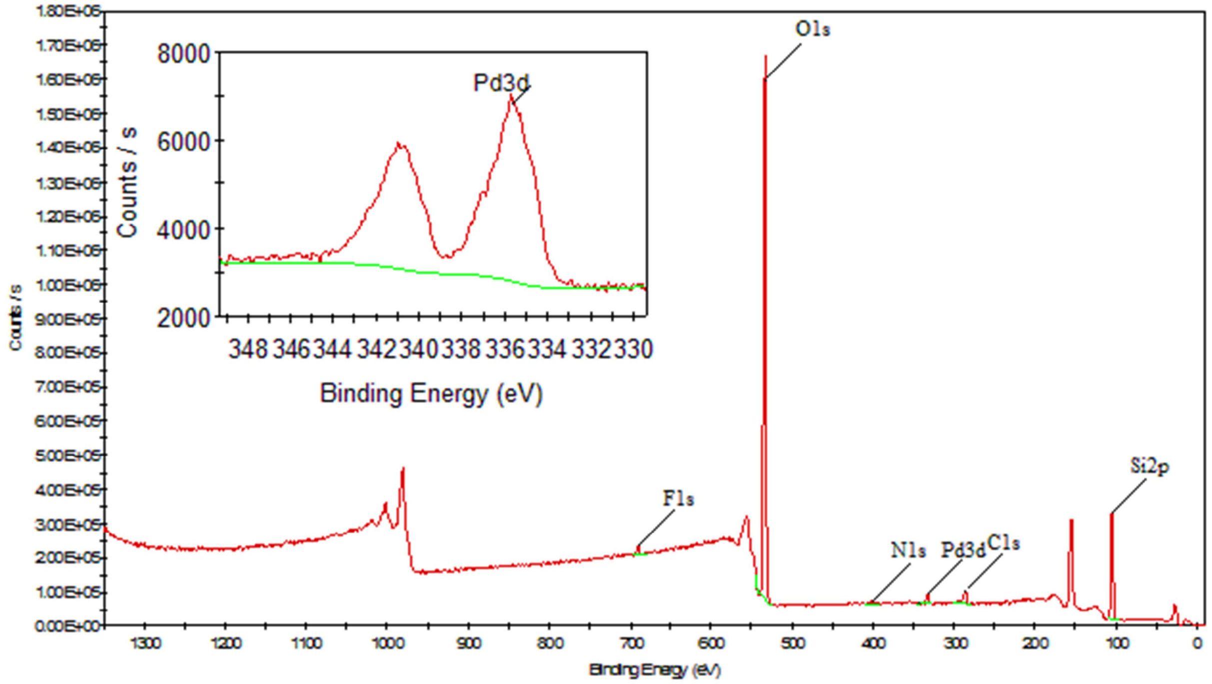


Fig. 5. XPS spectrum related to the elemental survey scan of SiO_2@*green tea*/Pd nanocomposite and peaks of the Pd 3d region (inset).

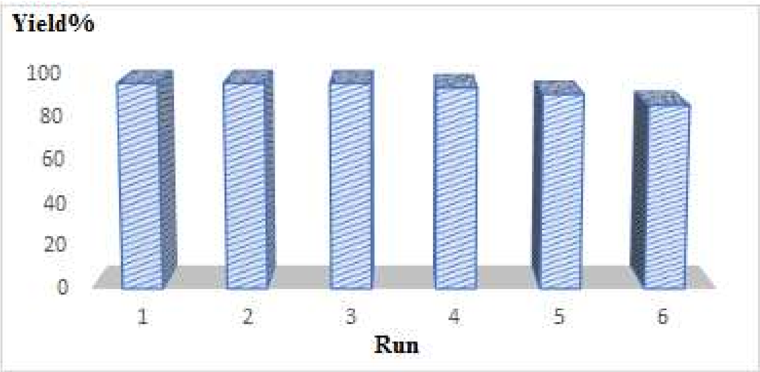


Fig.6. Recycling of catalyst for the B-H reaction between bromobenzene and morpholine.

Graphical Abstract

Decorated palladium nanoparticles over *green tea* extract-modified silica gel as a heterogeneous and recyclable nanocatalyst for Buchwald-Hartwig C–N cross coupling reactions

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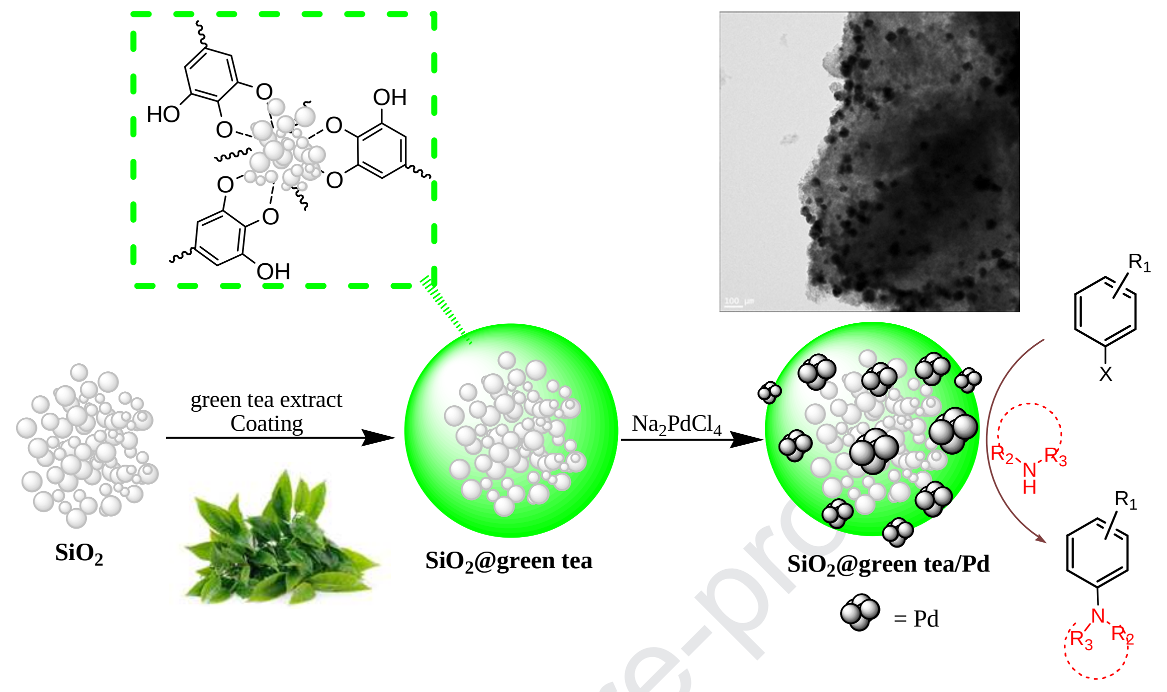
HO
O
O
O
O
OH
O
O
OH
SiO2
green tea extract
Coating
SiO2@green tea
Na2PdCl4
SiO2@green tea/Pd
= Pd
R1
X
R2
N
R3
H
R1
N
R3
R2

Highlights

- In situ–generated palladium nanoparticles anchored to green tea extract–coated silica gel
- Excellent performance as a reusable catalyst in Buchwald-Hartwig C–N cross-coupling reactions
- Excellent yield of the products
- Catalyst used up to six times

Conflict of Interest

The authors report no conflicts of interest in this work.