Low cost hydrothermal synthesis of optically important graphene/zinc oxide nanocomposites

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Graphene oxide (GO)/Zinc Oxide (ZnO) nanocomposites were synthesized by low-cost hydrothermal route under high pressure and temperature. The Samples were characterized by optical, structural, and morphological characterizations. Increase absorbance in the visible region alongwith good luminescence is observed with an increasing ZnO concentration. X-ray diffraction (XRD) studies exhibit much more intense and sharper peaks in higher concentration sample GOZn3 than in GOZn1, confirming the highly crystalline nature of Nanoparticles at a higher amount of ZnO nanoparticles inclusion in GO. The average crystal size was found to be approximately 22 nm and 30 nm in the sample with lower and moderate concentrations GOZn1 and GOZn2 respectively. FTIR spectra analysis for functional groups present in Nanocomposites indicates the presence of aliphatic compounds, hydrocarbon bonding, olefin, hydroxyl, and aliphatic nitro compounds. FESEM micrographs indicate a sheet like the structure of GO and Zinc oxide nanoparticles arranged on a sheet in a regular pattern of hexagonal structures which are in good agreement with XRD results. The size of FESEM and XRD studies is almost the same it varies from 22 nm to 30 nm.

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1. Introduction

Graphene has sp2 hybridized and honeycomb-like structure. It has many properties like high mechanical strength, electrical conductivity molecular barrier abilities, etc [1-3]. However, the use of pristine graphene faces challenges due to difficult bottom-up synthesis [4] and poor solubility [5]. To overcome these limitations an alternate material similar to graphene, graphene oxide is used which is easily synthesized by the top-down method. The graphene oxide has hexagonal geometry and can be prepared by oxidation of graphite in protonated solvents leading to graphite oxide, which consists of multiple stacked layers of graphene oxide (GO). GO has tremendous hydrophilic, thermal, and electrical properties. GO can be taken advantage of in stimuli-responsive materials [6-8]. The diverse properties of GO permit development and incorporation of GO into multi-stimuli-responsive smart materials. it has shown potentials for use in highly humid environments and touchless sensing technology with electromechanical responses. Functionalization of GO with other nano compounds has opened many new optoelectronic applications [9-10]. On the other hand recently many polymer and grephene based composites also reported with metal oxides and metsl sulfides. Zinc oxide (ZnO) among the many inorganic semiconductors is one of the most potential candidate for optoelectronic applications. In general, the addition of ZnO filler in polymer or carbon matrices can alter the optical, electrical and mechanical properties of polymers [11–13]. In this regard S. M. AHMED [14] reported ZnO / PS nanocomposite samples, blend and in-situ method with significant improvement in mechanical properties of ZnO/PS nanocomposite along with optical properties. Recently Reduced graphene oxide/zinc sulfide nano composites with sonochemical route is reported by Rajshree et al. [15]. Reduced Graphene oxide/ZnS nanocomposites exhibit fluorescence property compared with pure

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ZnS and rGO. It also enhances the photocatalytic activity by efficient light harvesting, improved interfacial charge transfer, and suppressing charge recombination. Metal.

In this paper we have first time reported hydrothermally synthesized GO/ZnO nanocomposite and their optical, structural, and morphological characterizations

2. Experimental details

2.1. Material- Analytical grade materials Graphene oxide, ethanol, distilled water, Zinc chloride, and NH3OH were used purchased from CDH.

2.2. Method – The whole process was divided into three parts. First Preparation of ZnO Nanoparticles, preparation of graphene oxide solutions, and then Preparation of Graphene oxide solution hydrothermal method.

(a) Preparation of ZnO nanoparticles

0.1 mol of Zinc chloride dissolve in100ml of distilled water, magnetically stirred for one hour at 60^oC, and add 5 drops of liquid ammonia in it after 15 min of reaction. Kept the obtain solution in ultrasonicator for 30 mins. The remaining solution divided into 5ml, 10ml and 25ml for further synthesis.

