



SYNTHESIS AND CATALYTIC REDUCTION OF 4-NITROPHENOL USING AG NANOPARTICLE INCORPORATED POLYDOPAMINE STABILIZED Fe_3O_4 MAGNETIC NANOPARTICLES

Kalaivasan Natarajan ¹, Praveen Raj Perumal ²

¹ Department of Chemistry, Thanthai Periyar Government Institute of Technology, Vellore, Tamil Nadu, India- 632002.

² Department of Mechanical Engineering, Thanthai Periyar Government Institute of Technology, Vellore, Tamil Nadu, India- 632002.

ABSTRACT

A novel and facile strategy for the synthesis of $Fe_3O_4@Ag$ hybrid nanoparticles with the assistance of dopamine surface functionalization was brought forward. The surface of the Fe_3O_4 particles was first functionalized by polydopamine (PDA), and silver was then plated on the Fe_3O_4/PDA surface by electroless plating. The method had the advantage of being simple, nontoxic, controllable, and cost effective. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) were used to study the crystal structure, surface chemical compositions, and functional groups, respectively, of the hybrid nanoparticles. The results indicated that PDA was successfully deposited on the surfaces of $\alpha-Fe_3O_4$ nanoparticles without affecting their crystal structures. The size and uniformity of the silver nanoparticles could be well controlled by adjusting the concentrations of silver nitrate ($AgNO_3$) and polydopamine (PDA). The catalytic behaviour of silver nanoparticles also investigated to reduce 4-Nitrophenol in presence of $NaBH_4$. The catalytic reaction is found to be pseudo-first order and the resulting rate constant is comparable with previous reported results. The silver nanoparticles showed good stability on the Fe_2O_3 substrate even after they were subjected to an ultrasonic experiment for 30 min.

Keywords: Polydopamine (PDA), silver nanoparticles, stabilized Fe_3O_4 magnetic nanoparticles, 4-Nitrophenol

1. Introduction

Nanoparticle are submicron moieties (diameters ranging from 1 to 100 nm) according to the used term, although there are examples of NPs several hundreds of nanometers in size made of inorganic or organic materials, which have many novel properties compared with the bulk materials [1, 2]. On this basis, magnetic NPs have many unique magnetic properties such as super paramagnetic, high coactivity, low Curie temperature, high magnetic susceptibility, etc. Magnetic NPs are of great interest for researchers from a broad range of disciplines, including magnetic fluids, data storage, catalysis, and bioapplications [3, 4]. Magnetic iron oxide NPs became the strong candidates, and the application of small iron oxide NPs in invitro diagnostics has been practiced for nearly half a century [4, 5, and 11]. These strategies comprise grafting of or coating with organic molecules, including small organic molecules or surfactants, polymers, and biomolecules, or coating with an inorganic layer, such as silica, metal or nonmetal elementary substance, metal oxide or metal sulfide.

Fe_3O_4 , one of the most commonly occurring materials in the earth, is of technological and scientific importance as pigments, catalysts, and magnetic materials [6, 7, and 9]. Up to now, a variety of methods for the preparation of $\text{Fe}_3\text{O}_4@Ag$ nanoparticles have been reported, these particles not only retain their unique semiconducting and magnetic properties but also exhibit enhanced magnetic, chemical, optical, and catalytic properties compared with the individual components [8, 10]. Sun et al. [11] have reported a one-step fabrication of $\text{Fe}_3\text{O}_4@Ag$ core-shell composite nanoparticles at low temperatures. In the present work, a facile and environment-friendly approach involving dopamine oxide polymerization was used to prepare $\text{Fe}_3\text{O}_4@Ag$ core-shell nanoparticles. Polydopamine, an adherent coating, was deposited on the surface of the Fe_3O_4 nanoparticles by in suit spontaneous oxidative polymerization, followed by electrolessplating of silver on the functionalized Fe_3O_4 surfaces. The crystal structure, chemical compositions, morphology and size of the nanoparticles have been investigated. Herein we report a novel strategy for synthesis and catalytic reduction of 4-nitrophenol using Ag nanoparticle incorporated polydopamine stabilized Fe_3O_4 magnetic nanoparticles.

