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Bio-inspired synthesis of palladium nanoparticles fabricated magnetic Fe₃O₄ nanocomposite over *Fritillaria imperialis* flower extract as an efficient recyclable catalyst for the reduction of nitroarenes

Hojat Veisi¹✉, Bikash Karmakar²✉, Taiebeh Tamoradi¹, Reza Tayebee³, Sami Sajjadifar¹, Shahram Lotfi¹, Behrooz Maleki³ & Saba Hemmati¹

This current research is based on a bio-inspired procedure for the synthesis of biomolecule functionalized hybrid magnetic nanocomposite with the Fe₃O₄ NPs at core and Pd NPs at outer shell. The central idea was the initial modification of magnetic NP by the phytochemicals from *Fritillaria imperialis* flower extract, which was further exploited in the green reduction of Pd²⁺ ions into Pd NPs, in situ. The flower extract also acted as a capping agent for the obtained Pd/Fe₃O₄ composite without the need of additional toxic reagents. The as-synthesized Fe₃O₄@*Fritillaria*/Pd nanocomposite was methodically characterized over different physicochemical measures like FT-IR, ICP-AES, FESEM, EDX, TEM, XPS and VSM analysis. Thereafter, its catalytic potential was evaluated in the reduction of various nitrobenzenes to arylamines applying hydrazine hydrate as reductant in ethanol/water (1:2) medium under mild conditions. Furthermore, the nanocatalyst was retrieved using a bar magnet and recycled several times without considerable leaching or loss of activity. This green, bio-inspired ligand-free protocol has remarkable advantages like environmental friendliness, high yields, easy workup and reusability of the catalyst.

The catalytic society in recent days has shown significant interest and applied extensive thrust on the development of engineered heterogeneous catalysts as compared to their homogeneous analog. Their easy handling and facile isolation from the reaction mixture has made them advantageous^{1–4}. Among them, the magnetite nanoparticles (MNPs) have acquired remarkable attention as catalyst support or as the core of nanohybrid composites to serve as a potential reusable green catalyst^{5–7}. The features like easy availability, abundance, small size thereby high surface area, excellent reactivity, high biocompatibility, good magnetic permeability, presence of plenteous hydroxyl groups for surface engineering and straightforward magnetic isolation has made them a fascinating material^{8–14}. However, due to high surface energy, they are highly prone to self-aggregation which reduces their catalytic activity significantly^{15–18}. This is somewhat minimized by surface functionalization. In recent years, the biogenic green approach for synthesis of NPs has come into prominence^{19–24}. Plants have been a ubiquitous and rich source in this regard. There are reports of using plant leaves, fruits, flowers, barks, and roots' extract as the cheap and abundant precursors of corresponding biomolecules for functionalization^{25–33}. Following the trend of our earlier report towards the bio-inspired synthesis of stable and active nanocomposite catalysts^{34–40}, we demonstrate herein the *Fritillaria imperialis* flower as bio-resource to fabricate Fe₃O₄ NP. The flower is grown widely in the plateau areas of Turkey, Iraq and Iran border and Himalaya foothills (Fig. 1). The

¹Department of Chemistry, Payame Noor University, Tehran, Iran. ²Department of Chemistry, Gobardanga Hindu College, North 24, Parganas, India. ³Department of Chemistry, Hakim Sabzevari University, 96179-76487 Sabzevar, Iran. ✉email: hojatveisi@yahoo.com; bikashkarm@gmail.com



Figure 1. *Fritillaria imperialis* flower image.

herb contains numerous phytochemicals including polyphenols, flavonoids, mild acids alkaloids and terpenoids. We further modified the biomolecule supported NPs by fabricating its exterior layer with tiny Pd NP as active catalytic phase. Finally, the catalytic application of the magnetic biogenic nanocomposite was demonstrated in the reduction of nitroarenes, a fundamental and significant chemical reaction in various organic transformations^{41,42}. Particularly, 4-nitrophenol is a detrimental organo-pollutant in water and dreadful for all living creatures^{43,44}. The reduced amines find wide applications in the synthesis of fine chemicals, agrochemicals, pharmaceuticals, dyes, polymers, pesticides, cosmetics and photography^{45–48}. In view of such consequences we designed our catalyst to carry out the reduction in a facile and green chemical pathway using hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) as a mild and effective reductant. The magnetic core helps in efficient and effortless recoverability of the catalyst from the reaction mixture. Our protocol has been so proficient that a wide variety of nitro compounds has been converted to resultant amines within quick interval in aqueous ethanol producing outstanding yields and TOF.

Experimental

Synthesis of magnetite NPs. Following a typical co-precipitation method, a mixture of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (2.0 g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5.2 g) were taken into deoxygenated water (25 mL) containing few drops of conc. HCl and subsequently, 250 mL of 1.5 M NaOH solution was added dropwise. The whole mixture was stirred vigorously at 60 °C. Immediately, brown colored Fe_3O_4 NPs were formed which were isolated using a magnetic stick. It was washed thrice with 200 mL deionized water and dried in air at 40 °C.

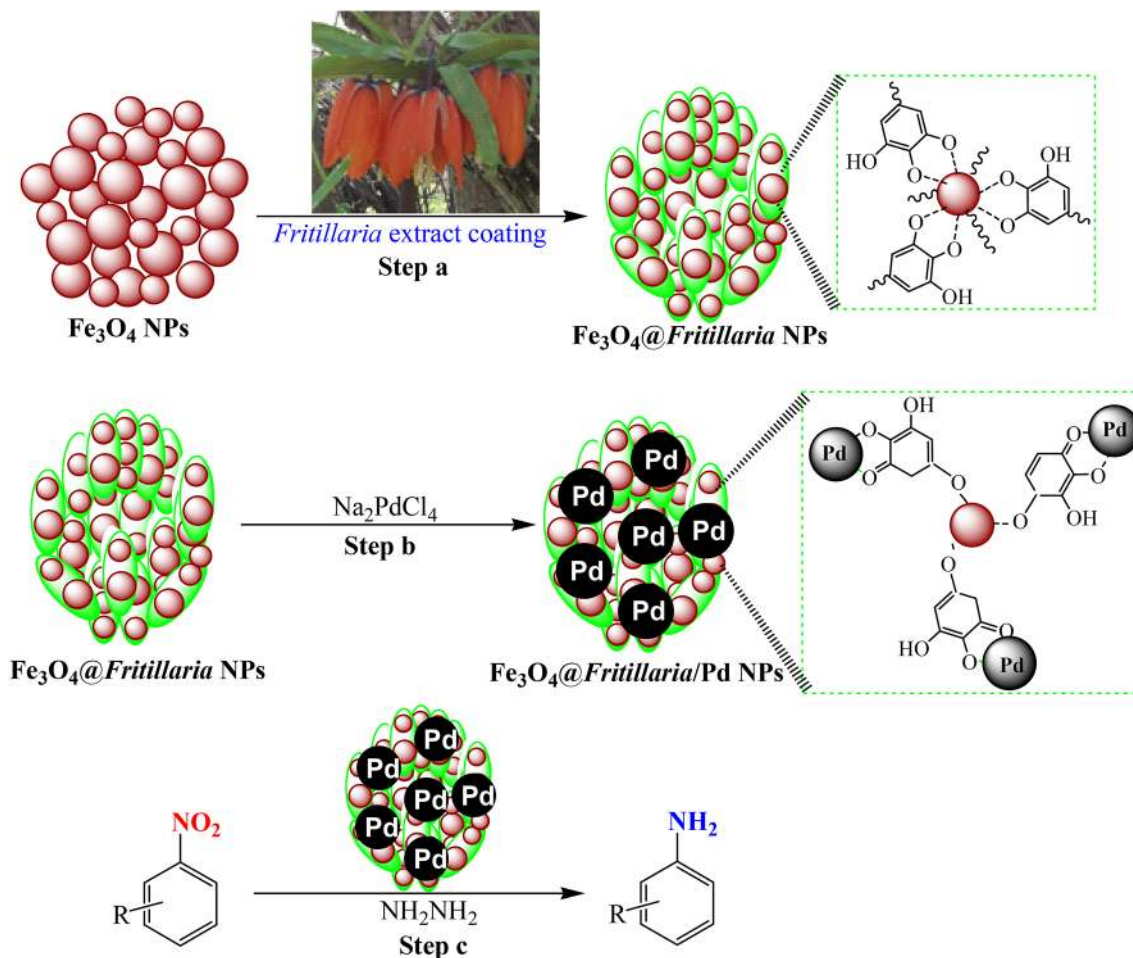
Preparations of Fe_3O_4 @*Fritillaria* using the plant extract. 0.5 gm *Fritillaria* flower powder was extracted into 50 mL of Milli-Q water by swirling at 50 °C for 20 min. It was filtered over Whatman 1 paper and the filtrate was centrifuged at 4000 rpm for 5 min to precipitate out the impurities. The clear upper layer was preserved for the next step. For the preparation of Fe_3O_4 @*Fritillaria* NPs, the magnetite NPs (0.5 g) were first dispersed in water by sonication for 20 min and the flower extract was added dropwise into it. The mixture was then stirred for 24 h at room temperature. Finally, the Fe_3O_4 @*Fritillaria* nanocomposite was collected magnetically, washed thoroughly over DI- H_2O and dried in vacuum at 40 °C overnight.

