

Synthesis and Characterization of Graphene Oxide Coated Au Nano Particles and The Study of its Application on Electro Catalytic Activity of Nitric Oxide

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Abstract

Synthesis of graphene oxide has enticed good dispense of consciousness due to their vast utilization in different fields in modern days. In the present investigation, we report on the preparation of graphene oxide via a modified Hummer's method. The nanocomposites were isolated and then characterized by using various analytical techniques to understand the composition and the surface morphology of the nanocomposites. The structure as well as morphology of the nanocomposites were analyzed using SEM Instruments. The electro chemical behavior of the compound was studied by cyclic voltammetry in various supporting electrolyte. The electrocatalytic behavior of the nanocomposites monitored over the oxidation of nitric oxide (NO). Copyright © VBRI Press.

Keywords: Graphene oxide/gold nanoparticles, sensor, cyclic voltammetry, Hummer's method, nitric oxide, electrocatalytic activity.

Introduction

Now a days nano particles are widely used in industries, batteries, and research institutions etc., various preparation techniques are available to synthesis nano particles some techniques are molecular beam epitaxy, chemical vapour deposition thermal deposition etc., metal nano particles are great scientific interest as they are effectively bridge between bulk material and nano materials. The applications are the metal nano particles and its composites are therapeutic drugs, information storage, environmental applications, catalyst, sensors, nano-structured electrodes etc. [1-4].

Graphene is a powerful compound it has a great definite sector and high adaptability, high thermal conductivity, high optical transmittance and good conductivity material [5, 6]. Graphene oxide has field of reactive O₂ functional groups, which has fine mentioned application among others through chemical functionalizations [7]. The synthetic graphene oxide has been the many applications are polymer compound, energy materials, sensors, and biological applications, to fit high electrical, mechanical and thermal properties [8-11].

Nitric oxide (NO) is biotic signaling compound and fit great role in cell functioning for nervousus,ticker and immunize systems and NO intimate in the

parthenogenesis of these system as seen in cancerous growth maturation and idiopathic disease. Therefore, quick detection of NO is crucial to understand as well as to supply a plate form for experimental application like clinical identification [6].

Experimental

Materials and methods

Graphene powder, con. sulphuric acid, potassium per sulphate, phosphorous pentoxide, potassium permanganate, Auric chloride, Sodium nitrate, Hydrogen peroxide, Trisodim citrate, Glutathione, Sodium nitrate were utilize as such without further purification.

Preparation of Graphene oxide (GO)

GO was prepared from graphite powder based on modified Hummer's method [7, 13]. The powdered graphite (4g) was oxidized in hot solution (80°C) of Con. Sulphuric acid (24 mL) containing potassium thiosulphate (8g), and Phosporous pentaoxide (8g). The final compound dark blue mixture was thermally isolated and slowly cooled to room temperature nearly 6 h. The mixture was diluted to 300 mL, and then filtrated with a filter membrane and dried at 60°C for

12 hrs. These preoxidized graphite powder (2g) was added to 92 mL of cold sulphuric acid (0°C), to which potassium permanganate (12g) was slowly added under constant stirring in ice-bath. After 15 min, sodium nitrate (2 g) was added to the above reaction mixture. The solution was more stirred for 2 h at 35 °C and distilled water (200 mL) was added. The reaction was stopped with the addition of a mixture of 560 mL of distilled water and 10 mL of Hydrogen peroxide (30 %). The compound was washed with Hydrochloric acid (1:10) and then with water, and then suspended in distilled water. The brown dispersion was extensively dialyzed to remove residual metal ions and acids, and then exfoliated via sonication for 1.5 h (300 W). Noncomparable graphene oxide was removed by centrifugation.

Synthesis of graphene oxide/gold nanocomposites

Preparation of Graphene oxide/Gold nanocomposite was based on the depletion of gold (III) compound by trisodium citrate [14, 15]. 2.5 ml of graphene agitator (1.5mg/ml) were added to 50 ml of auric chloride solution. The final compound was ancient during 30 min to develop the reaction of gold ions with the graphene superficial portion. After that, the ancient was heated up to 80°C, after which 940 µL of sodium citrate (0.085mol/dm) was added drop wise. The reaction mixture kept at these conditions during 1h [16, 17]. The resultant nano compound was washed with DI water using centrifugation to remove the unreacted gold nanocompound that formed in solution. The final compound was dried and used for characterization.