2. Experimental Section

2.1. Chemicals.

Anhydrous iron (III) chloride (FeCl_3) was purchased from Acros organics. Anhydrous sodium acetate (NaOAc), ethylene glycol (EG), silver nitrate (AgNO_3) and Dopamine hydrochloride. Ultrapure water prepared with a Millipore Milli-Q water purification system (MA, USA) was used for all experiments. The solvent was used without further purification. 2-Amino-2-hydroxy methylpropane-1, 3-diol (Tris). Potassium chloride (AR), Sodium phosphate and sodium dihydrogen phosphate was purchased from SRL chemicals, India.

2.2. Synthesis of Fe₃O₄ magnetic nanoparticles.

The magnetic particles were prepared via solvothermal method. (1) Briefly 1.36g of FeCl₃.6H₂O and 3.6g of anhydrous sodium acetate were dissolved in 50mL of Ethylene Glycol under vigorously stirring for 5hrs. The obtained yellow homogeneous solution was transferred to a Teflon-lined stainless steel autoclave. The autoclave was heated at 200 °C for 8 hrs and then cooled to room temperature (25 °C). The obtained black products were washed with ethanol for ten times and then dried in vacuum at room temperature.

2.3. Synthesis of Fe₃O₄@Polydopamine (PDA) Core–Shell nanoparticles.

To prepare PDA@Fe₃O₄ composites, 0.4g of the as prepared Fe₃O₄ was dispersed in 200mL of Dopamine solution (2mg mL⁻¹, pH 8.5, 10mM Tris buffer), and allowed to proceed for 24 hrs under stirring at a room temperature.

The resulting product was separated and collected with magnet, followed by washing with deionised water three times and then dried in vacuum at room temperature.

2.4. Synthesis of Fe₃O₄@PDA@Ag nanoparticles.

The Ag Nanoparticles were deposited on the PDA@Fe₃O₄ microspheres by the mixing of 0.02g of AgNO₃ aqueous solution (80mL) with PDA@Fe₃O₄ and stirred for 24 hrs at a room temperature.

The resultant nanocomposite was separated and rinsed with deionised water for at least three times, and dried under vacuum for further use. Then, Fe₃O₄@PDA@Ag microspheres were obtained.

2.5. Preparation of Phosphate Buffer solution

Buffer solution with pH of 7 was prepared by mixing of 0.1M NaH₂PO₄ and 0.1M Na₂HPO₄ in 250mL standard flask using Milli-Q water. The pH of the solution was tested using Elico-pH meter at 25°C.

2.6. Catalytic reduction of 4-nitrophenol using Fe₃O₄@PDA@AgNPs

Typically, 0.05 mg of catalyst was mixed to 2.5 mL of 4-NP aqueous solution (2.5 mmolar) in a beaker and stirred constantly for 1 min. Next, 25 mL of freshly prepared aqueous NaBH₄ (250 mmolar) was added into the mixture. The concentration of 4-NP in the supernatant was monitored by UV–vis spectroscopy at wavelength of 400 nm. At certain intervals, the mixture was centrifuged and 1.0 mL of the solution extracted then diluted to 25 mL for further UV–vis absorption analysis.

2.7. Instrumentation

UV spectrometer (UV-VIS; Hitachi inc., U-3900) was used to measure the optical absorption properties of BGO. Powder X-Ray Diffraction was collected at room temperature on Shimadzu XRD-6000 diffractometer with a graphite filtered Cu-K α source (0.154 nm), 40 kV, and 30 mA. Fourier transform infrared (FT-IR) spectra (4000-400 cm⁻¹) in KBr were recorded using Nicolet Nexus 670 FT-IR spectrometer (Nicolet, USA).

1. Results and Discussion

The procedure for the preparation of α -Fe₃O₄@Ag core-shell structure nanoparticles by polydopamine-assisted electroless silver plating. It consists of the deposition of PDA on the surfaces of α -Fe₃O₄ nanoparticles and the electroless plating of silver nanoparticles onto the α -Fe₃O₄/PDA surfaces. To date, the mechanism of dopamine in situ spontaneous oxidative polymerization is still not clear. They reported that the oxidation of dopamine, as occurs during the curing of secreted mussel glue, dramatically results in the formation of high-strength irreversible covalent bonds on an organic surface. The synthesized compound characterized by UV-Vis Spectroscopy, X-Ray diffraction, FT-IR, nitrophenol reduction, photocatalytic activity and electrochemical studies.

