

Catalytic reduction of 4-Nitrophenol by Poly (ϵ -caprolactone) encapsulated Ag and Fe₃O₄ nanocomposite systems

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ABSTRACT: The catalytic reduction of p-nitrophenol (NiP) was carried out at room temperature with the aid of sodiumborohydride (NaBH₄) in the presence of different polymer nanocomposite systems. The reduction of NiP into aminophenol (AP) was quantitatively monitored with the help of UV-visible spectrophotometer. From the UV-visible absorbance value, the apparent rate constant (k_{app}) was calculated. The FESEM images confirmed the nanosize of the Ag and Fe₃O₄ systems. The k_{app} values were compared based on the size of the nanohybrids.

Key words: Polymer nanocomposite, p-nitrophenol, catalytic reduction, FESEM, k_{app}

INTRODUCTION

Recently, the material scientists turned their attention towards the development of novel homogeneous and heterogeneous catalysts for the reduction purpose. They need a catalyst with a dual behavior such as not only act as a simple catalyst to catalyze the reaction but also sometimes it should initiate the ring opening polymerization (ROP) of ϵ -caprolactone (CL). Such a catalyst with dual activity is carried out in the present investigation. Reduction of NiP is a standard model for the catalyst system because it follows the pseudo first order

kinetics. Here, the catalyst is first functionalized with dye moiety followed by the ROP of CL. Meanwhile, let us do review the available literature in this regard. In 2015, Gu et al [1] reported the Au nanoparticle (NP) mediated reduction of NiP. Hydrogenation of NiP was carried out in the presence of Ni/TiO₂ catalyst system [2]. For the reduction of NiP different catalysts like Iron niobate [3], Au NP [4,5], layered double hydroxides [6], Ag [7], quantum of clusters of Ag [8], Au NP supported titania [9] and hydroxyapatite [10] were used. By thorough literature survey we could not

found any report on NiP reduction using PCL encapsulated Fe_3O_4 and Ag nanocomposites. Reduction activity of fluorescent Fe_3O_4 and Ag is the novelty of the present investigation.

EXPERIMENTAL

Materials and methods

Sodiumborohydride (NaBH_4 , Himedia, India), nitrophenol (NiP, Himedia) and tetrahydrofuran (THF, CDH, India) solvent were purchased and used as received. Double distilled water (DDW) was used for the purpose of solution preparation. Polymer nanocomposite samples were received from our research team and followed the procedure as mentioned in the literature [11-13].

Catalytic reduction study

Two mg of NP was dissolved in 10 mL THF:Water (1:1) mixture solvent. 0.10g of PCL-Ag/AF or PCL- Fe_3O_4 /AF and 15 mg of NaBH_4 were added with the same 10 mL solvent mixture. From the reaction mixture, 2 mL aliquot was taken and subjected to UV-visible spectral measurement at a regular interval of time. The absorbance at 404.6 nm was regularly monitored.

Characterization Techniques

UV-visible spectrum was measured by dissolving the samples in THF solvent. Shimadzu 3600 NIR, Japan instrument is used from 250-600 nm. FESEM was used to examine morphological behavior of polymer nanocomposites with the help of FESEM – Hitachi S4800 Japan, instrument.

RESULTS AND DISCUSSION

The main aim of the present investigation is to prove the surface catalytic effect of both Ag and Fe_3O_4 NP. In order to prove the same, the reduction of NiP with the aid of NaBH_4 was carried out at room temperature at different time interval by using different capping agents. The catalytic reduction of NiP was quantitatively monitored by UV-visible spectroscopy. Figure 1(a-i) indicates the UV-visible spectrum of NiP at different time interval in the presence of PCL-Ag/AF system. The spectrum shows one peak at 404.6 nm corresponding to the NiP [10]. While increasing the reduction reaction time, the absorbance at 404.6 nm was slowly reduced. This is due to the conversion of NiP into AP. The reduction rate constant (k_{app}) was determined by plotting time against $\ln(C/C_0)$ (Fig. 1j). From the slope value the k_{app} value was calculated as $9.90 \times 10^{-3} \text{ sec}^{-1}$. The intercept value yielded the induction time (T_i) as 0.039 sec (Table 1). Both the k_{app} and T_i confirmed the surface catalytic activity of Ag NP. A very high surface catalytic effect is possible only when the Ag NP should be existed in the nanosize. Because in the absence of Ag NP, the catalytic reduction was absent. In order to confirm the nanosize of the Ag, the FESEM (Fig. 1k) image was recorded and the confirmed the size of Ag less than 100 nm. Actually, the size of Ag NP was varied between 40 and 100 nm. The circled area confirmed the same.

