

# Review on Zinc Oxide-Graphene Oxide Nanocomposites: Synthesis Techniques, Properties and Applications

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**Abstract:** Graphene-oxide nanocomposites have promising applications like chemical sensor, photocatalysts, fuel cells, super capacitors etc. and are useful for monitoring the toxicity, inflammability, and explosive nature of chemicals. Metal oxides like ZnO, TiO<sub>2</sub>, SnO<sub>2</sub>, when combined with graphene oxide in the form of nanocomposites have excellent potential for detecting trace amounts of hazardous gases and chemicals. ZnO-GO nanocomposites have various applications like gas sensors, humidity sensors, UV sensors, water purification, capacitors and optoelectronic applications. Various techniques have been used by researchers for the synthesis of ZnO, GO and ZnO-GO nanocomposites. This paper presents a comprehensive review of the available synthesis techniques, properties and applications of ZnO-GO nanocomposites.

**Keywords:** Graphene Oxide, Zinc Oxide, Nanocomposite, photocatalysis, sensors.

## I. INTRODUCTION

Nanocomposites composed of two or more materials with desired performance are recently one of the most studied areas, mainly due to the synergic effect between the materials that are essential for technological applications in various fields.

Zinc Oxide (ZnO) and Graphene Oxide (GO) nanomaterials have been area of wide research in the past few years due to its properties in sensor application and photocatalytic applications. ZnO is an important metal oxide that could be easily grown and it is described as a functional, promising, and versatile inorganic material of interest to many applications [1]. It is a II-VI semiconductor and is suitable for industrial, technical and medical applications due to its diverse properties which have been found to strongly depend on their morphology [1]-[5]. It holds unique optical, chemical sensing, semiconducting, electric conductivity, and piezoelectric properties. Graphene is one of the carbon allotropes that have electron conductivity, and one atom thick layers arranged in a honeycomb two-dimensional (2D) crystal structure. It has optical, electrical, catalytic, thermal, and mechanical properties leading to numerous applications. Graphene has very high electron mobility and a high surface area making it an attractive material for photocatalysis applications [6]-[7]. Its 2D structure consists of single layer carbon atoms and reveals many features such as high electron mobility, high thermal conductivity and excellent mechanical stability [8]. Graphene oxide is produced by oxidation of highly pure graphite [8]-[9]. It is a layer of graphene decorated with oxygen functionalities, such as hydroxyl (OH), carbonyl (C=O) and alkoxy (C-O-C) groups. It possesses unique properties that are different from graphene due to the existence of various oxygenated functional groups on the surface of GO. These properties include the adsorption of various molecular structures on its surface and attractive optical properties [8]. Organic pollutant molecules can be effectively adsorbed by using graphene oxide, due to its highly acidic nature of the components on the surface. A composite of GO with other nanoparticles can be very much useful in enhancing the adsorption efficiency. There are various reports for the synthesis of ZnO -GO nanocomposites using methods like spray pyrolysis, Physical vapor deposition, Chemical vapor deposition, Sol-gel Method, RF Plasma Method, Pulsed Laser Method, Thermolysis and Solution Combustion Method, Colloidal Method, hydrothermal process. This paper presents a focussed review of the synthesis techniques and properties of ZnO -GO nanocomposites based on its different applications.

## II. ZnO-GO NANOCOMPOSITES FOR CAPACITOR APPLICATIONS

Murugan Saranya, Rajendran Ramachandran, Fei Wang [10] reported the preparation of nanocomposites of Graphene-ZnO (G-ZnO) by facile solvothermal method. Crystalline ZnO nanoparticles with size in the range of 30-70 nm are uniformly deposited on the graphene sheets. The electrochemical properties of the nanocomposites were examined by measuring the specific capacitance in 6M KOH solution using CV and electrochemical impedance spectroscopy. XRD evolution demonstrates wurtzite structure of ZnO and a particle size of 150 nm as determined from SEM. G-ZnO nanocomposites showed a good capacitive behavior with a maximum

specific capacitance of 122.4 F/g as compared to GO (2.13 F/g) and rGO (102.5 F/g) at 5 mV/s scan rate. The G-ZnO electrode is a promising material for high-performance supercapacitor applications.

