Optical Sensor for Hydrogen Peroxide using Copper@Graphene Oxide Nanocomposites

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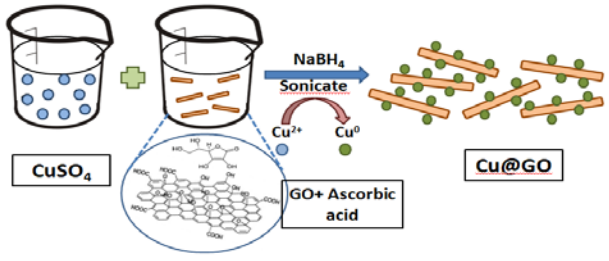
Abstract - In recent years, copper nanoparticles have gained increased attention due to their interesting properties and low cost of preparation. It finds application in Catalysis, conductive inks and sensing applications. The present study describes the synthesis of copper-graphene oxide nanocomposite (Cu@GO) at room temperature for the first time and their application towards the optical sensing of H_2O_2. It is found to be an excellent colorimetric sensor for sensing highly reactive oxygen species such as hydrogen peroxide. The synthesized nanoparticles were further characterized by using UV-Visible spectrophotometry, scanning electron microscopy (SEM) analysis, energy-dispersive X-ray spectroscopy (EDAX) and Fourier transform infrared spectroscopy (FT-IR). It shows a characteristic UV-Visible absorption at around 598 nm. The SEM analysis of the fabricated nanoparticles shows spherical nanoparticles with approximate size ranging from 50 nm to 80 nm. It contains copper (1.08%), carbon (26.72%) and oxygen (24.18%) which is confirmed by EDAX spectrum. Colorimetric sensing of H_2O_2 was carried out by introducing H_2O_2 solution into Cu@GO dispersion and by taking the UV-Visible Spectra. It was found that the Olive green colour of Cu-GO NPs changed into bright yellow colour which doesn't show a SPR peak at 598 nm instead has a small peak at around 388nm.

Keywords: Cu@GO Nanocomposite, Surface plasmon resonance, Hydrogen peroxide sensing.



I. INTRODUCTION

Carbon based nanoparticles such as graphene oxide(GO), Graphene, carbon dots, fullerenes etc have find application in diverse fields including sensors, medicine, drug delivery, catalysis and photo voltaic devices etc[1,2]. Graphene consists of a two-dimensional, single layer of sp^2 hybridized carbon atoms. It is found to possess various unique properties owing to their high specific surface area; high sorption capacity and large delocalized pi-electron system which can easily forms bond with benzene ring system [3]. Due to the lack of functional groups on the surface of the graphene, the interaction with metal ions is poor. Graphene oxide(GO), the precursor of graphene on the other hand bears several hydroxyl, epoxide, carbonyl and carboxyl groups on its hexagonal two dimensional carbon network which makes it highly hydrophilic in nature[4]. The presence of oxygen allows them to show both electrostatic and co-ordinate interaction with several metal ions.

Hydrogen peroxide (H_2O_2) is the simplest peroxide, which is miscible with water and is widely used as an oxidizer, bleaching agent and an antiseptic. The peroxide ion will cause the oxidation of proteins, membrane lipids and DNA [5]. Hydrogen peroxide toxicity is via three main mechanisms: corrosive damage, oxygen gas formation and lipid peroxidation. Exposure to concentrated H_2O_2 may result in local tissue damage as it is a well known caustic [6]. Therefore fast and reliable detection of H_2O_2 at ultra trace level is of great importance. There are several papers describing the usage of noble metal nanoparticles for the colorimetric sensing of H_2O_2 [7-13]. Usually copper nanoparticles are employed for the electrochemical detection of H_2O_2 [14-16]. In the present study, we report the synthesis of copper nanoparticles stabilized by graphene oxide and its application for the sensing of H_2O_2. The Cu@GO dispersion was prepared by reducing copper (II) sulphate using sodium borohydride in presence of GO, under ultrasonication. Ascorbic acid is used as the stabilizing agent. $NaBH_4$ reduces Cu^{2+} into Cu^0 which is then stabilized by the functional groups present in GO. The colour changes from light brown into dark olive green. The formation of copper nanoparticles protected by GO was confirmed by the characteristic surface plasmon resonance (SPR) band at 598 nm in the UV-Vis absorption spectrum. Copper nanoparticles synthesized in the absence of GO shows an absorption peak at 567 nm [17,18]. We are mainly relying on the shift in the SPR of Cu@GO dispersion upon treatment with H_2O_2 for detecting its presence in the sample. The fabricated materials were further characterized using scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDAX) and Fourier transform infrared spectroscopy (FT-IR).