Preparation of the Fe_3O_4 @*Fritillaria*/Pd NPs. Five gram of the Fe_3O_4 @*Fritillaria* NPs was dispersed over deionized water (100 mL) in sonicator for 20 min. An aqueous solution of Na_2PdCl_4 (40 mg in 20 mL H_2O) was poured into dispersion and refluxed for 12 h to assure the complete reduction of Pd(II) ions. The Fe_3O_4 @*Fritillaria*/Pd nanocomposite was isolated as previous, rinsed with H_2O /acetone mixture to eliminate the adhered organic substances and dried likewise. The whole preparative schedule has been presented in Scheme 1. Pd content in the material was 0.08 mmol/g, analyzed by ICP-AES analysis.

Catalytic reduction of nitrobenzene. In a stirring solution of nitrobenzene (1 mmol) and Fe_3O_4 @*Fritillaria*/Pd nanocomposite (0.1 mol% Pd, 13 mg) in H_2O /EtOH (2:1, 3 mL), the reducing agent $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ (3 mmol) was slowly dropped and the mixture was refluxed at 80 °C. After completion (by TLC, n-hexane/EtOAc: 5/2), EtOAc was added to the reaction mixture and stirred well. After removing the catalyst over a magnet, the water in reaction filtrate was soaked over anhydrous Na_2SO_4 . Finally, the collected organic layer was concentrated to have pure aniline in 96% yield.

Results and discussion

Catalyst characterizations and data analysis. The current work illustrates an environmental friendly and green protocol involving *Fritillaria* flower extract to fabricate the ferrite MNPs surface and further to introduce stable Pd NPs. The biomolecules of *Fritillaria* flower has a significant tendency to accumulate over Fe_3O_4



Scheme 1. Schematic representation for the synthesis of catalyst and its application; step a: synthesis of $\text{Fe}_3\text{O}_4@Fritillaria$, step b: synthesis of $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$, step c: Reduction of nitroarenes over the catalyst.

MNPs. The polyphenolic compounds of the flower extract contain hydroxyl and ketonic groups that chelate Pd^{2+} ions and subsequently reduce them green metrically (Scheme 1). The structural and physicochemical characteristics of the nanomaterial was characterized using diverse analytical techniques like FT-IR, ICP-AES, FE-SEM, TEM, EDX, XPS and VSM studies.

Figure 2 depicts comparative FT-IR spectra of bare Fe_3O_4 NPs, *Fritillaria* extract, $\text{Fe}_3\text{O}_4@Fritillaria$ and $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$ nanocomposite in order to illustrate the stepwise synthesis. In the spectrum of Fe_3O_4 NP (Fig. 2a), two broad peaks at 1622 and 3419 cm^{-1} correspond to the physisorbed H_2O and the surface OH groups. The characteristic peaks appeared at 584 and 439 cm^{-1} are due to the stretching and bending vibrations of Fe–O bond. Pure Fe_3O_4 structure is characterized by a peak at 632 cm^{-1} . Figure 2b represents the spectrum of *Fritillaria* extract which displays the significant peaks at 3385 cm^{-1} due to O–H groups of polyols⁴⁹ and C–H stretching vibration from hydrocarbons and flavonoids at 2926 cm^{-1} ⁵⁰. Additionally, due to the presence of quinones, ketones, and carboxylic acids functions in the biomolecules contained in it, the distinctive peaks of C=O and O–C–O appears at 1709 cm^{-1} and 1072 cm^{-1} respectively⁵¹. An FT-IR band is observed in the range of 1400–1600 cm^{-1} owing to aromatic C=C stretching vibrations. The corresponding spectrum of $\text{Fe}_3\text{O}_4@Fritillaria$ NPs is depicted in Fig. 2c. It is literally a combination of Fig. 2a,b indicating the successful functionalization of *Fritillaria* molecules over the ferrite NPs. These biomolecules actually perform as excellent capping agent, preventing the NPs from agglomeration and oxidation⁵². It also acts as reducing and stabilizing agent for immobilizing Pd NPs on the ferrite surface. The FT-IR spectrum of $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$ NPs (Fig. 2d) is almost alike Fig. 2c except a small shift in C–O, C=C and O–H stretching frequencies. These shifts account for the attachment of Pd NPs on the surface modified MNPs.

The structural morphology, size and shape of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@Fritillaria$, and $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$ nanocomposite were investigated with the FE-SEM analysis as shown in Fig. 3. The materials are of nanometric size and of quasi-spherical shape (Fig. 3a). In addition, a continuous biopolymer layer is seen on the nanocomposite surface indicating the surface modification (Fig. 3b,c). The bright spots in Fig. 3c signifies the in situ synthesized Pd NPs being spread over the $\text{Fe}_3\text{O}_4@Fritillaria$ composite.