3.1 Characterization of Fe₃O₄@PDA@AgNPs

Fig 1 shows the UV-Vis spectra for Fe₃O₄@PDA@AgNPs. The UV-Vis spectra Fig 1(a&b) shows band in the wavelength region of 278 nm for Fe₃O₄@PDA and (c) shows band in the wavelength region of 375 nm for Fe₃O₄@PDA@AgNPs. These adsorbent bands demonstrate the presence of Fe₃O₄@PDA@AgNPs. Fig.2 shows the pattern of the Fe₃O₄@PDA shows peaks at 2 θ values of 32°, 57.1° and 63.2° corresponding to the reflections of the (220), (511) and (440) crystalline planes indicates face-centered cubic (fcc) structure (JCPDS card No.19-629). In Fe₃O₄@PDA@Ag nanoparticles shows peaks at 2 θ values of 36°, 46.1° and 78.2° corresponding to the reflections of the (111), (200) and (311) crystalline planes, respectively, of the face-centered cubic (fcc) crystal structure of Ag, which was consistent with ASTM standard (JCPDS Card No. 04-0783) and confirmed that the Ag nanoparticles on the surface of the composite nanoparticles exist in the zero valent state.

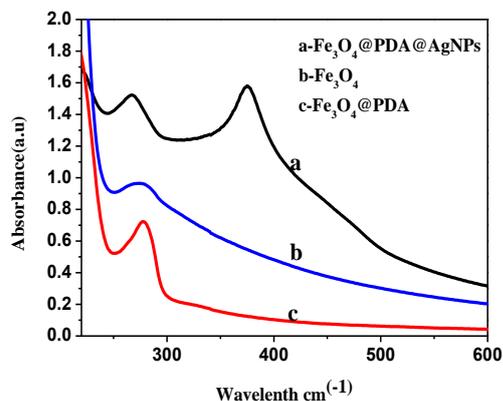


Fig. 1: UV-Vis (a) $\text{Fe}_3\text{O}_4@PDA@AgNPs$ and

(b) Fe_3O_4 and (c) $\text{Fe}_3\text{O}_4@PDA$

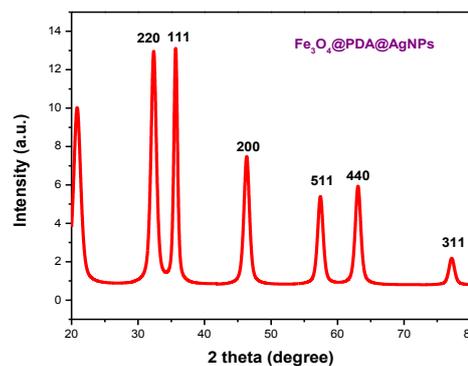


Fig. 2: XRD Pattern for $\text{Fe}_3\text{O}_4@PDA@AgNPs$

Fig 3 shows the FT-IR spectra of (C) $\text{Fe}_3\text{O}_4@PDA@AgNPs$. The absorption peaks at $2,976\text{cm}^{-1}$ were attributed to the asymmetric CH_2 stretching and the symmetric CH_2 stretching, respectively. The intense peak at $1,640\text{cm}^{-1}$ was due to the overlapping of the absorption bands of the carboxyl groups. The aromatic ring stretching vibration, phenolic $-\text{OH}$ and amide N-H stretching frequencies which indicates that the iron oxide nanoparticles are modified with polydopamine. These peaks are shifted in $\text{Fe}_3\text{O}_4@PAD@AgNPs$ which confirms the modification of $\text{Fe}_3\text{O}_4@PAD$ by silver nanoparticles.

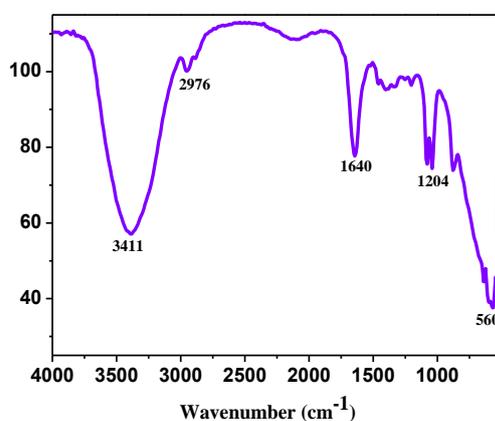


Fig. 3: FT-IR Spectra of $\text{Fe}_3\text{O}_4@PDA@AgNPs$

3.2. Evaluation of the catalytic activity of $\text{Fe}_3\text{O}_4@PDA@AgNPs$ through the reduction of 4-nitrophenol

4-NP solution exhibits a strong absorption peak at 317 nm in neutral or acidic conditions. Upon the addition of NaBH_4 , a red shift of the peak of 4-NP to 400 nm was observed. This is due to