The FE-SEM images showed that the synthesized Cu@GO Nano composite (NC) were spherical in shape with size ranging from 50nm to 80 nm. After the addition of H_2O_2 into the Cu@GO, the peak at 598 nm is found to disappear and a new peak emerges at 388 nm, which becomes more intense with higher H_2O_2 concentrations.

II. EXPERIMENTAL

2.1. Chemicals and materials

Graphite flakes were synthesized by Hummers method reported earlier [19]. Chemical reagents such as copper sulphate ($CuSO_4$), sulphuric acid (H_2SO_4, 98%), potassium permanganate ($KMnO_4$, 99.9%), phosphoric acid (H_3PO_4, 85%), hydrogen peroxide (H_2O_2, 30%) were purchased from Merck. L(+)-ascorbic acid (AA) was purchased from Sisco research laboratories, sodium borohydride ($NaBH_4$) is from Sigma-Aldrich. All the other chemicals used were of analytical grade and used without further purification.

2.2. Preparation of Cu@GO Nanocomposite

The preparation method of Cu@GO nanocomposite was as follows. Initially, GO was prepared by modified Hummer's method. About 3 mg of GO was dispersed in 10 mL of DI water using a sonicator at 50 W in a RB flask. Then, added 500 µl of $CuSO_4$ (0.01 N) to the above solution and is sonicated again for another 10 min. After that, 500 µl of 5 mM freshly prepared sodium borohydride ($NaBH_4$) solution was added to the $CuSO_4$-GO mixture. The colour of the solution initially changes to blackish brown, then into olive green. Sonication is continued for another 10 more minutes to ensure complete reduction of Cu^{2+} into Cu^0.

III. CHARACTERIZATION

3.1. Instrumentation

A bath sonicator operating at (500 W, 50 Hz) was used for synthesizing Cu@GO Composite. Absorption spectra were measured by using V-550 JASCO UV–Visible spectrophotometer. The FT-IR measurements were carried out in JASCO FT-IR 4100 model. A drop of the sample was put in a transparent KBr pellet and allowed to dry. Then the spectrum was recorded in the transmittance mode as a function of the wavenumber ranging from 400 to 4000 cm^{-1}. High resolution scanning electron microscopy (FE-SEM) images were obtained from a CARL ZEISS GEMINI FE-SEM 300, operating at 200 kV. For this, 10 µL of the sample solution was dropped on a glass plate and allowed to dry and the scanning microscopic image is recorded. The EDAX analysis was obtained using AMETEK Octane Plus model. The FT-IR spectra were collected using Jasco FT/IR-4100 model.

IV. RESULTS AND DISCUSSIONS

4.1 Characterization of Cu-GO Composite

Optical studies: The formation of copper nanoparticles can be observed visually as it gives a dark reddish-brown color. But here the Cu@GO composite is found to appear as an Olive green solution. The surface plasmon resonance peak of Cu@GO Nanocomposite was at 598 nm, whereas that of copper nanoparticles synthesized without GO has SPR at around 567 nm and has a reddish brown colour.

UV-Vis spectroscopy: The absorbance of the sample solution was measured using a Jasco V-550 UV-Vis spectrophotometer with de-ionized water as the reference over the range of 300 to 900 nm. The UV-Visible spectroscopy of Cu NPs shows a surface plasmon resonance pear at around 567 nm and appears brown in colour. But, in the case of Cu@GO composite, there is a SPR peak at 598 nm and it appears as a olive green solution.

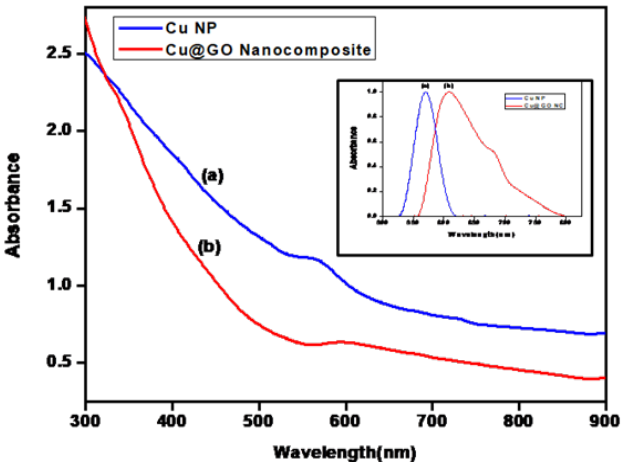


Figure.1. (a)UV-Visible Spectroscopic image of Copper nanoparticles reduced by $NaBH_4$ in presence of Ascorbic acid has an SPR at 567 nm and (b)Copper nanoparticles synthesized in presence of graphene oxide and Ascorbic acid has an absorption maximum at 598 nm. The shift in the SPR can be clearly seen from inset.

