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Single Step Synthesis of Poly(o-Anisidine) Lignosulfonate Composite Protected Silver Nanoparticles and Study of Their Application on Reduction of Nitrophenol and Textile Dyes

D. Mohana Soundari, K. Pandian*

Department of Inorganic Chemistry, University of Madras, Guindy Campus, Chennai – 600 025, Tamilnadu, India.

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ABSTRACT

Lignosulfonate doped poly(o-anisidine) and poly(o-anisidine)/lignosulfonate polymer composite protected silver nanoparticles (AgNPs) were synthesized by interfacial polymerization method by mixing of an equal molar ratio of o-anisidine and lignosulfonate using silver nitrite as oxidizing agent. The polymerization reaction was carried out under reflux condition at 80 °C for 3 hours. The resulting AgNPs nanocomposite was isolated and then characterized by using various instrument method including UV-visible spectroscopy, FT-IR, and FE-SEM analysis. The catalytic behaviour of the polymer protected silver nanoparticle was studied for the reduction of 4-nitrophenol (4-NP) and textile dyes like methylene blue (MB) and Congo Red. The reduction of 4-nitrophenol using AgNPs/poly(o-anisidine) nanocomposite reaction follow the pseudo first order kinetics and the resulting rate constant was found to be 10 min^{-1} for 4.0×10^{-4} M concentration of 4-NP using 10 mg/L of catalyst. On the other hand, the catalytic behaviour of the nanocomposite was investigated toward the degradation of some of the textile dyes such as MB and Congo Red. The percentage of degradation of dye was monitored by UV-visible spectral studies and found to be superior to the other catalyst used for the degradation studies. The present method was employed for the effective removal of textile dyes and reduction of 4-nitrophenol with a minimum amount of catalyst.

1. Introduction

Recently conducting polymers and metal nanoparticles dispersed conducting polymer nanocomposites were widely used in various field of research. Among the conducting polymers polyaniline and its derivatives have attracted much attention due to its easy way of synthesis either by chemical or electrochemical polymerization approach [1-6]. Mostly ammonium persulfate was used as oxidation agent for the chemical oxidative preparation of polyaniline by chemical method. Although the chemical method offers a mass production of polyaniline with a reasonable cost; it is difficult to solubilize in various organic solvent. On the other hand, electrochemical method has some advantages like direct deposition of polyaniline on electrode surface with controlled film thickness and morphology which are essential parameter for electronic devices and sensor applications [8-10].

Various metal nanoparticle dispersed polyaniline composite were prepared either by direct method or by interfacial polymerization method to obtained a nanoparticle dispersed polyaniline composite. Here we present a simple method for the preparation of POA/LGS/AgNPs nanocomposite by an in-situ chemical oxidative polymerization of o-anisidine in presence of LGS as dopant using silver nitrate as oxidation agent at reflux condition [7]. Already silver nanoparticles dispersed polyaniline and derivatives were used for various applications including removal of mercury, electrochemical sensors a removal of textiles dyes and gas sensors [11-14]. Here we have shown the catalytic reduction of 4-NP and MB and CR using and POA/LGS/AgNPs composite under various experimental conditions and the results are comparable with previously reported values and found that a present system exhibit superior catalytic activity [15].

2. Experimental Methods

2.1 Chemicals

Sodium lignosulfonic acid (LGS) and o-anisidine were purchased from Sigma Aldrich bio-carpals Bengaluru, India. Silver nitrate ($AgNO_3$) and sodium borohydride ($NaBH_4$) were purchased from SRL chemical, India whereas 4-nitrophenol (98%), methylene blue (99%) and Congo red (99%) were obtained from Merck chemical company, India. All the chemical used were of analytical grade and used as such without any further purification Double distilled water (DD H_20) was used to prepare all stock solution.