(b) Preparation of Graphene oxide solution

0.4 g Graphene oxide is dissolved in 40 ml of ethanol, continuously stirred for one hour then placed in an ultrasonicator for another half an hour. After the sonicator, the solution divides the mixture into four equal parts 10ml each.

(c) Formation of Graphene oxide / ZnO nanocomposites with hydrothermal method

1. For the formation of Graphene oxide, the first 10ml part of the solution is kept in a hydrothermal reactor and placed in the oven at 180^oC for 3 hours. After three hours the reactor cooled under room temperature and filtered the solution with whatsman filter paper dried the filter at 30^oC.
2. For the Composite, Added 5ml of ZnO solution into10ml of Graphene oxide solution slowly and stirred continuously for good saturation. After two or three mins kept the solution in the PPL lining autoclave reactor and placed in the oven for 3h at 180^oC. cooled the reactor at room temperature and filtered the solution with whatsman filter paper with multiple washing of particles by distilled water. The same method is used in the synthesis of various ratios of ZnO in graphene oxide the pure graphene oxide has coded with (a) GO and doped graphene oxide with various concentrations of ZnO nanoparticles coded with (b) GOZn1, 10:5 (C) GOZn2, 10:10 and (d) GOZn3, 10:25.

3. Results and discussion

3.1. XRD(Structural studies)

The samples were analyzed by X-Ray Diffraction (XRD) Using 300/650 Miniflex in the range $2\Theta$from $20^o$to 80^o. The surface morphology of Samples was studied with FESEM (Nova Nano SEM 450) studies from IIT Mandi, Himachal Pradesh. FTIR (Functional Analysis Carried using Perkin Elmer, absorption studies carried by UV- Visible Spectroscopy Perkin Lambda – 25 And PL Studies Also Carried By Elmer Perkin LS-55 From ITM University, Gwalior.

The diffraction pattern of Graphene oxide and Graphene oxide and Zinc oxide nanocomposites. (a) GO (b) GOZn1 (c) GOZn2 (d) GOZn3 shown in Fig.1. The peaks observed at 2 theta 31.8^0 34.4^0 36.4^0 47.7^0, 56.7^0, 63.6^0, 66.4^0 68.2^0 and 69.3^0 corresponding crystal planes (100), (002), (101) , (102), (110), (103), (200), (112) and (201) is good agreement of zinc oxide peaks according the JCPDS NO- 79-0205. According to this file hexagonal wurtzite

structure is exhibited by GOZNO nanocomposites. The fig1. shows that the GO has two peaks at 11.60 and 26.6 0 corresponding to (001) and (002) plane, as the zinc oxide is incorporated into it the intensity of peaks decreases, and peaks are split into another number of peaks that are zinc oxide peaks and some other peaks are observed due to solvent and precursors used that can be neglected. The peaks are shifted throughout towards a higher 2theta value which is ascribed to the strain present in the sample.

The crystallite size (D) and microstrain(ε) of the obtained nanocomposites can be calculated from the peak broadening in the XRD patterns using Williamson-Hall analysis. As illustrated from eq. (2), the total line broadening considers two physical factors; the first one is responsible for the crystallite size (D), while the second one reflects the strain (ε) effects: β

$$\beta = \beta D + \beta\varepsilon \tag{1}$$

The Williamson-Hall equation can be written as in the following:

$$\beta\ Cos\theta = \frac{k\lambda}{D} + 4\varepsilon\ Sin\theta \tag{2}$$

The size broadening (βD) is proportional to cos-1θ and the strain broadening (βε) is proportional to tanθ. In order to calculate the crystallite size and microstrain of the ZnO nanoparticles, a relationship between $\beta\ Cos\theta$ and sinθ is drawn for prepared sample and is shown in fig (1). The average crystallite size 20nm, 23nm, 38nm, and 42nm, while its microstrain value is about 0.47 to 0.196 and exhibit positive strain confirms the presence of tensile strain. The size of the Nanocomposite particles calculated by eq.(30debye Scherer equation[16-17].

