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Synthesis and structural properties of Mn-doped ZnO/Graphene nanocomposite

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ABSTRACT

Zinc oxide (ZnO) is a promising metal oxide semiconductor with various applications, especially in the photocatalytic destruction of environmental pollutants. However, this nanoparticle has some limitations, such as poor dispersion, aggregation, and a wide energy gap. As such, the doping of metal oxide semiconductor has been strongly recommended. Addition of manganese (Mn) has proven effective in resolving these issues. On the other hand, addition of carbon-based materials (e.g., graphene) could improve the stability and photocatalytic efficiency of ZnO. Graphene oxide acts as an electron- transport and electron-acceptor agent, controlling the charge transfer in the ZnO/graphene nanocomposite interface. The present study aimed to synthesize manganese-doped graphene/ZnO nanocomposites and determine its structural properties. Some techniques were employed to characterize the prepared composites, including scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), dynamic light scattering (DLS), and zeta potential analysis. According to the FTIR analysis, the peak in the range of 3467 cm^{-1} was due to the presence of zinc groups in the graphene structure, and the peak observed at 439 cm^{-1} also indicated the presence of Mn in the compound. Furthermore, the results of AFM analysis showed that graphene to be a layered sheet with the mean thickness of 1.48 nanometers. The results of the DLS analysis showed the mean diameter of GO-ZnO-Mn to be 37 nanometers, which reduced after graphene modification. According to the findings, addition of Mn and ZnO to graphene could effectively result in doping.

Keywords: Graphene, Nanocomposite, Doping

Introduction

Today, nanotechnology has become a prominent science owing to the remarkable properties of materials within the range of 1-100 nanometers.[1] Some of the most important applications of nanotechnology in the environment include the reduction of pollutant emissions, eliminating pollution and environmental monitoring, green products, and water purification.[2]

In this technology, nanoparticles are used as a catalyst or pollution sensor. In addition, the use of light and ultrasound to activate these nanoparticles has enabled the design of green oxidation technologies to eliminate environmental pollution.[3] The photocatalyst eliminates contaminants through decomposing pollutants or their conversion into less harmful substances in the presence of ultraviolet (UV) light or the lights that are close to this range.[4] These processes are based on the decomposition of pollutants by active radicals, such as OH°.[5]

Photocatalytic oxidation by UV radiation is an essential process in advanced oxidation, which occurs in the presence of catalysts for the removal of organic pollutants. The ability to repeatedly use the catalyst and effective removal of chemical pollutants have attracted the attention of researchers considering the high efficiency of the process.[6] Some of the

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nanoparticles with photocatalytic properties include titanium dioxide, zirconium dioxide, zinc oxide, and grapheme.

Today, zinc oxide (ZnO) is used for the oxidation of a wide range of organic compounds and is considered to be an important semiconductor owing to its direct gap energy, as well as the binding energy of 60 mega-electrons, stability of the particles against optical and chemical corrosion, non-toxicity, insolubility, ability to decompose toxic organic compounds and absorb a wide range of electromagnetic waves, and photocatalytic radiation in radiation exposure.[7]

Graphene is a graphite layer, which is a two-dimensional allotrop of carbon with a honeycomb, grid plate structure. This compound is the building block of carbon nanotubes and large fullerenes.[8] Graphene has exhibited extraordinary physical characteristics, which have not been formerly observed on a nanoscale. Some of the significant properties of graphene include High Young's modulus (approximately 1,000 gpa), high resistance to failure (130 gpa), good thermal conductivity (5,000 $Wm^{-1}K^{-1}$), electrical conductivity (200,000 $cm^2V^{-1}s^{-1}$), specific surface area (2,600 $m^2 g^{-1}$), surprising transitional phenomena (e.g., Hall quantum effect), absorption of some metal ions and water and soil pollutants, and catalytic properties.[9, 10]

The present study aimed to synthesize manganese (Mn)-doped graphene/ZnO nanocomposites and determine their structural properties.

Materials and Methods

Experimental Materials

The required chemicals, including graphite, manganese acetate, zinc acetate, sulfuric acid, and nitric acid, were purchased from Merck Co. (Germany).

Synthesis of Graphene/ZnO Nanocomposites Doped with Mn

Graphene oxide (GO) and graphene/ZnO nanocomposites were synthesized using the modified hummer's method and solo-thermal technique, respectively. GO was dissolved in 80 milliliters of ethylene glycol (EG) through ultrasound for two hours in ambient conditions and centrifuged to obtain a brown dispersion.