The second system is Fe_3O_4 /AF system. The UV-visible spectrum of NiP in the presence of Fe_3O_4 /AF-PCL system is shown in Fig. 2 (a-k). Here also the

reduction reaction was carried out under identical experimental condition as mentioned above. The present system too exhibited the same trend (i.e.) while increasing the reduction reaction time, the absorbance at 404.6 nm was slowly decreased due to the reduction of NiP into AP. Further, the k_{app} was determined from the plot of time against $\ln(C/C_0)$ (Fig. 2l) as $3.32 \times 10^{-3} \text{ sec}^{-1}$ (Table 1). In comparison, the Ag NP system exhibited ~ 3 times higher k_{app} . This is ascribed to the size of the Ag NP. This is in accordance with the literature report [10]. Table 1 confirmed the slow induction time for the present system (0.470 sec).

The second aim of the present investigation is to test the effect of different functional groups on the surface functionalization and catalytic reduction reaction. The AF contains amine, aminocation and sulphonate like functional groups. AR contains ketone, hydroxyl and sulphonate groups whereas Safranin contains amine, tertiary amine and tertiary amine cation like functional groups. So for, the k_{app} and T_i were compared for Ag and Fe_3O_4 nanocomposite systems. The next target is to analyze the influence of functional groups on the k_{app} and T_i . While increasing the reaction time the absorbance at 404.6 nm {Fig. 3 (a-o)} was found to be continuously decreased. This is due to the conversion of NiP into AP [10]. The k_{app} (Table 1) can be determined by plotting time versus $\ln(C/C_0)$ (Fig. 3p) as $2.85 \times 10^{-3} \text{ sec}^{-1}$. The T_i was determined from the intercept as

0.188 sec. When compared with the Ag NP, the Fe_3O_4 NP system availed higher T_i value. When compared among the Fe_3O_4 NP system, the present system yielded lowest T_i . This may be associated with the functional groups like keto and hydroxyl groups, because they are ready to offer hydrogen bonding.

The last system for comparison is PCL- Fe_3O_4 /Safranin. Here also both k_{app} and T_i were determined. The UV-visible spectrum taken at different time interval is given in Fig. 4 (a-h). The k_{app} and T_i were determined from time versus $\ln(C/C_0)$ (Fig. 4i) plot as $5.75 \times 10^{-3} \text{ sec}^{-1}$ and 0.234 sec respectively (Table 1). Among the Fe_3O_4 NP systems, the Safranin functionalized Fe_3O_4 system yielded the highest k_{app} . This is due to the functional groups. But the Fe_3O_4 -AR system produced the lowest T_i . It means, Fe_3O_4 -Safranin catalyzed the reduction reaction immediately in a very fast manner.

From the above study, the following queue was made based on the k_{app} :

Ag-AF > Fe_3O_4 -Safranin > Fe_3O_4 -AF > Fe_3O_4 -AR

Based on the T_i value the following queue was made:

