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Synthesis and Characterization of CuO/ZnO/GO Nanocomposites for Enhancement of Photocatalytic and Antibacterial Activities

N. Nejanthan[1], J. Raffiea Baseri[2], J.Manikandan[3], S.Chandra[4] and J. Alice puspharani[5]
Department of Chemistry, PSG College of Arts and Science, Coimbatore, Tamilnadu, India

Corresponding Author: **J. Raffiea Baseri**

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Abstract

In this work, CuO/ZnO/GO nanocomposite was prepared by chemical method. Graphene oxide was prepared by using Hummer method and characterized by using SEM, XRD and TEM analysis. SEM results confirm that CuO/ZnO/GO has nanorod like shape. XRD analysis reveals that the CuO/ZnO/GOnanocomposite has the typical hexagonal wurtzite structure with the particle size of 38.8nm. TEM images show that the CuO/ZnO/GO composites have a rod shape and are well-dispersed on the GO surface. From the antibacterial studies, it shows that ZnO nanoparticles exhibit antibacterial activity against both E. coli and Staph, compared to Neomycin sulphate as a control. The degradation of Methylene Blue dye shows that CuO/ZnO/GO composite can be used as a good absorbent.

Keywords: Graphene oxide, monoclinic CuO/GO, and antibacterial activity, Methylene blue.

1. Introduction

Nanotechnology is considered to be the rapidly growing technology in the field of science such as medicines, cosmetics, environmental health, energy science and space industries.Various researchers are showing the interest in the field of green chemistry in several applications such as anti-microbial, anti-fungal, anti-cancer and anti-tumour agents[1]. Recently, the development of green chemistry has been implemented to reduce the usage of hazardous chemicals to human health and environment. Nanoparticles can be prepared using various approaches including chemical, physical, and biological methods, though chemical method require short time for synthesis of high yield of nanoparticles and requires capping agents for size stabilization of the nanoparticles[2].

Recently copper oxide nanoparticles have been used more due to their large surface area, excellent stability in solutions, good electrochemical activity and proper redox-potentialand they show various applications as sensors/ biosensors, antifouling coatings, energy storage devices and biocidal agents.Nanotechnology in medicinal field have a good development in research activities[3]. Zinc oxide nanoparticles are widely used and known for their antibacterial activity and also, they are used as a semiconducting material. Graphene oxide is the promising material, used in many applications because of its unique chemical, optical and electronic properties.

Antibacterial activity of copper and zinc that readily interacts with cell memberane of the bacterias through its surfaces and leads to the bacterial death and also this is used in the treatment of burns. In this work, the prepared CuO/ZnO/GO nanocomposites were examined using a gram positive and a gram negative-bacterias [4].

The photocatalytic dye degradation activity of CuO/ZnO/GO is tested using methylene blue and this has improved the photocatalytic activity against methylene blue dye and it can be employed in waste water-treatment as an excellent adsorbent[5].

Experimental procedure

Materials and method

Preparation of Graphene oxide (GO)

Graphene oxide was synthesized by using modified hummers method in which graphite flakes and sodium nitrate were taken in 1:1 molar ratio and mixed with 90ml of conc.sulphuric acid(98%) in a beaker and kept on a icebath. After 2hour of stirring, 12g of $KMnO_4$ were added gradually below 15°C and this was stirred at the temperature of 35°Cfor 2hours[6]. 50ml of water is added to the solution and this process is said to be quenching yellowish brown colour solution is which is kept on a water bath for 15 minutes and the temperature should be maintained to 90-100°C[7]. To this solution 150ml of distilled water was added along with 10ml of H_2O_2[added gradually], the solution is centrifuged at 3000rpm for 30 minutes and washed with 5% dil.HCl and dried in a hot air oven to obtain graphene oxide powder.

Preparation of CuO/GO Nanocomposites

25ml of 0.1M $CuCl_2$ were taken in a beaker and stirred on a magnetic stirrer. To this solution, 10ml of 0.2M of NaOH were added in a dropwise and stirred for 4hours along with 10mg of graphene oxide under room temperature.Then the colloidal solution was filtered using Whatman (no.40) filtered paper. The filterate is transferred to silica crucible and dried in muffle furnace at 400°C for 4hours[8,9].