EDX analysis of the material was conducted in order to know the chemical composition. The spectrum obtained on recording of signals at random points of the catalyst surface showed the presence of Fe, Pd as

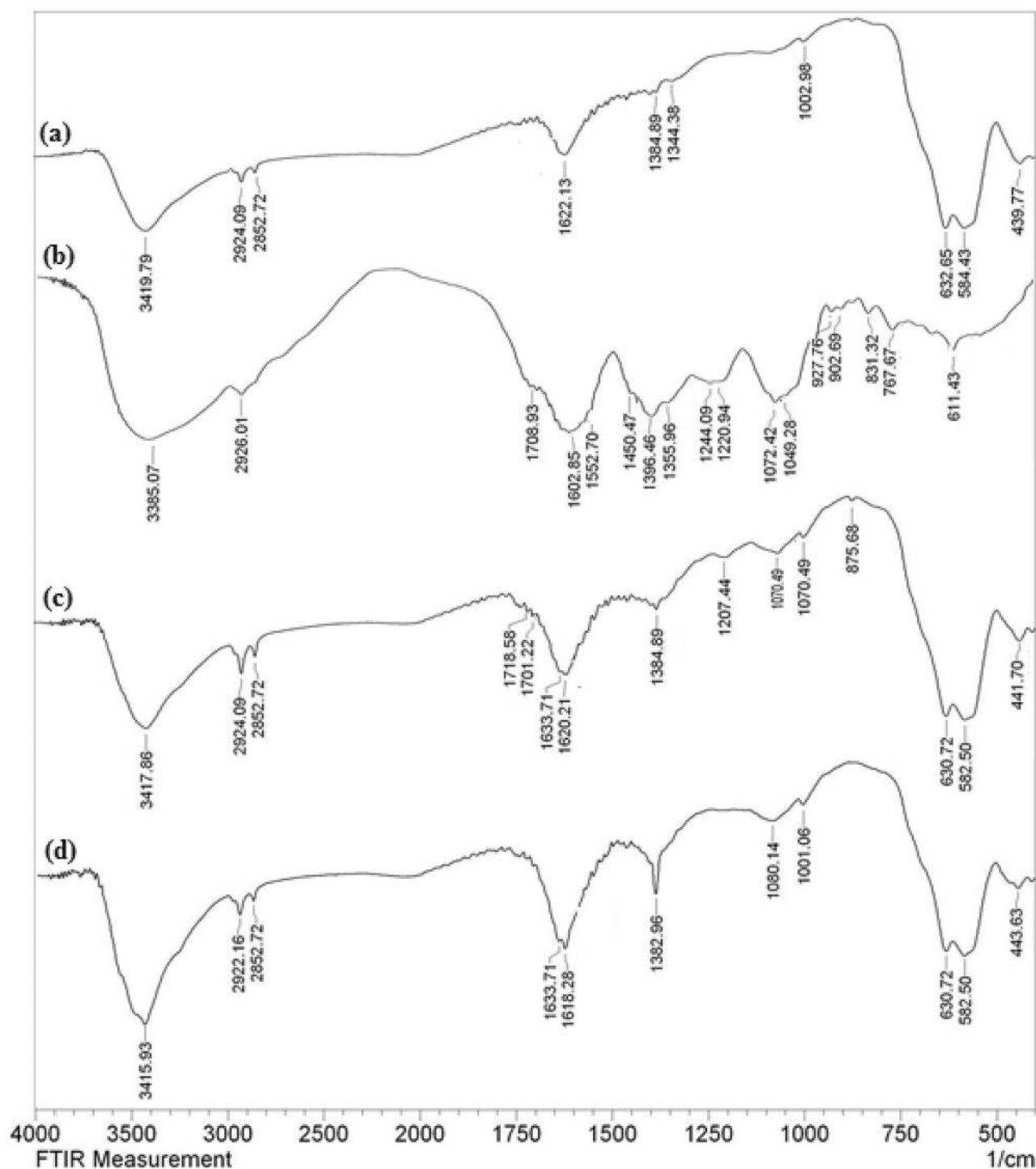


Figure 2. FT-IR spectrum of (a) Fe_3O_4 , (b) *Fritillaria* extract, (c) $\text{Fe}_3\text{O}_4@Fritillaria$ NPs, and (d) $\text{Fe}_3\text{O}_4@Fritillaria/Pd$ NPs.

metallic and C, O as non-metallic components. The non metals justify the attachment of phyto-compounds in the composite (Fig. 4).

In addition to the EDX analysis, elemental mapping of $\text{Fe}_3\text{O}_4@Fritillaria/Pd$ nanocomposite also carried out to have the knowledge of component distributions over the catalyst surface. X-ray scanning of a segment of the FE-SEM image reveals the homomorphic dispersion of all the components on the nanocomposite (Fig. 5). The uniform distribution of the active site definitely has a significant role behind its catalytic superiority.

The TEM image of the $\text{Fe}_3\text{O}_4@Fritillaria/Pd$ NPs exhibits that the Pd NPs are formed with almost globular morphology (Fig. 6). As can be seen in the image (Fig. 6a), the ferrite NPs are of 10–20 nm in dimension that are coated by thin layers of *Fritillaria* extract. The biomolecular layers from the extract acts as the green reducing

