

Immobilization of Pt nanoparticles on magnetite–poly (epoxyamine) nanocomposite for the reduction of *p*-nitrophenol

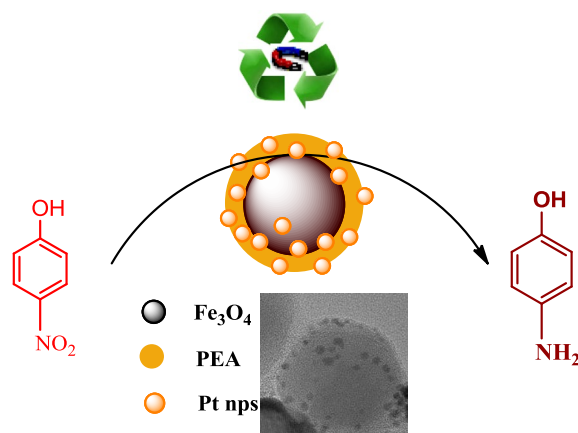
Kannappan Lakshmi¹ · Rajmohan Rangasamy¹  · E. Prathibha¹ · A. Sridhar¹

© Springer Nature Switzerland AG 2019

Abstract

Recently the magnetic nanoparticle earns more attention in the field of catalysis for their enhanced loading capacity and magnetic recyclability. In this study, we intended to focus the synthesis of polymer coated iron oxide nanoparticle as support for the immobilization of metal nanoparticles. The typical synthetic strategy involves the synthesis of 1,4-diaminobutane functionalized superparamagnetic Fe_3O_4 nanoparticle, followed by epoxyamine polymer coating on amine functionalised Fe_3O_4 using 1,4 diaminobutane and epichlorohydrin monomers through one pot method. Further, ultrafine Pt nanoparticle was immobilised onto poly (epoxyamine) coated Fe_3O_4 . These materials were characterized using FT-IR, XRD, VSM, EDS, SEM HRTEM etc. The semiheterogenous catalytic efficiency of the material was examined in aqueous phase reduction of *p*-nitrophenol. The catalyst was reused up to 5 times without loss of activity.

Graphic abstract



Magnetite-poly (epoxyamine) platinum nanocomposite

Keywords Magnetite · Poly (epoxy amine) · Nanocomposite · Platinum nanoparticle · Immobilization · *p*-nitrophenol

✉ Rajmohan Rangasamy, rangagncchem@gmail.com | ¹Department of Chemistry, Guru Nanak College, Velachery, Chennai, Tamil Nadu 600042, India.



SN Applied Sciences (2019) 1:1121 | <https://doi.org/10.1007/s42452-019-1137-5>

Received: 24 May 2019 / Accepted: 20 August 2019 / Published online: 29 August 2019

1 Introduction

Magnetic iron oxide nanoparticles being robust with greater surface area have wide spread applications in the field of drug delivery [1], magnetic resonance imaging [2], storage devices [3], catalysis [4] etc. Recently many researchers reported the iron oxide nanoparticle as catalyst support due to their easy recoverability by magnetic separation method [5]. Generally, Fe_3O_4 nanoparticles can be synthesized from iron precursors by various method such as chemical reduction, coprecipitation, thermal decomposition, sonochemical method etc. [6]. But while synthesizing Fe_3O_4 few factors to be considered like particle size, uniform shape, less aggregation, fine dispersion etc. Numerous methods have been developed to synthesis iron oxide nanoparticles by using surfactants [7, 8] organic ligands [9], polymers [10], dendrimers [11] as stabilizers. Among these methods, chemical reduction using amines is simple and convenient for the synthesis of Fe_3O_4 nanoparticles with enhanced features. [12]. Further, the surface of the iron oxide nanoparticles have functionalized in order to synthesis specific catalysis. The surface modifications of Fe_3O_4 nanoparticles can be carried out by using polymer [13], mesoporous silica [14], metals [15], metal oxides [16] etc. Besides, polymer coating strategy on the Fe_3O_4 nanoparticles facilitates numerous sites for further modification and fine dispersion. Many organic polymers such as polyester [17], polyethylene glycol [18], poly styrene [19] etc., have been reported which forms an organic shell around the iron oxide nanoparticles. These polymer matrix provides an avenue to immobilize metal nanoparticles for catalysis [20]. Normally, metal nanoparticles can be immobilized on the polymer coated iron oxide nanoparticles by following two strategies i.e. to deposit pre-synthesized metal nanoparticles on the polymer coated iron oxide nanoparticle, but the metal nanoparticles can be leached after catalysis. The second method is to directly grow the metal nanoparticle on the polymeric surface with controllable size. Since polymer possess greater multifunctional atoms and favorable structural features, it provides excellent support for direct synthesis of size-controlled metal nanoparticles. Recently, noble metals such as silver, gold, platinum, palladium nanoparticles were immobilized on solid-support and used for the reduction of *p*-nitrophenol. As we are aware that *p*-nitrophenol is a significant compound in pharma sector and which remains as pollutant too. Hence, it has to be reduced to *p*-aminophenol by greener method in aqueous medium using recoverable and reusable catalysts [21–23].

In this research work, we have demonstrated the efficient two step synthetic protocol for immobilization of platinum nanoparticle onto spherical magnetite–poly

(epoxyamine) nanocomposite with uniform size, shape and monodispersion of Pt nanoparticles. Efficacy of this material has been tested for aqueous phase catalysis of reduction of *p*-nitrophenol to *p*-aminophenol.

2 Experiment and methods

2.1 Materials

Ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), 1,4-diaminobutane (DAB), epichlorohydrin, sodium borohydride (NaBH_4), *p*-nitrophenol were purchased from SRL. Chloroplatinic acid (H_2PtCl_6) was purchased from Sigma Aldrich. Double Distilled (DD) water was used wherever necessary. Reactions were carried out using Remi mechanical overhead stirrer provided with Teflon blade.