A specific amount of manganese acetate (5 wt. %) and 80 milligrams of zinc acetate were dissolved in 80 milliliters of EG, and the resulting solution was added to the brown dispersion with magnetic stirring. Afterwards, 20 milligrams of dissolved soda was dissolved in 20 milliliters of distilled water, and the obtained solution was added to the mixture and stirred for one hour in order to obtain a homogeneous suspension.

In the next stage, the suspension was preserved in a stainless steel Teflon autoclave (200 ml) for 24 hours at the temperature of 160 ºC in order to reduce GO and achieve the ZnO deposition. Finally, the prepared composite was recovered through centrifugation and washed five times with ethanol and distilled water. The synthesized nanocomposite was dried in a vacuum oven at the temperature of 80 ºC for 24 hours.[11, 12]

Properties of Synthesized Nanoparticles

Figures 1-a and 1-b depict the images of scanning electron microscopy (SEM) (Mira 3, Tescan, Czech Republic) of GO and GO-ZnO-Mn. X-ray diffraction (XRD) (INEL-Equinox-3000) was used to investigate the structure of the materials, nanoparticle size, and network parameters (Figure 2). The reflected diffraction was collected and analyzed within the angle range of 10-110 θ. The size of the nanoparticles was calculated using the Scherrer formula at the peak of 101, as follows:

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

where D is the crystal size (nm), β represents the width of the peak in half of the maximum intensity (radians), θ shows the Bragg angle of the peak (degree), and λ denotes the X-ray wavelength (nm).

A Fourier infrared spectrometer (Bruker, Tensor 27, Germany) was applied to investigate the chemical structure of the nanoparticles. In addition, an anatomic power microscope (ARA Research Co., model: No.0101/A of Iran) was used to analyze the surface roughness and surface properties of the nanoparticles.

The electrical potential of the nanoparticles was measured using the zeta potential analysis (Nanobrook Omni, USA), and the UV-Vis absorption spectra were measured using a spectrophotometer (DR5000- HACH) at the wavelength of 200-800 nanometers.

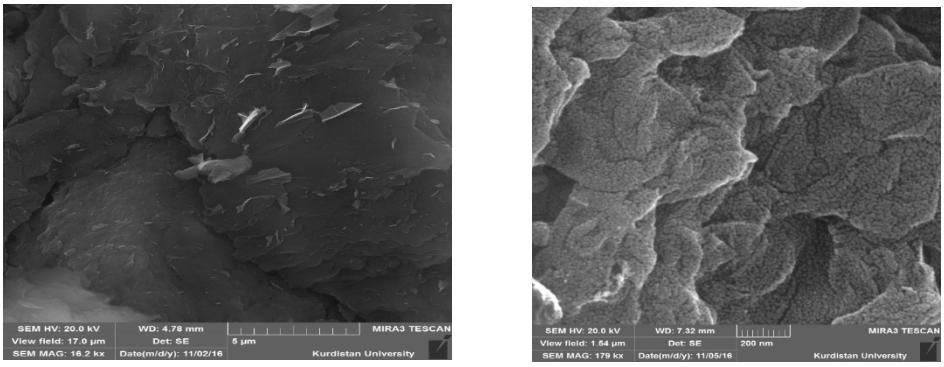
Results and Discussion

Properties of the Nanocomposites

As can be seen in the SEM image of GO in Figure 1-a, GO had a transparent structure and was properly exploited to single-layer and low-layer sheets. The fracture of the sidewalls of the GO sheets reflected the layer structure in all parts of this compound.

As is depicted in Figure 1-b, the addition of ZnO and Mn to the graphene nanoparticles produced an appearance with a grain-like cover. The spherical and dense particles (mean size: 20-40 nm) are normally distributed onto the graphene layers. This size is in accordance with the size obtained based on the Scherrer formula through XRD. In this regard, our findings are consistent with the study by Xie *et al.*[13]

Figure 2 shows the normal distribution diagram of ZnO and Mn nanoparticles on the GO surface.