Instrumentation

UV- Visible Spectrometer

Ultraviolet-visible absorption spectrum was recorded Shimadzu UV-1800 spectrophotometer. All galvanization investigations were carried out on a CHI620A galvanostat instrument in a conventional three electrodes cell. All spectra were collected averse to the background spectrum of solvents.

Fourier Transform Infrared (FTIR) Spectroscopy

FT -IR spectrum were taken down using a Perkin-Elmer 360 model IR double beam spectrophotometer. The spectrum were collected from 4000 to 400 cm⁻¹ with 4cm⁻¹ resolution over 40 scans. All spectrum were collected against the background spectrum of KBr.

Cyclic voltammetry

Electrochemical studies were taken at room temperature. Cyclic voltammograms were obtained on CHI 600A, Electrochemical Analyzer, USA. The studies were carried out under Nitrogen atmosphere using in single compartment electrochemical cell in which glassy carbon (GC) electrode, or the substance coated on the ITO glass plate was the working

electrode, Ag wire was the reference electrode and platinum wire was used as auxiliary electrode. All potentials were determined against Ag wire as reference electrode. For the electrochemical studies, the suspension of the samples was drop coated on electrode surface and dried under nitrogen.

Scanning electron microscopy

The images were collected without light waves are rendered black and white. SEM images were obtained with a FE-SEM Hitachi SU6600 instrument, Germany. The liquid samples were drop coated on a microscopic glass plates (0.5cm × 0.5cm) and dried under N₂ atmosphere.

Result and discussion

UV-Measurement

In recent years, numerous researches focused on the synthesis and application of graphene oxide. Here with, in our work, synthesis of graphene oxide modified gold NPs was stabilized by the form of Hummers method [8, 18]. The UV-vis absorbance spectral studies of graphene oxide shows in Fig. 1 GO sonicated at different time interval shows peaks at 227, 222, 219 nm and the characteristic peak of gold nanoparticles is observed at 520 nm.

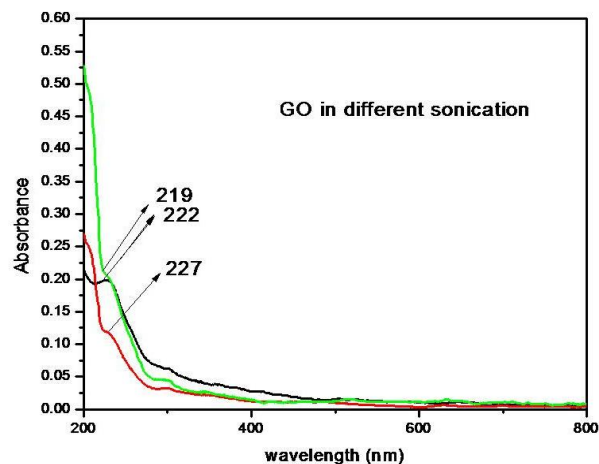


Fig. 1. UV-visible spectra of graphene oxide.

Fourier transforms infra-red spectroscopy

FTIR spectral studies of GO and GO-Au nanoparticles are shown in Fig. 2. In this spectra, the peak at 3450 cm⁻¹ due to the appearance of -OH stretching vibration and the bands at 1650 and 1400 cm⁻¹ attributed to the carboxyl groups of C=O and C-O and also the epoxy response (C-O) at 1200 cm⁻¹ observed. The band at 1100 cm⁻¹ is for alkoxy C-O groups located in the GO nanosheets edges. The oxygen containing groups reduced while the formation of AuNPs, which confirmed by the intensity losses at the band at 3450 cm⁻¹ which is confirmed the interaction between hydroxyl oxygen groups with AuNPs and also it confirm the interaction between chemically converted

GO nanosheets with AuNPs are strongly ensure by these spectra even after the external washing and ultra-sonication [19].

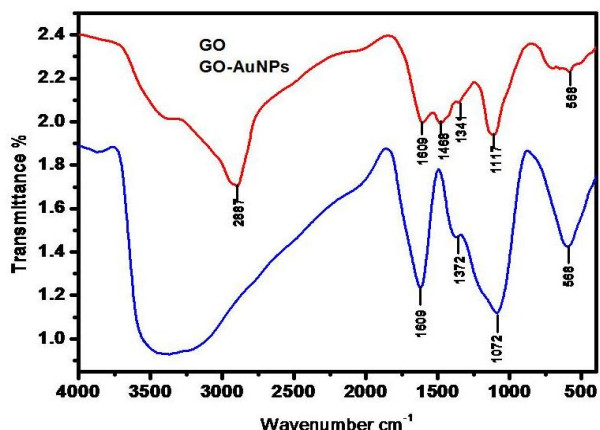


Fig. 2. FTIR spectra of GO and Au-GO nanocomposites.