2.2 Characterization methods

Images were taken using High Resolution Transmission Electron Microscope (HRTEM), JEOL Japan JEM 2100 at 200 kV model with LaB_6 electron gun. The grid was placed under electron beam and images were captured. X-ray diffraction patterns were recorded in Bruker USA D8 Advance, Davinci using $\text{CuK}\alpha$ radiations with wavelength 0.154 nm. The measurements were made between the angles 10° and 70° . Magnetic behavior of the nanocomposite materials synthesized were analyzed by using Vibrating Sample Magnetometer Lakshore, 7410 series with a maximum field of 3.1 Testla at room temperature having field setting resolution of 30 mOe. FTIR spectra was obtained from Perkin Elmer instrument in transmittance mode for measurements in the range of $4100\text{--}400\text{ cm}^{-1}$ using KBr pellets sampling method.

2.3 Synthesis of poly (epoxyamine) functionalized Fe_3O_4 nanocomposite ($\text{Fe}_3\text{O}_4/\text{PEA}$)

0.278 g (1 mM) of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in DD water and stirred vigorously. To this solution, about 10 equivalence i.e. 0.8 mL of DAB (10 mM) was added under continuous stirring, the solution turned green. This suspension turned black when heated at 80°C for 6 h. The black particles $\text{Fe}_3\text{O}_4\text{--NH}_2$ got attracted towards magnet [7]. To the above $\text{Fe}_3\text{O}_4\text{--NH}_2$ black suspension, equal amount of DAB (2 mL, 20 mM) and epichlorohydrin (1.6 mL, 20 mM) were added and stirred at 80°C for 24 h [24]. Magnetite–poly (epoxyamine) nanocomposite obtained was separated by external magnet and washed thrice with DD water, thrice with acetone and dried in vacuum for 24 h.

2.4 Immobilization of Pt nanoparticles on Fe₃O₄/PEA nanocomposite (Fe₃O₄/PEA/Pt)

100 mg of the Fe₃O₄/PEA nanocomposite was suspended in 50 mL DD water, to this suspension 0.2 mL of chloroplatinic acid (4.8 μM) were added under continuous stirring for 15 min. Then Pt⁴⁺ was reduced with aqueous NaBH₄ (2.4 mM, 91 mg) in cold condition, stirring was continued for 30 min at room temperature. Fe₃O₄/PEA/Pt nanoparticles obtained was washed thrice with DD water, thrice with acetone and dried in vacuum for 24 h.

2.5 Determination of amine concentration by conductometric titration method

Exactly 10 mg of the nanomaterial was dispersed in 20 mL of standardized hydrochloric acid (1 mmol) and stirred mechanically for 30 min. Afterwards, the nanomaterial was isolated by magnetic separation, 5 mL of supernatant solution was titrated against standardized NaOH solution, the variations of conductance was measured for each 0.2 mL addition of NaOH solution. From the measured conductance, the value of concentration of HCl remaining in the solution which were not absorbed by the Fe₃O₄/PEA/Pt nanocomposite was determined. Henceforth, HCl consumed by the nanomaterial can be determined and that is equivalent to the concentration of amine groups available on the nanocomposite material.

2.6 Catalysis of reduction of *p*-nitrophenol

1 mM of *p*-nitrophenol solution was stirred with 7 mg of Fe₃O₄/PEA/Pt catalyst at room temperature. 10 mM of NaBH₄ was added to the above suspension in cold condition under continuous stirring. During the course of the reaction the light-yellow colored *p*-nitrophenol solution turned intense yellow colored solution, it has faded gradually and turned brown in 21 min. This colour change conformed the conversion of *p*-nitrophenol into *p*-aminophenol.

3 Results and discussion

Synthesis of Pt nanoparticle immobilised Fe₃O₄ poly (epoxyamine) nanocomposite was obtained from convenient one-step synthetic protocol. Initially, amine stabilized Fe₃O₄ nanoparticle was synthesized from the reduction of FeSO₄ using DAB in the ratio 1:10. DAB acts as the reducer as well as stabilizer to afford spherical shaped monodispersed diamino butane protected Fe₃O₄ nanoparticles. Further, the presence of amino groups on the Fe₃O₄ nanoparticles provides added advantage for polymer

functionalization on it. Additionally, DAB is one of the monomers for the polymer functionalization on iron oxide nanoparticles. Hence, removal of excess DAB has not been implemented and then equimole of DAB and epichlorohydrin were added to the diamine stabilized Fe₃O₄ nanoparticles, which was allowed to undergo polycondensation for a period of 24 h to yield poly (epoxyamine) functionalized magnetite nanocomposite.

Polymer functionalization on the Fe₃O₄ nanoparticle protects the iron oxide core from chemical degradation, prevents agglomeration, to enhance the spherical morphology and to achieve well dispersibility in solvents. Besides, the magnetic property of Fe₃O₄, also preserved to exhibit the material for high throughput application especially as recyclable catalyst support. Subsequently, Pt nanoparticles were immobilized on the Fe₃O₄/PEA nanocomposite by a simple wet impregnation method. The actual formation of Pt nanoparticle was taken place while mixing the H₂PtCl₆ with magnetite–poly (epoxyamine) composites, which enables chemical interaction between Pt⁴⁺ and amine group. The Pt⁴⁺ coordinated to the amine was reduced to Pt⁰ by means of aq. NaBH₄ solution to produce Pt nanoparticle decorated magnetite–poly (epoxyamine) composite. The precise size and uniform distribution of the Pt nanoparticle on the surface of the nanocomposite was attributed by effective stabilization of Pt nanoparticles on polymer functionalized magnetite particles (Scheme 1).

