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Gold Reduced Graphene Oxide (rGO) Nanocomposites as a Catalyst for the Reduction of o-nitroaniline

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ABSTRACT

Carbon-based nanocomposites are an emerging material which is of great interest due to their extraordinary properties upon the addition of nanoparticles onto it. Herein, we report the in-situ synthesis of gold-rGO nanocomposites by the chemical reduction method using two reducing agents-chitosan and ascorbic acid. Chitosan is a natural polysaccharide polymer which exhibits good adhesion, biocompatibility and biodegradability. The adhesive nature of chitosan enables the binding of gold ions on the chitosan matrix, thereby reducing it. The mechanical properties of the rGO enhances by the addition of chitosan stabilized gold nanoparticles forming a nanocomposite. UV-Vis, FT-IR, XRD and FESEM were used to characterize the nanocomposites. The synthesized Au-rGO nano composites with a crystallite size of 64.79nm were confirmed by X-ray diffraction spectra. The scanning electron microscope image revealed that spherical shaped gold nanoparticles dispersed on the chitosan matrix and graphene sheets. The synthesized gold-rGO nanocomposite exhibits good catalytic activity towards the reduction of o-nitro aniline. The findings of this research could be useful in the development of catalysts for the reduction of organic contaminants in industrial wastewater.

Keywords: Gold-rGO nanocomposite, Chitosan, o-nitroaniline.

INTRODUCTION

Graphene is a single layer of carbon atom which is of sp^2 hybridized packed into a honeycomb crystal lattice. It has received great attention because of its fascinating properties like electronic, optical, thermal and mechanical which makes it suitable for a variety of applications[1-4]. The reducing agents such as hydrazine and sodium borohydride are used to modify the surface of graphene which results in the formation of reduced graphene oxide (rGO). However, GO undergoes agglomeration and precipitation in non-aqueous medium due to the presence of strong Π-Π stacking and van der Waals forces between the carbon layers, thereby reducing its surface area. To overcome this problem, graphene oxide is immobilized with inorganic nanostructures which exhibit higher surface area, excellent catalytic properties, higher specificity etc.[5]. Among the metal nanoparticles, gold nanoparticles are found to be important due to their unique physical and chemical properties. Due to the presence of oxygen functional groups, GO/rGO can easily hold gold nanoparticles onto it which creates negative zeta potential thereby coupling with positively charged gold nanoparticles[6]. There are several reducing agents available to synthesize the gold nanoparticles. However, strong reducing agents are poisonous and unstable. As a result, an effective, low-cost, non-toxic, and environmentally begin green reducing agent is required, and chitosan is one such substance that can be used as a reducing agent. Chitosan is a non-toxic, biodegradable, and biocompatible polymer with mucoadhesion properties and it is composed of β-(1,4) connected D-glucosamine and N-acetyl-D-glucosamine units. It is a deacetylated derivative of chitin. Chitosan possesses the amino and hydroxyl groups which enhances its reducing ability due to the electrostatic interactions of NH_3^+ of chitosan and $AuCl_4^-$ present in the metal precursor[7-10]. o-nitroaniline are used as intermediates in pharmaceuticals, pesticides, pigments, dyes, and rubber chemicals. They are toxic contaminants to the environment. Different methods, such as adsorption, thermal decomposition, photocatalysis, biological degradation, and catalytic reduction have been examined to remove the o-niroaniline from effluents[11-13]. The most preferred method of nitroaniline removal in aqueous solution is catalytic reduction because the products of catalytic reductions are applied in various fields. o-Phenylenediamine is used as a precursor in the synthesis of pharmaceuticals, dyes, and antiseptic agents[14]. As a result, the catalytic reduction of nitroaniline to o-phenylenediamine is chosen over alternative approaches. In the present work, we have synthesized gold (Au-rGO) nanocomposite using two reducing agents-chitosan and L-ascorbic acid in a greener way. Chitosan plays a dual role as both reducing and stabilizing agent. The catalytic activity of the synthesized nanocomposite is determined using reduction of o-nitro aniline as a model reaction.

