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Synthesis of Ag-rGO nanocomposite for the catalytic reduction of p-nitrophenol

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In this study, we have reported an eco-friendly, very simple, in-situ method for the synthesis of silver-reduced graphene oxide nanocomposite (Ag-rGO) by using ascorbic acid and chitosan as stabilizing and reducing agents. Chitosan is a naturally occurring polysaccharide polymer with excellent adhesion properties which allows the binding of silver ions to the chitosan matrix, thereby reducing it. The addition of chitosan-stabilized silver nanoparticles to rGO increases its mechanical properties, yielding a nanocomposite. The catalytic activity of the synthesized silver-rGO nanocomposite for the reduction of p-nitrophenol is examined. The Ag-rGO exhibits good catalytic activity for the reduction of p-nitrophenol within a very short duration of time.

Keywords: Ag-rGO nanocomposite, Chitosan, p-Nitrophenol

Introduction

Graphene, which is a monoatomic thin sheet of carbon with a honeycomb crystalline lattice, holds great promise for future research. They are exceedingly thin and exhibit remarkable properties such as adsorption, electrical transportation, antibacterial activity, and mechanical strength, which holds a great future for the creation of various carbon-based technical gadgets and composites[1]. Graphene could be easily synthesized by the chemical reduction of graphite[2,3]. Graphene oxide (GO), an important derivative of graphene, is a promising material for researchers due to its high surface area and it can be easily synthesized by the oxidation of graphene[4]. GO consists of various reactive functional groups such as hydroxyl, epoxy, and carboxylic acid on its planes and edges so that it is easily susceptible to further chemical modifications[5,6]. GO is hydrophilic due to the activation of the oxygenated groups so that it is easily dispersed in water and polar organic solvents[7,8]. Due to the high surface area of GO, it can act as a carrier for nanoparticles. Consequently, there has been a lot of interest in manipulating the interfacial property of graphene or GO through functionalization or loading of metal/metallic oxide nanoparticles. However, due to the presence of strong π-π stacking and van der Waals forces between the carbon layers, GO agglomerates and precipitates in a non-aqueous medium, reducing its surface area [9]. It could be overcome by the immobilization of GO with inorganic nanostructures and the resulting nanocomposites possess high surface area, more catalytic capabilities, improved specificity, and so on[10].

The physical and chemical properties of reduced graphene oxide (rGO) are similar to those of graphene. The high electrical conductivity of rGO is of particular importance for application in nano-devices. Despite significant research efforts, optimizing the number of layers and morphology of graphene sheets on a substrate, as well as the synthesis of chemical-free graphene at low temperatures, continue to be significant challenges[11,12]. There is a significant amount of research devoted to the reduction of GO and the controlled growth of graphene[13-15]. Applying techniques based on chemical or thermal treatments can result in the simultaneous reduction of the number of layers and a higher degree of graphene reduction[16-20]. Chemical reduction is the most popular and, widely employed method using conventional reducing agents. However, the widely used chemical approaches typically involve the use of toxic chemicals such as hydrazine and it can be a challenge to remove the residual agents. In recent years, researchers have focused on the synthesis of rGO using mild and green reducing agents. Green reducing agents such as ascorbic acid, also known as Vitamin C, have achieved a great deal of attention for the reduction of GO. GO/rGO has proven to be a promising substrate for the production of nanoparticle-decorated GO/rGO due to its unique properties.

Metal nanoparticles decorated graphene composites were synthesized using a variety of chemical and electrochemical reduction methods. Much research has previously been conducted on graphene-based nanocomposites[21,22], but, the research into the decorating of various metal ions on graphene is still in its early stages. Silver has the potential to be used in metal nanocomposites due to its good conductivity and biocompatibility [23]. Most previous investigations on the production of AgNPs-GO composites used toxic reducing agents such as sodium borohydride, formaldehyde, and hydrazine. Multiple steps and complex operations are involved in this synthesis processes[24]. Accordingly, an efficient, inexpensive, non-toxic, and ecologically friendly reducing agent is necessary, and chitosan is one such chemical that can be utilized as such. The nanocomposite based on chitosan films has obvious advantages of both easier handling for recycling compared with other powdery catalysts, and hence we were attracted by the material and chose the same [25,26].