The formation of iron oxide nanoparticles and the presence of amino groups on their periphery has been confirmed primarily through FTIR spectrum (Fig. 1A). Absorbance band around 580 cm⁻¹ attributes for Fe–O vibrations of Fe₃O₄ and absorbance around 3350 cm⁻¹ attributes to the –NH stretching, 1625 cm⁻¹ attributes to the –NH bending of the amine present on the periphery of the iron oxide nanoparticle. The X-ray diffraction pattern of amine stabilized iron oxide nanoparticle has been proved to be magnetite (inverse spinel cubic structure) showing sharp peaks for 2θ values at 30.25°, 35.66°, 45.34°, 57.37°, 62.7° corresponds to the respective lattice planes (220), (311), (400), (511), (440) (Fig. 2A). These XRD patterns matched well with JCPDS patterns of magnetite (JCPDS card No. 19-0629). The magnetic behavior of the synthesized amine stabilized Fe₃O₄ nanoparticles were evidenced to be superparamagnetic through the VSM studies (Fig. 3A). These nanoparticles acquired magnetic saturation value of 68.8 emu/g even when high magnetic field in the order of 1500 KOe was applied. Additionally, these nanoparticles have less magnetic retentivity such that negligible hysteresis loop was observed. Thus, the magnetometry studies authorizes the amine stabilized Fe₃O₄ nanoparticles behaves like temporary magnet which acquires magnetic moment only in the presence of an external magnet. The

Scheme 1 Synthesis of Pt nanoparticle decorated on magnetite–poly (epoxy-amine) nanocomposite

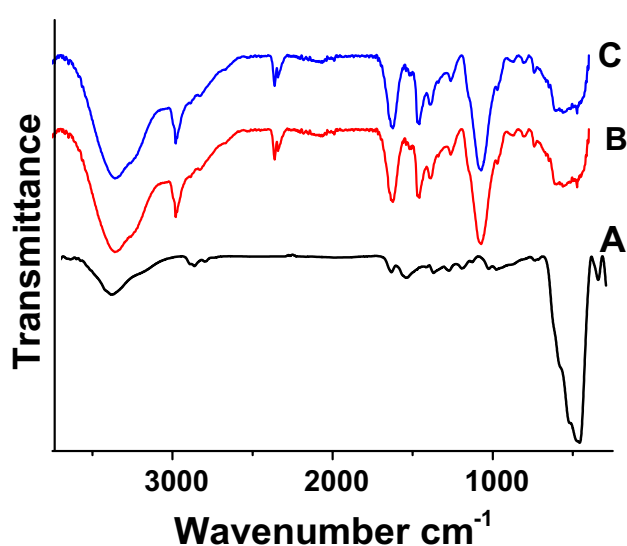
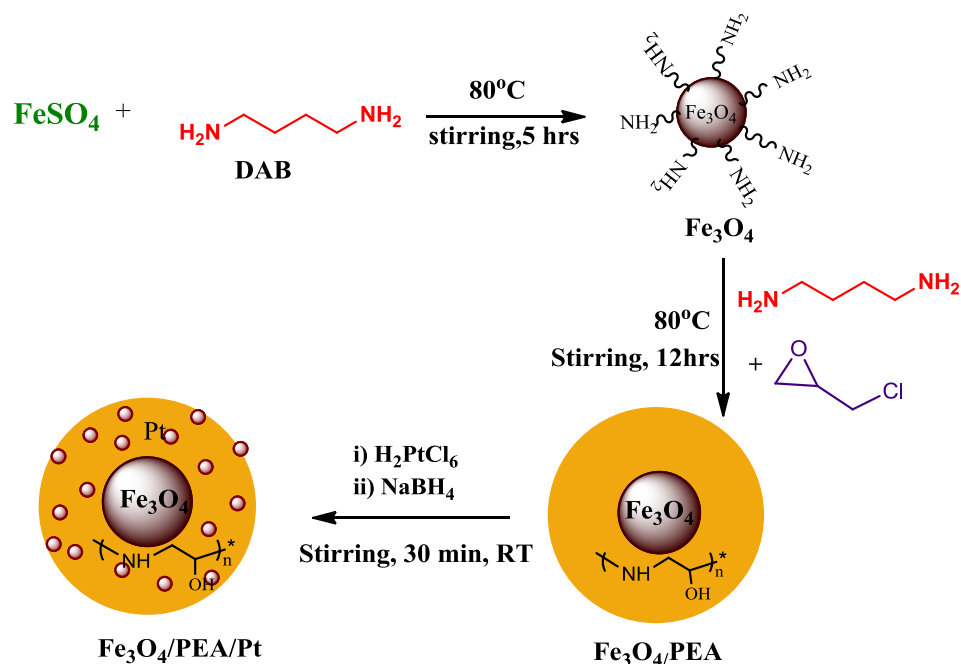


Fig. 1 FTIR spectra of (A) Fe_3O_4 nanoparticle, (B) $\text{Fe}_3\text{O}_4/\text{PEA}$ nanocomposite, (C) $\text{Fe}_3\text{O}_4/\text{PEA}/\text{Pt}$ nanocomposite

superparamagnetic property of $\text{Fe}_3\text{O}_4\text{-NH}_2$ nanoparticle provides credential to the material to serve as excellent catalyst support. The concentration of amine groups present on the periphery of amine stabilized Fe_3O_4 nanoparticle were determined by conductometric titrations and was found to be 2.14 mmol/g of amine groups.