EXPERIMENTAL

MATERIALS AND METHODS

Chloroauric acid and chitosan (low molecular weight) were purchased from CDH. Graphite fine powder, potassium permanganate, sulfuric acid, hydrochloric acid, sodium borohydride, L-ascorbic acid and acetic acid were procured from Merck. o-nitro aniline was purchased from Fischer scientific & co. All chemicals used were of analytical grade and were used as such without any purification.

Synthesis of GO

The modified hummer's method[15] was used to synthesize graphene oxide from graphite powder. At 0°C, 2.5 g of graphite fine powder was dispersed in 60 mL of concentrated sulphuric acid with continuous stirring. Then, 7.5 g potassium permanganate was added slowly to the above reaction mixture and the temperature is maintained at 0°C and stirring was continued for 30 minutes. To the above solution, 110 mL of distilled water was added slowly under stirring. Again, the solution was diluted with 350 mL of distilled water and 3 mL of H_2O_2 was added slowly. The solution became yellow brown in color. The resulting solution was filtered and washed with 5% hydrochloric acid and water until it reached a neutral pH, then centrifuged at 3000 rpm for 30 minutes[16,17]. The obtained precipitate was dried at 90°C in an oven for 1 day. Finally, a dark brown powder was obtained.

Synthesis of Au-rGO nanocomposite

To synthesize Au-rGO nanocomposites, 0.25 g of chitosan was dissolved in 2% acetic acid. Then, 0.025 g of GO was dispersed in 25 mL of distilled water added to the above reaction mixture and stirred for 1 hour. To the above mixture, 25 mL of 0.1 M ascorbic acid solution and 25 mL of 0.001 M $HAuCl_4.3H_2O$ were added. The mixture was heated to 60°C with reflux under magnetic stirring for 1 hour. Ruby red color solution shows the formation of Au nanoparticles. The resulting solution was centrifuged at 6000 rpm for 30 min, and the precipitate was separated, dried at 50°C in an oven for one hour to get Au-rGO nanocomposite[18]. UV-Vis, FT-IR, XRD, and SEM were used to characterize the nanocomposite.

Catalytic activity of Au-rGo nanocomposite

The reduction of o-nitroaniline to o-phenylene diamine was used as a model reaction to evaluate the catalytic activity of gold-rGO nanocomposite. About 2.5 mL of 0.03 M ice-cold aqueous solution of $NaBH_4$ was mixed with 2.5 mL of 0.0038 M aqueous solution of o-nitroaniline and magnetically stirred for 30 minutes. To the above reaction mixture, 10 mg of gold-rGO nanocomposite was added. The bright yellow solution faded as the reaction progressed after the addition of the catalyst. 2 mL of the reaction mixture was placed in a 2 mL cuvette, and the reduction reaction was monitored continuously at room temperature using a UV-Visible spectrophotometer.

RESULTS AND DISCUSSION

Absorption spectrum

Figure 1. Illustrates the UV-Visible spectrum of the gold-rGO nanocomposite. It shows a sharp narrow peak at 565 nm, which corresponds to the surface plasmon resonance peak of gold nanoparticles. The size and shape of the gold nanoparticles determine the frequency and width of the SPR band. The formation of spherical gold nanoparticles is indicated by the presence of a single SPR peak[19].

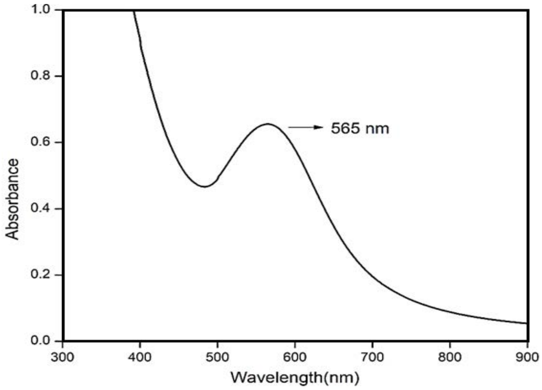

Fig. 1. UV-visible spectrum of gold-rGO nanocomposite

Infrared spectrum of Graphene oxide and gold-rGO nanocomposite

The complete oxidation of graphite to graphene oxide was confirmed by Infrared spectroscopy. Fig. 2 shows the FT-IR spectrum of graphene oxide. The peaks at 3471 cm^{-1}, can be assigned to the stretching vibration of -OH group. The peak at 2933 cm^{-1} can be assigned to -CHO and -C=O at1695 cm^{-1} and –C-O at 1272 cm^{-1} respectively. It clearly indicates that the graphite was completely oxidized to graphene oxide[20].

