

# Synthesis and characterization of rGO + SnO<sub>2</sub> composite for bio sensor application

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**Abstract:** In the present work, Graphene oxide (GO) was prepared using improved modified Hummer's method. Reduced Graphene oxide (rGO) is synthesized by cow urine extract using sonication and refluxing process. Tin Oxide quantum dots were synthesized using wet chemical method. RGO/SnO<sub>2</sub> based pellets were prepared using hydraulic press. These pellets were characterized for glucose. Structural and optical characterization of GO, rGO and SnO<sub>2</sub> quantum dots was performed using XRD, UV-visible and FTIR. The sensors show good response towards glucose.

Keywords: graphene oxide, reduced graphene oxide, quantum dot, glucose sensor

## Introduction

Nanotechnology and nanostructured materials provide new and exhilarating opportunities for exploring biosensing applications [1–3]. In recent years, an increasing number of researchers have explored the production of novel nano-scale metal oxides, noble metal-doped metal oxides, metal oxide-CNTs nanocomposites, and metal oxide-polymer composites. . It is reported that during the last two decades tremendous efforts have been made for the detection of glucose based on nanostructured metal oxides and their composites Graphene, graphene oxide (GO) and reduced graphene oxide (rGO) composites with metal oxide quantum dots and nanoparticles are very useful for large scale production of selective chemical and biosensors. Numerous processes and methodologies have been developed for creating new glucose biosensors such as electrochemical methods [4], colorimetry [5], conductometry [6], optical methods [7], and fluorescent spectroscopy [8]. Among them, the electrochemical glucose sensors have attracted the most attention over the last 40 years because of their unbeaten sensitivity and selectivity. Additionally, electrochemical techniques show lower detection limit, faster response time, better long term stability and inexpensiveness. The catalytic ability of metal oxides as candidate electrode materials has been extensively investigated to develop biosensors with high sensitivity, fast response and stability for glucose determination through electrochemical oxidation.[9-11]. Graphene has extraordinary potential as a bio sensing material due to good electrical conductivity, biocompatibility, flexibility and ease of functionalization. Sensors based on graphene do not require high impedance circuit [12]. Recent progress shows that graphene based bio sensing materials can have profound impact on applications such as real time health monitoring ,early diagnosis of life threatening diseases like cancer and biosensors namely pH sensor, DNA sensor, glucose sensors etc.[13 ]. Given the good electron transfer ability and unsaturated dangling bonds of rGO, as well as the ample electro catalytic active sites of quantum-sized SnO<sub>2</sub> NPs on unfolded rGO sheets, the fabricated SnO<sub>2</sub>-rGO nanocomposite exhibited excellent performance in the non-enzymatic electrochemical detection of glucose molecules.

### Preparation of Grapheme Oxide:

In the present work, improved modified Hummer's method was used for the preparation of graphene oxide (GO) [14]. It has two phases the solid phase is a mixture of 10 g of graphite powder and 5 g  $\text{NaNO}_3$ . The liquid phase contains 216 ml of concentrated  $\text{H}_2\text{SO}_4$  mixed with 24 ml concentrated  $\text{H}_3\text{PO}_4$ . The liquid phase ratio was maintained as 9:1 (wt %). After addition of 30 g of potassium permanganate, the mixture was stirred for 1 hour at temperature of  $100^\circ\text{C}$ . Addition of 30 ml of  $\text{H}_2\text{O}_2$  into the mixture resulting in yellow color represents great level of oxidation. For the complete removal of  $\text{SO}_4^{2-}$ , solution was repeatedly washed with 5% HCl and DI followed by centrifuge (4000 rpm). Finally the material was air dried for nearly 24 h and a brown black sample was collected.

### Preparation of rGO using cow urine extract.

The prepared graphene oxide solution was mixed with 10 ml concentration of cow urine extract. The solution was heated to  $95^\circ\text{C}$  using water bath to get homogeneous heating under reflux condition for 15 hrs. The solution was centrifuged at 4000 rpm for 20 min. The precipitate collected was washed repeatedly using DI water and re-centrifuged to obtain reduced graphene oxide.