In recent years, rGO-based nanocomposite catalyzed chemical processes have received a lot of attention in the field of organic synthesis. p-Nitrophenol (p-NP) is a hazardous and refractory contaminant in wastewater originating from the industrial manufacturing processes of agrochemicals, pigments and pharmaceuticals. Instead, p-aminophenol (p-AP) is very beneficial and important in many fields that include analgesic and antipyretic drugs, photographic developer, corrosion inhibitors, and anticorrosion lubricants. Although there are many methods available for the removal of hazardous p-NP, its catalytic reduction to p-AP over an appropriate catalyst (e.g. metal and metal oxide nanoparticle) has emerged as a hot research topic [27-30]. Therefore, we wish to report here, the synthesis of Ag-rGO nanocomposite using ascorbic acid and chitosan as a reducing and stabilizing agent and its application as a highly efficient catalyst for the reduction of p-NP.

Experimental Section

Materials and Methods

Silver nitrate and chitosan (low molecular weight) were procured from CDH. Graphite fine powder, potassium permanganate, sulfuric acid, hydrochloric acid, sodium borohydride, L-ascorbic acid and acetic acid were obtained from Merck. p-nitrophenol was supplied by Fischer Scientific & co. All chemicals used were of analytical grade and were utilized as such without any purification.

Synthesis of Graphene oxide (GO)

The modified Hummers method was used for the synthesis of graphene oxide from pure graphite power[31]. Sulphuric acid (27 mL) and phosphoric acid (3 mL) were taken in the volume ratio of 9:1 and were mixed and stirred for about 20 min. To this solution, 0.225 g of graphite powder was added with constant stirring. Then potassium permanganate (1.32 g) was added slowly and the whole mixture was stirred for 6 h till the solution became dark green. 0.7 mL of hydrogen peroxide was added and stirred for 10 min to remove excess potassium permanganate. The exothermic reaction occurred and let it cool down. Deionized water (30 mL) and hydrochloric acid (10 mL) were added to the above reaction mixture and centrifuged for 7 min at 2000 rpm. The supernatant was then decanted, and the residuals were rewashed three times with HCl and deionized water. Then, the supernatant was decanted away and the residuals were then rewashed with HCl and deionized water until it reached a neutral pH. The residue was dried in an oven at 90°C for 24 h and GO powder was obtained[32,33].

Synthesis of Ag-rGO nanocomposite

Ag-rGO nanocomposite was prepared by a simple solution cast method. To synthesize the nanocomposite, simultaneous chemical reduction of GO and Ag was performed in situ in the presence of chitosan and ascorbic acid. 0.05 g of GO ultrasonically dispersed in 50 mL deionized water. About 0.5 g of chitosan previously dissolved in 2% acetic acid, was added to GO and stirred for 1 h. After stirring for an hour, 50 mL of 0.1 M ascorbic acid and 50 mL of 0.001 M $AgNO_3$ were added and the reaction mixture was heated to 60°C with reflux under magnetic stirring for 1 h. The resultant solution was centrifuged at 6000 rpm for 30 min, the resulting homogeneous mixture was poured onto a Petri dish and dried at room temperature. Then the films were dried in an hot air oven at 105°C. The dry films were peeled off from the Petri dish. UV-visible absorption, FT-IR, XRD, and FESEM techniques were used to characterize the GO and Ag-rGO nanocomposite.