4.2. Optical sensing of Hydrogen peroxide

The optical detection of oxidizing species such as Hydrogen peroxide was carried out using Jasco V-550 UV-Visible Spectrophotometer. The calibration characteristics of H_2O_2 using Cu@GO as an optical sensor were studied.

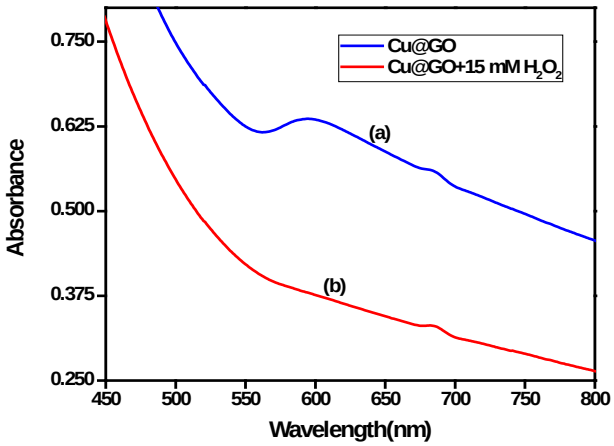


Figure. 2. (a)Cu@GO nanocomposite showing SPR at 598 nm and (b) the disappearance of SPR upon treatment with H_2O_2 solution.

This was performed by adding varying amounts of 0.1 M H_2O_2 prepared to the Cu@GO composite and taking the UV-Visible Spectra. 2 mL of Cu@GO was taken in a bottle and added varying amounts of H_2O_2, shaken well, and allowed to a react. The formation of bubbles in the solution was observed, due to the decomposition of H_2O_2 by the Cu@GO Composite. After that the absorption spectra of Cu@GO solution containing different amounts of $H_2O_2$was recorded and analyzed.

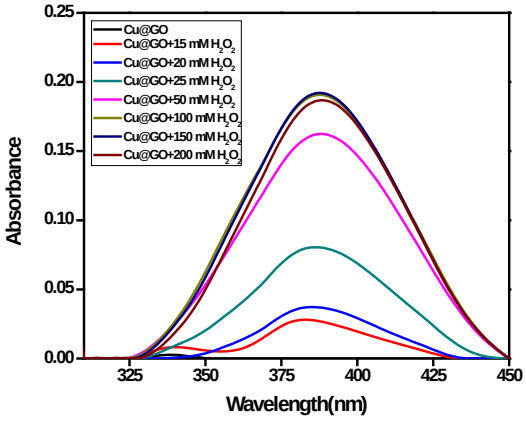


Figure.3. Appearance of a new peak at 388 nm which is directly proportional to the amount of H_2O_2 used.

Figure. 4. Photographic image of Cu@GO composite before and after treatment with H_2O_2.

A higher concentration of H_2O_2 solution causes a higher colour change of Cu@GO composite which can be observed even with the naked eye, in which the colour change is directly proportional to the amount of H_2O_2 solution added to the dispersion.

4.3. Interferences

It is possible that certain amino acids and common metal ions may interfere in the sensing of H_2O_2. So we carried out the experiment with all these possible interfering species such as Thiamine, Alanine, Glycine, Cysteine, $CaCl_2$, $PbCl_2$, $ZnSO_4$, $MgCl_2$, $C_2O_4^{2-}$ and, $HgCl_2$ to make sure that Cu@GO is specific for H_2O_2 sensing. It was found that all these species doesn't produce any visible colour change from green to yellow upon treatment with Cu@GO making it a reliable optical/ colorimetric sensor for H_2O_2.