Ag-AF > Fe_3O_4 -AR > Fe_3O_4 -Safranin > Fe_3O_4 -AF

CONCLUSION

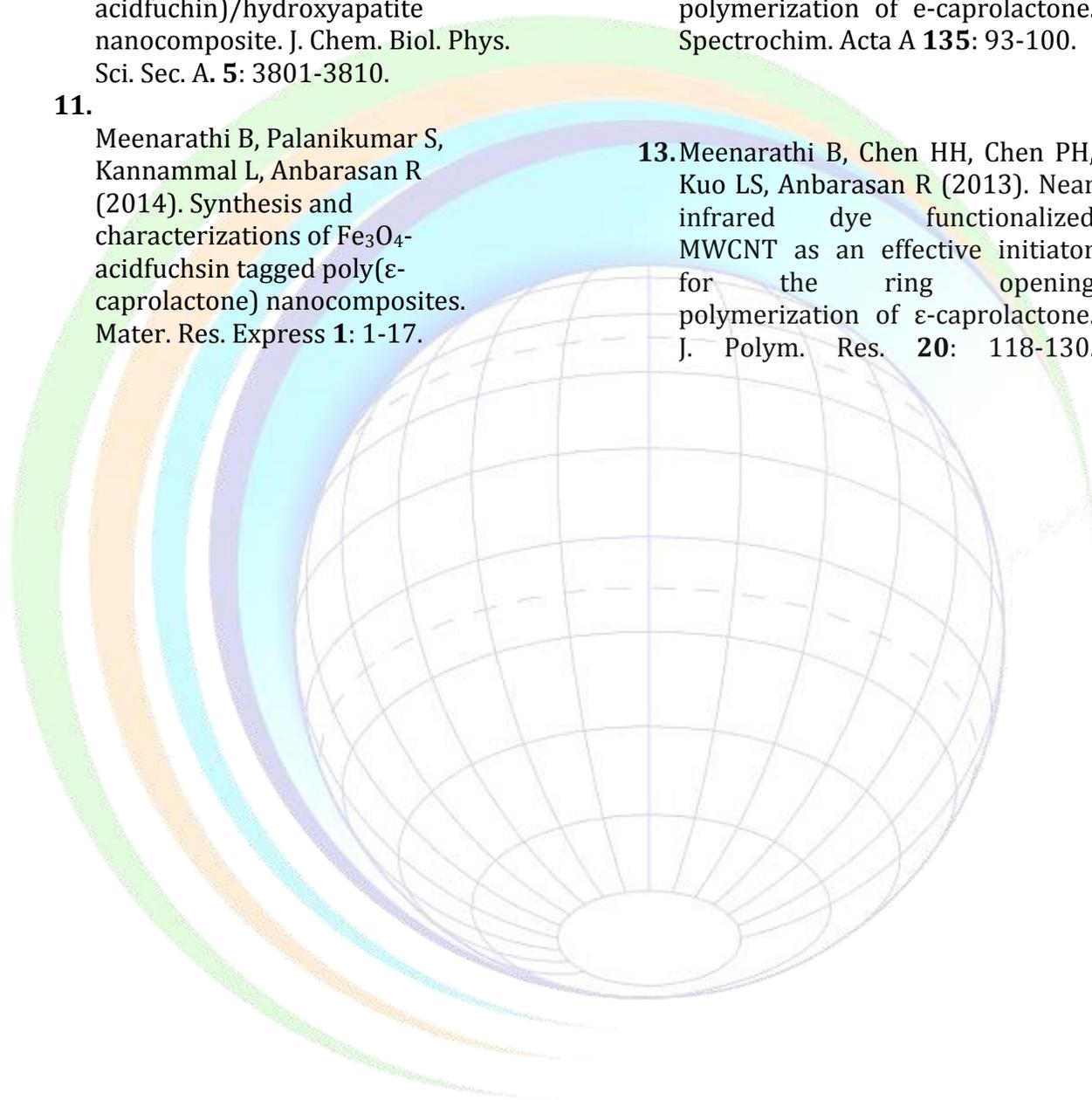
From the above comparative study the following points are presented here as conclusion. The FESEM image of PCL-

Ag/AF system confirmed the nanosize of Ag NP. The Ag NP system exhibited the high k_{app} value and with very low induction time due to the smaller size of Ag NP. The present research communication concluded that for the reduction purpose the experiment needs a smaller sized nano material with suitable functional groups.