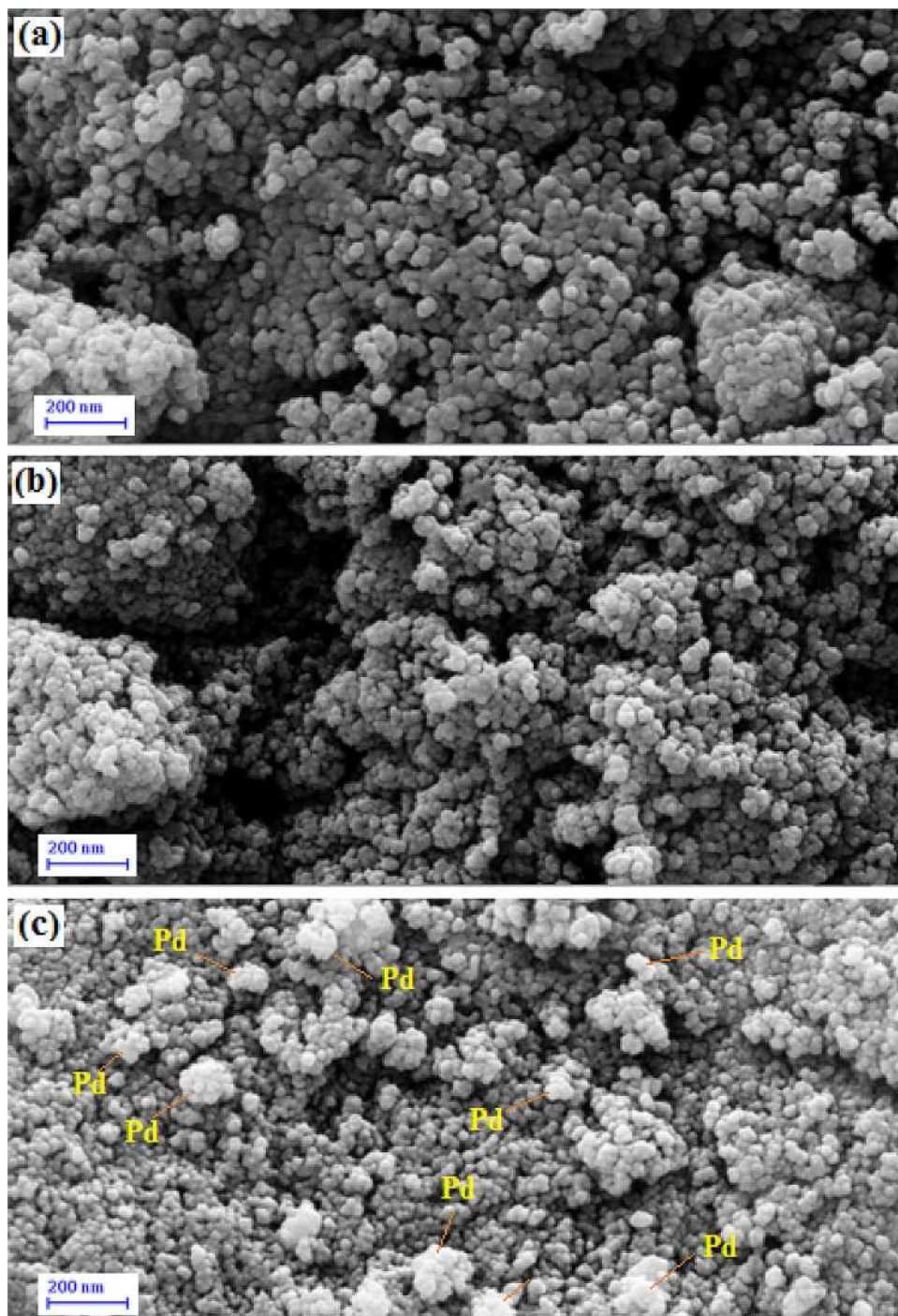


Figure 3. FE-SEM images of the (a) Fe_3O_4 NPs, (b) $\text{Fe}_3\text{O}_4@Fritillaria$ NPs, (c) $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$ NPs.

agent of the Pd ions as well as the stabilizing agent of Pd NPs. It easily detectable that the dark Pd NPs are of $\sim 20\text{--}30$ nm being entrapped in the modified iron oxide surface (Fig. 6b).

Figure 7 illustrates XRD patterns of Fe_3O_4 and $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$ nanocomposite. Evidently, XRD profile of the latter carries all the significant peaks that of cubic spinel Fe_3O_4 NPs. The XRD peaks found at $2\theta = 30.3^\circ$, 35.7° , 43.4° , 53.9° , 57.4° and 62.9° can be attributed to diffraction on (220), (311), (400), (422), (511) and (440) planes respectively (JCPDS No. 19-0629). It also implies that the interior structure remains undisturbed even after bio-functionalizations and Pd anchoring. The Pd attachment can also be demonstrated by the distinctive peaks observed at $2\theta = 40.1^\circ$, 46.6° and 67.9° , being ascribed to the (111), (200) and (220) crystalline planes of Pd fcc structure.

Magnetic characteristics of the $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$ NPs was assessed through VSM analysis and the magnetization curve has been shown in Fig. 8. From the corresponding hysteresis curve, the maximal saturation

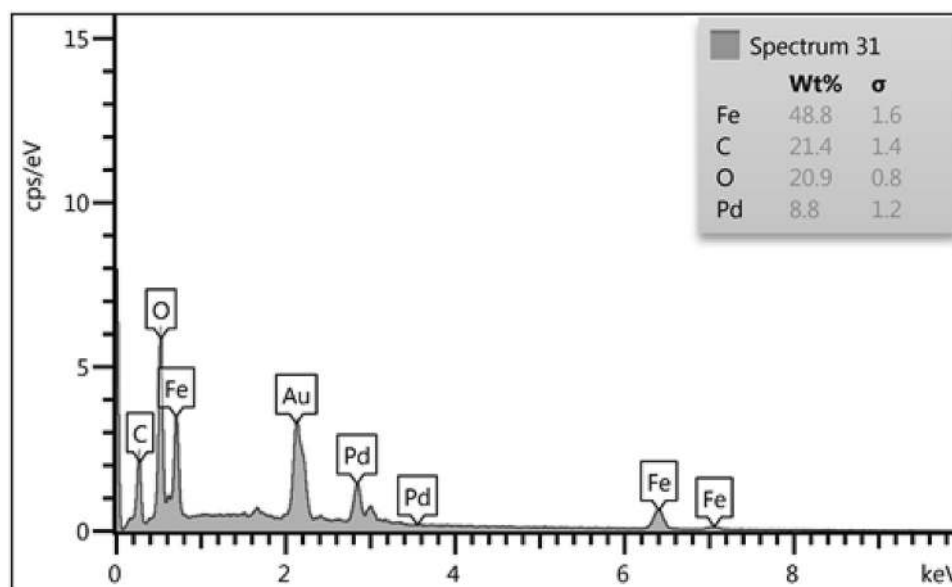


Figure 4. EDX of the $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$ NPs.

magnetization of $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$ NPs was found to appear at 42.5 emu g^{-1} . However, the value is much lower than bare ferrite NP (64.2 emu g^{-1}) due to surface operations. Still, in the modified material the magnetization goes down from plateau state to zero on removal of the magnetic field which justifies it to be superparamagnetic⁵³.

Catalytic applications of $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$ nanocomposite. So as to explore the catalytic application of $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$ nanocomposite and finding optimum reaction conditions, we selected the reduction of nitrobenzene as a model reaction. The effect of various conditions including temperature, solvents, catalyst load, amount of reductant and time reaction were studied over the reaction. The outcomes were documented in Table 1. Primarily, the model reaction was examined in various solvents like dimethyl formamide (DMF), EtOH, MeOH, CH_3CN , $\text{H}_2\text{O}/\text{EtOH}$ and H_2O . Among them, $\text{H}_2\text{O}/\text{EtOH}$ afforded the best yield and thereby selected as the optimum solvent. The amount of $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$ nanocomposite was also explored for the model reaction. Based on the study, 0.1 mol% catalyst was the most convenient for 1 mmol of nitrobenzene. Finally, the best result for the reduction of nitrobenzene was obtained using 3.0 mmol $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ as reductant and 0.013 g $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$ (0.1 mol% Pd) catalyst respectively in $\text{H}_2\text{O}/\text{EtOH}$ (2:1) solvent at 80°C . We also performed the reduction of nitrobenzene using the bare $\text{Fe}_3\text{O}_4@Fritillaria$ NPs but only a trace of aniline was obtained. This indicates that the interaction between the Pd NPs and $\text{Fe}_3\text{O}_4@Fritillaria$ is very important for catalytic success.

After resolving the required optimizations, the next endeavor was to generalize them over a range of differently functionalized (electron-donating and electron-withdrawing groups) nitroarenes. The results in terms of reaction yield and TOF are shown in Table 2. All the reactions were executed superbly with all kind of substrates without noticeable influence of functional groups on the reaction. All the reactions were completed within 0.5–2 h.

Recyclability of $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$ catalyst. For every heterogeneous catalytic system, the isolation and recycling of catalyst is a crucial feature in view of sustainable and industrial concern. The reusability of $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$ was examined over the reduction of nitrobenzene under optimized conditions. After finishing a fresh batch of reaction the catalyst was recovered using a bar magnet and washed several times with ethanol and water. It was regenerated after drying at moderate temperature. To our delight, we could have reused it for eight consecutive cycles of reaction without noticeable loss in its activity (Fig. 9). We further analyzed the structural morphology of $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$ nanocomposite after recycling 7 times by using TEM and EDX. As clearly can be seen from the TEM image (Fig. 10), the catalyst retains its initial morphology and particles size without any sign of agglomeration. Alongside, there occurs no change in elemental composition as evident from EDX data (Fig. 10), which in turn validates the robustness of our material.