The morphology of amine stabilized Fe_3O_4 nanoparticle were evidently clearly seen from SEM images. SEM images observed for amine stabilized Fe_3O_4 nanoparticle shows spherical morphology with minimal

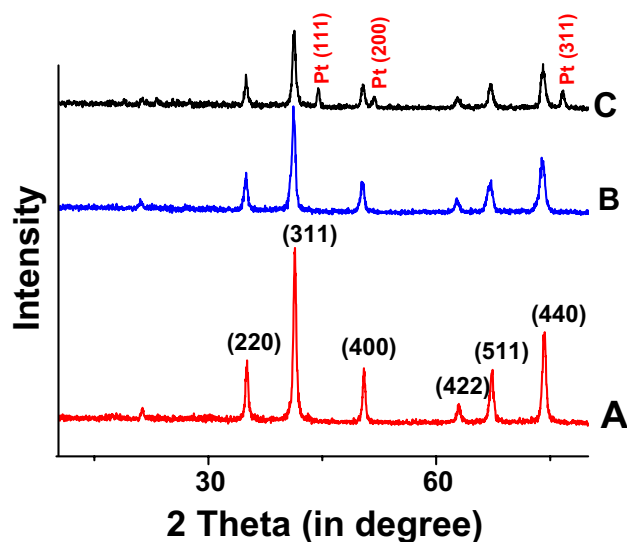


Fig. 2 X-ray diffraction patterns of (A) Fe_3O_4 nanoparticle, (B) $\text{Fe}_3\text{O}_4/\text{PEA}$ nanocomposite, (C) $\text{Fe}_3\text{O}_4/\text{PEA}/\text{Pt}$ nanocomposite

agglomeration (Fig. 4a), since the Fe_3O_4 nanoparticle were stabilized with DAB. These observations of amine stabilized Fe_3O_4 nanoparticle were further confirmed from HRTEM images (Fig. 5a). The size of the nanoparticles was found to be around 35 ± 5 nm from HRTEM images, which holds in good agreement with the size calculated from XRD from Scherrer formula. The FWHM was determined for 311 lattice plane and the crystallite size of the magnetite nanoparticle was calculated from

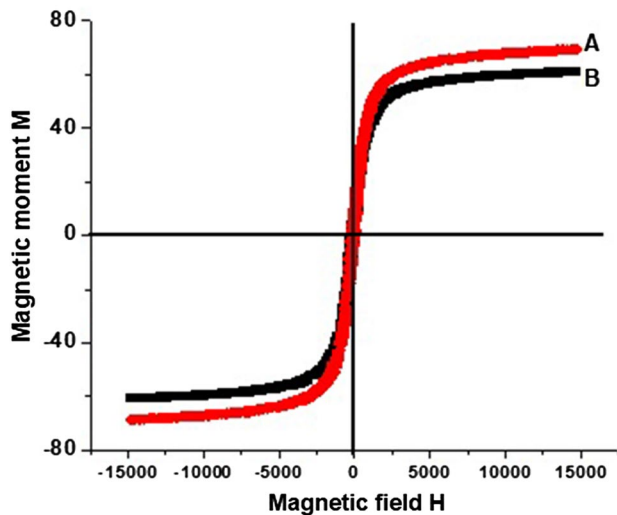


Fig. 3 VSM studies of (A) Fe_3O_4 nanoparticle, (B) $\text{Fe}_3\text{O}_4/\text{PEA}$ nanocomposite

the Scherrer equation $D = (K \cdot \lambda) / (\beta \cdot \cos \theta)$ where $K = 0.69$, $\lambda =$ wavelength of X-ray, $\beta =$ FWHM.

$\text{Fe}_3\text{O}_4/\text{PEA}$ nanocomposite material was synthesized by the condensation polymerization of DAB and epichlorohydrin on amine stabilized Fe_3O_4 nanoparticle. It was confirmed through FTIR (Fig. 1B) from increased intensity of absorption band around 3350 cm^{-1} for $-\text{NH}$ as well as $-\text{OH}$ stretching, appearance of new band at 3250 cm^{-1} for $-\text{CH}$ stretching and decreased intensity of absorption band at 580 cm^{-1} for $\text{Fe}-\text{O}$ vibration due to functionalization

of PEA on iron oxide nanoparticles compared with the FTIR spectrum obtained for amine stabilized Fe_3O_4 nanoparticle. Hence, these absorption band depicts that the formation of $\text{Fe}_3\text{O}_4/\text{PEA}$ nanocomposite. The XRD pattern for $\text{Fe}_3\text{O}_4/\text{PEA}$ nanocomposite does not show any new characteristic peak other than the patterns observed for magnetite nanoparticle, confirming that the magnetite crystallite structure has not been disturbed even after polymer functionalization (Fig. 2B). In addition to these analytical observations, VSM study validates the persistence of superparamagnetic character of $\text{Fe}_3\text{O}_4/\text{PEA}$ nanocomposite. The observed magnetic saturation values for Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{PEA}$ is 68.8 emu/g and 60.2 emu/g respectively. The decline in magnetic saturation values from 68.8 to 60.2 emu/g provides the insight information about the polymer functionalization of magnetite nanoparticle (Fig. 3B). Moreover, the superparamagnetic behavior still exists favoring the easy recoverability of the nanoparticle by using external magnet. The polymer functionalization on Fe_3O_4 nanoparticle was also observed from HRTEM images (Fig. 5b). Independent $\text{Fe}_3\text{O}_4/\text{PEA}$ nanocomposite were found, having boundary for each entity of $\text{Fe}_3\text{O}_4/\text{PEA}$ nanocomposite. The diamine present on iron oxide nanoparticles serves as monomer and it facilitates the polymerization with epichlorohydrin on Fe_3O_4 nanoparticle consistently, such that they appear to be monodispersed with less agglomeration.