$$D = {}^{0.9\lambda}/_{\beta Cos\theta} \tag{3}$$

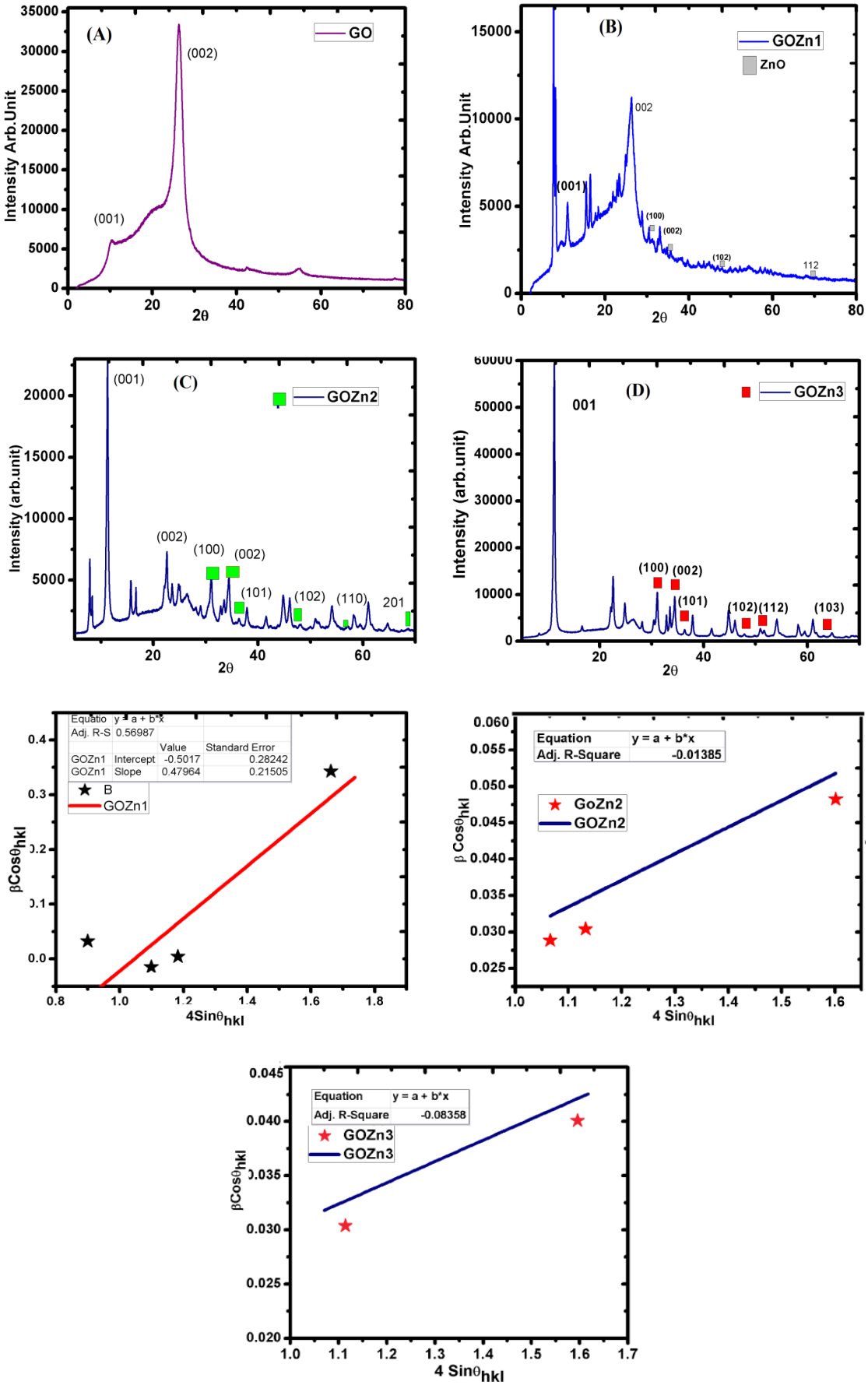

Fig. 1. XRD diffraction peaks and W-H plot of Graphene oxide Nanocomposites.(A) GO (B) GOZn1 (C) GOZn2 (D) GOZn3.