Heterogeneity test for $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$ catalyst. The Sheldon's test was carried out to assure heterogeneous nature of the synthesized material, whether any Pd species leached out in the filtrate solution. The reduction of nitrobenzene was continued over the catalyst under optimized state for 15 min and then the reaction mixture was divided into two-halves. From one portion of the reaction mixture the catalyst was removed by a magnetic bar and both the part reactions were further continued for another 15 min. On gas chromatographic analysis, it was revealed that no significant progress in reaction was achieved under non-catalytic conditions

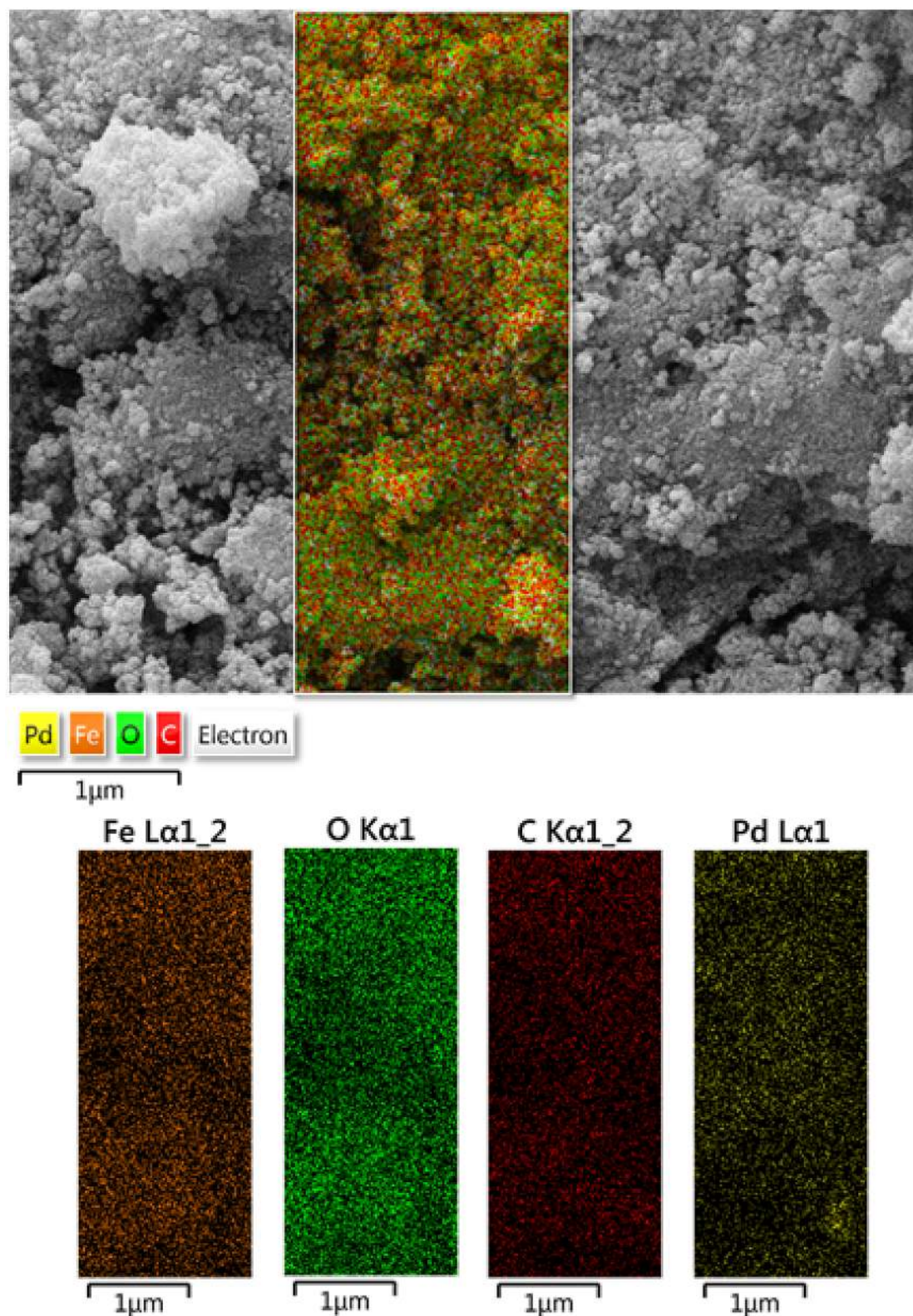


Figure 5. Elemental mapping of $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$ nanocomposite.

(60% conversion) while the other portion led to completion. The result is shown in Fig. 11. This further suggests that there was hardly any leaching of Pd NPs took place in the reaction mixture justifying its true heterogeneity.