Preparation of CuO/ZnO/GO nanocomposites.

1.74g of copper oxide and 2.87g of zinc oxide were dispersed in 100ml of distilled water, later 1g of Graphene oxide also dispersed in required quantity of distilled water separately, then introduced to CuO dispersion and stirred for 4hour and centrifuged at 6000rpm and then the product was washed with ethanol and placed on oven for 8hours at 60°C to yield the nanocomposite product[10,11,12].

Results and Discussion

XRD Analysis for CuO/GO and CuO/ZnO/GO nanocomposites

The X-ray diffraction (XRD) analysis of the sample, termed "CuO," predominantly exhibits the characteristic peaks of monoclinic CuO. The observed 2θ values at 15.7°, 32.5°, 35.52°, 38.78°, 46.3°, 48.76°, 53.76°, 58.36°, 61.76°, 66.15°, and 67.94° correspond to the respective planes (110), (111), (200), (112), (202), (020), (021), (113), (311), and (220). These coincide with the JCPDS file no.48-1548 for monoclinic CuO[13].

The characteristic peak were observed at 36.3°,56.7°,62.9°indicating the peak of ZnO. A significant observation is the near absence of the (001) reflection peak associated with graphene oxide (GO), suggesting a high degree of exfoliation or dispersion of the GO layers within the composite. Such behaviour is consistent with prior studies indicating that the typical XRD peak related to GO's stacking diminishes when its sheets are effectively exfoliated [14]. This interpretation is further supported by SEM data, emphasizing a scenario where CuO particles dominantly interact with, and perhaps modify, the GO surfaces. Consequently, the combined insights from both XRD and SEM analyses present a composite with CuO as the dominant phase and GO layers that appear to be considerably dispersed or altered in their structural arrangement[15].It is significant to know the crystallite size of the product. Crystallite size was computed using Debye–Scherrer equation. D Kλ/ β cos θ ; where D= crystallite size, K = Scherrer constant, λ = wavelength = 1.540560 Å, β = FWHM, θ = angle (°)

$$D = K\lambda / \beta \cos\theta$$

SEM analysis for CuO/GO and CuO/ ZnO/GO nanocomposites.

At a lower concentration of CuO (0.1M), the SEM images suggest that the copper oxide (CuO) is distributed on the basal plane of the graphene oxide (GO)[16]. This spatial arrangement avoids agglomeration, allowing for a more uniform distribution of CuO/ZnO on GO.

TEM analysis of CuO/GO and CuO/ZnO/GO nanocomposites

The TEM images reveal monodispersed spherical copper nanoparticles on the graphene oxide sheets. The average diameter of the copper nanoparticles is around 5 nm. Copper nanoparticles are uniformly distributed on the graphene oxide sheets with minimal aggregation[19,20].

This composite presents a mix of both spherical copper and rod like nanoparticles on the GO sheets. Copper nanoparticles average at about 5 nm in diameter, while zinc nanoparticles have an average edge length of 6 nm[21]. Both copper and zinc nanoparticles show uniform distribution, though there are a few regions where the nanoparticles cluster together, possibly indicating some interaction or alloying between copper and zinc[22].

Antibacterial activity of CuO/GO and CuO/ZnO/GO composites.

The antibacterial activity of CuO/ZnO/GO nanoparticles and a control antibiotic, Neomycin sulphate, against two bacteria

The results indicate that CuO/ZnO/GO has notable antibacterial activity against E. coli, although slightly less than that of the control antibiotic,Compared to E. coli, CuO/ZnO/GO showed reduced activity against Staphylococcus The zone of inhibition is notably smaller for CuO/ZnO/GO in comparison to Neomycin sulphate when tested against Staph.

The antibacterial activity of CuO/ZnO/GO composites is believed to be the better antibacterial agents due to the generation of reactive oxygen species (ROS) which cause oxidative stress in bacterial cells, leading to cell death[23,24,25]. Other mechanisms might include damage to the bacterial cell membrane or interference with cellular processes.

The antibacterial properties of CuO/ZnO/GO nanoparticles could make them valuable in various applications, including in coatings, medical devices, or even in formulations where antibiotics are facing resistance issues[26,27].