Table 1. Calculate size of Nanoparticles by debye schrrer formula and intercept and strain by W-H plot of Graphene oxide Nanocomposites. (A) GO (B) GOZn1 (C) GOZn2 (D) GOZn3.

Sample	size in (nm)	FWHM	Intercept	Strain
GO	22	0.0635		
GOZn1	42.7	0.0332	-0.5017	0 .47
GOZn2	38.8	0.0421	-0.00675	0.037
GOZN3	41	0.038	0.01077	0.196

3.2. FESEM

Figure 2 FESEM micrographs show the composition of Graphene Oxide and its Composites with Zinc oxide. According to FESEM micrographs of GO/ZnO nanocomposites have wurtizite hexagonal, small size and bigger sized particles well arranged on the surface of graphene oxide sheet. which reveals the XRD results and size of these particles is varies from 20nm to 26nm is calculated by imaje J .

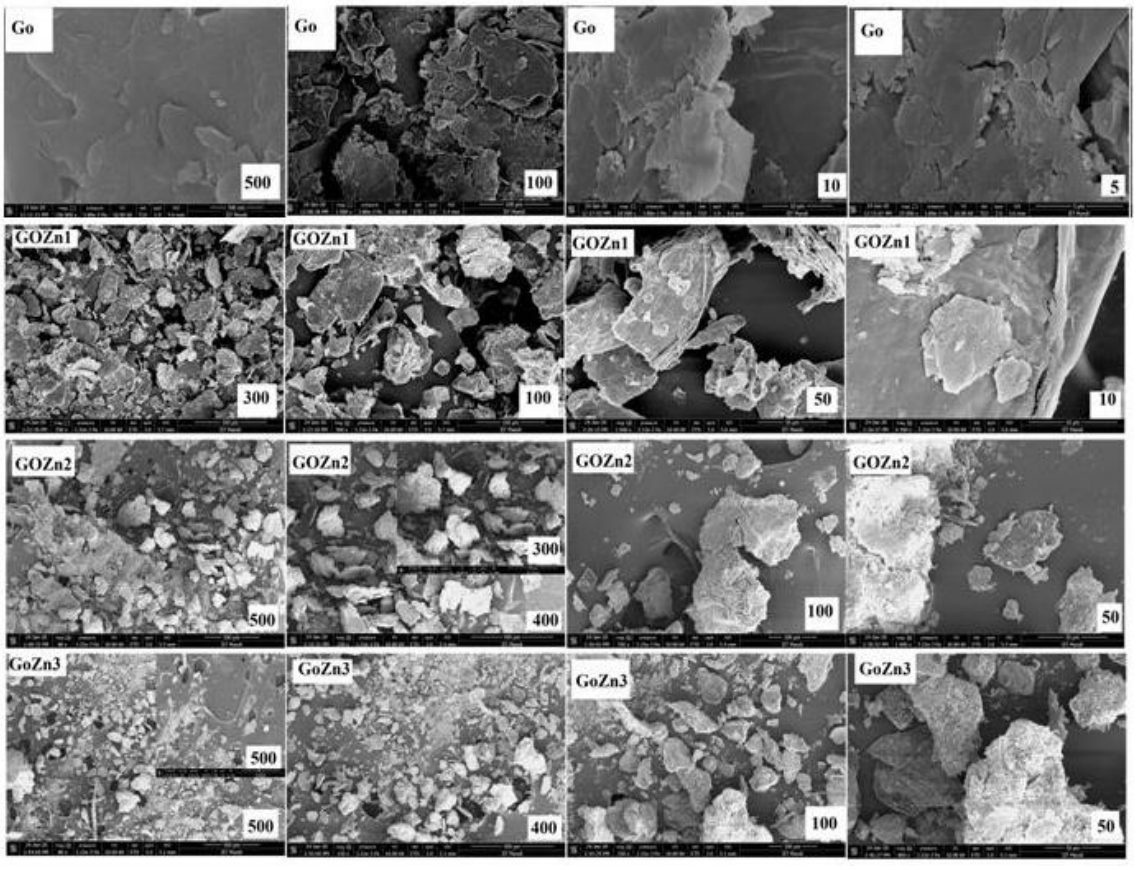

Fig. 2. FESEM micrographs of Graphene oxide /ZnO nanocomposities(a) GO (b) GOZnO1 (c) GOZnO2 (d) GOZnO3.