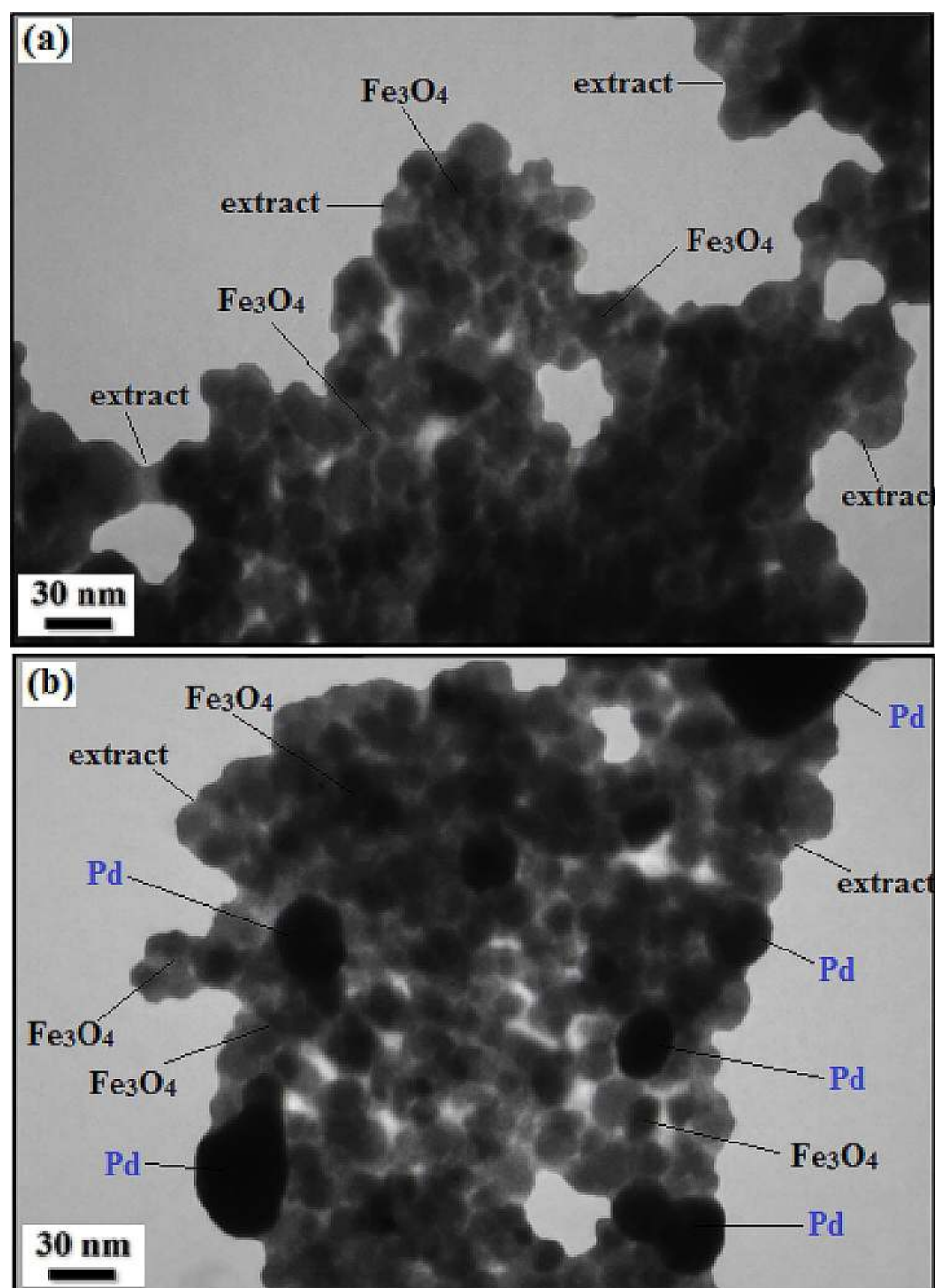


Figure 6. TEM images of (a) Fe_3O_4 @*Fritillaria* NPs and (b) Fe_3O_4 @*Fritillaria*/Pd NPs.

Study of reaction mechanism. Based on earlier published works, a probable reaction pathway has been documented in Scheme 2^{54–57}. The reaction goes through several intermediates. At the outset, hydrazine gets adsorbed on the surface of Pd NPs (I) which subsequently generates N_2 and nascent hydrogen by bond cleavage. This hydrogen is captured by the active Pd NPs to form metal hydride (II). In the meantime the substrate nitroarenes also get adsorbed over the catalyst surface and gets reduced by hydride transfer from II to form active nitroso derivative (III). This moiety is then further reduced to amine via hydroxylamine (IV) intermediate through hydrogen transfer. The hydrogenation of hydroxylamine is considered to be slow and rate determining step. Finally, the desired product leaves behind the catalyst surface to be used for the next cycle.

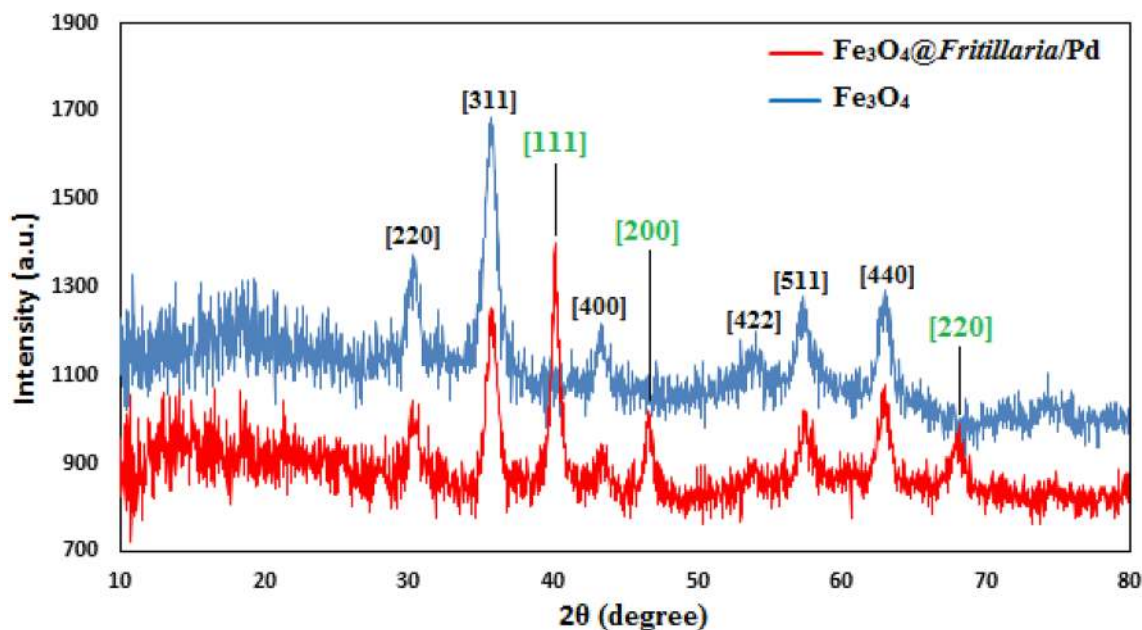


Figure 7. XRD profile of Fe_3O_4 NPs and the $\text{Fe}_3\text{O}_4@Fritillaria/Pd$ nanocomposite.

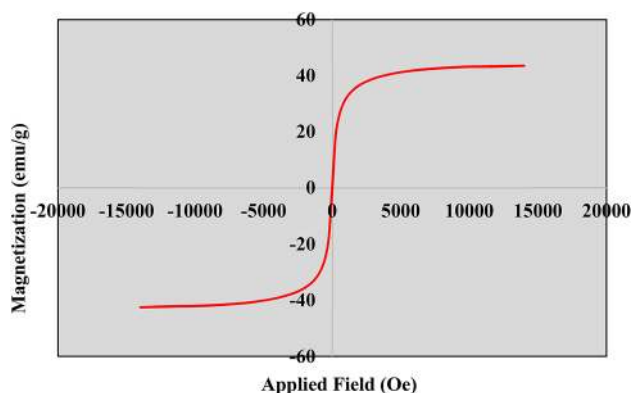


Figure 8. Magnetism study of $\text{Fe}_3\text{O}_4@Fritillaria/Pd$ NPs.

Uniqueness of our result. The individuality of our protocol was affirmed by comparing the catalytic performance between our methodology and the reported procedures in the reduction of 4-nitrophenol. The results are shown in Table 3 which evidently displays that the $\text{Fe}_3\text{O}_4@Fritillaria/Pd$ nanocomposite is much superior to others in terms of reaction time and yield.

Conclusion

We introduce a facile procedure for the synthesis of a heterogeneous and reusable Pd NPs decorated on *Fritillaria imperialis* flower extract modified magnetic ferrite nanoparticles by post functionalization approach. Catalytic performance of the $\text{Fe}_3\text{O}_4@Fritillaria/Pd$ nanocomposite material was studied in the competent reduction of nitroarenes without the use of any added base. The protocol worked proficiently using hydrazine hydrate as the reducing agent under eco-friendly conditions affording various aromatic amines with excellent yields. In addition, due to strong magnetic nature, the $\text{Fe}_3\text{O}_4@Fritillaria/Pd$ nanocatalyst could be reused as much as eight cycles in the reduction process emphasizing its true heterogeneity. In view of the outstanding catalytic behavior, the engineered material is anticipated to be a versatile support to feed many other noble metals like Ag, Au, Cu etc. towards many catalytic transformations and might find an excellent exposure in chemical industry.