2.2 Instrumental Methods

The chemical composition as morphology of this composite were analyzed using a FE-SEM (Hitachi, H-7100, and Japan) with an acceleration voltage of 200 kV. FTIR spectra of NZVI were determination by a Fourier transform infrared spectroscopy (FTIR Nicolet 5700, Thermo Corp., USA). Measurement was preferred by mixing of 1% (w/w) specimen with 100 mg of KBr powder. The catalytic degradation experiment was carried out by UV-visible spectrum by record over 200-800 nm range with a UV-Visible spectrophotometer (UV-1800 PC-Shimadzu, Japan).

2.3 Synthesis of POA/LGS/AgNPs Nanocomposite

100 mg of 10 mM sodium lignosulfonate and 15 mg of (5 mM $AgNO_3$) were dissolved in 20 mL of distilled water in a 100 mL RB flask and then added 100 µL of o-anisidine to the reaction mixture drop by drop under constant stirring. The reaction was carried out constant stirring at 80 °C for 3 h under reflux condition. The color change of the solution from orange brown to gray color indicates the formation of poly(o-anisidine)/LGS/AgNPs composite and the resulting precipitate was isolated by filtration. The dried product was obtained and used for further studies.

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*Corresponding Author:jeevapandian@yahoo.co.uk(K. Pandian)

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3. Results and Discussion

3.1 Synthesis of POA/LGS/AgNPs

The silver nanoparticle dispersed POA/LGS/AgNPs was synthesized by single step method at 80 °C under reflux condition. Here, o-anisidine was used as a reducing agent to convert Ag^+ to Ag^0 and the reduction reaction was slow at room temperature. In order to enhance the reduction rate, the reaction was carried out at 80 °C under reflux condition. The progress of the reaction was monitored continuously by UV visible spectral studies at different time interval. We note that the reaction was completed within 3 h under the above experimental condition and the product was analyze by UV- visible spectroscopy, FT-IR, and SEM studies to identify the nature bonding and surface morphology.

3.2 UV-Visible Spectral Analysis of POA /LGS/AgNPs Composite

Fig. 1 showed UV-visible spectral results POA/LGS/AgNPs in both stirring as well as reflux conditions. A sharp plasmon band was observed at 400 nm which is due to the formation of colloidal silver nanoparticle during the reduction process and a broad peak was observed in the higher wavelength side which is attribute for n–π* transition of benzenoid to quinoid ring (poly o-anisidine backbone). Other two peaks in the lower wavelength region (330 nm and 220 nm) are due to the unreacted o-anisidine and LGS respectively. In the case of LGS/AgNPs and POA/LGS/AgNPs (stirring condition), the SPR band was a broad in shape which is due to insufficient reduction of silver nitrite under stirring condition. From these studies it is clearly understand that o-anisidine play a vital role for the in-situ single pot synthesis of poly(o-anisidine)/LGS/AgNPs composite.

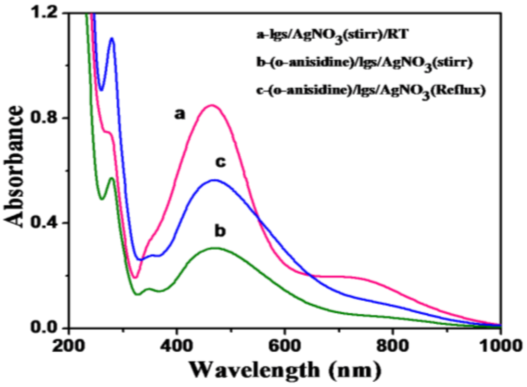

Fig. 1 UV spectra for a) LGS/AgNPs b) POA/LGS/AgNPs (Stir) and c) POA/LGS/AgNPs (reflux) composite

The bandwidth of the all three UV–visible peaks were measured for LGS/AgNPs and the band half peak width maxima is 1.6 cm whereas the POA/LGS/AgNPs is 1.5 cm for room temperature for 3 h stirring. A slight shift in band width was observed POA/LGS/AgNPs (is about 2.0 cm) under the reflux condition. In all three systems the band width was measured in which a sharp peak was obtained for LGS/AgNPs at 468 (2.6 eV) and POA/LGS/AgNPs was noted at 462 (2.68 eV) at room temperature stirring. Under reflux condition the peak position was observed at 470 (2.69 eV). The appearance of the sharp is due to the formation of narrow size distribution of the particle sizes.