REFERENCES

1. Gu S, Kaiser J, Marzum G, Ott A, Lu Y, Wagener P (2015). Ligand free gold nanoparticle as a reference material for kinetic modeling of catalytic reduction of 4-nitrophenol. *Catal. Lett.* **145**: 1105-1112.
2. Chen R, Du Y, Xing W, Xu N (2006). The effect of titania structure on Ni/TiO₂ catalysts for p-nitrophenol hydrogenation. *Chin. J. Chem. Eng.* **14**: 665-669.
3. Ghorai TK (2015). Synthesis of spherical, mesoporous titania modified iron niobate nanoclusters for photo catalytic reduction of 4-nitrophenol, *J. Mater. Res. Technol.* **4**: 133-143.
4. Reddy GB, Madhusudhan A, Ramakrishna D, Ayodhya D, Venkatesh A, Veerabhadram G (2015). Green chemistry application for the synthesis of gold nanoparticles with gum kondagogu: characterization, catalytic and antimicrobial study. *J. Nanostruct. Chem.* **5**: 185-193.
5. Dash SS, Sikder AK, Bag BG, Bandyopadhyay S (2013). Phoenix dactylifera seed extract mediated green synthesis of gold nanoparticles and its application as a catalyst for the reduction of 4-nitrophenol to 4-aminophenol. *Int. J. Nanometer. Biostruct.* **3**: 42-46.
6. Ma H, Wang H, Wu T, Na C (2016). Highly active layered double hydroxide derived co-nano catalysts for 4-nitrophenol reduction. *Appl. Catal. B. Env.* **180**: 471-479.
7. Hsu KK, Chen DH (2014). Green synthesis and synergistic catalytic effect of Ag/reduced grapheme oxide nanocomposites. *Nanoscale Res. Lett.* **9**: 484-493.
8. Leelavathi A, Rao TUB, Pradeep T (2011). Supported quantum clusters of Ag as enhanced catalysts for reduction. *Nanoscale Res. Lett.* **6**: 123-131.
9. Yazid H, Adnam R, Farruk MA (2013). Au nanoparticle supported on titania for the reduction of 4-nitrophenol. *Ind. J. Chem.* **52A**: 184-191.

10. Sowmiya S, Sowmiya S, Kanchana K, Jeyaselvi J, Anitha M, Meenarathi B, Anbarasan R (2015). Synthesis, characterization and catalytic reduction activity of poly(epichlorohydrin-g-acidfuchin)/hydroxyapatite nanocomposite. *J. Chem. Biol. Phys. Sci. Sec. A*. **5**: 3801-3810.
11. Meenarathi B, Palanikumar S, Kannammal L, Anbarasan R (2014). Synthesis and characterizations of Fe₃O₄-acidfuchsin tagged poly(ϵ -caprolactone) nanocomposites. *Mater. Res. Express* **1**: 1-17.
12. Meenarathi B, Palanikumar S, Kannammal L, Anbarasan R (2015). Synthesis, characterization and catalytic activity of Ag-acidfuchsin nanohybrid system towards the ring opening polymerization of ϵ -caprolactone. *Spectrochim. Acta A* **135**: 93-100.
13. Meenarathi B, Chen HH, Chen PH, Kuo LS, Anbarasan R (2013). Near infrared dye functionalized MWCNT as an effective initiator for the ring opening polymerization of ϵ -caprolactone. *J. Polym. Res.* **20**: 118-130.