						
Entry	Catalyst (mol%)	Solvent	N ₂ H ₄ ·H ₂ O (mmol)	Condition	Time (h)	Yield (%) ^b
1	–	EtOH	3	Reflux	24	0
2	0.1	EtOH	3	Reflux	2	75
3	0.1	MeOH	3	Reflux	2	70
4	0.1	H ₂ O	3	Reflux	6	60
5	0.1	DMF	3	Reflux	2	55
6	0.1	CH ₃ CN	3	Reflux	2	50
7	0.1	H ₂ O/EtOH (1:1)	3	Reflux	1	90
8	0.1	H ₂ O/EtOH (2:1)	3	Reflux	0.5	98
9	0.05	H ₂ O/EtOH (2:1)	3	Reflux	1	85
10	0.1	H ₂ O/EtOH (2:1)	2.5	Reflux	1	90
11	0.1	H ₂ O-EtOH (2:1)	3.5	Reflux	0.5	98
12	0.1	H ₂ O/EtOH (2:1)	3	r.t	2	45

Table 1. Standardization of reaction conditions in the reduction of nitrobenzene over Fe₃O₄@Fritillaria/Pd nanocomposite^a. ^aReaction conditions: nitrobenzene (1.0 mmol), solvent (3.0 mL), open air; ^bIsolated yield.

Entry	RC ₆ H ₄ NO ₂	Time (h)	Yield (%) ^b	TOF (10 ^{−3}) (s ^{−1}) ^c
1	H	0.5	98	544
2	4-OH	0.5	98	544
3	2-OH	1	92	256
4	4-NH ₂	1	95	264
5	4-CH ₃	0.5	96	533
6	4-OCH ₃	0.5	95	528
7	4-CN	1	92	256
8	2-NH ₂	2	88	122
9	4-CHO	1.5	85	157
10	4-Cl	1.5	80	148

Table 2. Reduction of aromatic nitroarenes catalyzed by Fe₃O₄@Fritillaria/Pd NPs^a. ^aReaction conditions: Nitroarene (1.0 mmol), NH₂NH₂, H₂O (3.0 mmol), catalyst (0.1 mol%), EtOH:H₂O (1:2, 3.0 mL), 80 °C; ^bIsolated yields; ^cturnover frequencies (TOF = (Yield/Time)/Amount of catalyst (mol)).

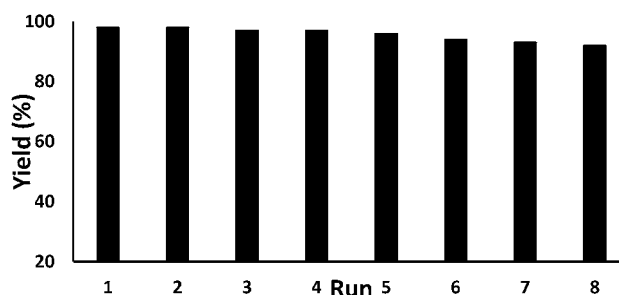


Figure 9. Reusability of Fe₃O₄@Fritillaria/Pd catalyst for reduction of nitrobenzene.

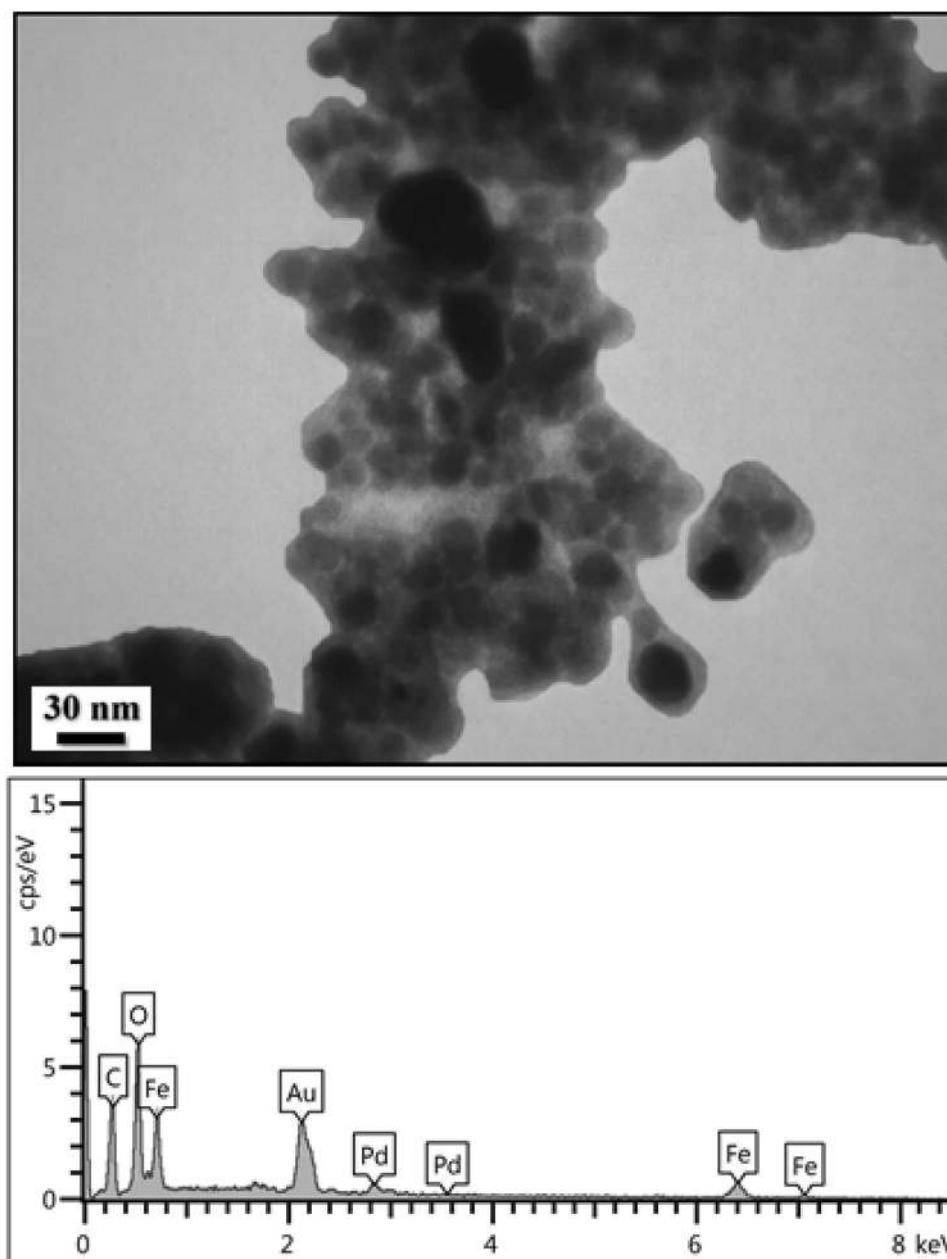


Figure 10. TEM and EDX data for reused $\text{Fe}_3\text{O}_4@Fritillaria/\text{Pd}$ catalyst after 7 runs.