As discussed earlier, Pt nanoparticle were immobilized on $\text{Fe}_3\text{O}_4/\text{PEA}$ via coordination of Pt^{4+} with amino group of the polymer followed by reduction of Pt^{4+} to

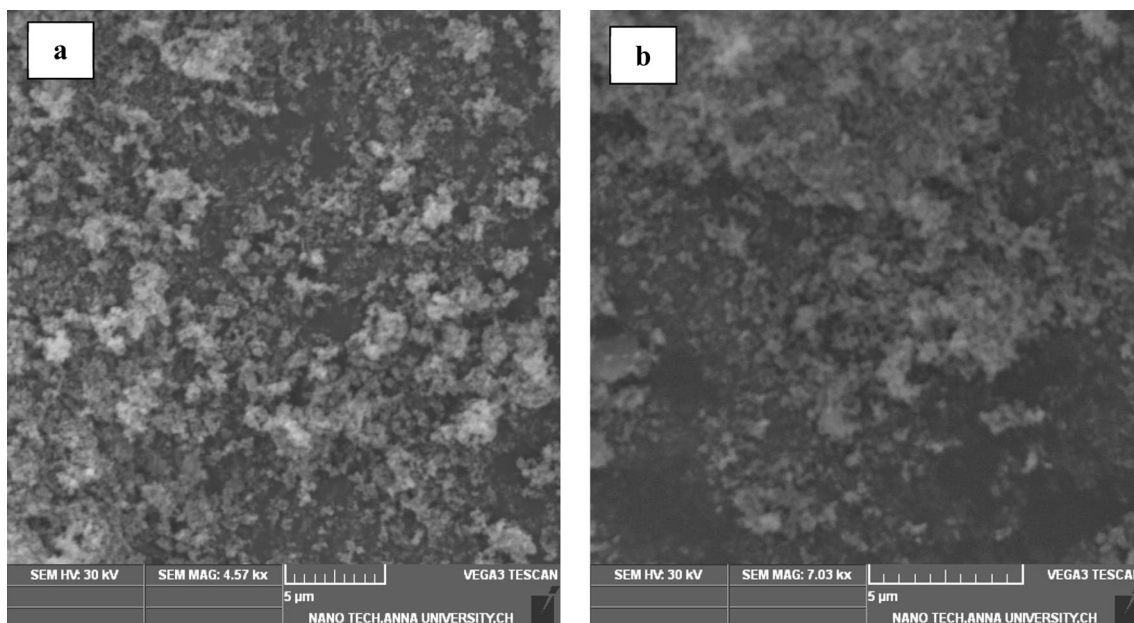


Fig. 4 SEM images of **a** Fe_3O_4 nanoparticle, **b** $\text{Fe}_3\text{O}_4/\text{PEA}$ nanocomposite