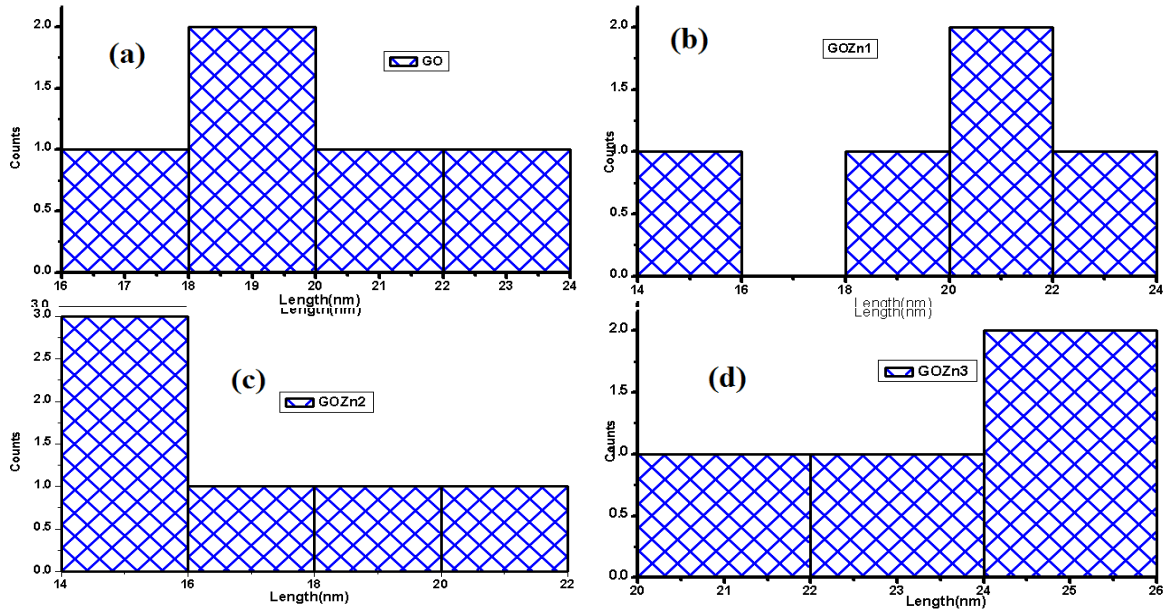

Fig. 3. Histograms of FESEM micrographs for calculating the average length of particles.of (a) GO (b) GOZn1 (c) GOZn2 and (d) GOZn3.

3.3. FTIR

In Fig4. IR spectroscopy shows that Graphene oxide and its composites have well prepared the peaks present at 3499cm^{-1} corresponding to stretching frequencies of oxide C-O bond and free –OH Bond. The intensity of peaks increases on adding ZnO nanoparticles in GO. The peaks at 1600cm^{-1} are attributed to the stretching frequency of carbonyl C=O bond and at peak 2157Cm^{-1} which shows CH_2.

