

# Exploring the Effect of Graphene on Structural and Optical Properties of Graphene-ZnO Nanocomposite

P. B. Rathod<sup>1</sup>, S. A. Waghuley<sup>2</sup>

<sup>1</sup>Assistant Professor, Department of Physics Padmashri Vikhe Patil College of Art, Science and Commerce, Pravaranagar, Ahilyanagar, Maharashtra, India

<sup>2</sup> Professor, Department of Physics, Sant Gadge Baba Amravati University, Amravati, Maharashtra, India

DOI: 10.5281/zenodo.15728333

## ABSTRACT

*The present research paper, we studied the effect of graphene on structural and optical properties of graphene-ZnO nanoparticles. The graphene used in this work was synthesized by electrochemical exfoliation and ZnO nanoparticles was synthesized by using the co-precipitation method. The ex-situ approach using weight percent ratio was adopted for the preparation of nanocomposite. Based on x-ray diffraction (XRD) and field scanning electron microscopy (FE-SEM) the nanoparticles and nanocomposite shows good crystalline nature and graphene sheets decorated with ZnO. The ultraviolet-visible (UV-Vis) and photoluminescence spectroscopy of as prepared materials show intense absorption in the UV-Vis region and its corresponding optical band gaps were found to be 3.14 eV and 2.96 eV for ZnO nanoparticles and 1 wt. % graphene-ZnO nanocomposite.*

**Keyword :** - ZnO nanoparticles; graphene; nanocomposite; structural properties, optical properties.

## 1. INTRODUCTIONS

Graphene is a two-dimensional system in which electric current is carried by massless quasiparticles [1,2]. Graphene having its high specific surface area for a large interface, high mobility up to  $10000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , and tunable band gap, it should be a very promising electron acceptor in photovoltaic devices [3]. Graphene loaded with metal oxides can considerably modify their electronic properties and put forward more surprising results [4]. Nanocomposites especially graphene loaded provide an important milestone to improve the application performance of metal oxide nanoparticles. The hybrids are multipurpose and tailor-made properties with performances superior to those of the individual oxide nanomaterials. To date, various kinds of metal oxides are synthesized and reported on graphene, which include  $\text{SnO}_2$  [5], ZnO [6],  $\text{TiO}_2$  [7],  $\text{In}_2\text{O}_3$  [8] and  $\text{Al}_2\text{O}_3$  [9]. Out of these ZnO nanoparticles are a widely studied semiconductor due to its wide bandgap (3.3 eV) and large exciton binding energy of 60 MeV [10]. The decoration of such nonmaterials on the graphene surface is highly desirable for tuning surface morphology, electronic structure, and intrinsic properties of graphene [11]. In present work, we study synthesis, structural and optical properties of ZnO nanoparticles and graphene-ZnO nanocomposite. The graphene and ZnO nanoparticles are synthesized by using modified fast electrochemical exfoliation method and co-precipitation method. The nanocomposite of graphene-ZnO is prepared by ex-situ approach using weight percent ratio. The ZnO and graphene-ZnO nanocomposite are used for further characterization such as XRD, FE-SEM, UV-Vis and PL spectroscopy. The reference number should be shown in square bracket [1]. However the authors name can be used along with the reference number in the running text. The order of reference in the running text should match with the list of references at the end of the paper.

## 2. EXPERIMENTAL

ZnO nanoparticles were synthesized by AR grade chemicals such as zinc nitrate and hexamethylenetetramine (HMT) and applied for fabrication of PV cell using spin coating. ZnO nanoparticles were synthesized using co-precipitation method using zinc nitrate and HMT in 1:1 M quantity. The chemical solution of zinc nitrate and HMT was heated at 50 °C with stirrer continuous for 1 hour and kept half an hour without any disturbance. The obtained

chemical solution was ultrasonication and centrifugation for 20-20 min, respectively. The final product was collected and followed by calcinations at 350 °C in a muffle furnace for 3 hours. The ZnO nanoparticles were synthesized with a practical yield of ~51%. Graphene used in this work was synthesized from graphite rod using a modified fast electrochemical exfoliation method with thickness 0.5577 nm and reported in details in our previous work [12]. The phase purity and structural of the as-prepared ZnO and graphene-ZnO were determined by x-ray diffraction (XRD, PW 1830; Philips), and FE-SEM (JEOL JSM-7500F). For the preparation of nanocomposite first, graphene (1 wt. %, with respect to ZnO to be synthesized) was dispersed in 10 mL acetone as an organic media at room temperature. Then, ZnO nanoparticles (1 gram constant) are added in same 10 mL acetone. The graphene-ZnO nanocomposite was kept overnight for evaporation of acetone and dried in muffle furnace at 100 °C for 2 hours for complete evaporation of acetone. Introduction related your research work Introduction related your research work

## 2.1 Materials Characterizations

To study the structural and optical properties of as-synthesized samples were characterized through x-ray diffraction (XRD, Rigaku, Miniflex-II) using CuK $\alpha$  radiation ( $\alpha=1.54$  Å), Field Emission-Scanning Electron Microscope (FE-SEM) from JEOL JSM-7500F, Ultraviolet-visible (UV-Vis) of samples were acquired on Perkin Elmer UV spectrophotometer and Photoluminescence (PL) spectroscopy was performed on fluorescence spectrophotometer HITACHI, F-7000.