Graphene/ZnO nanocomposites as electrode material for electrochemical capacitors was successfully synthesized by Ejikeme Raphael Ezeigwe et.al.[11] from highly pyrolytic graphite via a green, facile, effective and scalable solvothermal technique. The XRD analysis shows the formation of pure ZnO structure from the zinc nitrate hexahydrate precursor during solvothermal synthesis. The surface characteristics and elemental composition of the nanocomposites have been studied by FESEM, EDS and TEM. The electrochemical properties of the Graphene/ ZnO nanocomposites were examined by galvanostatic charge–discharge, electrochemical impedance spectroscopy (EIS) and CV. The Graphene/ZnO nanocomposites weight ratio of 1:8 (G:ZnO) displayed an improved capacitive performance of 236F/g at a scan rate of 10mV/s, excellent cyclic performance, and an average energy and power density of 11.80Wh/kg and 42.48kW/kg respectively. The improved electrochemical performance of the nanocomposites can be ascribed to the good electroactive property of ZnO and the high electrical conductivity of the synthesized pristine graphene.

### III. ZnO-GO NANOCOMPOSITES AS SENSORS

Ehab Salih et.al. [12] reported the synthesis of Zinc oxide/Graphene oxide (ZnO/GO) nanocomposite in an electrochemical system. The formation of a ZnO/GO nanocomposite was confirmed by HRTEM, XRD, FESEM and attenuated total reflectance spectroscopy. HRTEM showed that ZnO nanocrystals (NCs) are well formed on the GO surface and average size of ZnO NCs was found to be about  $21.7 \pm 2.3$ nm from the XRD patterns. The effect of ZnO/GO nanocomposite concentrations incorporated into the electrode was investigated and found highest electrochemical signal. The results shows that the developed nanocomposite with the high surface area and electrocatalytic activity offer great promise for a non-enzymatic biosensor.

Yi Xia, Ran Li, Ruosong Chen, Jing Wang, Lan Xiang [13] reported the 3D architected Graphene/Metal Oxide Hybrids for Gas Sensors. Graphene/metal oxide based materials have been demonstrated as favourable candidates for gas sensing applications due to enhanced sensing performance. Numerous metal oxide such as ZnO, SnO<sub>2</sub>, WO<sub>3</sub> etc. have been hybridized with graphene to modify the gas sensing properties. Reduced GO/ZnO films showed higher room temperature sensing performance owing to their superior high surface area, porosity, functionalized structures and the synergistic effects. Therefore, 3D graphene/metal oxide composites could play important roles as promising candidates for room temperature hazardous gas sensing.

### IV. ZnO-GO NANOCOMPOSITES AS HUMIDITY SENSOR

Dongzhi Zhang et.al.[14] prepared layer-by-layer self-assembled ZnO/GO film device for ultrahigh humidity sensing. The morphological and compositional properties of ZnO/GO hybrid were characterized by SEM and XRD. The sensing performance of the ZnO/GO hybrid film device toward humidity was investigated, and an unprecedented response was yielded, which surpasses the existing conventional humidity devices. This device exhibits an ultrahigh response and recovery speed capable of detecting human breath, recovery times, acceptable repeatability, stability, which is vital for its commercial application.

### V. ZnO-GO NANOCOMPOSITES AS UV SENSOR

Morget Martin et.al. [15] reported the optical, phonon properties of ZnO–PVA, ZnO–GO–PVA nanocomposite free standing polymer films for UV sensing. PVA based composite films under UV radiations, polymer based films of ZnO, GO and ZnO/rGO powders were prepared by solution casting method at room temperature. The samples were characterized by XRD, UV–Visible absorption spectroscopy, AFM and Raman spectroscopic technique. The photo-sensitivity of the films towards UV radiation was studied by current–voltage measurements UV irradiation and under visible. The electric field produced by the UV radiation can pull the holes to the surface whereas at the surface the adsorbed oxygen ions will trap the photo-generated holes by the recombination of surface electrons and holes, which results in the increase of photocurrent gain. A better response was observed for the ZnO/rGO polymer composite film because of large surface roughness and localized electrons within the GO sheet.

M. Al-Fandi et.al. [16] reported that a new prototype UV nanosensor using ZnO-NP/GO on silicon substrate. The synthesis of high quality hybrid ZnO-NPs/GO nanocomposites via simple and cost-effective method by mixing of ZnO-NPs and GO solution was characterized successfully. The hybrid nanocomposite structure has been developed by an optimized hydrothermal process at low temperature. In hybrid nanosensor, the ZnO nanoparticles act as UV absorbing and charge carrier generating material, while graphene with its superior electrical conductivity. The EDX spectra confirmed the exact chemical composition of the structure. UV-VIS measurement shows an enhanced optical absorption of UV-light at an absorption band centered on 375 nm. The optical and electrical properties were observed at an optimum relative concentration of 1:10. These results can be promising for future enhanced UV- sensing applications.

