

MORPHOLOGICAL AND OPTICAL PROPERTIES OF POLYMER CAPPED ZnO NANOPARTICLES

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We report on the effect of ZnO nanoparticles capping on Polyethylene and polyaniline (PANI) polyethylene composite. The polyethylene/Polyaniline (PANI)/ZnO nanocomposite was successfully fabricated by co-precipitation method of ZnO via in situ polymerization of the polymers. Our results showed that the prepared ZnO nanoparticles were uniformly dispersed and highly stabilized throughout the polymer chain and formed uniform metal oxide-conducting polymer nanocomposite material. UV-Vis spectra of polymer/ZnO nanocomposite were studied to investigate the optical behaviour using UV-spectrophotometer and the morphology was studied using Scanning Electron Microscopy (SEM). Our result revealed that inclusion of ZnO nanoparticle gives rise to the blue shift of π - π^* transition of the composite. The nanocomposite was found to have as size in the range of 243 to 246 nm.

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1. Introduction

Multi-composite nanomaterials with wide range of compositions and tunable morphology displays multiple functions and novel properties that makes them good candidates for applications in biological detection and sensing, drug delivery, magnetic data storage photoelectric conversions etc. [1]. Crystalline Zinc Oxide (ZnO) has a wurtzite structure at ambient temperature [1]. In wurtzite hexagonal structure of ZnO, each anion is surrounded by four cations at the corners of the tetrahedron, which shows the tetrahedral coordinates and hence exhibits sp^3 covalent bonding. ZnO has wide bandgap energy of 3.370 eV and 3.437eV at room temperature and 4 K respectively [2]. The refractive index is of the order of 2.008 [3]. These unique properties and others makes ZnO nanoparticles good candidates for various applications. Biological applications of ZnO nanoparticles has been reported by many authors [4]. Such applications includes the complete inhibition of *Escherichia coli* (E. coli), *Staphylococcus aureus* (S.aureus) etc [4]. The use of ZnO particles in the preferential killing of cancer cells have also been reported [5]. ZnO nano particles are also used in the collection of solar energy. A collection efficiency of 0.75 has been reported using ZnO [6]. ZnO is also applied in photo reactivity and in cosmetics [7].

Generally, polyethylene is prepared from gaseous ethylene under very high pressures (up to about 350 megapascals and high temperatures (up to about 350 °C in the presence of oxide initiators [6]. These processes yield a polymer structure with both long and short branches. The branches prevent the polyethylene molecules from packing closely together in hard, stiff, crystalline arrangements, LDPE is a very flexible material. Its melting point is approximately 20 °C - 110 °C. Principal uses are in packaging film, trash and grocery bags, agricultural mulch, wire and cable insulation, squeeze bottles, toys, and housewares [8].

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Conductive polymers had been the topic of the large number of investigations during last decades because of their unique properties such as mechanical strength, electrical conductivity, corrosion, stability and possibility of both oxidative and electrochemical synthesis [9]. Thus PANI is useful in wide area of application: such as solar energy conversion, rechargeable batteries, electro chromic displays, electrochemical sensors, capacitors and active corrosion protector. Polyaniline is probably the most important industrial conducting polymer today. The type of dopant anion also affects the stability of the conductivity in PANI at different atmospheres and temperatures. Changing the nature of the anion also has a significant influence on the kinetics and conversion in the electrochemical polymerization of aniline [6]. However, in this study we report on the morphology and optical properties of ZnO nanoparticles (ZnO NPs) blended with polyethylene and polyaniline (PANI) and the possible applications.