Catalytic activity of Ag-rGO nanocomposite

The catalytic activity of the Ag-rGO nanocomposite was assessed using the reduction of p-NP to p-AP as a model reaction. A mixture of 3 mL of 0.0002 M p-NP solution and 0.3 mL of 0.02 M ice-cold $NaBH_4$ aqueous solution was magnetically swirled for 30 min. 0.02 g of Ag-rGO nanocomposite was added to the aforementioned reaction mixture**.** At 5 min intervals, 2 mL of this solution was taken in a 2 mL cuvette and the reduction reaction was continuously monitored using UV-visible spectrophotometer at room temperature.

Results and Discussion

Characterization of Ag-rGO

The Ag-rGO nanocomposite was prepared with chitosan and ascorbic acid as a reducing agent. Initially, GO and chitosan were mixed to generate a GO/chitosan composite. Ascorbic acid was used here as a stabilizing and reducing agent for synthesizing the Ag-rGO. The prepared nanocomposite was confirmed by UV-visible spectroscopy. The absorption spectrum of the prepared nanocomposite exhibits two peaks at 305 nm and 430 nm (Fig. 1). The peak at 305 nm indicates the restoration of the π -conjugated network, while the appearance of surface plasmon resonance peaks at 430 nm confirms that the silver nanoparticles are stabilized successfully on the rGO–chitosan to yield Ag-rGO nanocomposite.[34]

Infrared spectrum of GO and Ag-rGO nanocomposite

The complete oxidation of graphite to GO was confirmed by Infrared spectroscopy. In the FTIR spectrum of GO (Fig. 2) vibrations at 3415cm^{-1} (O–H stretching vibrations) and 1636cm^{-1} (C=O stretching vibrations) can be used to detect various oxygen functionalities in GO[35]. Peaks at 2361 cm^{-1}, and 1100 cm^{-1} are assigned to the stretching vibration of C -H bonds and the alkoxy C-O vibrations, respectively [36]. As a result, it confirms the presence of many hydroxyl groups and oxygenous groups in GO, making it appropriate for advanced modification using metal NPs such as Ag NPs[1].

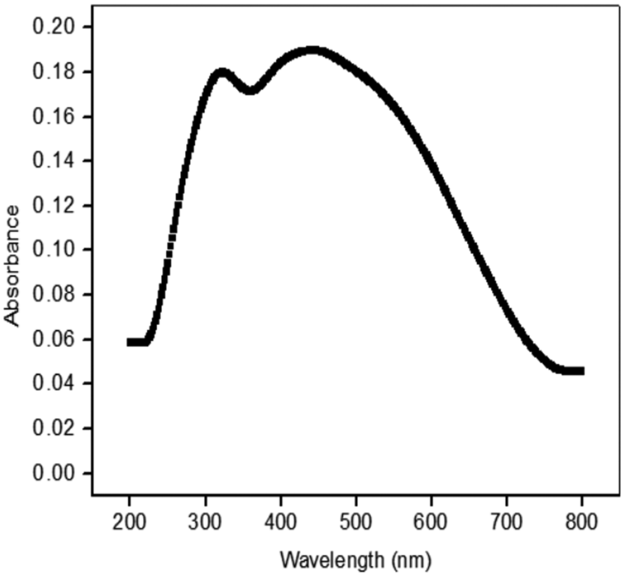

Fig. 1 — UV-visible spectrum of Ag-rGO

Fig. 3 depicts the IR spectrum of the Ag-rGO nanocomposite. The peak at 2364 cm^{-1}, 1585 cm^{-1}, 1394 cm^{-1} are assigned to -COO, -C=O, C-O stretching vibrations, respectively. It indicates that Ag-rGO still possesses oxygenated species such as carboxylic, carbonyl, and hydroxyl groups that can act as Ag^+ binding sites. These groups also contribute to the hydrophilicity of rGO [37]. The peak at 1304 cm^{-1} is attributed to the C-N bonds and other peaks appeared at 2959 cm^{-1}and 2304 cm^{-1} are attributed to C−H