### VI. ZnO-GO NANOCOMPOSITES FOR WATER PURIFICATION

Ying Tao Chung et.al. [17] reported that Zinc oxide nanoparticles were well-known for the enhanced antifouling and antibacterial properties. The functionalization of ZnO onto GO nanoplates was targeted for better distribution and both ZnO and ZnO-GO NPs were synthesized using sol-gel method. The nanoparticles characterized by XRD, TEM, and FESEM. The Polysulfone-nanohybrid membranes were successfully fabricated with various percentage of ZnO (1, 2, 3 wt%) nanoparticles and ZnO-GO (0.1, 0.3, 0.6 wt%) nanoparticles. The optimum membrane performance was shown in membrane with 2 wt% of ZnO and 0.6 wt% of ZnO-GO. The unique characteristics of ZnO and ZnO-GO NPs were established with several analyses i.e. XRD, TEM and FESEM and the enhancement of membranes was explored by varying the concentrations of the NPs. Both membranes presented significantly improved performance such as enhanced hydrophilicity, high permeability and porosity, improved humic acid rejection, pore size, rejection tendency rate as well as good antifouling and antibacterial control. Hence, ZnO and ZnO-GO NPs were superb nanomaterials in the fabrication of PSF-nanohybrid membranes with significant hydrophilicity and fouling control enhancement which was suitable in various separation and purification applications.

Majid Azarang et.al. [18] synthesised and characterized ZnO NPs/rGO nanocomposite by sol-gel method in a gelatin medium as highly efficient photo-degradation of MB. The XRD pattern of the ZnO-NPs/rGO indicated a hexagonal phase for the product. FESEM and TEM images showed that the ZnO NPs were decorated and spread on the rGO. HRTEM images of the NPs show that the ZnO NPs were single crystals without any defects. The FTIR results showed that the post-annealing method removed the gelatin medium and formed the ZnO structure and it shows GO was transformed into RGO by the post-annealing process. The photocatalyst activity revealed the high MB removal efficiency of the ZnO-NPs/rGO as compared to the ZnO NPs. This technique may be used for the large-scale removal of pollutants from wastewater.

Wei Liu et.al. [19] prepared ZnO/rGO Nanocomposite for the determination of Cadmium(II), Lead(II), Copper(II), and Mercury(II) in Water. A hydrothermal one-pot method was employed to fabricate a new ZnO/rGO nanocomposite and a proper amount of graphene oxide was used to cover the ZnO nanoparticles. The obtained ZnO/rGO composite was employed to determine Cu(II), Cd(II), Hg(II) and Pb(II) in aqueous solutions. The limits of detection for Cu(II), Cd(II), Hg(II) and Pb(II) were measured to be 0.04 μM, 0.03 μM, 0.06 μM and 0.03 μM, respectively.

Seyed A. Hosseini, Shabnam Babaei [20] studied the photocatalytic performance of GO/ZnO nanocomposite for degradation of methylene blue (MB) from wastewater and was compared with that of ZnO, GO and carbon nanotube(CNT)/ZnO. The properties of the GO/ZnO nanocomposite were characterized by XRD, FTIR, SEM and TEM. The SEM and TEM results revealed the nanostructure of the composite. The photocatalytic process was modeled by response surface methodology (RSM). The removal of MB over GO/ZnO was 99% under the optimum conditions and the other photocatalyst such as ZnO and CNT/ZnO exhibited higher activity in MB decolorization. Therefore, ZnO/GO could be a promising photocatalyst for decolorization processes.

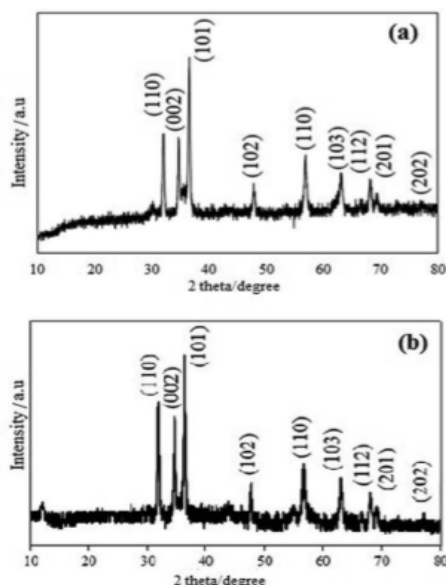


Fig. 1 XRD spectrum for (a) ZnO and (b) ZnO/GO nanocomposite.