## 3. RESULTS AND DISCUSSIONS

Figure 1 (a) and (b) shows XRD patterns for ZnO nanoparticles and 1 wt. % graphene-ZnO nanocomposite. The XRD patterns of the samples were recorded using a Rigaku Miniflex-II in the  $2\theta$  range from  $20^\circ$ - $80^\circ$  in steps of  $0.02^\circ$ . The fig. 1 (a) shows the sharp peaks for ZnO at  $2\theta$  values of 31.8, 34.4, 36.3, 47.5, 56.6, 62.9, 66.4, and 68.0 can be indexed to (100), (002), (101), (102), (110), (103) and (112) crystal planes, respectively. It is seen that the graphene-ZnO nanocomposite with 1 wt. % addition of graphene exhibit similar XRD patterns as that of ZnO nanoparticles. Notably, in Fig. 1. (b) small broad peak appears at  $2\theta=26^\circ$  as a (0 0 2) inside nanocomposite is the characteristics peak for graphene. The sharp and broad peaks appear in graphene-ZnO nanocomposite show ZnO nanoparticles were very well decorated on graphene nanosheets. The average crystallite sizes are determined by using the classical Scherer's formula [13].

$$D = K\lambda / (\beta \cos \theta) \quad (1)$$

where, D is the average crystallite size, K is the shape factor, which can be assigned a value of 0.9 if the shape is unknown,  $\theta$  is the diffraction angle at maximum peak intensity, and  $\beta$  is the full width at half maximum of diffraction angle in radians. When, Eq. (1) is applied to the sharp peaks of ZnO and graphene-ZnO nanocomposite the average crystallite sizes are found to about 67 nm and 75 nm.

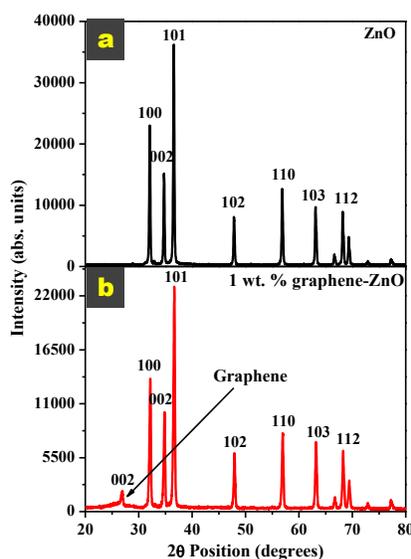
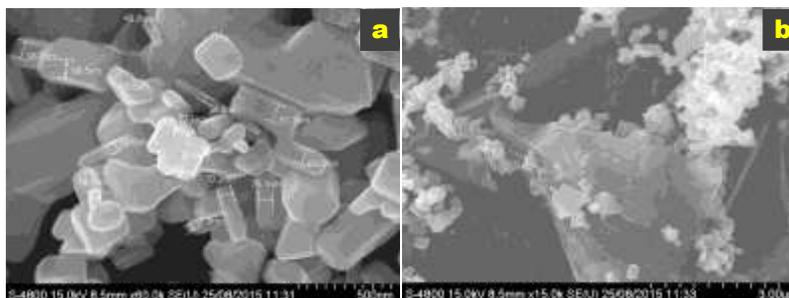


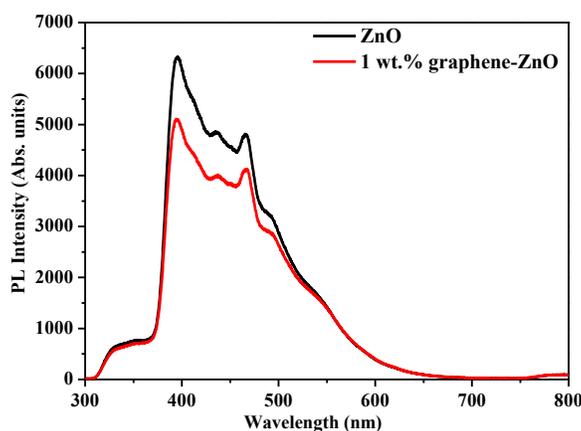
Fig -1: XRD pattern of (a) ZnO nanoparticles and (b) 1 wt. % graphene-ZnO nanocomposite