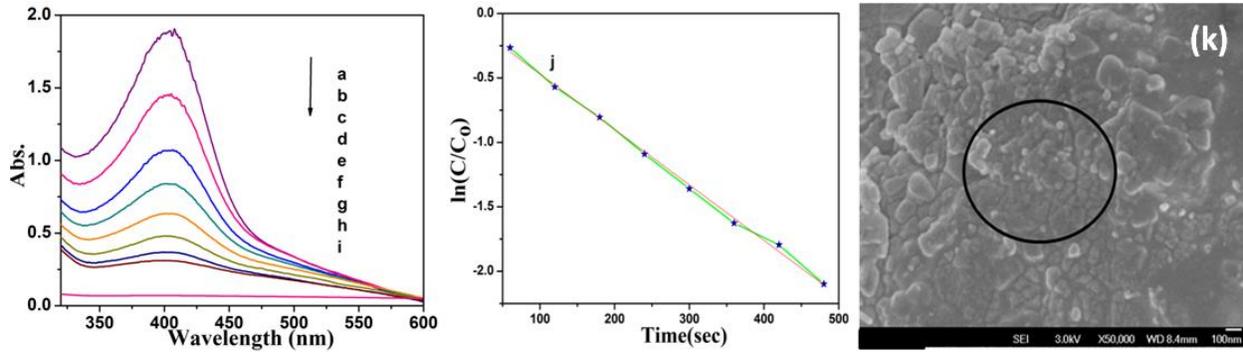


Figure 1: UV-visible spectrum of NiP at different time interval (a-i), the plot of time against $\ln(C/C_0)$ (j), FESEM image of PCL-Ag/AF nanocomposite system (k).

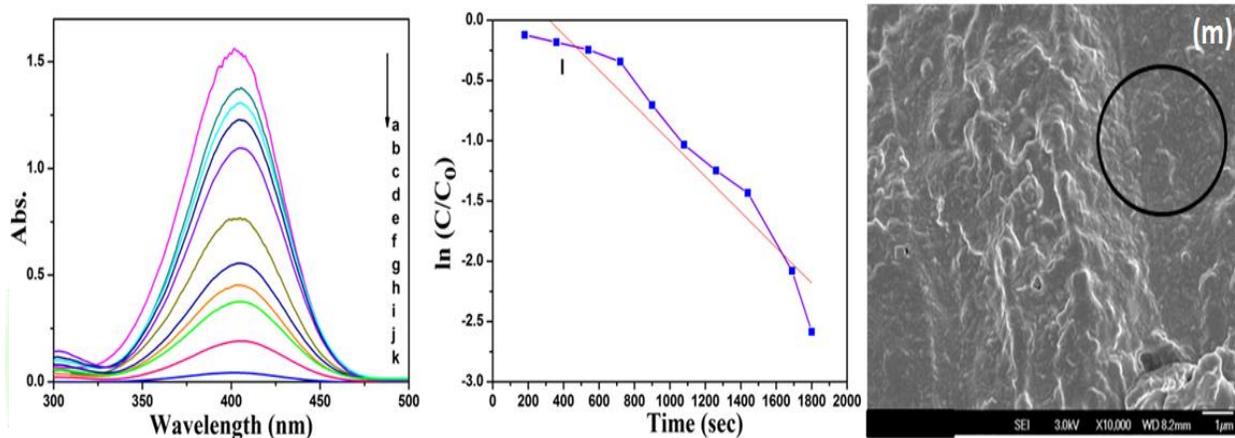


Figure 2: UV-visible spectrum of NiP at different time interval (a-k), the plot of time against $\ln(C/C_0)$ (l), FESEM image of PCL-Fe₃O₄/AF nanocomposite system (m).