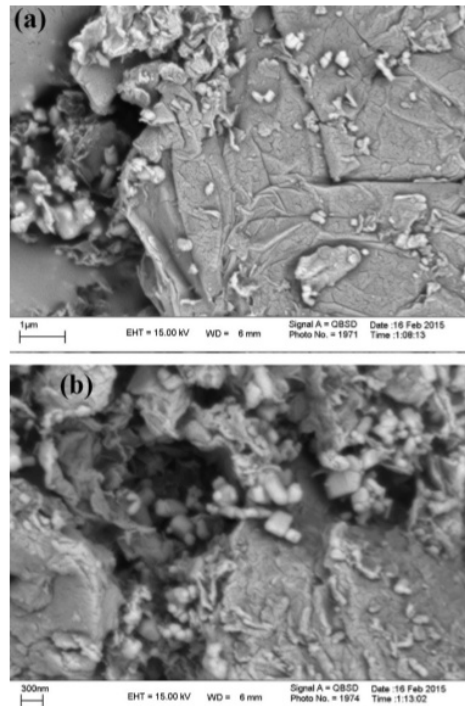


Fig. 2 SEM images of ZnO/GO nanocomposite. The scale bars in the images of (a) and (b) are 1  $\mu\text{m}$  and 300 nm, respectively.

Fatin Saiha Omar et.al. [21] synthesised ZnO/rGO nanocomposites in the presence of diethylenetriamine (DETA) via a facile microwave method. The stability of coordination structure between DETA and  $\text{Zn}^{2+}$  plays an important role for the morphology of the ZnO and ZnO/rGO nanocomposites. The photocatalytic activities and adsorption of the nanocomposites are dependent on the proportion of rGO. The nanocomposites show higher photocurrent response than ZnO, which is in agreement with the photocatalysis result, that manifest the possibility of using the nanocomposite for application in waste water treatment.

#### VII. ZnO-GO NANOCOMPOSITES FOR OPTOELECTRONIC APPLICATIONS

I. Boukhoubza et.al. [22] synthesised GO/ZnO nanorods (NRs)/GO nanocomposites by simple hydrothermal method. It is a very efficient candidate for various optoelectronic applications. The XRD showed that the samples had hexagonal wurtzite structure, with (100) as a preferred orientation for the growth of the ZnO nanorods. SEM images shows the formation of sandwich-like nanocomposites structure by the insertion of the ZnO nanorods between the inter-layer of GO. Therefore, results can be used to enhance the efficiency of some optoelectronic applications.

F. S. Ghoreishi et.al. [23] synthesised G-ZnO nanocomposite by a simple method of thermal treatment of GO-ZnO paste which reduces the graphene oxide into the graphene and leads to the formation of the G-ZnO nanocomposite. The structure, morphology and optical properties of nanocomposites are characterized by XRD, FESEM, FTIR and Raman spectroscopies. The XRD analysis shows the formation of graphene decorated by hexagonal ZnO nanoparticles with average size of 50 nm. CdS quantum dots are deposited on G-ZnO nanocomposite structure and is integrated as a photo anode in CdS quantum dot sensitized solar cells (QDSSCs). The cell with GZnO/CdS photo anode indicated two times higher photoelectric conversion efficiency than pure ZnO photo anode. Therefore, G/ZnO nanocomposite can be a promising candidate for better photovoltaic performance in QDSSCs.

#### VIII. CONCLUSION

ZnO combined with graphene in the form of nanocomposites have excellent potential for applications like gas sensors, humidity sensors, UV sensors, water purification, capacitors and optoelectronic. A review of the work done in this field specifically for the different applications has been done in this paper. Among the several available techniques for synthesis of these composites, Sol gel method has been most preferred. The photocatalytic performance is dependent on the proportion of GO. The ZnO nanoparticles act as UV absorbing and charge carrier generating material, while GO shows superior electrical conductivity. These composites can be thus be prospective candidates for different sensor applications also.



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