### Synthesis of $\text{SnO}_2$ quantum dots.

0.4 g of tin chloride was dissolved in 80 ml of methanol under magnetic stirring for 3 h. After complete dissolution of the  $\text{SnCl}_2$  source,  $\text{NH}_3$  solution was added drop wise and the pH of the solution was maintained as 9. The prepared solution was heated at  $80^\circ\text{C}$  for 2 hours till the tin hydroxide precipitate was formed. The precipitate was separated by centrifugation and washed repeatedly with DI water and ethanol for the removal of by-products. The calcination of the precipitate was carried out at  $400^\circ\text{C}$  for 2 hours to obtain tin (di) oxide quantum dots.

### Preparation of rGO/ $\text{SnO}_2$ composite

$\text{SnO}_2$  and rGO at a ratio of 1:2 by weight were mixed with HPMC and PVA at a ratio of 3:2 by weight to form nanocomposites. Few drops of DI water were added to prepare pellet using hydraulic press. The pellet was annealed at  $100^\circ\text{C}$  for 1 hour. The diameter of the pellet was 9 mm with thickness of about 2mm. Pellets were prepared by considering the proportions of  $\text{SnO}_2$ , rGO, HPMC and PVA to form nanocomposites as shown in table 1. Few drops of DI water were added to prepare pellet using hydraulic press.

**Table 1: composition of Pellet**

Pellet No	rGO (wt %)	$\text{SnO}_2$ (wt %)	HPMC (wt %)	PVA (wt %)
1	50	-	25	25
2	-	50	25	25
3	50	25	15	10

## Structural characterization

X-ray diffraction (XRD) patterns of the samples were recorded using Phillip, Holland instrument with  $\text{CuK}\alpha$  radiation (0.1541 nm) in the range of  $5^\circ$  to  $85^\circ$  with scanning rate  $2^\circ$  per minute.

## Optical characterization

Fourier Transform Infrared (FTIR) and UV-visible spectra of the samples were recorded on Perkin-Elmer FTIR Spectrometer RXI and Shimadzu UV-2450 UV visible spectrophotometer respectively.

## Results and discussion:

### XRD analysis

Figure 1 depicts XRD pattern of graphite powder, prepared GO, rGO and rGO+SnO<sub>2</sub> nanocomposites.

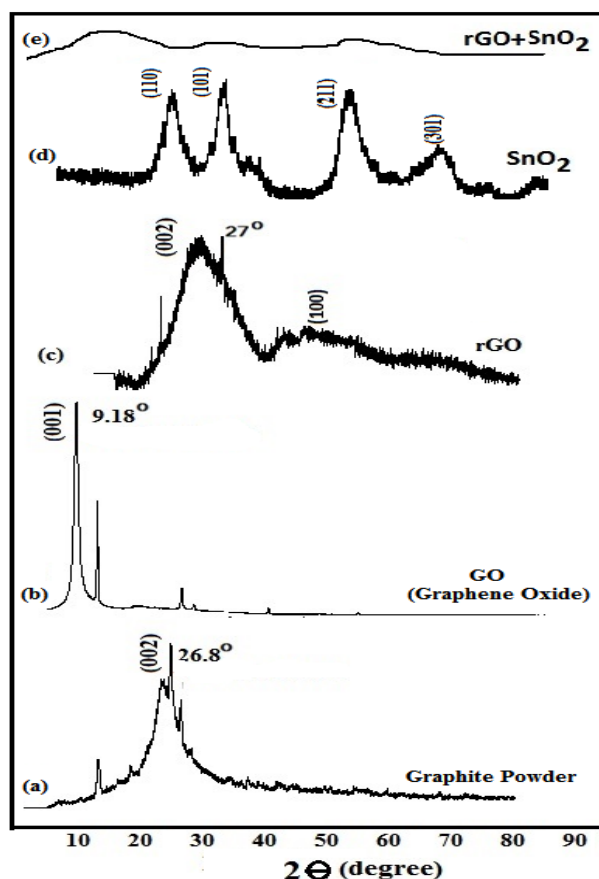


Fig. 1: XRD pattern of (a) graphite (b) GO (c) rGO (d) SnO<sub>2</sub> and (e) rGO + SnO<sub>2</sub>