formation of 4-nitrophenolate ions under alkaline condition with NaBH_4 . As shown in Fig 4 (a and b), during the reaction process, the absorption intensity of 4-NP at 400 nm decreases, accompanied by the appearance of the new peaks at about 300 nm corresponding to 4-AP. The absorption peak at 400 nm is fully disappeared after about 60 s in the presence of $\text{Fe}_3\text{O}_4@\text{PDA}@Ag\text{NPs}$ catalyst (7.0 mg). In the absence of catalyst, the reduction of 4-NP does not proceed within 3 h.

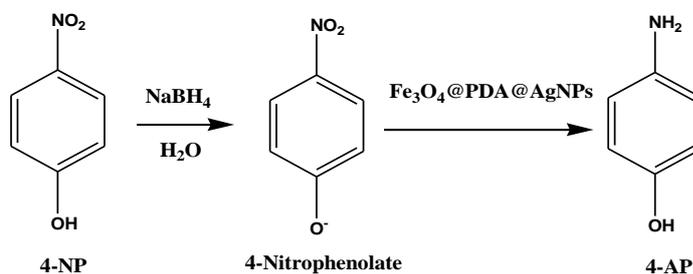


Fig.4: (a) The absorption intensity of 4-NP at 400 nm decreases, accompanied by the appearance of the new peaks at about 300 nm corresponding to 4-AP

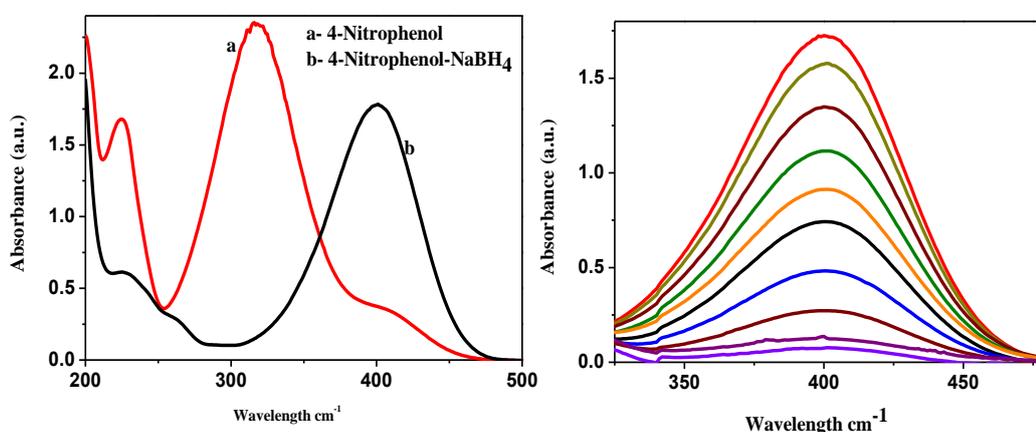


Fig. 4: (b) (A) UV-vis spectra for MPs in catalytic reduction by NaBH_4 and $\text{Fe}_3\text{O}_4@\text{PDA}$ Ag core-shell microspheres. (B) First-order kinetics plot of catalytic reduction in the presence $\text{Fe}_3\text{O}_4@\text{PDA}-Ag$ core-shell microspheres.

In our reaction system, the concentration of NaBH_4 is significantly higher than that of 4-NP and can be considered as constant during the reaction period. So, the pseudo-first-order kinetics could be applied to evaluate the rate constant for 4-NP reduction [13]. The kinetic equation for the reduction could be written as

$$dC_t/dt = dA_t/dt = kC_t \text{ or } \ln(C_t/C_0) = \ln(A_t/A_0) = -kt$$

Fig.5 shows a linear correlation between $\ln(A_t/A_0)$ and the reaction time at room temperature. The pseudo first-order rate constant (k) is 0.055 s^{-1} , which is comparable to those reported previously [14].