The formation of Au-rGO was confirmed by IR spectroscopy. The peak at 3724 cm^{-1} can be assigned to NH_2 group of chitosan molecule. The broad peak at 3120 cm^{-1} shows the intermolecular hydrogen bonding of OH group of graphene oxide[20] (Figure 3).

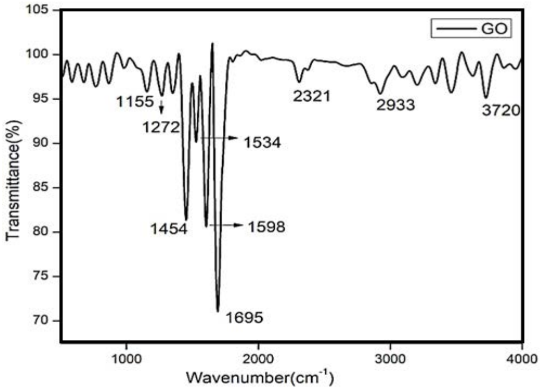

Fig. 2. FT-IR spectra of GO

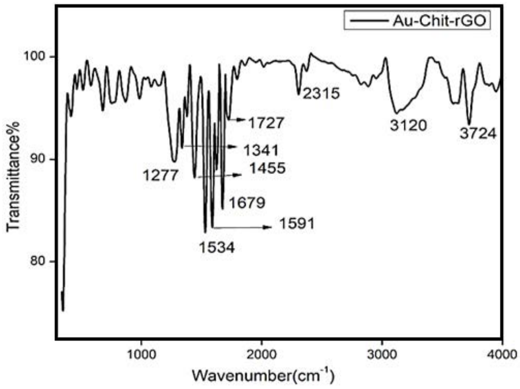

Fig. 3. FT-IR spectra of Au-rGO nanocomposite

X-ray diffraction study

Figure 4 shows the XRD pattern of Au-rGO nanocomposite. It shows peaks at 2Θ=38.700, 44.270, 47.270, 64.400 and 77.390 which correspond to the reflection planes (111), (200), (220), (311), and (222) of gold nanoparticles in a face-centered cubic lattice (JCPDS No- 04-0784). The diffraction peak indexed to 38.700 is very sharp and intense, when compared to other peaks indicating that gold nanoparticles have predominantly grown (111) planes. The broad peak at 26.700 corresponds to the rGO which indicates that the graphite was completely converted into reduced graphene oxide (JCPDS no- 12-0212)[21]. The crystallite size of Au-rGO is 64.79 nm.

Field Emission Scanning Electron Microscopy study (FESEM) studies

FESEM was used to investigate the structural properties of Au-rGO nanocomposite (Fig.5). The images confirmed the spherical shape of the gold nanoparticles well dispersed on the chitosan matrix and graphene sheets. The SEM image also shows the formation of graphene layers on which gold nanoparticles are uniformly dispersed[22].