The characteristic peak (002) at  $2\theta = \sim 26.8^\circ$  with interlayer distance of 0.39 nm represents few un-oxidized graphite. It can be seen that after oxidation of graphite into GO, the sharp peak of graphite disappears and new peak appears at  $2\theta \sim 9.18^\circ$  corresponding to (001) plane. Due to formation of functional groups on both sides of loosely arranged graphite sheets interlayer distance increases to 0.54 nm. The broad peak to  $2\theta \sim 27^\circ$  observed in figure 1(c) depicts layered formation of rGO sheets corresponding to (002) plane. XRD pattern of SnO<sub>2</sub> nanoparticles (Figure 1d) shows the diffraction peaks of (110), (101), (211) and (301) planes at various values of  $2\theta$   $26.2^\circ$ ,  $33.4^\circ$ ,  $51.7^\circ$  and  $66.4^\circ$  respectively which magnificently matches with JCPDS card # 77-0452. The average crystallite size was estimated according to the Scherer equation

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

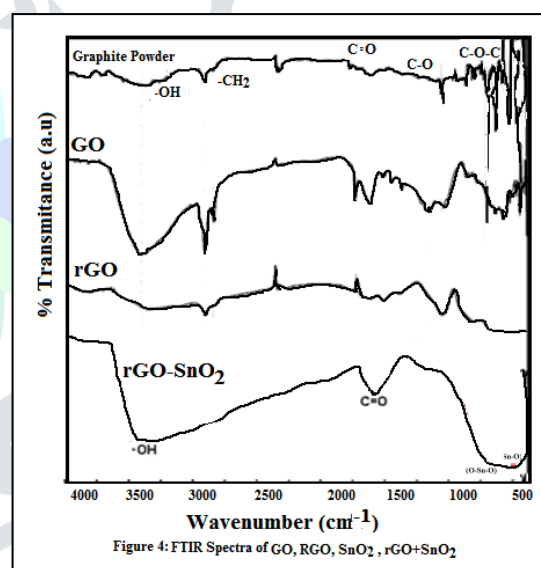
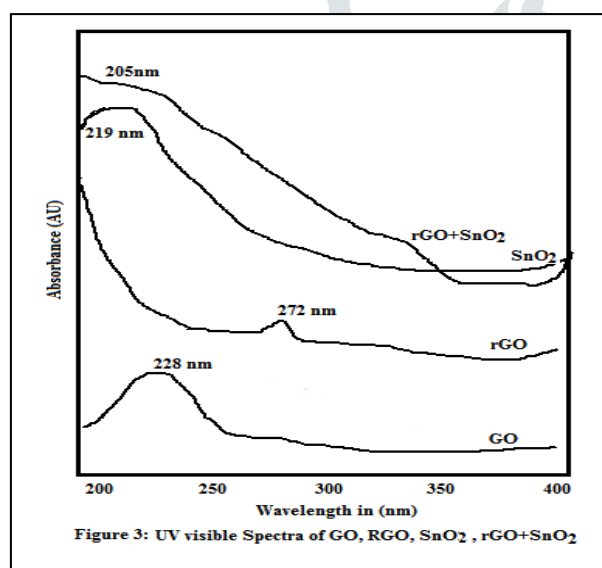
The average crystallite size was  $\sim 2$  nm. The XRD pattern of rGO-SnO<sub>2</sub> nanocomposites (Fig. 1e) shows SnO<sub>2</sub> peaks but the intensity of the peaks are reduced and broaden when compared with XRD pattern of individual rGO and SnO<sub>2</sub>.