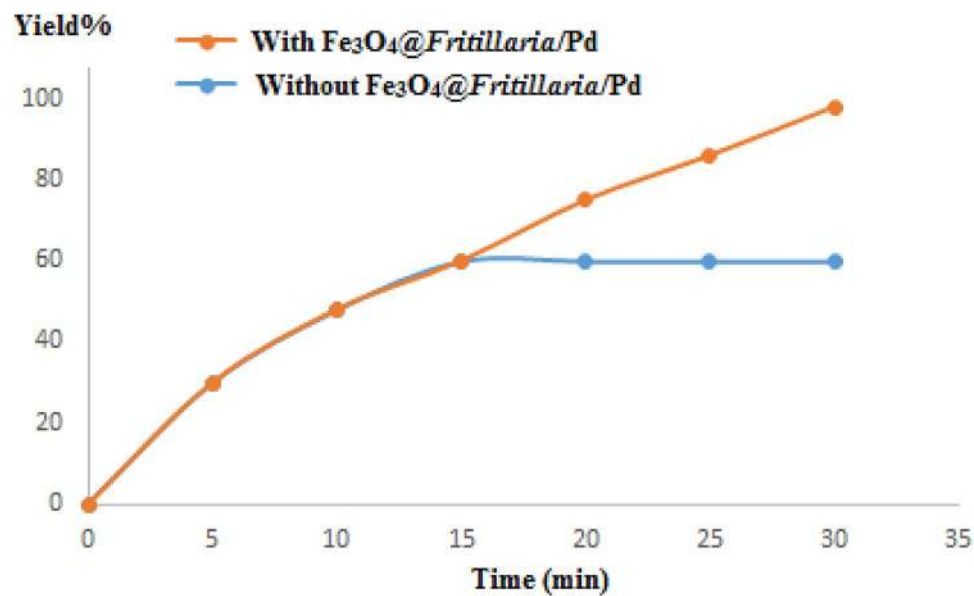
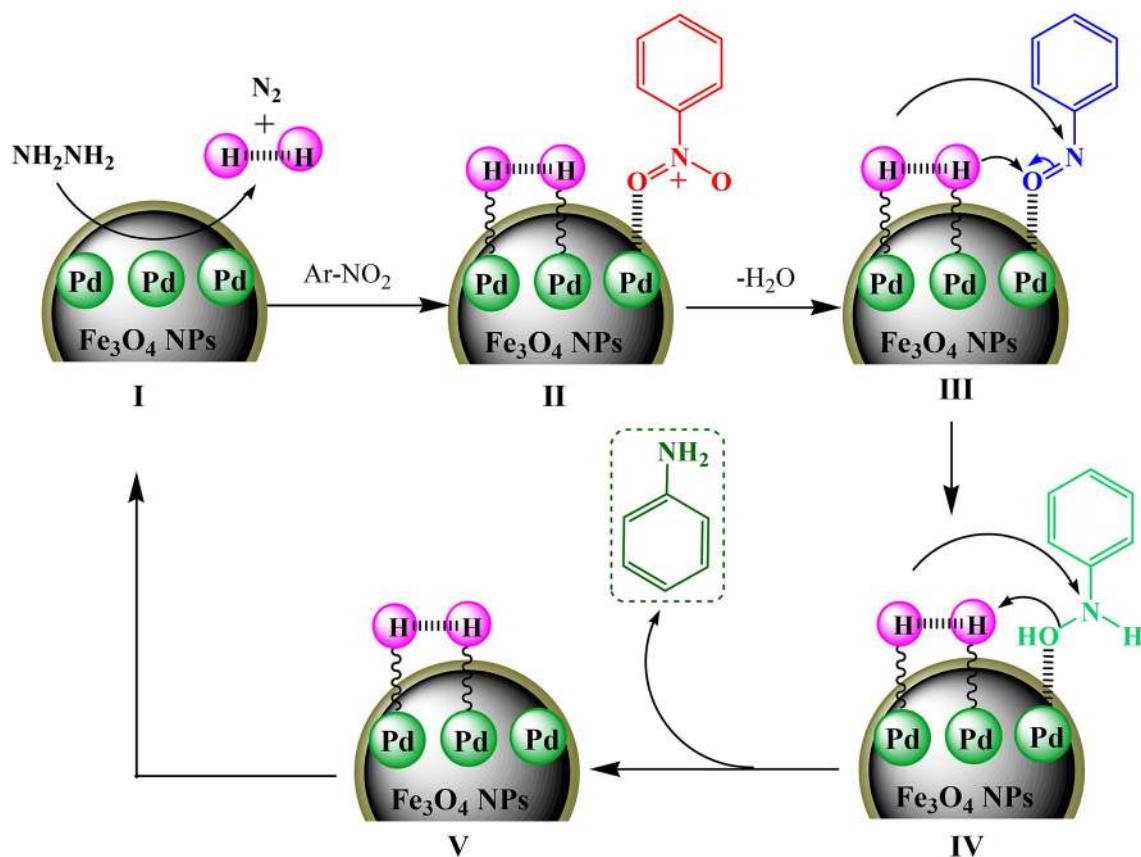


Figure 11. Hot filtration and leaching test of $\text{Fe}_3\text{O}_4@Fritillaria/Pd$ in the reduction of nitrobenzene.



Scheme 2. Reaction mechanism for the reduction of nitrobenzene over $\text{Fe}_3\text{O}_4@Fritillaria/Pd$ catalyst.

Entry	Catalyst (mol%)	Conditions	Time (h)	Yield (%)	References
1	Au/MTA	NaBH ₄ , EtOH, RT	3	90	⁵⁸
2	Fe ₃ O ₄ Ni MNPs	Glycerol, KOH, 80 °C	3.5	88	⁵⁹
3	Pd NPs/RGO	NaBH ₄ , EtOH:H ₂ O, 50 °C	1.5	97	⁶⁰
4	Fe-phenanthroline/C	N ₂ H ₄ , H ₂ O, THF, 100 °C	10	97	⁶¹
5	Nickel-iron mixed oxide	N ₂ H ₄ , H ₂ O, propan-2-ol, Reflux	1.75	93	⁶²
6	[Pt]@SiC ₆	AcOEt, H ₂ , RT	3	99	⁶³
7	Rh	N ₂ H ₄ , EtOH, 80 °C	2.5	94	⁶⁴
8	Rh-Fe ₃ O ₄ nanocrystals	N ₂ H ₄ , EtOH, 80 °C	1	99	⁶⁵
9	PdCu/graphene	NaBH ₄ , EtOH:H ₂ O (1:2), 50 °C	1.5	98	⁶⁶
10	Fe ₃ O ₄ @Fritillaria/Pd	N ₂ H ₄ , H ₂ O, EtOH:H ₂ O (1:2), 80 °C	0.5	98	This work

Table 3. Catalytic comparison in the reduction of 4-nitrophenol.

Received: 24 July 2020; Accepted: 4 February 2021

Published online: 25 February 2021

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Acknowledgements

We are thankful to Payame Noor University (PNU) for financial supports. BK thanks Gobardanga Hindu College for providing research facilities.

Author contributions

T.T., R.T., S.S., S.L., B.M. and S.H.: Visualization, Writing original draft, Formal analysis. H.V.: Funding acquisition, Methodology, Supervision. B.K.: Writing original draft, Formal analysis, Writing-review and editing.

Competing interests

The authors declare no competing interests.

Additional information

Correspondence and requests for materials should be addressed to H.V. or B.K.

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