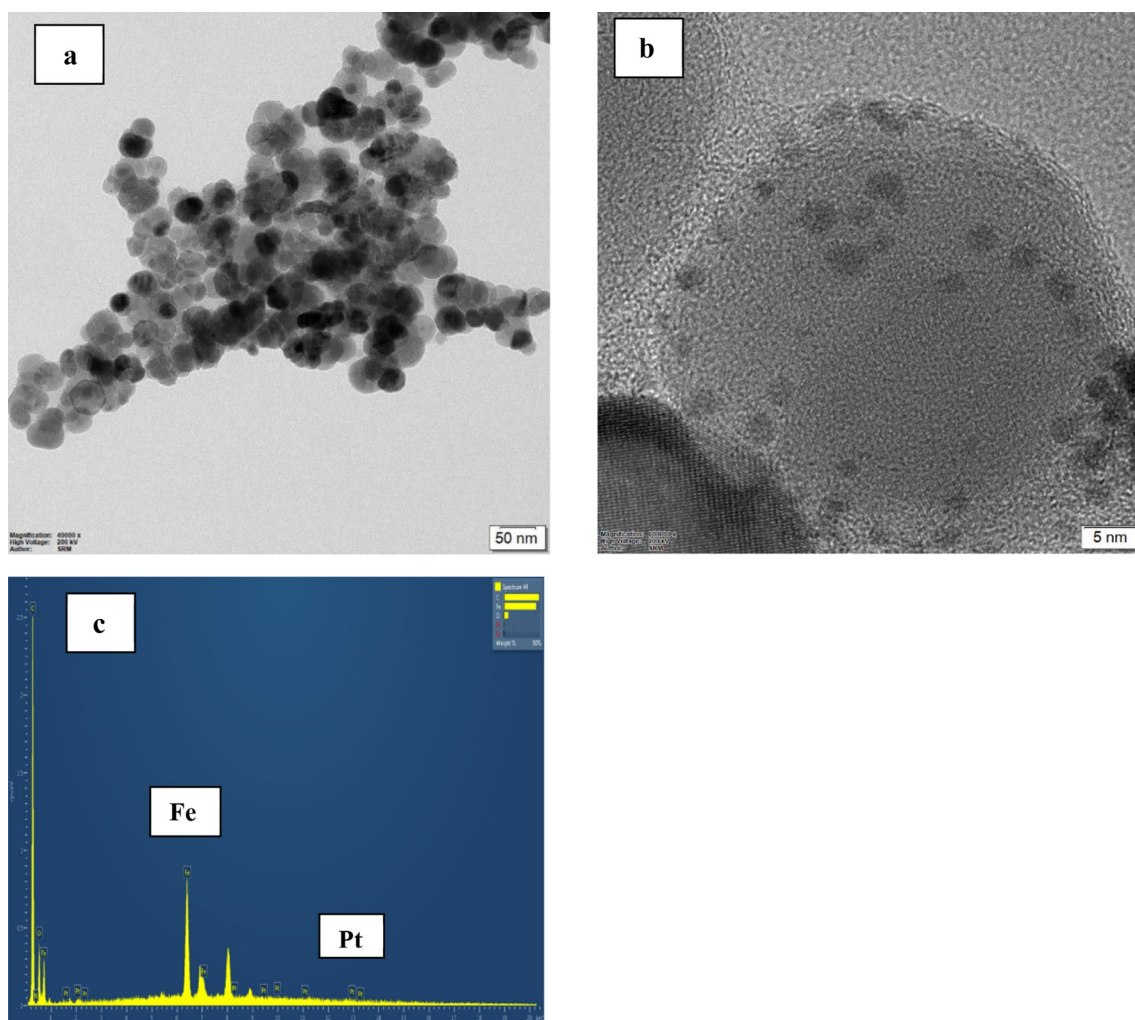


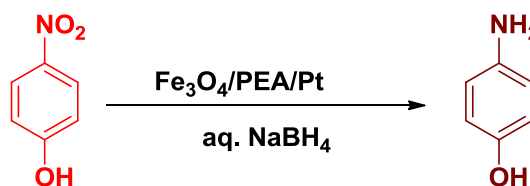
Fig. 5 HRTEM images of **a** $\text{Fe}_3\text{O}_4/\text{PEA}$ nanocomposite, **b** $\text{Fe}_3\text{O}_4/\text{PEA}/\text{Pt}$ nanocomposite, **c** EDS spectrum of $\text{Fe}_3\text{O}_4/\text{PEA}/\text{Pt}$ nanocomposite

Pt^0 using aq. NaBH_4 . Pt nanoparticles were evenly distributed on the surface of the $\text{Fe}_3\text{O}_4/\text{PEA}$ nanocomposite that can be attributed due to the presence of more availability of functional atoms such as nitrogen and oxygen available on the polymer stabilizes the metal nanoparticle. The Pt nanoparticles immobilized on the matrix was confirmed from the XRD pattern obtained for $\text{Fe}_3\text{O}_4/\text{PEA}/\text{Pt}$ nanocomposite which showed new peak for platinum crystal structure for the lattice plane 111, 200, 311 and this in addition to the magnetite crystallite lattice planes [25]. Further, HRTEM images envisages $\text{Fe}_3\text{O}_4/\text{PEA}$ nanoparticle entity contains ultrafine Pt nanoparticle that additionally supports the increase in loading capacity of the polymer (Fig. 5c). Hence, the synthesized $\text{Fe}_3\text{O}_4/\text{PEA}/\text{Pt}$ nanocomposite will serve as better catalyst for reduction reactions.

4 Catalysis

4.1 Reduction of *p*-nitrophenol to *p*-aminophenol using $\text{Fe}_3\text{O}_4/\text{PEA}/\text{Pt}$ nanocomposite

The catalytic activity examination of $\text{Fe}_3\text{O}_4/\text{PEO}/\text{Pt}$ nanocomposite was evaluated for the reduction reaction of *p*-nitrophenol to *p*-aminophenol (Scheme 2). Usually,



Scheme 2 Reduction of *p*-nitrophenol to *p*-amino phenol

Palladium and gold nanoparticles were employed for various reduction reactions. Platinum metal being stable and inert, it was chosen for immobilization on magnetic nanoparticle support in order to carry out the reduction reaction of *p*-nitrophenol to *p*-aminophenol which has been the major source for preparation of paracetamol. In normal practice *p*-Nitrophenol does not undergo reduction reaction with NaBH_4 in the absence of catalyst. Therefore the $\text{Fe}_3\text{O}_4/\text{PEA}/\text{Pt}$ was used as semiheterogeneous catalyst of activate NaBH_4 and *p*-nitrophenol which inturn facilitates the reduction reaction with much faster rate. Since the particle size of the catalyst is in nanodimension, it is easily dispersed in reaction medium and leads to semiheterogenous phase catalyst. The yellow colored solution started to fade and turned brown at 20 min, which indicated the reduction of *p*-nitrophenol to *p*-aminophenol. Further, the conversion of products was confirmed through UV-Vis absorption measurement, *p*-nitrophenol showed absorbance spectrum at 400 nm for the protonation of *p*-nitrophenolate ion with aq. NaBH_4 . After the addition of the catalyst, absorption peak at 400 nm was diminished and disappeared after 20 min, that infers the complete reduction of *p*-nitrophenol to *p*-aminophenol (Fig. 6). Finally, the $\text{Fe}_3\text{O}_4/\text{PEO}/\text{Pt}$ nanocatalyst was separated by magnetic attraction and regenerated by washing thrice with water, acetone and dried (Fig. 7). The recycling efficiency of the regenerated catalyst was tested up to five cycles. The catalyst showed remarkable efficiency even after fifth cycle for reduction of *p*-nitrophenol, without any significant loss in catalytic activity and loss in weight of the catalyst also.