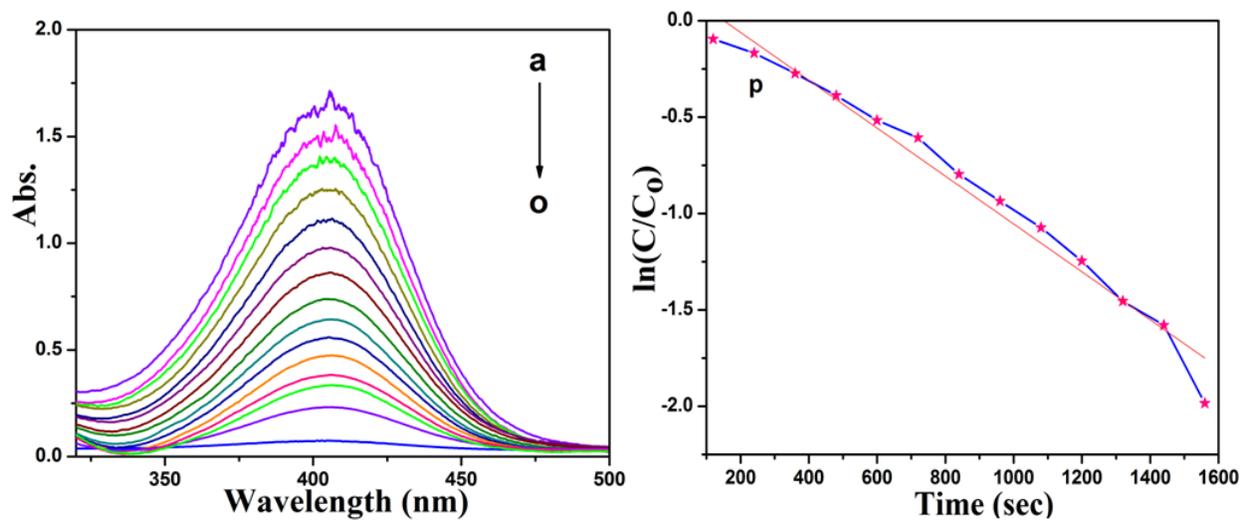


Figure 3: UV-visible spectrum of NiP at different time interval (a-o), the plot of time against $\ln(C/C_0)$ (p) of PCL-Fe₃O₄/AR nanocomposite system.

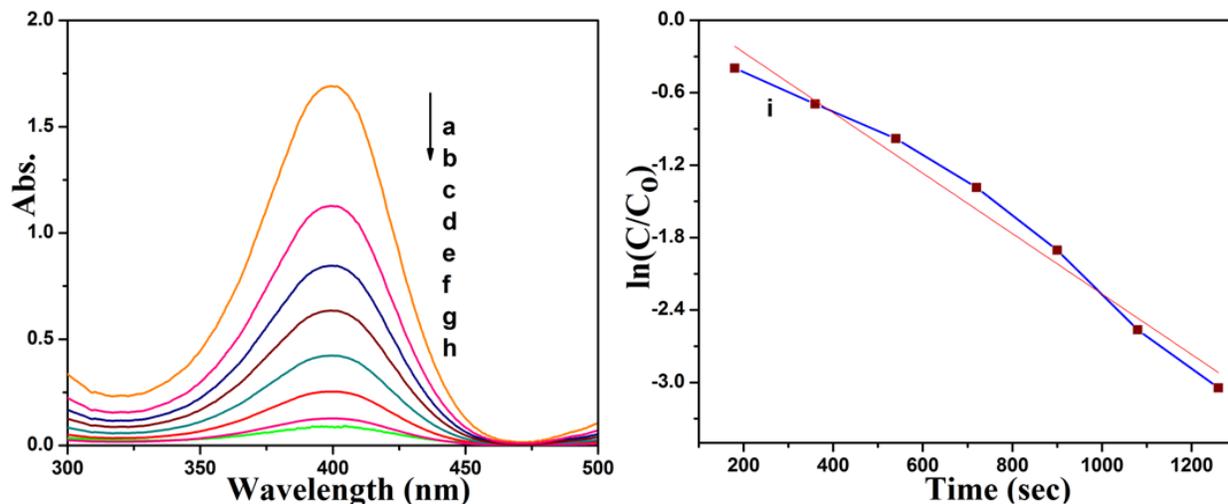


Figure 4: UV-visible spectrum of NiP at different time interval (a-h), the plot of time against $\ln(C/C_0)$ (i) of PCL-Fe₃O₄/Saf. nanocomposite system.

Table 1: Effect of nanomaterial on the apparent rate constant and induction time

System	Code No.	$k_{app} \times 10^3$ (sec ⁻¹)	Induction time (sec)
Ag-AF-PCL	1	9.90	0.039
Fe ₃ O ₄ -AF-PCL	2	3.23	0.470
Fe ₃ O ₄ -AR-PCL	3	2.85	0.188
Fe ₃ O ₄ -Saf-PCL	4	5.75	0.234