a b

Fig. 1. SEM Image of a) Graphene Oxide (GO) and b) GO-ZnO-Mn Nanocomposite

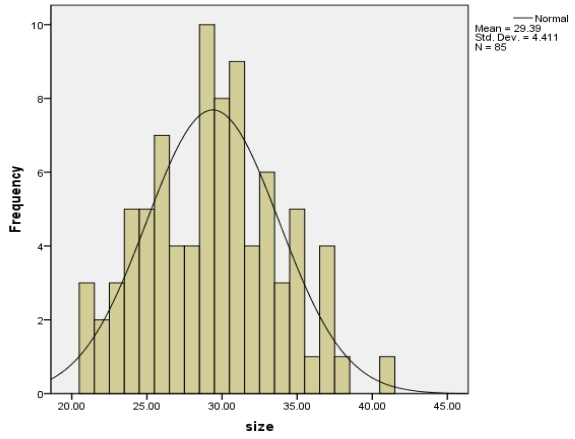


Fig. 2. Normal distribution of ZnO-Mn Nanocomposites on GO Surface

According to the results of FTIR (Figure 3), the peaks appearing at 3,458, 2,923, and 1,051-1,388 cm^{-1} could be attributed to the stretching frequency of the O-H, C-H, and C-O groups of carbonyl carbonate. Another peak, which was observed at 1,627 cm^{-1}, was attributed to the stretching frequency of the C=C groups. The peaks observed at 532, 543, and 450 cm^{-1} were attributed to the presence of the ZnO groups in the compound.

Since graphene initially reduced in the solvothermal process, and the nanocomposite was synthesized afterwards, the peak observed at 3467 cm^{-1} could be due to the presence of zinc groups in the graphene structure. On the other hand, the peak observed at 439 cm^{-1} indicated the presence of Mn in the compound.[12]

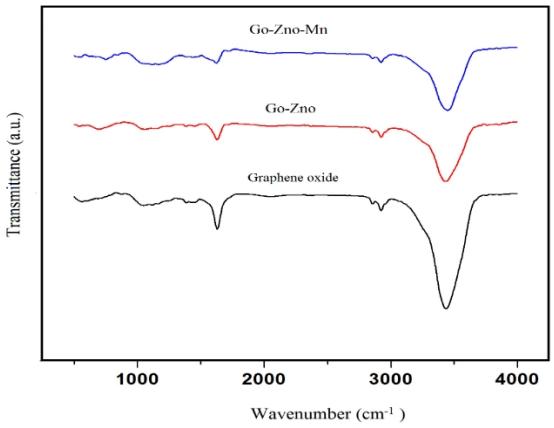


Fig. 3. FTIR Spectra of GO, GO-ZnO, and GO-ZnO-Mn Nanocomposites

As is depicted in Figure 4, the XRD pattern of GO showed a high-intensity peak with the structure of 001 at the angle of 2θ=110, indicating a large gap between the graphene layers due to graphite oxidation and formation of functional groups, such as carboxyl, hydroxyl, and epoxy. The peak reduced significantly after the synthesis of the nanocomposites due to the decreased GO. Moreover, high-intensity pixels were observed in the 100, 002, 101, 110, 200, 112, 201, and 202 structures, indicating the high purity and wurtzite hexagonal structure of ZnO.

With the addition of Mn, the XRD peaks slightly decreased possibly due to the reduced crystallite size and crystallinity. Therefore, it could be inferred that the Mn-ZnO nanoparticles were well placed on the graphene sheets. The size of the nanoparticles and parameters of the nanocomposite network are presented in Table 1.

According to the Scherrer formula, the size of the GO-ZnO nanoparticle was approximately 2.35 nanometers, while the size of the GO-ZnO-Mn nanoparticles was estimated at 35 nanometers. These sizes reduced following the addition of Mn, and the difference was attributed to the magnetism of Mn since the magnetic interaction between zinc and manganese ions is greater compared to that of zinc ions. As a result, the length of the ionic ZnO-Mn bond was less than that of ZnO-ZnO, and the size of the nanoparticles decreased.

According to the current research, the addition of Mn increased the network constants since the ion radius of Mn^{2+} was 0.66 Angstrom instead of Zn^{2+}, with an ion radius of 0.6 Angstroms.[14]