3.3 FT-IR Spectral Studies of POA/LGS/AgNPs Composite

The nature of interaction between poly(o-anisidine) and lignosulfonate dopant in presence of silver nanoparticles can be obtained from FT-IR studies. Fig. 2 displayed the FT-IR pattern of both LGS and POA/LGS/AgNPs. The characteristic POA peaks were observed at 3415, 3460, 1600, 1210, 1130, and 800 cm^{-1} was in agreement with the literature reported. The peak at 3400 cm^{-1} is due to the N–H stretching vibration of secondary amine, the aromatic C–H stretching vibration at about 3100 cm^{-1}, C–N stretching vibration at 1600 cm^{-1}, and the in-plane C–H bending at about 1140 cm^{-1} reveal the characteristic bands of POA. The peak at about 800 cm^{-1} is characteristic of the para disubstituted aromatic rings that indicate polymer formation. The bands at approximately 1390 and 1570 cm^{-1} are due to the benzenoid and quinoid ring units, respectively. The peaks at 1036–1043 cm^{-1} ranges are corresponding to S=O symmetric stretching of the sulfonic groups present in the LS chains. Two absorption bands at 1570–1604 and 1487–1500 cm^{-1} were associated with the stretching of quinoid and benzenoid rings of LGS/POA chains, respectively. Due to doping of LGS into the POA polymer backbone some of the peak positions were shifted and the FT-IR Pattern are similar in Fig. 2. Detailed assignment of FT-IR peak position is given in Table 1.

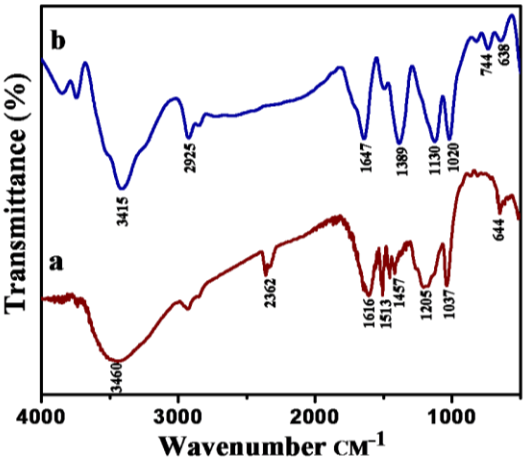

Fig. 2 FT-IR spectra of a) LGS and b) POA/LGS/AgNPs composite

Table 1 FT-IR spectra of a) LGS and b) poly(o-anisidine)/LGS/AgNPs composite

Characteristic peak	Wavenumber (cm^{-1})	
	LGS	POA/LGS/AgNPs
N-H stretching	3460	3415
C-H stretching vibration	-	2925
C-N stretching vibration	1616	1647
C-H plane stretching	-	1130
S=O symmetric stretching	1037	1020
C=N quinoid stretching	-	1389
C=C benzenoid stretching	-	1500
C-H out plane bending	644	744

3.4 FE-SEM Image of POA/LGS/AgNPs Composite

Fig. 3 shows the SEM image of AgNPs dispersed POA/LGS nanocomposite are clearly shown at different magnifications. From the SEM images the approximate size and shape of the silver nanoparticles can be clearly seen. The average sizes of the particles are following 20 to 30 nm size ranges. Further TEM studies is need to understand the exact size and shape of the silver nanoparticles present in the polymer composite.