Scanning electron microscope analysis

The SEM images of GO (A) and GO-Au (B) were shown in Fig. 3. The morphology of the GO are look flakes like structure and GO-Au look cluster like structure [20].

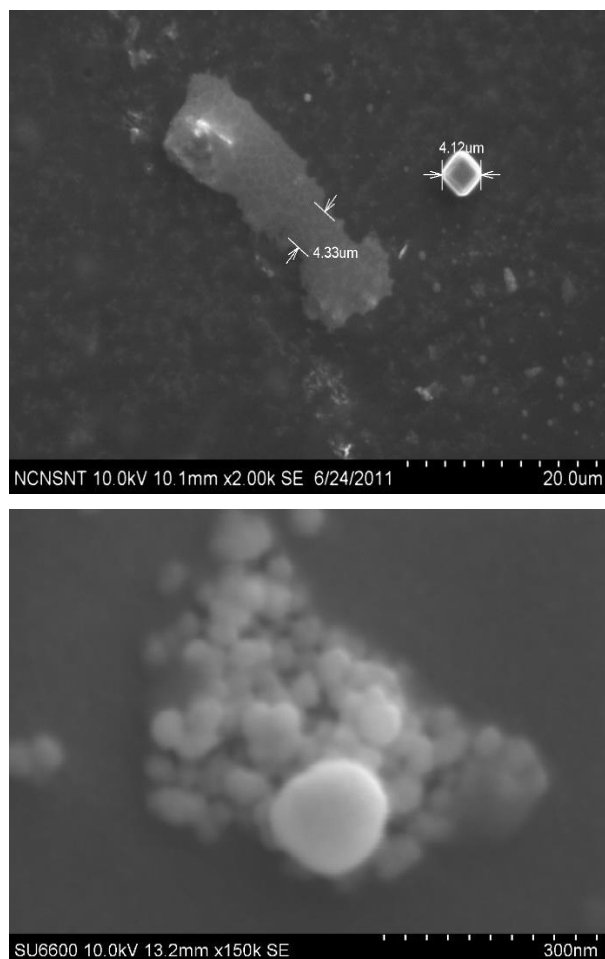


Fig. 3. FE-SEM image of GO and GO-Au nanocomposites.

Electrochemical response of the GO-Au/GCE modified electrode

The electrochemical responses of GO-Au/GCE was analyzed using in the electrolyte medium of $[\text{Fe}(\text{CN})_6]^{3-}$ (10 mM) in 1 M KCl solution. The cyclic voltammogram of GO-Au/GCE is shown in Fig. 3A were obtain by different scan rate (10-60 mV). In these spectra, the anodic and cathodic responses at +0.2 V and +0.16 V due to the responses of nanocomposites, which has the high redox and reversible properties while increasing scan rate. The redox current was increased linearly by the immobilization of the AuNPs on the nanosheets and its corresponding calibration plot (Fig. 3B) is reveal the redox nature of the nanocomposites by the increasing redox current. The redox behavior of the prepared electrode can elaborately explained by the following equation [15].

$$i_p \propto \omega^{1/2} \quad \text{and} \quad i_p \propto \omega^{1/2} \quad \text{KDv} = 2 \beta \text{KTv}$$

and the GO-Au/GCE modified electrode is tested over the determination of nitric oxide in 0.1 M phosphate medium at the scan rate 50 mV/S. The determination of nitric oxide concentration (10-50 μM) concentration of NO was subject over the GO-Au/GCE modified electrode and the peak current was observe at +0.96 V is due to the oxidation of NO. The anodic peak current was increase linearly with respect to increasing the concentration of the analyte.