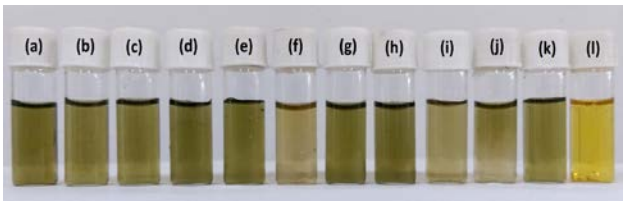


Figure. 5. Photographic image of Cu@GO treated H_2O_2 and some common chemicals that may interfere in the H_2O_2 sensing. (a)Cu@GO Control, (b)Thiamine, (c)Alanine, (d)Glycine, (e)Cysteine, (f)$CaCl_2$, (g)$PbCl_2$, (h)$ZnSO_4$, (i)$MgCl_2$, (j)$C_2O_4^{2-}$, ,(k)$HgCl_2$ and (l)H_2O_2. It is well evident that only H_2O_2 is able to produce a yellow colour upon treatment with Cu@GO.

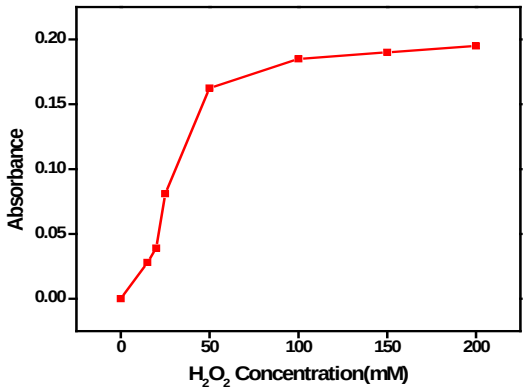


Figure. 6. The plot showing the dependence of the absorbance at λ_{max} against H_2O_2 concentration

It is observed that the curve is linear at lower concentrations of H_2O_2 and after reaching an optimal concentration of H_2O_2, the difference in the absorbance becomes less significant.

EDAX analysis: Energy-dispersive X-ray spectroscopy analysis was done to get an idea about the elemental composition of the fabricated material.

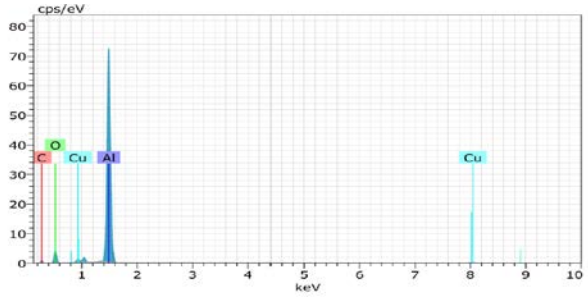


Figure. 7. EDAX spectrum of Cu@GO coated on an aluminum sheet.

As can be seen in the EDAX spectrum, there are peaks at around 1 keV and 8 keV belonging to Copper. Other elements such as carbon (C) has peak at 0.2 keV and that of oxygen appears at 0.5 keV. The appearance of carbon and oxygen peaks confirms the presence of graphene oxide

in the sample. The EDAX thus obtained was used for the elemental analysis. It contains Copper (1.08%), Carbon (26.72%) and Oxygen (24.18%) respectively which is confirmed by the EDAX spectrum.

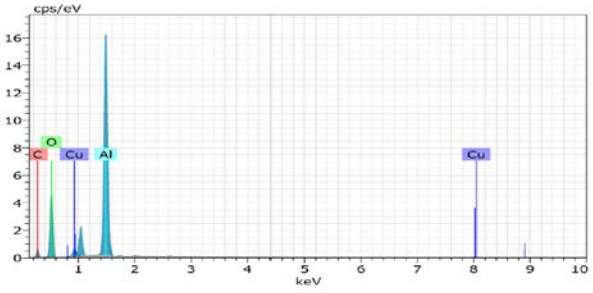


Figure. 8. The EDAX spectrum of Cu@GO after treatment with H_2O_2.

Cu@GO after treating with H_2O_2 contains copper (0.37%), carbon(24.89%) and oxygen(48.97%) respectively.

FT-IR measurement: To identify the presence of graphene oxide in the Cu@GO composite, we carried out the Fourier transform infrared spectroscopic analysis.

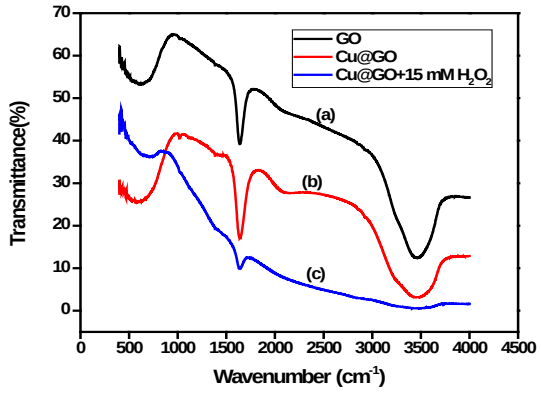


Figure. 9. Fourier Transform Infrared Spectrum of (a)Graphene Oxide, (b)Cu@GO Composite and (c)Cu@GO after treatment with H_2O_2.