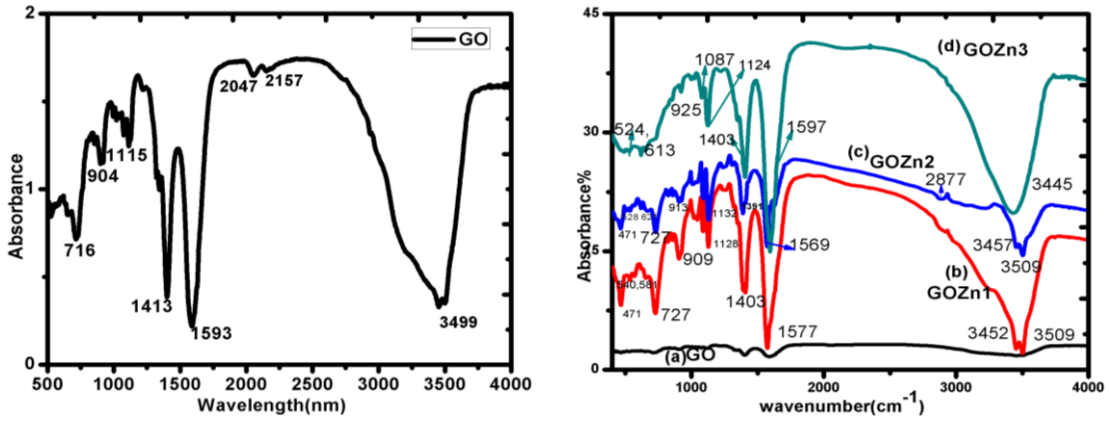

Fig. 4. IR spectroscopy of graphene /ZnO nanocomposities(a) GO (b) GOZn1 (c) GOZn2 (d) GOZn3.

Table 2. for FTIR analysis and attributed peaks of GO-ZNO nanocomposites.

Bending and vibrations	GO	GOZn1	GOZn2	GOZn3
-OH	3499	3452,3509	3457,3509	3440
C=O	2157,2047		2877	1600
C=C	1593,1413	1577,1403	1569,1387	1597,1403,1399
C-OH	1115,904	1128,909	1132,913	1124,1087,925
ZnO	716	727,609,535,471	727,624,528,471	613,524

3.4. UV-VIS spectroscopy

The optical band gap with direct transition can be calculated from the following Tauc relationship.

$$(\alpha h\nu)^{2} = D\,(h\nu - Eg) \tag{4}$$

where hν is a photon energy, *B* is a parameter which depends on the transition probability, α is the absorption coefficient, Eg is the optical band gap and n is a number characterizing the transition process which may take values of 1/2 and 3/2 for direct allowed and forbidden transitions, respectively. Fig.(5) shows plots of (αhν) 2 vs hν. The values of the optical band gap Eg of GOZn1, GOZn2 and GOZn3 nanocomposites sample was determined to be (a)3.98eV (b)3.9eV (c) 3.6eV (d)3.62eV. The optical band gap of GO/ZnO nanocomposites are decreases as the ZnO Nanoparticles concentration increases in GO. The decrease in the band gap of GO/ZnO can be explained by the increase in the surface charge between ZnO and GO, which results in the optical band gap shifting to a higher wavelength.