Catalytic degradation of methylene blue dye

The degradation of dye has attracted significant attention in recent years. Methylene blue (MB) is a model cationic dye, and its degradation is of particular interest due to its widespread use in various industries.

The coupling of metal nanoparticles with GO provides a synergistic effect that enhances the photocatalytic degradation of organic pollutants. Copperoxide-graphene oxide (CuO/GO) and zinc-graphene oxide (CuO/ZnO/.GO) are two such combinations[28,29].

Catalytic Mechanism:

The oxygen-containing functional groups on GO can adsorb methylene blue molecules, thus facilitating the interaction between the pollutant and the catalyst, Upon light irradiation (usually under UV or visible light), the metaloxide nanoparticles (CuO or ZnO) on GO can produce electron-hole pairs[30]. These electron-hole pairs can further react with water and oxygen to produce reactive oxygen species (ROS) such as hydroxyl radicals and superoxide ions[31]. These ROS are responsible for the degradation of methylene blue.

Comparison between CuO/GO and CuO/ZnO/GO:

The efficiency of photocatalytic degradation can vary between CuO/GO and CuO/ZnO/GO. The MB degradation was monitored spectrophotometrically at a wavelength of 664 nm[32].

Both CuO/GO and CuO/ZnO/GO demonstrated promising results in the catalytic degradation of methylene blue. While CuO/ZnO/GO showed slightly higher degradation efficiencies than CuO/ZnO/GO under the studied conditions, both catalysts proved effective and showcased potential for reusability[33]. The degradation efficiency was observed to be temperature-dependent, with better performance at 35°C. Further studies are needed to optimize conditions and investigate the mechanistic aspects of the degradation process[34,35,36].

Conclusion

By using the chemical method, the CuO/ZnO/GO nanocomposites was synthesized and characterized by using XRD, SEM and TEM analysis. XRD analysis reveals that the CuO/ZnO/GO has the typical hexagonal wurtzite structure with the particle size of 38.8nm. From the SEM analysis, the results emphasize the importance of material concentration in achieving desired morphologies in nanocomposites.The uniform coverage of CuO on GO at lower concentrations implies a potential interaction between the two materials that aids in the dispersion. The affinity between CuO particles and the GO basal plane may be driven by a combination of factors, possibly including electrostatic interactions or surface energies. Such morphologies can have significant implications for the composite's properties, making them suitable for specific applications, such as photocatalysis, where rod-like structures can provide more reactive sites, or in electronics, where a sandwiched structure might influence conductivity and influence their electronic and optical properties. TEM images show that the CuO/ZnO/GO nanoparticles have a rod shape and are well-dispersed on the GO surface.

In conclusion, CuO/ZnO/GO nanoparticles exhibit antibacterial activity against both E. coli and Staph, although the efficacy varies between the two bacteria and is lower than the control antibiotic, Neomycin sulphate and catalytic degradation of methylene blue dye against nanoparticles from different ppm proves that CuO/ZnO/GO has the higher degradation efficiency.

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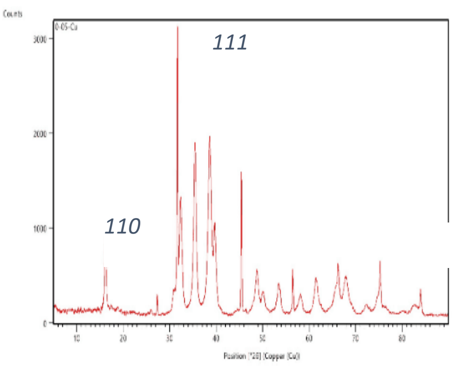
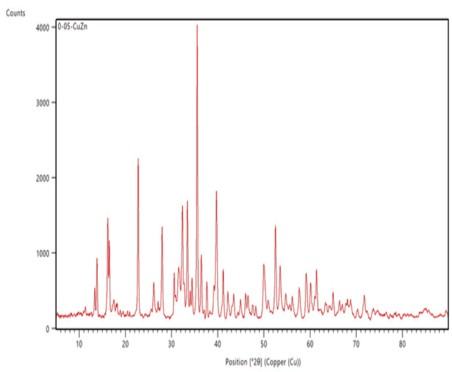
Figure captions