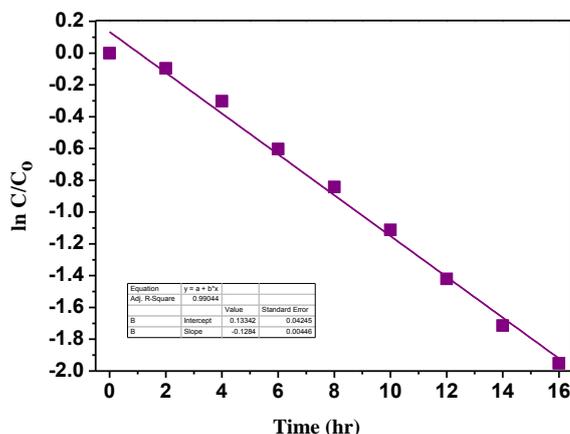


Fig. 5: Linear correlation plot

4. Conclusion

Fe₃O₄@AgNPs was successfully synthesized by polydopamine assisted electroless plating. Dopamine could be spontaneously polymerized on the surface of the Fe₃O₄ nanoparticles in an oxygen environment. The polydopamine shell with well preserved catechol and indole functional groups was used not only as the adhesion layer between the Fe₃O₄ substrate and Ag nanoparticles, but also as the chemisorptions sites for the silver particles during electroless silver plating. The silver nanoparticles were uniformly dispersed on the surface of the Fe₃O₄/PDA substrate. The size and uniformity of the silver nanoparticles could be well controlled by adjusting the concentrations of AgNO₃. The synthesized composite material was used for catalytic reduction of 4-nitrophenol using Ag nanoparticle incorporated polydopamine stabilized Fe₃O₄ magnetic nanoparticles. It also exhibit bifunctional properties with high magnetization and excellent catalytic activity toward P- Nitrophenol reduction. The high catalytic activity of the catalyst might be attributed to its high surface area and the synergistic effect on the delivery of electrons between Ag NPs and Fe₃O₄.

References

1. LaConte. L, Nitin. N, Bao. G, *Mater. Today*, **2005**, 32, 8, doi: 10.1016/S1369-7021(05)00893-X
2. Patel. D, Moon. J.Y, Chang. Y, Kim. T.J, Lee. G.H, *Colloid Surf.* **2008**, 91, 313–314, doi:10.1016/j.colsurfa.2007.04.078
3. Gupta. A.K, Gupta. M, *Biomaterials*, **2005**, 3995, 26, doi:10.1016/j.biomaterials.2004.10.012
4. Cornell. R.M, Schwertmann. U, *The Iron Oxides: Structures, Properties, Reactions, Occurrences and Uses*, **2003**, (Wiley-VCH, Weinheim).
5. Cordova. G. et al., *Nano Biomedicine and Engineering*, **2014**, 6, 31.
6. Xie. J, and Jon. S, *Theranostics*, **2012**, 2, 122.
7. Laurent S. et al., *Chem rev.* **2008**, 108, 2064.
8. Simon. J. D, Peles, D. N. *Acc. Chem. Res.* **2010**, 43, 1452.
9. Mitra. S, Das. S, Mandal. K, Chaudhuri. S, Synthesis of - Fe₂O₃ nanocrystal in its different morphological attributes: growth mechanism, optical and magnetic properties, *Nanotechnology*, **2007**, 18 (27), 275608.

10. Hong. R.Y, Fu. H.P, Di. G.Q, Zheng. Y, Wei. D.G, Facile route to - Fe₂O₃/SiO₂ nanocomposite used as a precursor of magnetic fluid, *Materials Chemistry and Physics*, **2008**, 108 (1), 132.
11. Sun. Y.Y, Guo. G.Z, Yang. B.H, Zhou. X, Liu. Y.Q, Zhao. G.Z, One-step fabrication of Fe₂O₃@Ag core-shell composite nanoparticles at low temperature, *Journal of Non-Crystalline Solids*, **2011**, 357(3), 1085.
12. Lee. H, Dellatore. S.M, Miller. W.M, Messersmith. P.B, Mussel-inspired surface chemistry for multifunctional coatings, *Science*, **2007**, 318 (5849), 426.
13. Li. S, Guo. S, Yang. H, Gou. G, Ren. R, Li. J, Dong. Z, Jin. J, Ma. J, Hazard. *J. Mater.* **2014**, 270, 11.
14. 49. Choi. Y, Son Bae. H, Seo. E, Jang. S, Hyun Park. K, Kim. B.S, *J. Mater. Chem.*, **2011**, 21, 15431