2. Materials and methods

Zinc oxide nanoparticles (ZnO NPs) were prepared in the conventional chemical method [2]. Typically, 0.45 M aqueous solution of Zinc nitrate was prepared in the standard way and kept in a beaker. Similarly, 0.9 M aqueous solution of sodium hydroxide was also prepared and heated to a temperature of 55° C. The Zn (NO₃)₂ solution was carefully and slowly added drop wise to the heated NaOH solution for 40 minutes under high-speed stirring. The beaker was sealed under this condition for 2 hours to allow for the precipitation of ZnO NPs. The precipitated ZnO NPs is now washed with double deionized water and ethanol and then allowed to dry at a temperature of 60° C. Polyaniline (PANI) was polymerized in formic acid medium using (NH₄)₂S₂O₈ as oxidizing agent. In this report, 1 M of aniline was dissolved in 25 ml of 85% formic acid at room temperature. The resulting solution was cooled to about 2° C in an ice bath. A solution of 0.0107 M (NH₄)₂S₂O₈ was dissolved in 25 ml of formic acid and added drop wise into the cold aniline – acid solution under constant stirring for about 30 minutes. The resulting mixture was kept at a temperature of 2° C and stirred continuously for 2 hours. The dark- green solid formed in the reaction bath is then filtered rinsed with deionized water and methanol. Sachet water bags were collected washed with distilled water allowed to dry and cut into smaller sizes. About 0.15 g of the polyethylene were dissolved in 30 ml of toluene at a temperature of about 60°C under stirring. The resulting colloidal solution was spin coated on a petri dish and left over night to enable the solvent to evaporate completely. Finally, 0.1 g of ZnO NPs were dispersed in 0.1g of polyethylene and PANI respectively. A 0.1 g of ZnO NPs was also dispersed on composite containing equal ratio of polyethylene and PANI all prepared by spin coating in a petri dish. The morphology of the films was investigated using Scanning Electron Microscopy (SEM), and the transmittance and reflectance versus wavelength measurements was done using UV-Spectrophotometer technique.

3. Results and discussion

Figs. 1(a), (b), (c) and (d) illustrate the SEM micrographs of polyethylene, PANI, ZnO NPs and polyethylene/PANI/ZnO NPs composite respectively. It is observed that all the micrographs displayed uniformity and good adhesion of the films. The micrograph of zinc oxide nanoparticles show little sphere- like particles distributed throughout the scanned area. It is also observed that the individual grain shows a distinguished contrast on the surface. Different facets with sharp edges were also observed in the micrographs. No visible facets were observed in the SEM analysis of ZnO NPs which shows good crystallinity of the ZnO NPs. The micrographs of polyethylene, PANI and polyethylene/PANI/ZnO NPs composite show some rope-like nanostructures on the surface.