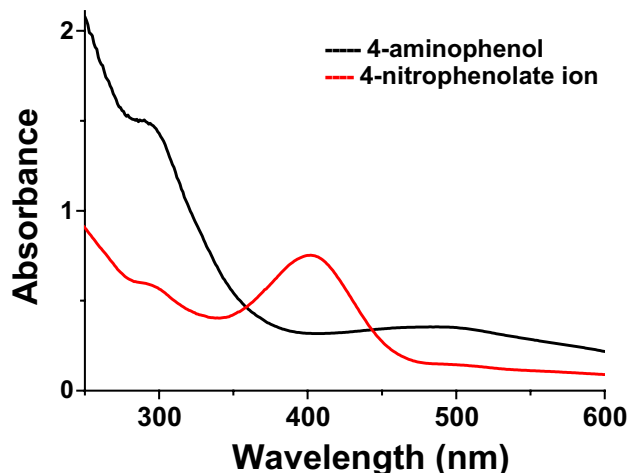


Fig. 6 UV-Vis absorbance for the reduction of *p*-nitrophenol to *p*-aminophenol

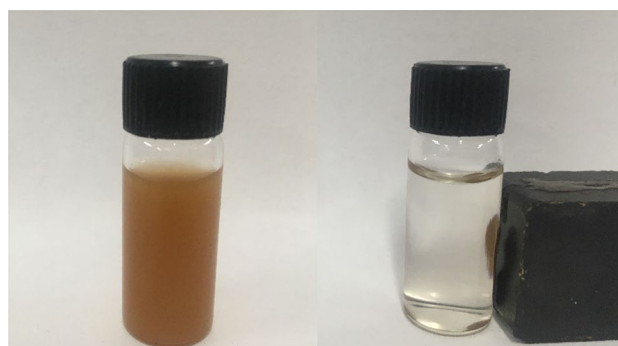
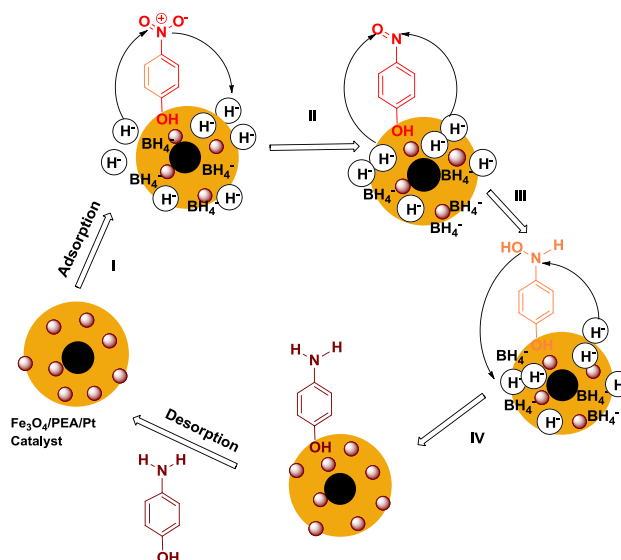


Fig. 7 Photograph for the magnetic separation of the $\text{Fe}_3\text{O}_4/\text{PEA}/\text{Pt}$ nanocomposite

4.2 Mechanism for the catalytic reduction of *p*-nitrophenol

The actual mechanism for the reduction of *p*-nitrophenol using platinum nanoparticle immobilized on poly (epoxyamine) coated iron oxide nanoparticle catalyst has described in Scheme 3. The typical mechanism involves the steps such as (I) adsorption of the borohydride anion and *p*-nitrophenol on the surface of the platinum nanoparticle, (II) formation of *p*-nitrosophenol, (III) formation of *p*-hydroxyaminophenol, (IV) hydride transfer for the formation of *p*-aminophenol compound, (V) desorption of the product *p*-aminophenol and borohydride ions [26, 27].



Scheme 3 Proposed mechanism for the catalytic reduction of *p*-nitrophenol to *p*-aminophenol

5 Conclusion

We have successfully demonstrated the one-pot synthesis of magnetite–poly (epoxyamine) nanocomposite with controlled particle size, uniform shape and fine dispersion. Platinum nanoparticles were decorated onto magnetic polymer matrix. The synthesized nanocomposite was proved to be an efficient catalyst for the reduction of *p*-nitrophenol, also the recycle efficiency of catalyst was examined up to five cycles without any significant loss of their catalytic activity. Hence, the nanocomposite material will replace the existing catalyst for reduction reactions in industries and further many organic transformations can be achieved.

Acknowledgements RR thank SERB, India for financial support (EEQ/2017/000374). We dedicate this research work to our beloved teacher Dr. M. Selvaraj, Principal, Guru Nanak College. We acknowledge HRTEM facility at SRMIST set up with support from MNRE (Project No. 31/03/2014-15/PVSE-R&D), GoI. Analytical facilities rendered from IIT Kanpur, IIT Guwahati, MNIT Jaipur are gratefully acknowledged.