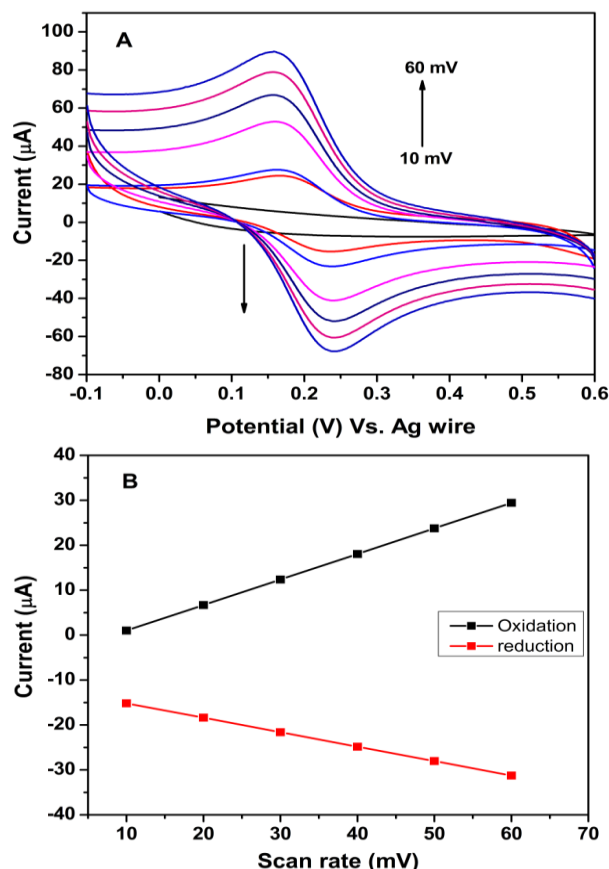


Fig. 4. The electrochemical behavior of GO-AU/GCE (A) in 10 mM $[\text{Fe}(\text{CN})_6]^{3-}$ in 1.0 M KCl using scan rates of (10-60 mV/S) and its corresponding calibration plot (B).

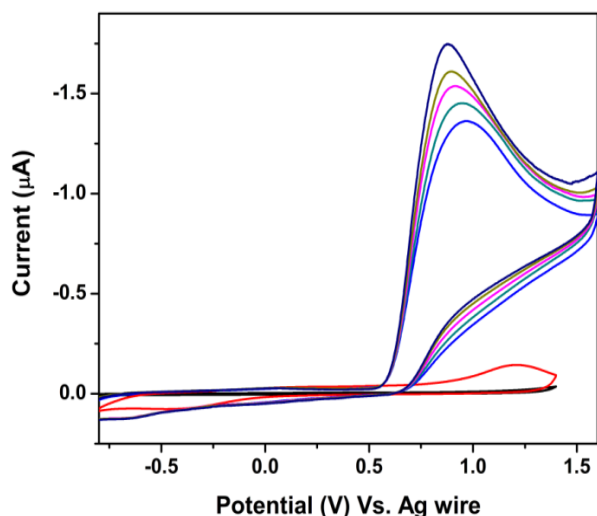


Fig. 5. The electrochemical behavior of GO-AU/GCE in 0.1 M PBS at scan rate 50 mV/S over the concentration of NO (10-50 μM).

Amperometry studies

Generally in the oxidation of NO has two-step mechanism, first the conversion of NO to NO^+ and the second one is NO_2^- to NO_3^- [21]. But in this investigation, we observed on the direct oxidation of NO to NO_3^- because of the oxidative current has excellent linearity over the relationship of NO concentration [18]. The Amperometric determination carried out in different medium (0.1 M PBS at pH 7.0 and acetate buffer pH 3.0) at fixed potential +0.9 V. The oxidation responses obtained very fast and it has excellent reproducibility over the addition of NO in every 25 s time intervals. The obtained oxidation current was well and good linearity over the addition concentration of NO and GO-Au/GCE modified electrode has very good stability over the oxidation of NO [16, 17].

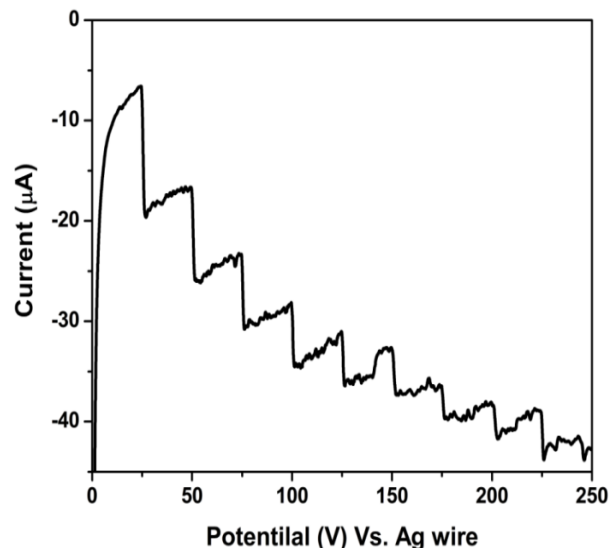


Fig. 6. Typical Amperometry responses of GO-Au/GCE electrode in PBS (pH 7.0) buffer at +0.9 V applied potential over the addition of NO (10-90 μM) in every 25 s.