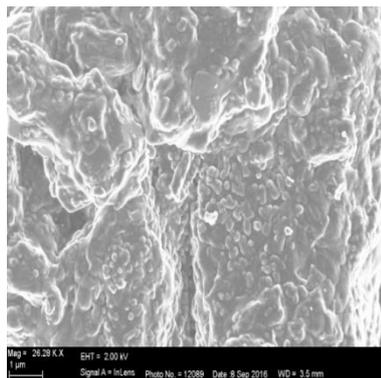


Fig.1a: SEM for polyethylene

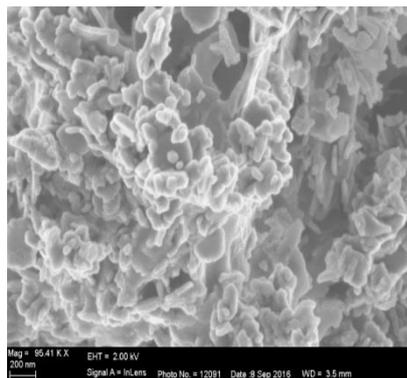


Fig.1b: SEM for PANI

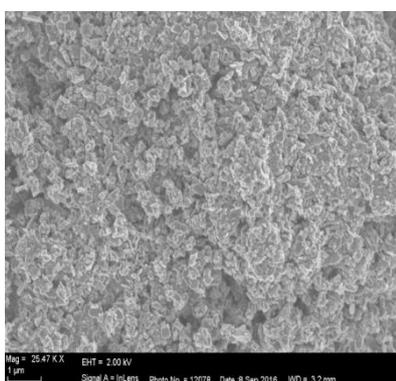


Fig.1c: SEM for ZnO

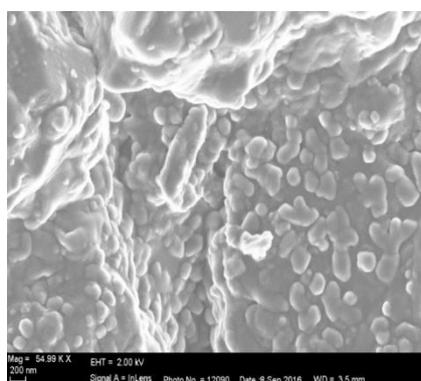


Fig.1d: SEM for ZnO/Poly/PANI composite

Fig. 1(d) shows the SEM of the blend of ZnO NPs with polyethylene and PANI. The SEM clearly indicates uniform distribution of the ZnO NPs in mesh like structure built by the polyethylene and PANI chains. The size of the nanocomposite is in the range of 243 to 246 nm. The SEM depicts the porous nature of the nanocomposite. The observed nature of the SEM show that the blend of polyethylene/PANi and polyethylene/Pani/ZnO are very interesting towards applications in electronic devices and bio-delivery.

4. Optical study

The plot of percentage transmittance against wavelength for polythene is shown in figure 2. The plot shows that the polyethylene nanostructure has an absorption edge around 300nm with the transmittance increasing gradually as the photon energy decreases. Maximum transmittance of about 24% is recorded by the polyethylene nanostructure. The transmittance spectra of PANI is displayed in fig. 3. The plot shows a slight shift in the absorption edge. As in the polythene, the transmittance increases with decrease in the photon energy. The transmission behaviors of the polymer can be linked to the fact that polymers are known to be mixture of amorphous and crystalline regions as also evident in the SEM results, The amorphous regions depicts area where the chains are irregular and entangled while the crystalline regions are the area where the chains are regularly or orderly arranged. In the crystalline regions because of presence of hindering structural units (higher density), the chains moves with greater difficulty [2, 9].

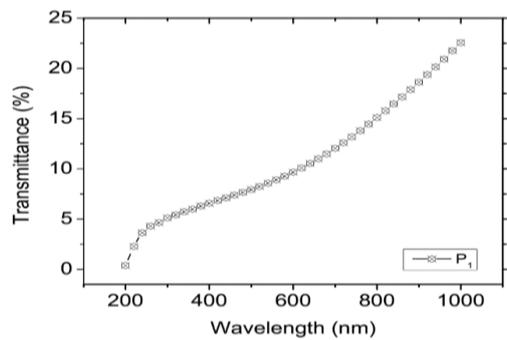


Fig. 2. Transmittance Vs Wavelength for polyethylene (P_1)

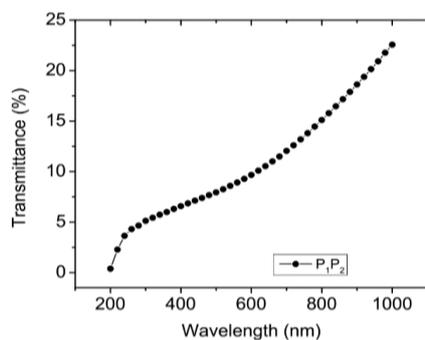


Fig. 3. Transmittance Vs Wavelength for polyethylene/PANI blend (P_1P_2)

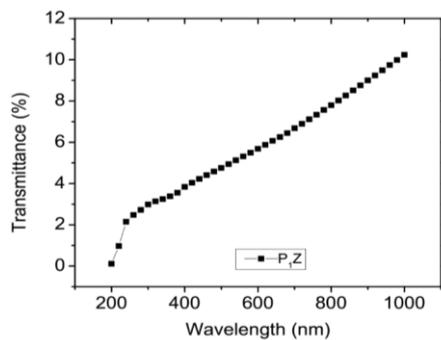


Fig. 4. Transmittance Vs Wavelength for polyethylene/ZnO blend (P_1Z)