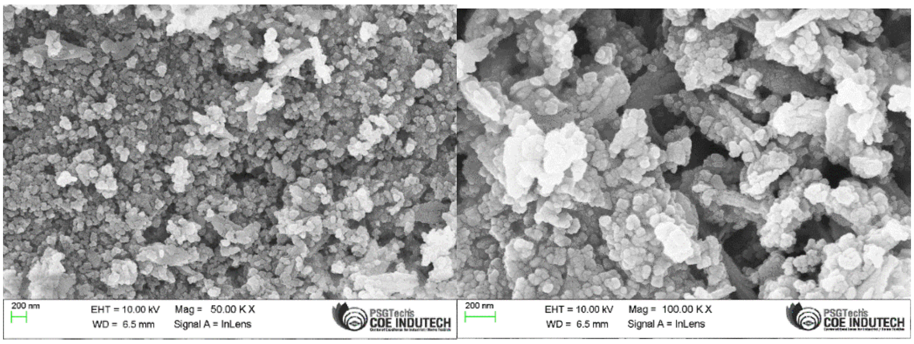
1. **Figure3.1 XRD image of 0.1MCuO/GO and 0.1MCuO/ZnO/GO nanocomposites**
2. **Figure3.2 SEM images of 0.1M CuO/GO and 0.1MCuO/ZnO/GO nanocomposites**
3. **Figure 3.3 TEM image of CuO/GO and CuO/ZnO/GO nanocomposites**
4. **Figure 4..1 Antibacterial activity results for CuO/GO and CuO/ZnO/GO.**
5. **Table 1. zone of inhibition table for CuO/GO and CuO/ZnO/GO**
6. **Figure 4.2 Catalytic degradation image of CuO/GO and CuO/ZnO/GO composites**

Table and figure





XRD images



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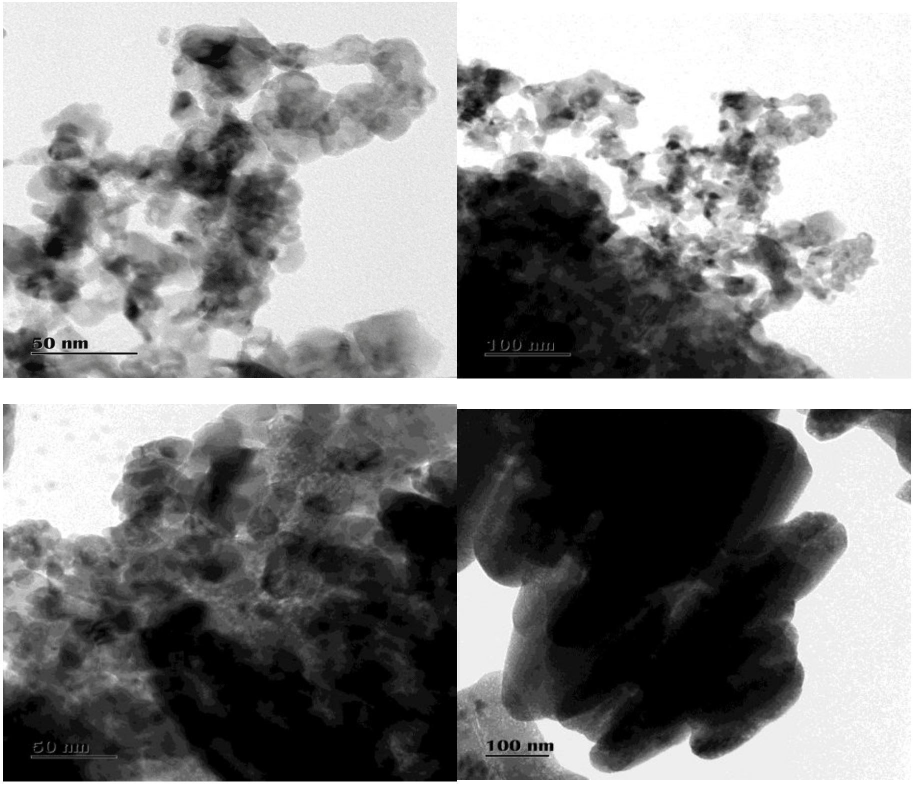
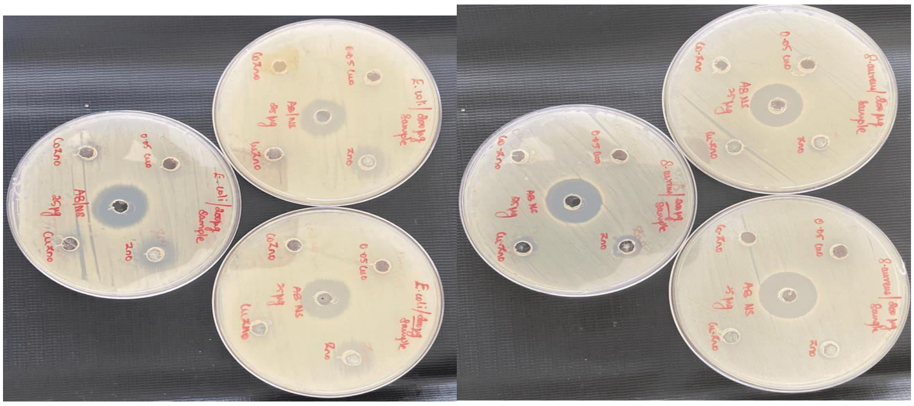