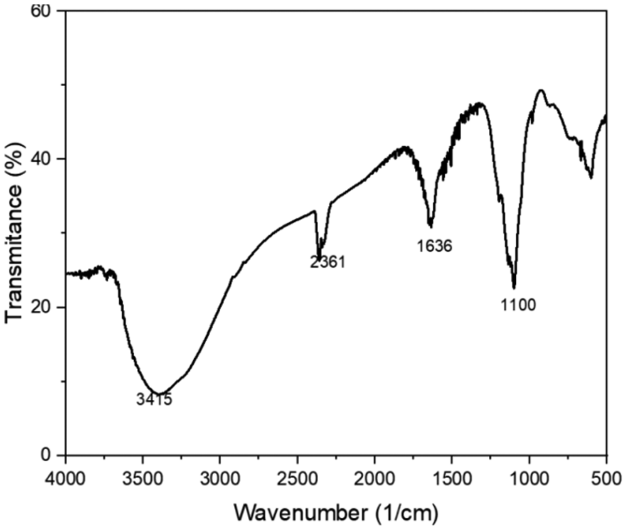

Fig. 2 — FT-IR spectrum of GO

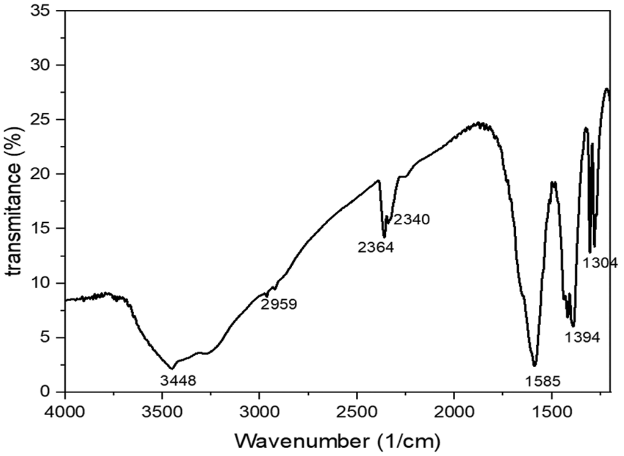

Fig. 3 — FT-IR spectrum of Ag-rGO

stretching vibration. The FT-IR spectrum of Ag-rGO clearly showed that the O-H stretching vibrations at 3448 cm^{-1} were significantly reduced due to deoxygenation[38]. The peak appearing at 3448 cm^{-1} is attributed to the stretching vibration of free –NH and O–H groups of grafted chitosan polymer which indicates the formation of Ag-rGO.

Powder X-ray diffraction studies

The X-ray diffraction pattern of Ag-rGO nanocomposite is shown in Fig. 4. The peaks at 38.7°, 43.7°, 64.2° and 77.7° correspond to the (111), (200), (220), (311) planes of the face centered cubic lattice of silver nanoparticles[39,40]. The crystalline size of the silver nanoparticles was found to be 23.52 nm. The diffraction peaks of the samples were sharp and were well indexed with JCPDS card no. 04-0783 which suggests the typical fcc phase structure of Ag. The most common peak for rGO is $2\theta = 23°$ (Ref.41). An analysis of Ag-rGO shows graphitic (002) peak at 26.6° and it implies that when graphitization takes place, oxygen moieties are thermally removed from the carbon surface. The small sharp diffraction peaks at 21° correspond to the semi-crystalline chitosan polymer.