Conclusion

This study confirms the NO sensing can exhibit the high physiological solution such as cell culture media or real sample serum can be used for monitoring of NO. These study clearly shows that our sensor can be used to detect NO in complex biological sample with good sensitivity and rapid response along with GO-Au nano composites.

References

1. Parvez, K.; Wu, Z.S.; Li, R.; Graf, R.; Feng, X.; Mullen, K.; *JACS*, **2014**, *136*(16), 6083.
2. Zhu, Y.; Murali, S.; Cai, W.; Li, X.; Suk, J. W.; Potts, J. R.; Ruoff, R. S.; *Adv. Mater.*, **2010**, *22*, 3906.
3. Shalini, A.; Nishanthi, R.; Palani, P.; Jaisankar, V.; *Mater. Today Proc.*, **2016**, *3*, 1633.
4. Paulraj, P.; Janaki, N.; Sandhya, S.; Pandian, K.; *Colloids Surf. A*, **2011**, *377*, 28.
5. Piovesan, J.; Santana, E. R.; Spinelli, A.; *J. Electroanalytical. Chem.*, **2018**, *813*, 163.
6. Dikin, D. A.; Stankovich, S.; Zimney, E. J.; Piner, R. D.; *J. Nature*, **2007**, *448*, 457.
7. Zhang, M.; Lu, X.; Wang, H.Y.; Liu, X.; Qin, Y.; Zhang, P.; Guo, Z.X.; *RSC Adv.*, **2016**, *6*, 35945.
8. Ng, S. R.; Guo, C. X.; Li, C. M.; *J. Electroanalysis*, **2011**, *23*(2), 442.
9. Prabakaran, E.; Parani, S.; Alexander, M.; Paulraj, P.; Pandian, K.; *J. Nanosci. Lett.*, **2013**, *3*, 1.
10. Paulraj, P.; Manikandan, A.; Manikandan, E.; Pandian, K.; Moodley, M. K.; Roro, K.; Murugan, K.; *J. Nanosci. Nanotechnol.*, **2018**, *18*, 3991.
11. Shalini, A.; Pandian, K.; Jaisankar, V.; *J. Eng. Chem. Fuel.*, **2017**, *2*, 61.
12. Lee, C.S.; Yu, S.H.; Kim, T.H.; *J. Nanomater.*, **2018**, *8*, 17.
13. Marcano, D. C.; Kosynkin, D. V.; Verlin, J. M.; Sinitiskii, A.; Sun, Z.; Lawrence A. S.; Alemany, V.; Lu W.; Tour, J. M.; *ACS Nano*, **2010**, *4*(8), 4806.
14. Prashant, V.; Kamat, *J. Phy. Chem. Lett.*, **2010**, *1*(2), 520.
15. Hu, W.; Peng, C.; Luo, W.; Li, X.; Fa, C.; *ACS Nano*, **2010**, *4*(7), 4317.
16. Lu, G.; Ocola, L. E.; Chen, J.; *J. Nanotech.*, **2009**, *20*(44), 445502.
17. Pumera, M.; Ambrosi, A.; Pon, H. L.; *J. TrAC.*, **2010**, *29*(9), 954.
18. Wolak, M.; Stochel, G.; Eldik, R. V.; *Inorg. Chem.*, **2006**, *45*(3), 1367.
19. Wu, Z. S.; Parvez, K.; Feng, X.; Mullen, K.; *J. Nature Commun.*, **2013**, *4*, 2487.
20. Yang, X.; Xu, M.; Qiu, W.; Chen, X.; Deng, M.; Zhang, J.; *J. Mater. Chem.*, **2011**, 8096.
21. Jiang, S.; Cheng, R.; Wang, X.; Xue, T.; Liu, Y.; Nel, A.; Huang, Y.; Duan, X.; *J. Nature*, **2013**, 2225, 1.