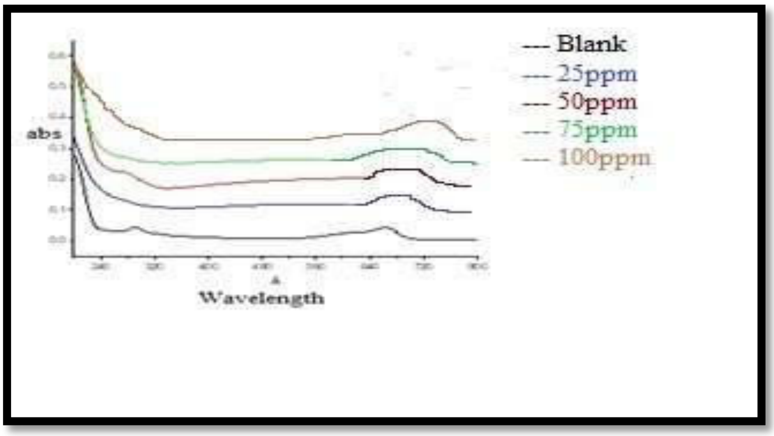
TEM images

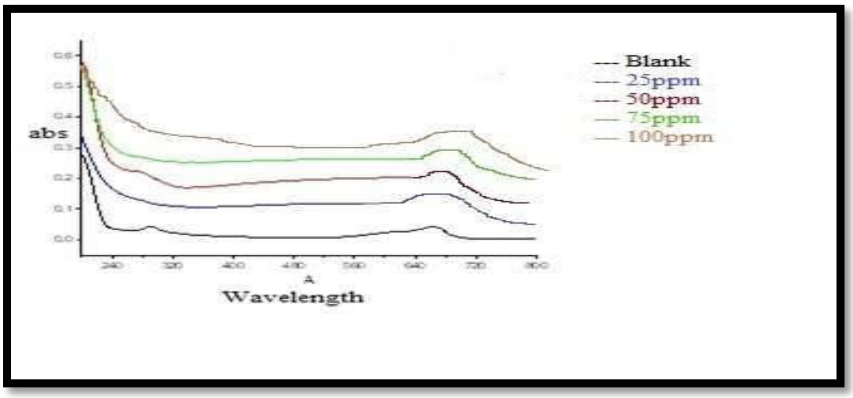


(a) (b)

Antibacterial

S.no	Nanoparticles	Escheria.coli			staphylococcus		
		20mg/ml	40mg/ml	60mg/ml	20mg/ml	40mg/ml	60mg/ml
1.	CuO/GO	9	8.5	8	9	8	7.5
2.	CuO/ZnO/GO	10	9.5	9	10	8.5	8.5





Photocatalytic degradation