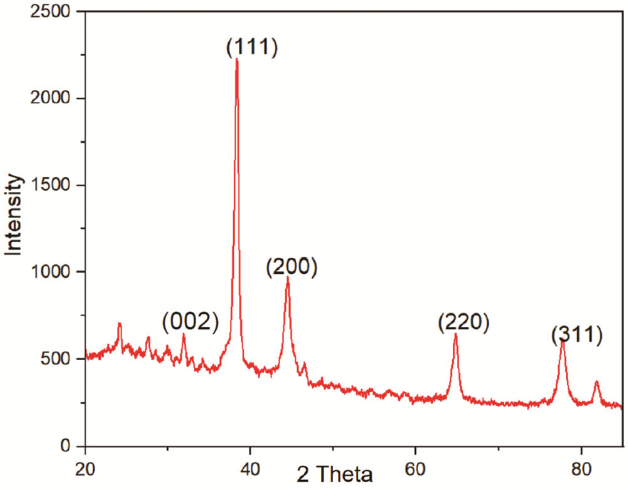

Fig. 4 — XRD pattern of Ag-rGO nanocomposite

Field Emission Scanning Electron Microscopy study (FESEM) studies

The morphology of the Ag-rGO nanocomposite was investigated using FESEM (Fig. 5). The images confirmed that the silver nanoparticles were spherical and evenly distributed across the chitosan matrix and graphene sheets. It also demonstrates the formation of graphene layers with uniformly dispersed silver nanoparticles[42] and the average diameter of silver nanoparticles was found to be 23 nm which is in good agreement with the XRD data.

Energy dispersive X-ray spectroscopy (EDX) is a microanalysis used in conjugation with FE-SEM. EDX was used to find elemental composition of the synthesized Ag- rGO nanocomposites. Fig. 6 illustrates the typical EDX pattern of the Ag-rGO nanocomposite. The elemental composition of Ag-rGO nanocomposite was found to be 66.27% of C, 24.80% of O and 04.10% of Ag. Thus, the presence of all the relevant elements in the Ag-rGO nanocomposite was confirmed by EDX analysis.