Figure 2 (a) and (b) shows FESEM image for pure ZnO nanoparticles and 1 wt. graphene-ZnO nanocomposite. The main structures of the ZnO nanoparticles represent small rods like structures (fig. 2 (a)) while graphene is shows transparent sheets (fig. 2 (b)). Compared with graphene sheets, uniform small rods shape ZnO nanoparticles with an average length of 67 nm was anchored on the graphene sheets as shown in fig. 2 (b). When graphene combined with ZnO, steps like graphene sheets decorated by ZnO. The further confirmation of prepared ZnO like rods and graphene/ZnO nanocomposite was examined by TEM microscopy as shown in fig. 2 (c) and (d). The fig. 2 (c) shows ZnO as small rods likes structures which are decorated on graphene sheet (fig. 2 (d)). The ZnO nanoparticles are connected to each other and also with graphene sheets. Such type of structure is very useful for transformation of photon generated electrons and holes for improving efficiency of PV cells.



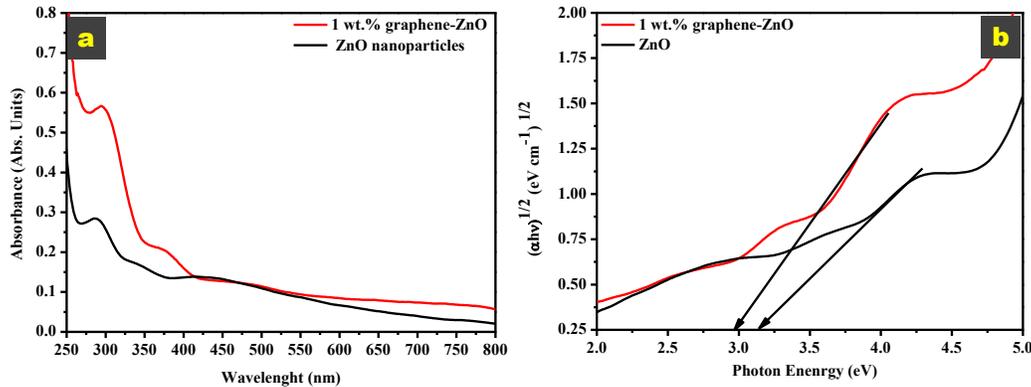
**Fig -2:** FE-SEM images of (a) ZnO nanoparticles and (b) 1 wt. % graphene-ZnO nanocomposite

Figure 3 shows the room temperature PL spectrum of ZnO nanoparticles and 1 wt. % graphene-ZnO nanocomposite. The PL spectrum of ZnO and nanocomposite are similar with different small emission peaks centered at 400 nm, 430 nm, and 470 nm. The different emission peaks at different wavelength is appears due to presence of surface defects and vacancies, which is distributed in ZnO nanoparticles. The maximum PL intensity in ZnO is reduced by the use of graphene with lower defects density. PL intensity of 1 wt. % graphene-ZnO nanocomposite is much lower than ZnO nanoparticles. Reduced in PL intensity is indicating the most efficient inhibition of charge carrier recombination, which seems to be well reproducible with its highest efficiency toward efficient PV cells. The very few defects in graphene involve relatively good electrical conductivity [14].



**Fig -3:** PL spectrum for ZnO nanoparticles and 1 wt. % graphene-ZnO nanocomposite

Figure 4 (a) and (b) shows UV-Vis absorbance spectrum and energy band gap plot for ZnO nanoparticles and 1 wt. % graphene-ZnO nanocomposite. The ZnO and nanocomposite shows linear UV-Vis absorbing nature (fig. 4 (a)). The 1 wt. % graphene-ZnO nanocomposite shows higher absorption magnitude as compared to ZnO nanoparticles. When graphene bonded with ZnO nanoparticles, nanocomposite as-formed show maximum absorption values and have linear red-shift towards higher wavelength. This phenomenon is results from the excellent conductivity of graphene that can facilitate separation of photogenerated electron-hole pairs. Fig. 4 (b) shows energy band gap spectrum for ZnO nanoparticles and 1 wt. % graphene-ZnO nanocomposite. The plot is direct optical band gap for ZnO and graphene-ZnO nanocomposite and estimated by plotting the  $(\alpha h\nu)^{1/2}$  versus photon energy (eV). The band gaps for pure ZnO and 1 wt. % graphene-ZnO nanocomposite were found to be 3.14 eV and 2.96 eV.