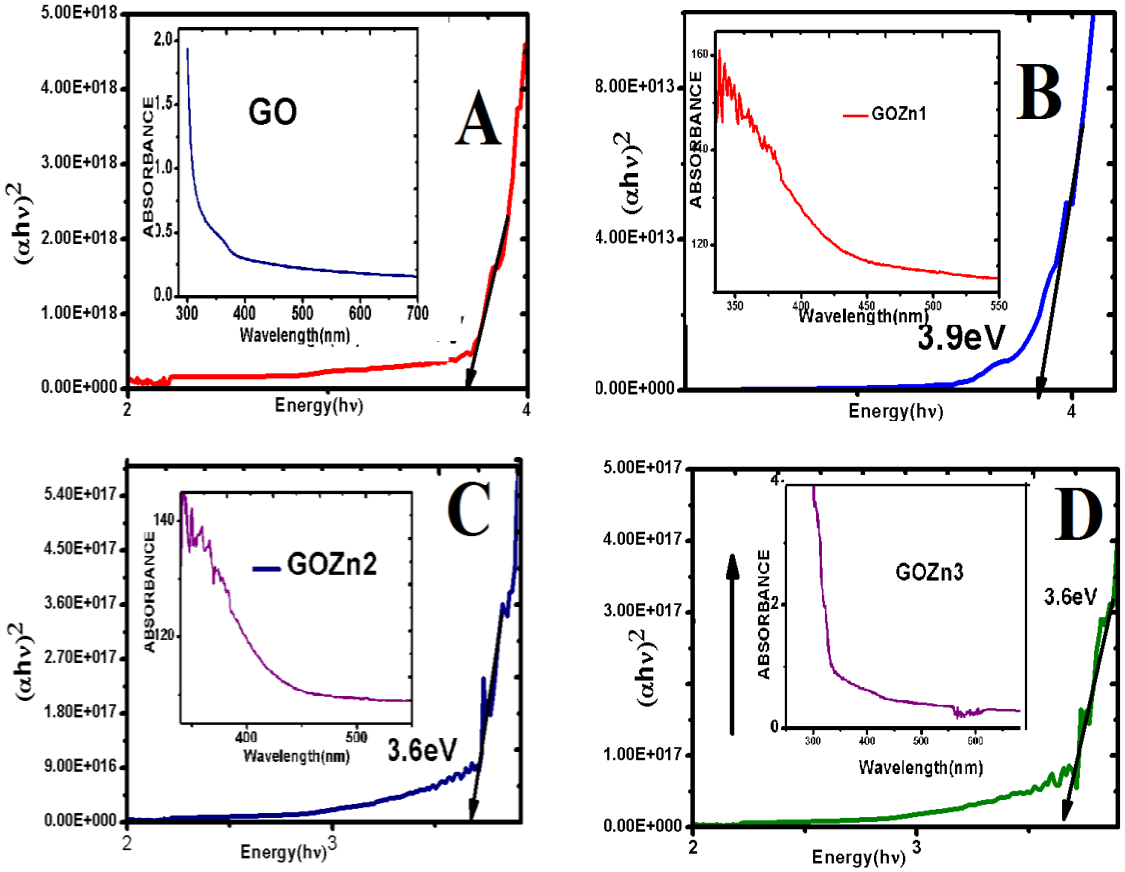

Fig. 5. UV-spectra and Tauc Plot of Graphene oxide and Graphene oxide/ZnO nanocomposities (a) GO (b) GOZnO1 (c) GOZnO2 (d) GOZnO3.

3.5. Photoluminescence (PL)

In Graphene Oxide Powder , We observe two broad Peaks at 350nm ,450nm and one small peak at 575nm and broad peak at 650nm having maximum intensity 225 arb.unit. But when we add metal oxide nanoparticles into Graphene oxide the intensity reduced. Intensity decreases, due to reduced the content of oxides[17].

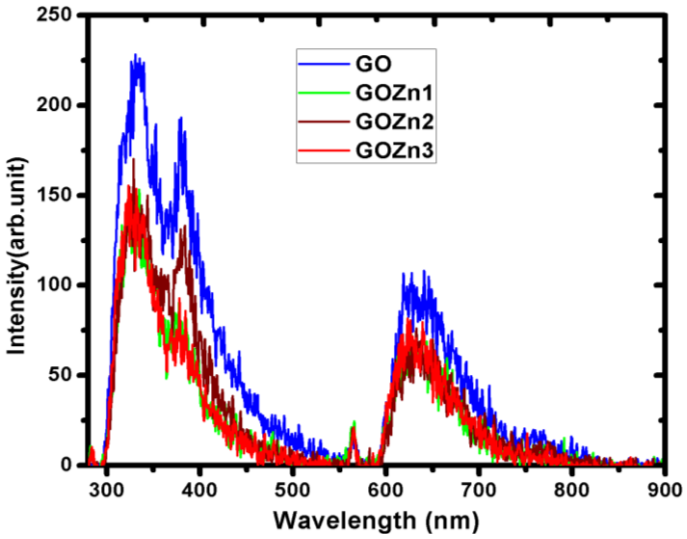

Fig. 6. PL studies of Graphene oxide based nanocomposites (a) GO (b) GOZn1 (c) GOZn2 (d) GOZn3.

4. Conclusions

Graphene oxide /ZnO nanocomposites were prepared by hydrothermal method, and the hexagonal zno nanoparticles, are well arranged on GO sheet. The average size of the GOZn nanoparticles was varying in different samples i.e, 20nm to 30nm. The composites show good luminescent behavior due to the intermediate transition levels, it increases the transition of electrons and enhanced the electrical conductivity of the material which is used in solar devices.

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