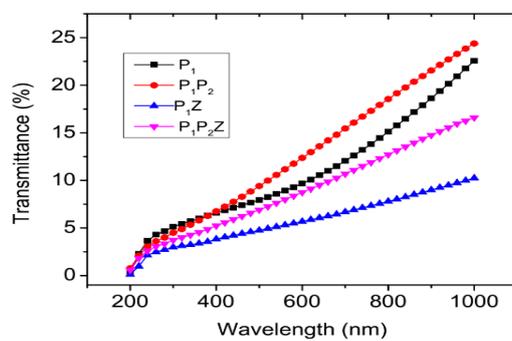


Fig. 5. Transmittance Vs Wavelength for polyethylene/PANI/ZnO blend

In Fig. 5, is compared the transmission spectrum of polyethylene, PANI, ZnO NPs and polyethylene/PANI/ZnO NPs composite thin film. The graph shows that the samples under study exhibit higher transmittances at longer wavelengths. The highest transmittance was by the polyethylene/PANI blend, while the lowest value of transmittance was recorded by the ZnO NPs, It is also observed that the entire film exhibit a sharp increase in transmittance near the fundamental absorption edge in the wavelength range of 200 – 425nm. It is also evident that the films show higher values of transmittance in the NIR with a little damping displayed by the polyethylene sample within that region. This could be attributed to the low density of free electrons. The transmittance value obtained for the polyethylene/PANI/ZnO NPs are observed to be in between values obtained for each polyethylene, PANI and ZnO, NPs which is indicative that there is reorganization of the atoms of the ZnO NPs within the mesh created by the polyethylene and PANI blend. This could also be attributed to the differential /multi nature of the absorption band due to the contribution of the individual compounds that make up the blend. Accordingly blue-shifting is observed in the transmittance curve and this could be attributed to the quantum confinement due to the reduced particle dimension in different blends indicating that the insertion of the ZnO NPs has the effect on the doping of the conducting polyaniline. This can be illustrated by the expression [10]

$$E_g(R) = E_g(\text{bulk}) + \frac{h^2}{8R^2} \left[\frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.8e^2}{\epsilon_2 R} + \frac{e^2}{R} \left(\sum_{m=1}^{\infty} \alpha_m \left(\frac{r}{R} \right) \right) \quad (1)$$

Where $E_g(R)$ and $E_g(\text{bulk})$ represents the bandgap energies of the nanoparticles of radius R and the bulk material with a dielectric constant ϵ_2 . In the expression, m_e and m_h represents the effective masses of the electron and the hole of the exciton, while e is the electronic charge and h is the Planck's constant. The effect of blueshift has been reported by other authors [11, 12] in the literature. It is also worthy to note that the ZnO, NPs atoms siting on the surface of the polyethylene/PANI enable thiolation and linkage of the molecules in the composite. This property profile can lead to new innovative applications in areas of photonics and optics as the the property of ZnO is tuned [4]. The bend observed at 378 nm can be assigned to the stretching vibration of C=N and C=C of the quinoid ring of the polyaniline. Hybridization between ZnO NPs polyethyelene and PANI molecules is excepted which results in intense vibration and the chemically adsorbed polymer structure caused an interface hybrid effect among the constituents of the composite [13, 14]. The transmittance behavior of the PANI/polyethylene/ZnO NPs blend suggest that it can be used as an additive in cosmetics as it has the ability to block UV-A radiation.

5. Conclusions

The study reported on the morphological and optical property of Znic oxide nanoparticles blended with polymer. Polyethylene prepared from used sachet water packets were blended with PANI to obtain polyethyelene/PANi. The blend was capped with ZnO NPs to obtain ZnO NPs/polyethyelene/PANi composite.

SEM micrograph reveals the amorphous cum crystalline nature of the polyethyelene and PANI and the crystalline nature of the ZnO NPs. Optical analysis shows that the capping of the ZnO, NPS with polymers significantly changed the optical behavior of ZnO,NPs. The properties exhibited by the composite suggests that it have wide range of applications including but not limited to electronic devices, bio-delivery etc.

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