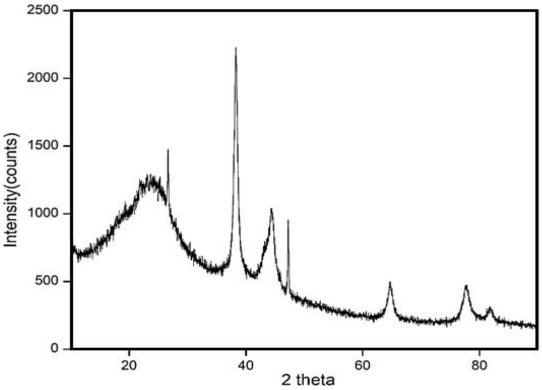

Fig. 4. XRD pattern of Au-rGO nanocomposite

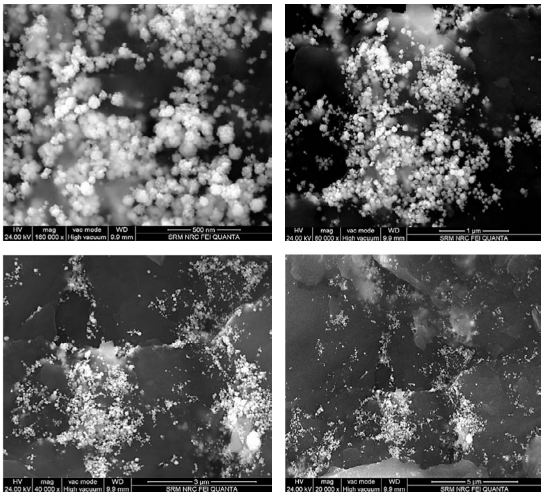

Fig. 5. FESEM images of Au-rGO nanocomposite

Catalytic activity

The reduction of aromatic nitro compounds with $NaBH_4$ over Au-rGO nanocomposites was employed as a model reaction to assess the catalytic activity of Au-rGO nanocomposites. The conversion of o-nitroaniline to o-phenylenediamine using $NaBH_4$ was studied to assess the catalytic activity of as-prepared gold-rGO nanocomposites (Fig. 6). UV-Visible spectrophotometer is used to monitor the reaction[23,24]. Initially, the control experiment was carried out using $NaBH_4$ without the addition of Au-rGO nanocomposites. The UV-Vis studies show that a very slow decrease in the intensity of the band corresponding to o-nitroaniline at 411 nm and 281 nm was observed. However, when Au-rGO nanocomposites were added to an aqueous reaction mixture containing $NaBH_4$ and o-nitroaniline, the intensity of the absorption bands at 411 and 281 nm were rapidly decreased. The reduction process can also be visually seen by the gradual change of the reaction mixture from yellow color to colorless. Fig. 7 shows the spectral changes observed for the reduction of o-nitroaniline by gold-rGO nanocomposite. The reduction process was completed within 10 min when gold-rGO nanocomposite was used as the catalyst. It can be mentioned that this reduction reaction occurs very slowly in the absence of gold catalyst. Hence, the gold nanocomposites serve as a heterogeneous catalyst for the reduction of o-nitroaniline to o-phenylenediamine and the catalyst can be easily isolated from the reaction mixture.

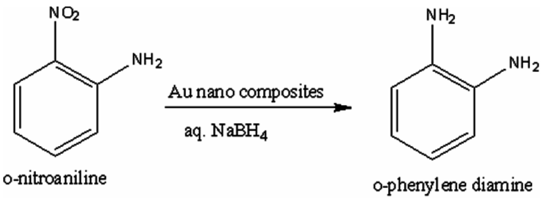

Fig. 6. Reaction scheme of reduction of o-nitroaniline to o-phenylene diamine using Au-rGO nanocomposites as catalyst

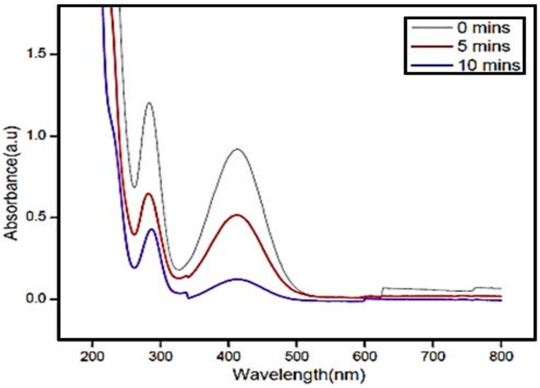

Fig. 7. UV-Visible spectra of reduction of o-nitroaniline using gold-chitosan-rGO nanocomposite

CONCLUSION

Gold-rGO nanocomposites were synthesized using two reducing agents such as ascorbic acid and chitosan. UV-Vis, FT-IR, XRD and SEM were used to characterize the sample. The synthesized gold-rGO nanocomposite was found to act as a better catalyst for the reduction of o-nitro aniline to o-phenylenediamine. Hence, it can be considered an economically very suitable catalyst for the reduction of aromatic nitro compounds.

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Conflicts of Interest

The authors declare no conflict of interest

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