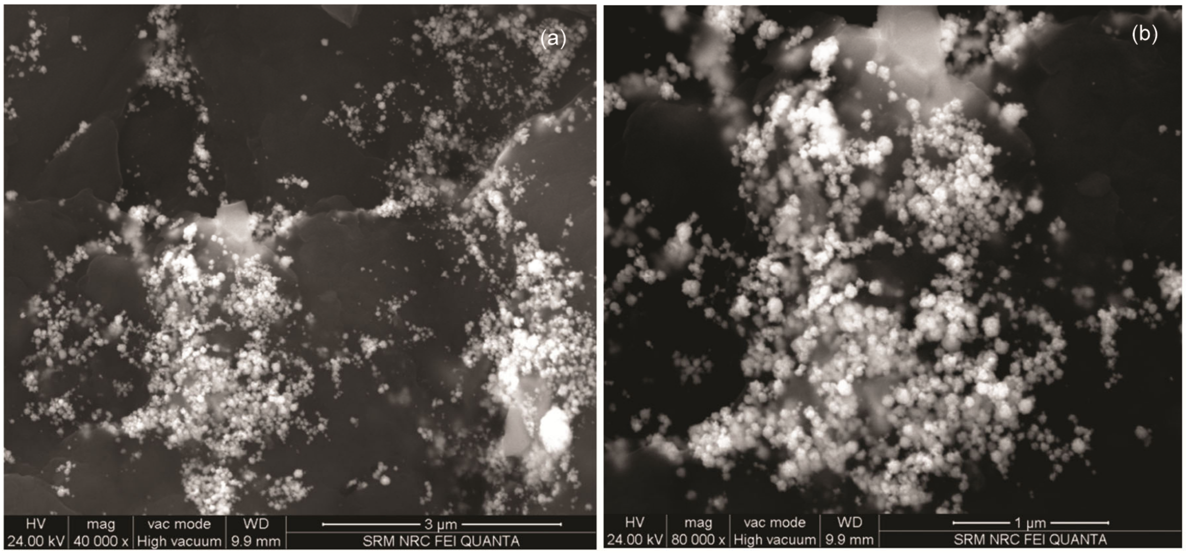

Fig. 5 — FESEM image of Ag-rGO nanocomposite

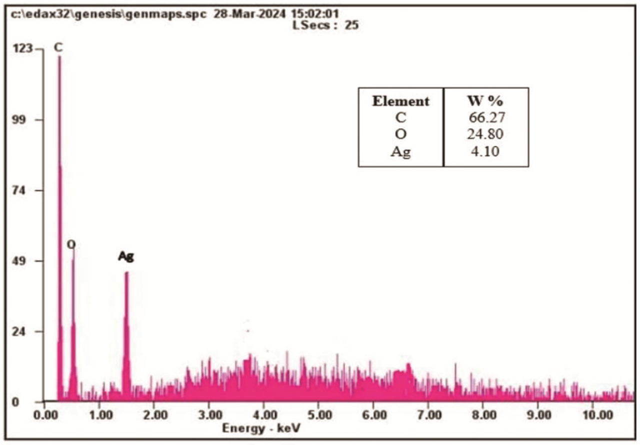

Fig. 6 — EDS of Ag-rGO

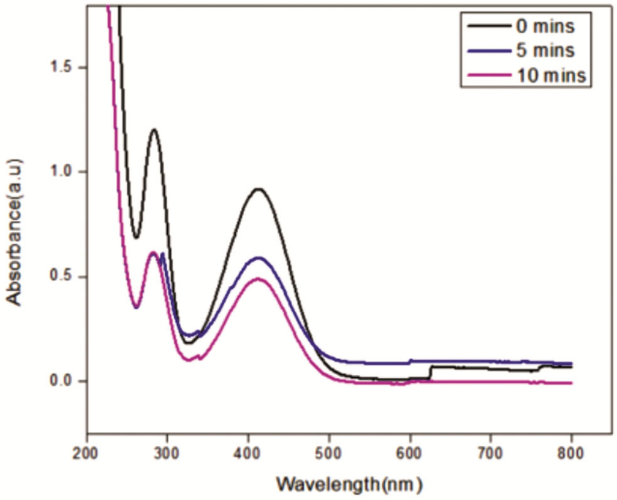

Fig. 7 — UV-visible spectra of reduction of p-nitrophenol using Ag-rGO nanocomposite

Catalytic activity

To check the catalytic activity of as-prepared Ag-rGO nanocomposites, reduction of p-NP using $NaBH_4$ was studied. The reaction was monitored using UV-visible in the 250–500 nm range. Initially, the control experiment was performed involving the reduction of p-NP using $NaBH_4$ without the addition of nanocomposites, a very slow decrease in the intensity of the band is observed. However, the addition of Ag-rGO nanocomposites into the aqueous reaction mixture containing $NaBH_4$ and p-nitrophenol resulted in a rapid decrease in the absorption band. Moreover, the peak shifts to 402 nm, confirming that 4-NP anions were formed[42]. The absorption intensity of p-nitrophenolate at 402 nm dropped during the reaction, and a new peak at 296 nm formed due to the production of p-AP [43] (Fig. 7). The reduction process can also be visually seen by the gradual change of the reaction mixture from yellow colour to colourless. It can be seen that the reduction of p-NP using Ag-rGO nanocomposite is faster. The reduction process was completed within 10 minutes when Ag-rGO nanocomposite was used as the catalyst. It can be mentioned that this reduction reaction does not occur without the Ag-rGO catalyst. Hence the nanocomposites serve as a heterogenous catalyst for the reduction of p-NP and the catalyst can be easily isolated from the reaction mixture.

Conclusion

In this study, we reported a very simple, easy, economical, green and environment friendly route for the synthesis of Ag-rGO nanocomposite using chitosan and ascorbic acid. The synthesized composite was characterized using UV-visible, FT-IR, XRD, and FESEM. In a relatively short period of time i.e., in 10 min, the Ag-rGO nanocomposite shown extremely good catalytic activity for the reduction of p-nitrophenol in the presence of $NaBH_4$. This method of synthesizing Ag-rGO can be utilized more generally to modify graphene's surface with different nanoparticles in the future for a variety of industrial uses.

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