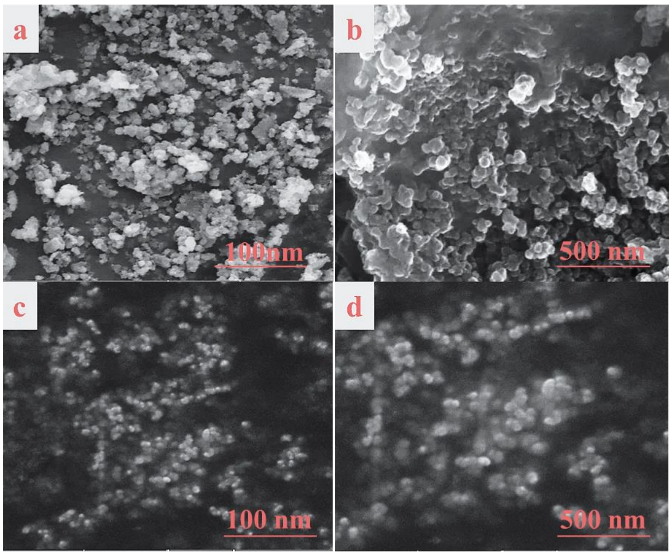

Fig. 3 FE-SEM image of POA/LGS (a&b) and POA/LGS/AgNPs composite(c&d)

3.5 X-Ray Diffraction of POA/LGS/AgNPs Composite

The X-ray diffraction pattern reflections at 20.6° 2θ value is assigned for the amorphous nature of POA-LGS and can also be ascribed to the periodicity parallel and perpendicular to the polymer chains of POA. The XRD pattern of POA nanocomposite is appeared a broad peak centered at 2θ ~12.5° and 25.3°, which are the characteristic of the semicrystalline nature of polymer. The POA/LGS/AgNPs exhibits the presence of many peaks which are corresponding to both poly(o-anisidine) such as 2θ ~ 12.5° and 25.3° and silver nanoparticles are 2θ ~ 38.2°, 44.4° and 64.6°. The XRD peaks of AgNPs are in good agreement with the JCPDS card no. 04-0783. The preponderant (111) reflection is indicative of the oriented growth of the silver nanoparticles.

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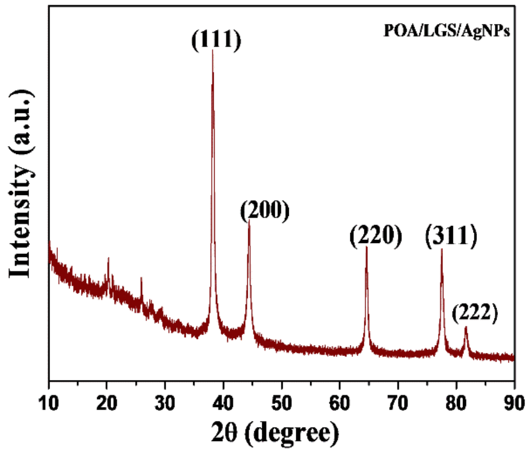

Fig. 4 XRD pattern of POA/LGS/AgNPs composite

3.6 Catalytic Activity of POA/LGS/AgNPs on Reduction of 4-NP

The catalytic behaviour of POA/LGS/AgNPs was studied against the reduction of 4-NP. The addition of different amount AgNPs influences the reduction of 4-NP as shown in Fig. 4. It was found that while increasing of amount of AgNPs catalyst the reduction of p-nitrophenol is also increases. The reduction of 4-nitrophenol was monitored by UV-visible spectroscopy. The complete reduction of 4-NP was observed at 36 min for 50 mg whereas the addition of 100 mg and 150 mg of catalyst, the reduction reaction was completed within 28 min and 10 min. which indicate the rate of the reduction of 4-NP is closely associated with concentration of catalyst added to the reaction medium. The reduction is considered as pseudo first order kinetics because less amount of catalyst is used in presence of a large quantity of water.