**Fig -4:** (a) UV-Vis absorption spectrum and (b) energy band gap plot of ZnO nanoparticles and 1 wt. % graphene-ZnO nanocomposite.

#### 4. CONCLUSIONS

In the present work, the small rods like ZnO nanoparticles and graphene-ZnO nanocomposite examined for structural and optical properties. In XRD analysis, nanocomposite shows sharp and broad peaks which indicate good interaction between constituent of composite. The same result was obtained from FESEM analysis. Such nanocomposite may be useful for transformation of photon generated electron-hole pairs and may enhance performance of various electronic devices. The reduced in emission intensity within PL spectra was shows that recombination rate of electron-hole pairs in nanocomposite is much lower than ZnO nanoparticles. The present result encourages to us to study in future application.

#### 5. ACKNOWLEDGEMENT

Authors are very much thankful to Principal, Padmashri Vikhe Patil College of Arts, Science and Commerce, Pravaranagar and Head, Department of Physics Sant Gadge Baba Amravati University for necessary facilities.

#### 6. REFERENCES

- [1]. C. Neto, A. H. Guinea, F. Peres, N. M. R., K. S. Novoselov, A. K. Geim, The electronic properties of graphene. *Rev. Mod. Phys.* 81 (2009) 109-162.
- [2]. F. Bonaccorso, Z. Sun, T. Hasan, A.C. Ferrari, Graphene photonics and optoelectronics. *Nature Photon.* 4 (2010) 611-622.
- [3]. Z. Liu, Q. Liu, Y. Huang, Y. Ma, S. Yin, X. Zhang, W. Sun, Y. Che, Organic Photovoltaic Devices Based on a Novel Acceptor Material: Graphene, *Adv. Mat.* 20 (2008) 3924-3930.
- [4]. Y. Li, Y. Zhao, H. Cheng, Y. Hu, G. Shi, L. Dai, L. Qu, Nitrogen-Doped Graphene Quantum Dots with Oxygen-Rich Functional Groups, *J. Am. Chem. Soc.*, 134 (2012) 15-18.
- [5]. S. A. Waghuley, Synthesis, characterization and CO<sub>2</sub> gas sensing response of SnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> double layer sensor, *Indian J. Pure Appl. Phys.* 49 (2011) 816-819.
- [6]. G. Y. Chai, O. Lupana, E.V. Rusuc, G.I. Stratanc, V.V. Ursaki, V. S. ontea, H. Khallaf, L. Chowa, Functionalized individual ZnO microwire for natural gas detection, *Sensors and Actuators A*, 176 (2012) 64-71.
- [7]. G. Telipan, M. Ignat, C. Tablet, V. Parvulescu, Synthesis, characterization and gas sensing properties of rutile TiO<sub>2</sub> doped with Pt obtained by sol-gel method, *J. Optoelectronics and Advanced Materials* 10 (2008) 2138-2141.
- [8]. G. Jimenez-Cadena, J. Riu, F. X. Rius, Gas sensors based on nanostructured materials, *Analyst.* 132 (2007) 1083-99.
- [9]. K. R. Nemade, S. A. Waghuley, Highly responsive carbon dioxide sensing by graphene/ Al<sub>2</sub>O<sub>3</sub> quantum dots composites at low operable temperature, *Indian J Phys* 88 (2014) 577-583.
- [10]. I. V. Kityk, J. Ebothe, A. Elchichou, M. Addou, A. Bougrine, B. Sahraoui, Linear Electro-Optics Effect in ZnO-F Film-Glass Interfac, *physica status solidi*, 234 (2002) 553-562.
- [11]. C. Hu, T. Lu, F. Chen, R. Zhang, A brief review of graphene-metal oxide composites synthesis and applications in photocatalysis. *Journal of the Chinese Advanced Materials Society*, 1 (2013) 21-39.

- [12]. P.B. Rathod, K.R. Nemade and S.A. Waghuley, Improvement in photovoltaic performance of TiO<sub>2</sub> nanoparticles by decoration of graphene nanosheets with spherical TiO<sub>2</sub> nanoparticles, *Materials Letters*, (2016) DOI: 10.1016/j.matlet.2016.01.110.
- [13]. K.R. Nemade, S.A. Waghuley, Low temperature synthesis of semiconducting  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> quantum dots, *Ceramics International* 40 (2014) 6109-6113.
- [14]. R. Sellappan, J. Sun, A. Galeckas, N. Lindvall, A. Yurgens, A. Yu. K. D. Chakarov, Influence of graphene synthesizing techniques on the photocatalytic performance of graphene-TiO<sub>2</sub> nanocomposites, *Phys. Chem. Chem. Phys.*, 15 (2013) 15528-15537.