## Optical characterization

### UV-visible analysis

**Figure 3 shows UV visible spectra of prepared GO, rGO and rGO+SnO<sub>2</sub> pellets**

The absorption peak for GO was observed at 228 nm depicts  $\pi \rightarrow \pi^*$  transition of C=C bonds [15]. The red shift in absorption peak from 228 to 272 nm is after the reduction of GO by reflux method using cow urine extract. The shift signifies deoxygenation of the GO sheets and the rebuilding of the sp<sup>2</sup> bonded hybridized carbon structure. This phenomenon shift has been used as a monitoring tool for the reduction of GO. During the reduction of GO, the colour of GO solution changes from yellow brown to black. This is in agreement with the work reported by few researchers [16]. The absorption band at 219 nm originates from the band gap transitions and leads to the existence of highly crystalline SnO<sub>2</sub>. The absorption band at 205 nm shows low absorbance of rGO/SnO<sub>2</sub> nanocomposites.



### FTIR analysis:

**Figure 4 indicates FTIR spectra of prepared Graphite powder, GO, rGO and rGO+SnO<sub>2</sub> nanocomposites.**

The FTIR of graphite powder shows various characteristic absorption hydroxyl, epoxy functional groups and bands of oxygen-containing groups. Analysis of Go shows broad absorption spectrum at 3457 cm<sup>-1</sup> equivalent to O-H stretching vibrations. This represents existence of water molecules and structural O-H groups in GO. The broad peak in GO indicates stretching in O-H and C-H bands. The band at 1734 cm<sup>-1</sup> can be related to C=O stretching of -COOH groups at the edges and defects in GO. The peak near 1750-1552 cm<sup>-1</sup> becomes wide and shifts to 1475 cm<sup>-1</sup>. This depicts presence of un-oxidized aromatic regions. The FTIR spectrum of Tin Oxide shows broad absorption band  $\sim 3457$  cm<sup>-1</sup> equivalent to O-H stretching vibration due to absorbed water molecules. A band at  $\sim 614$  cm<sup>-1</sup> relates to O-Sn-O stretching. Broad and

sharp absorption spectrum can be observed at  $\sim 3457\text{ cm}^{-1}$  corresponding O-H stretching vibration in rGO-SnO<sub>2</sub>. Peak at  $1640\text{ cm}^{-1}$  corresponding O-H bending vibration indicating existence of absorbed water molecules and structural O-H groups in rGO-SnO<sub>2</sub>. Similarly, a sharp band at  $\sim 614\text{ cm}^{-1}$  related to O-Sn-O stretching in rGO-SnO<sub>2</sub> refers to the integration of SnO<sub>2</sub> quantum dots.

### Resistance measurement for the glucose sensor

As prepared pellets were used to sense starch followed by amylase using drop casting method. Original resistance of pallet was measured with well calibrated 6 1/2 digit resistance meter. A drop of starch was placed on a pallet followed by diluted amylase. Change in resistance was measured at every stage. It was observed that the resistance of pellet decreases successively. This can be considered as one of the parameter for the capability of as prepared pellets towards glucose sensor. The change in resistance of pellets was as shown in Table 2.

**Table 2: Resistance measurements**

Pellet No	Original resistance	After placing a drop of Starch	After placing a drop of Amylase
1	45-50 K $\Omega$	11.5 K $\Omega$	10 K $\Omega$
2	1-2 M $\Omega$	90 K $\Omega$	23 K $\Omega$
3	700 K $\Omega$	7.5 K $\Omega$	10 K $\Omega$

In this class of biosensors, the enzyme is immobilized on a transducer surface and its capability to transform a substrate in an electroactive, measurable byproduct is exploited. Such biosensors rely on enzymes that belong to oxidases type. [17]

### Conclusions

The cow urine extract was successfully used as green reducing agent for reduction of graphene oxide (GO) into reduced graphene oxide (rGO). Tin Oxide quantum dots were synthesized using wet chemical method. Average crystallite size of SnO<sub>2</sub> quantum dots was  $\sim 2\text{ nm}$ . rGO/SnO<sub>2</sub> based pellets were characterized for starch and amylase and hence for glucose. Change in resistance was measured at every stage and it was observed that the resistance of pellet decreases consecutively. For rGO/SnO<sub>2</sub> based pellet the resistance decreases up to 10 K $\Omega$  from 700 K $\Omega$ . This proves that rGO/SnO<sub>2</sub> based pellets are capable of sensing glucose. The method reported in this work is sustainable, cost effective, bio safe and more ecofriendly. The sensors show good response towards glucose.

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