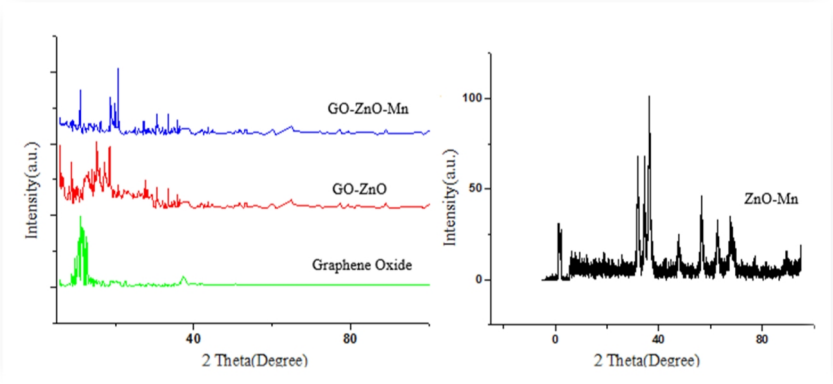


Fig. 4. XRD Patterns of GO, GO-ZnO, and GO-ZnO-Mn Nanocomposites

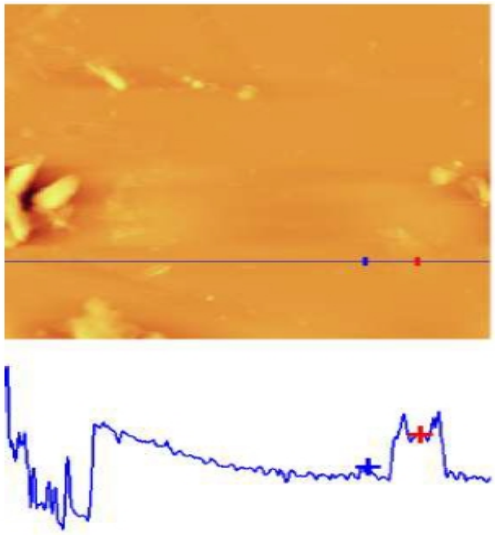
Table 1. Parameters of Nanocomposite network

Sample	Nanoparticles' size (nm)	a (Å)	c (Å)	c/a ratio	Volume (Å^3)
Go-ZnO	35.2	3.249	5.2070	1.6026	27.4825
Go-ZnO-Mn	35	5.84	5.84	1	99.5883

Figure 5 shows the two-dimensional graphene/ZnO image with the scan distance of 3×3 micrometers. The results of the AFM analysis indicated that the diameter of the nanoparticles was 37 nanometers, and the size between the graphene layers was estimated at 3-5 nanometers.

In order to determine the negative charge around the dual layer associated with the colloidal particle, zeta potential was used for the ionization of various functional groups. The surface charge in GO depends on the amount and type of the functional groups on the GO. During the synthesis of GO, functional groups (e.g., epoxy, hydroxyl, and carboxylic) are deposited on the GO plates. The hydroxyl and

carboxylic groups of GO sheets could cause negative charges in a solution.[15] Therefore, the negative charge of GO and GO-ZnO-Mn were investigated through zeta potential measurements at natural pH and temperature of 25 ºC (Table 2, Figure 6).



Analyse		
X1	4.27	µm
Y1	3.83	µm
Z1	-576.29	nm
X2	3.75	µm
Y2	3.83	µm
Z2	-577.77	nm
dX	0.52	µm
dY	0	µm
dZ	1.48	nm
dXY	0.52	µm
dXYZ	1.57	µm

Roughness		
Ra	0.9157	nm
Rq	1.1696	nm
Rv	-4.3153	nm
Rp	2.9498	nm

Fig. 5. AFM Images of GO and GO-ZnO-Mn Nanocomposite

According to the information in Table 2, the surface charge of GO and GO-ZnO-Mn was -18.59 and -11.65 mV, respectively, along with the increased charge on the GO surface after modification. This mode may be due to the reduced plate accumulation and presence of more carboxylic groups on the surface, as well as the increased colloidal stability.