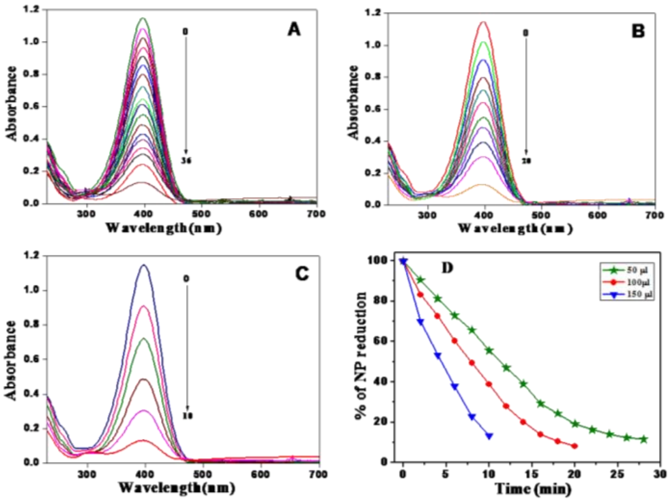

Fig. 5 UV-visible spectra capturing the conversion of 4-NP upon reaction with $NaBH_4$ in presence of 50 mg, 100 mg, and 150 mg of POA/LGS/AgNPs (A), (B), (C) respectively and (D) percentage plot (%) of 4-NP reduction

3.7 Catalytic Activity of POA/LGS/AgNPs on Reduction of Congo Red (CR)

Recently it has been reported that metal nanoparticles can be used as catalyst for reduction of textile dyes and chloro organic pollutants for the complete removal from effluent water sources in a faster rate. It is well-known that the catalytic activity of nanoparticle was strongly dependent on its composition, size and shape. Typically, a bigger surface-to volume ratio is given to show a higher catalytic activity [5]. It is a well-known fact that AgNPs and their composites show greater Catalytic activity in the case of dye reduction and removal. The use of CR, a heterocyclic aromatic dye, in the textile has increased in the last few years. The silver nanoparticles thus used as catalyst for the reduction of Congo red in presence of $NaBH_4$. The degradation rate of CR's color in the presence of $NaBH_4$was observed in the presence and absence of silver nanoparticle as catalyst. Fig. 5 shows that the reduction of CR with $NaBH_4$ in absence of silver nanoparticle (catalyst). This result proves that, although after 180 minutes of reaction between CR with strong reducing agent $NaBH_4$, there is no degradation of the dye CR is greatly enhanced. The disappearance of Red color of CR in solution (Fig. 6) was due to reduction of Congo red (CR).

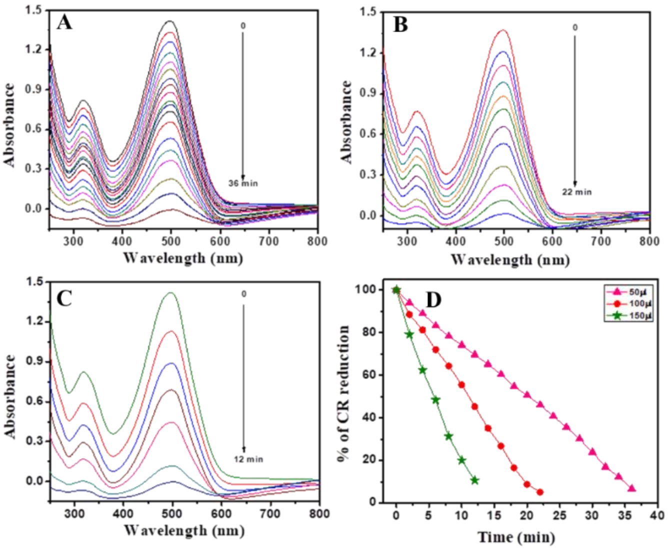

Fig. 6 UV-Visible spectra capturing the conversion of Congo red (CR) upon reaction with$NaBH_4$ in presence of 50 mg, 100 mg, and 150 mg of POA/LGS/AgNPs (A), (B, C) respectively and percentage (%) plot (D)

4. Conclusion

We have shown here the spherical silver nanoparticle can catalyst the degradation of 4-NP in the presence of sodium borohydride, producing a remarkable enhancement in the reaction rate. A poly(o-anisidine) nanoparticles was prepared in presence of in-situ polymerization. The synthesized catalyst is effectively degrading the textile dyes have been conducted, making them potentially useful for environmental remediation. Furthermore, the procedure is useful for synthesis of large-scale POA/LGS/AgNPs. The silver nanoparticles containing composite was used as catalysts for the degradation of hazardous dyes in a cost-effective manner. The degradation efficiency is increased due to their very high surface area as well as accelerate migration rate of electrons/hole to the surface of the nanoparticles.

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About the Conference…

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