The characteristic FTIR spectrum of GO nanosheets is shown in the above figure. The intense peak at 3467 cm^{-1} is attributed to the O-H group stretching vibration. The absorption bands at 1635 cm^{-1} can be assigned to C=O stretching of carboxylic and/or carbonyl moiety functional groups. The absorption peak at 1038 cm^{-1} is assigned to the C–O stretching vibrations. The FT-IR spectrum of Cu@GO has the same peaks as that of graphene oxide, indicating that GO has not been reduced by the ascorbic acid and $NaBH_4$ present in the solution. So the fabricated material is confirmed to be Cu@GO, not Cu@rGO (where rGO stands for reduced graphene oxide). After treating Cu@GO with H_2O_2, the major peak at 3457 cm^{-1} is too weak to identify and that at 1635 cm^{-1} has a significant decrease in its intensity.

SEM Analysis

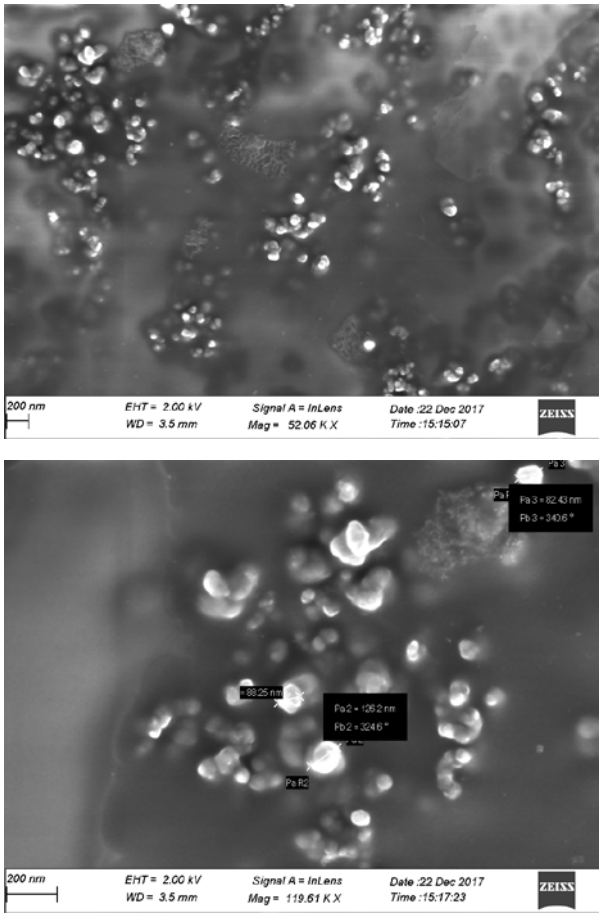


Figure. 10. Field emission scanning electron microscopic (FE-SEM) image of Cu@GO composite.

In this study, the fabricated Cu@GO composite was characterized by using scanning electron microscopic analysis, which can provide better information about the size and morphology of the fabricated nanoparticles. It was observed that the synthesized Cu@GO was having size in the nano range. They are all well dispersed without aggregation. The FE-SEM images of the fabricated Cu@GO nanocomposite showed that it has a spherical shape with size ranging from 50nm to 80 nm.

V. CONCLUSION

In the present study, the Cu@GO nanocomposite was fabricated by a simple chemical reduction method by reducing copper sulphate precursor with sodium borohydride and GO. Ascorbic acid is used as the stabilizing agent. The synthesized nanoparticle shows an SPR peak at 598nm and appears dark olive green in colour. The elemental composition, morphology, and other properties of the fabricated nanoparticles were characterized by using different techniques. The Cu@GO NC has spherical morphology with an average particle size ranging from 50 nm to 80 nm which is confirmed by the SEM Analysis. Thus formed Cu@GO dispersion is found to be excellent for detecting trace amounts of H_2O_2 by monitoring and analyzing the UV-Visible Spectra. The

shift in the SPR wavelength of Cu@GO gives an idea about the quantitative determination of H_2O_2. From the results, it is obvious that the SPR characteristics and colour of Cu@GO drastically got changed after H_2O_2 addition which is directly proportional to the H_2O_2 concentration. Thus we can conclude that Cu@GO can be synthesized by a simple, fast, and cost-effective method to be applied as a colorimetric sensor for H_2O_2 detection.

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