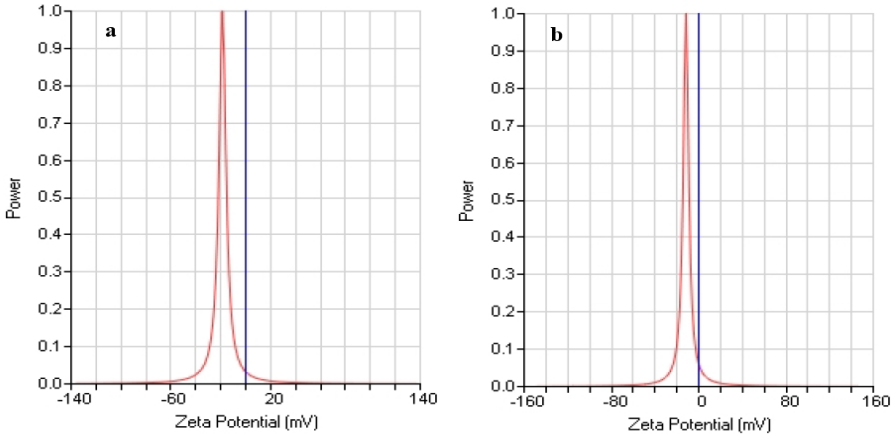


Fig. 6. Zeta Potential of a) GO and b) GO-ZnO-Mn Nanocomposites

Figure 7 shows the results of dynamic light scattering (DLS) for the graphene sheets and GO-ZnO-Mn with insignificant differences. In a GO sample, the distribution size varied within the range of 34-1,300 nanometers with an average size of 217 nanometers. In other words, the dispersion had a large distribution and could contain large particles or agglomerates that are not suitable for determining the size based on the DLS. However, these sizes were observed to reduce after graphene modification, reaching 156 nanometers (medium size) within the range of 23-1000 nanometers. As mentioned earlier, this could be due to the reduction of sheet density.

Figure 8 depicts the absorption spectra of the GO, ZnO, GO-ZnO, and GO-ZnO-Mn nanocomposites using UV-Vis diffuse reflectance. The absorption peak at 395 and 245

anometers demonstrated the presence of ZnO crystals and GOs, while in the GO-ZnO nanoparticles, the absorption peak was transferred to 420 nanometers.

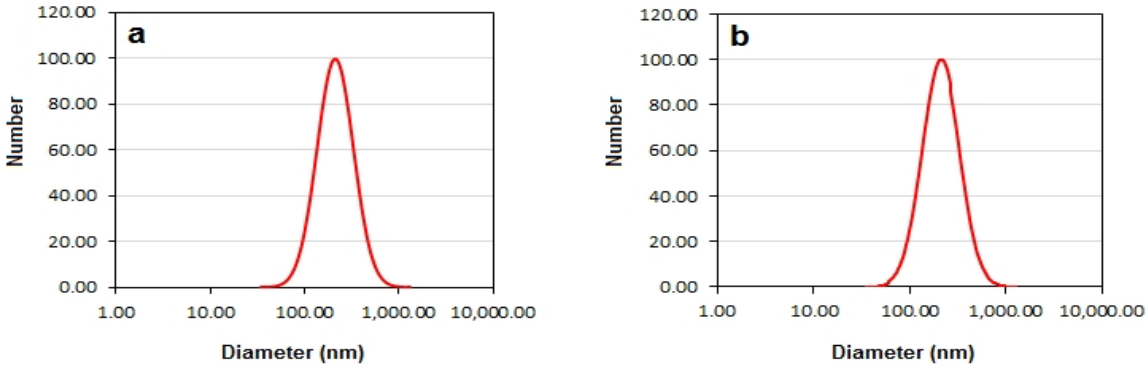


Fig. 7. Particle size distribution of a) GO and b) GO-ZnO-Mn Nanocomposites

Table 2. Zeta Potential of Nanoparticles

Nanoparticles	Zeta Potential (mV)	Zeta Potential Model	Mobility (μ/s)/(V/cm)
Go	- 18.59	Hückel	- 1.45
Go-ZnO-Mn	- 11.65	Hückel	- 0.91

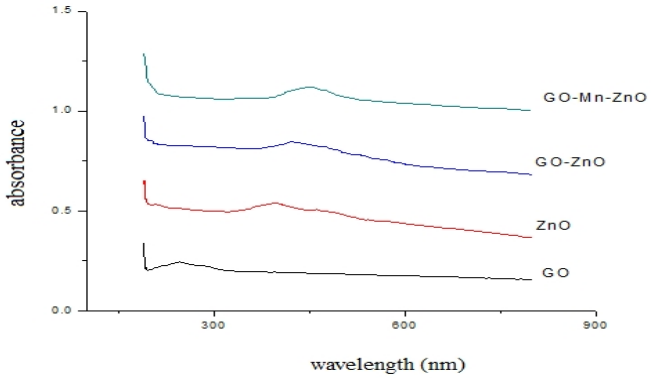


Fig. 8. UV-Vis Absorption Spectra of GO, ZnO, ZnO/grapheme, and GO-ZnO-Mn Nanocomposites

Conclusion

In the present study, graphene/ZnO doped by Mn was synthesized through the solvothermal process and characterized by XRD, SEM, FTIR, AFM, and DLS analyses. According to the results, graphene with a transparent structure was exposed to single-layer and low-layer sheets, and Mn-ZnO particles with a nanoscale size were well placed on the graphene plate structure. Moreover, FTIR confirmed the presence of zinc groups on the graphene structure and Mn in the compound. Therefore, it could be concluded that doping occurred successfully, and this nanocomposite could be used in photocatalytic decomposition processes of pollutants in sunlight.

Acknowledgments

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