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

1. Yoon HJ, Lim TG, Kim JH et al (2014) Fabrication of multifunctional layer-by-layer nanocapsules toward the design of therapeutic nanoplatform. *Biomacromolecules* 15:1382–1389. <https://doi.org/10.1021/bm401928f>
2. Joseph A, Villaraza L, Bumb A, Brechbiel MW (2010) Macromolecules, dendrimers, and nanomaterials in magnetic resonance imaging: the interplay between size, function, and pharmacokinetics. *Chem Rev* 110:2921–2959. <https://doi.org/10.1021/cr900232t>
3. Wang Q, Jiao L, Du H et al (2014) Fe₃O₄ nanoparticles grown on graphene as advanced electrode materials for supercapacitors. *J Power Sources* 245:101–106. <https://doi.org/10.1016/j.jpowsour.2013.06.035>
4. Baig NBR, Varma RS (2013) Magnetically retrievable catalysts for organic synthesis. *Chem Commun* 49:752–770. <https://doi.org/10.1039/C2CC35663E>
5. Shylesh S, Schünemann V, Thiel WR (2010) Magnetically separable nanocatalysts: bridges between homogeneous and heterogeneous catalysis. *Angew Chem Int Ed* 49:3428–3459. <https://doi.org/10.1002/anie.200905684>
6. Teja AS, Koh P (2009) Synthesis, properties, and applications of magnetic iron oxide nanoparticles. *Prog Cryst Growth Charact Mater* 55:22–45. <https://doi.org/10.1016/j.pcrysgrow.2008.08.003>
7. Aslam M, Schultz EA, Sun T et al (2007) Synthesis of amine stabilised aqueous colloidal iron oxide nanoparticles. *Cryst Growth Des* 7:471–475. <https://doi.org/10.1021/cg060656p>
8. Liu X, Wang L (2004) A one-pot synthesis of oleic acid end-capped temperature- and pH-sensitive amphiphilic polymers. *Biomaterials* 25:1929–1936. <https://doi.org/10.1016/j.biomaterials.2003.08.023>
9. Frankamp BL, Fischer NO, Hong R et al (2006) Surface modification using cubic silsesquioxane ligands. Facile synthesis of water-soluble metal oxide nanoparticles. *Chem Mater*. <https://doi.org/10.1021/cm052205i>
10. Kainz QM, Reiser O (2013) Polymer- and dendrimer-coated magnetic nanoparticles as versatile supports for catalysts, scavengers, and reagents. *Acc Chem Res* 47:667–677. <https://doi.org/10.1021/ar400236y>
11. Bronstein LM, Shifrina ZB (2011) Dendrimers as encapsulating, stabilizing, or directing agents for inorganic nanoparticles. *Chem Rev* 111:5301–5344. <https://doi.org/10.1021/cr2000724>
12. Wang L, Bao J, Wang L et al (2006) One-pot synthesis and bio-application of amine-functionalized magnetite. *Chem A Eur J* 12:6341–6347. <https://doi.org/10.1002/chem.200501334>
13. Adenier A, Cabet-deliry E, Lalot T, Pinson J (2002) Attachment of polymers to organic moieties covalently bonded to iron surfaces. *Chem Mater* 14:4576–4585. <https://doi.org/10.1021/cm0211397>
14. Lee J, Lee Y, Youn JK et al (2008) Simple synthesis of functionalized superparamagnetic magnetite/silica core/shell nanoparticles and their application as magnetically separable high-performance biocatalysts. *Small* 4:143–152. <https://doi.org/10.1002/smll.200700456>
15. Li J, Zheng L, Cai H et al (2013) Facile one-pot synthesis of Fe₃O₄@Au composite nanoparticles for dual-mode MR/CT imaging applications. *ACS Appl Mater Interfaces* 5:10357–10366. <https://doi.org/10.1021/am4034526>
16. Kim LJ, Jang JW, Park JW (2014) Nano TiO₂-functionalized magnetic-cored dendrimer as a photocatalyst. *Appl Catal B Environ* 147:973–979. <https://doi.org/10.1016/j.apcatb.2013.10.024>
17. Hazarika A, Deka BK, Kim D et al (2017) Microwave-synthesized freestanding iron-carbon nanotubes on polyester composites of woven Kevlar fibre and silver nanoparticle-decorated graphene. *Sci Rep* 7:1–11. <https://doi.org/10.1038/srep40386>
18. Nigam S, Chandra S, Newgreen DF et al (2014) Poly(ethylene glycol)-modified PAMAM-Fe₃O₄-doxorubicin triads with the potential for improved therapeutic efficacy: generation-dependent increased drug loading and retention at neutral pH and increased release at acidic pH. *Langmuir* 30:1004–1011. <https://doi.org/10.1021/la404246h>
19. Xie Y, Sougrat R, Nunes SP (2015) Synthesis and characterization of polystyrene coated iron oxide nanoparticles and asymmetric assemblies by phase inversion. *J Appl Polym Sci* 41368:1–11. <https://doi.org/10.1002/app.41368>
20. Murugan E, Rangasamy R (2010) Synthesis, characterization, and heterogeneous catalysis of polymer-supported poly(propyleneimine) dendrimer stabilized gold nanoparticle catalyst EAGAMBARAM. *J Polym Sci Part A Polym Chem* 48:2525–2532. <https://doi.org/10.1002/pola.24028>
21. Das TK, Bhawal P, Ganguly S et al (2018) A facile green synthesis of amino acid boosted Ag decorated reduced graphene oxide nanocomposites and its catalytic activity towards 4-nitrophenol reduction. *Surf Interfaces* 13:79–91. <https://doi.org/10.1016/j.surfin.2018.08.004>
22. Das TK, Ganguly S, Bhawal P et al (2018) A facile green synthesis of silver nanoparticles decorated silica nanocomposites using mussel inspired polydopamine chemistry and assessment its catalytic activity. *J Environ Chem Eng*. <https://doi.org/10.1016/j.jece.2018.10.067>
23. Kanti T, Sayan D, Poushali G et al (2018) Mussel inspired green synthesis of silver nanoparticles—decorated halloysite nanotube using dopamine: characterization and evaluation of its

- catalytic activity. *Appl Nanosci.* <https://doi.org/10.1007/s13204-018-0658-3>
24. Tepzz T, Reticules PDA (2006) *Eur. Pat. EP 1 831 266 B1* [0001]2010, 1, 1 WO 2006/043984 (27.04.2006 Gazette 2006/17). <https://doi.org/10.1007/s42452-019-1137-5>
 25. Abu-Reziq R, Wang D, Post M, Alper H (2007) Platinum nanoparticles supported on ionic liquid-modified magnetic nanoparticles: selective hydrogenation catalysts. *Adv Synth Catal* 349:2145–2150. <https://doi.org/10.1002/adsc.200700129>
 26. Das TK, Ganguly S, Remanan S, Ch N (2019) Temperature-dependent study of catalytic Ag nanoparticles entrapped resin nanocomposite towards reduction of 4-nitrophenol. *Chem Sel* 4:3665–3671. <https://doi.org/10.1002/slct.201900470>
 27. Kariper İA, Oğuzhan M, Zafer Ç (2018) Heterogeneous Au/Ru hybrid nanoparticle decorated graphene oxide nanosheet catalyst for the catalytic reduction of nitroaromatics. *Res Chem Intermed.* <https://doi.org/10.1007/s11164-018-3644-1>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.