

Nano Metal Oxide/Polymer Film: Spectral Features and Morphology Dependent by DC Glow Discharge Plasma

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Abstract: *This article deals with preparation of nano metal oxide on the surface of the polymer using two methods, Sol-gel process and dipcoating method. The prepared films were treated by DC glow discharge plasma technique. The plasma treated and untreated film are characterized by various analytical techniques such as X-ray diffraction, FT-IR Spectroscopy UV-VIS, SEM analysis is the results reveal that to assess the structural properties, peak position, presence of functional groups, spectral features, morphology has been related to the untreated film.*

1. Introduction

Nano composites are a special class of materials having unique properties and wide application potential in diverse areas. Novel properties of nano composites can be obtained from successful joined characteristics of parent constituents in a single material [1]. These materials are different, as both materials like pure polymers inorganic nanoparticles with some physical and chemical properties. Synthesis of inorganic particles in organic media is attractive because it produces particles with an organophilic surface originating from an organic medium or its degradation products [2-3]. CuO is a p-type semiconductor ($E_g = 1.2\text{eV}$) with excellent photovoltaic, electrochemical, catalytic properties. Also it is inexpensive and readily available. Copper oxide nanoparticles are used in a wide range of applications such as gas sensors, magnetic storage media, solar energy transformation and semiconductors [4]. Whereas poly (vinyl acetate) is a polymer material with outstanding optical properties and favorable mechanical as well as processing properties [5]. By combining the nano CuO and PVA polymer, providing that homogeneous particle distribution in the polymer is achieved. For that reason the particle surface needs to be hydrophobically modified [6-11]. In recent years several methods have been developed to modify polymer surface [12]. DC glow discharge plasma treatment has been successfully used as a dry process to alter the surface properties of polymers. The effect of plasma treatment depends on a variety of parameters such as the kind of plasma discharge power density, the pressure and the rate of gas or gas mixture, as well as the treatment time that significantly, reactive plasmas is used to add a polar function group (hydroxyl, carboxyl, ether, carbonyl, etc). In the present work Nano CuO /PVA films were treated with DC glow discharge plasma with an aim of improving the optical properties. The plasma treated Nano CuO /PVA film was characterized by X-Ray Diffraction, FT-IR spectroscopy, UV-Visible studies, scanning electron microscopy (SEM). From various results such as structural, absorptions, band gap energy and morphology of untreated films were compared with the plasma treated films.

2. Materials and Methods

2.1 Synthesis of CuO Nano Particles

Highly pure copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), sodium hydroxide and ethanol, poly vinyl acetate (PVA) used as precursor materials in this study without any further purification. The matrix sol was prepared by mixing copper chloride (1M) in 50ml of ethanol and another solution containing NaOH (1M) in 50ml of ethanol was used as solvent. The resultant solution was stirred at room temperature for 2hrs to yield a clear and homogeneous solution. Then, the precipitate was separated from the solution by centrifugation, washed several time with distilled water and then dried in air oven at 343K to obtain CuO nano particles.

2.2 Preparation of CuO NANO/ PVA Films

CuO nano particles doping with PVA solution. Before coating on the glass substrate, the substrates were thoroughly cleaned with chromic acid and water (1:10) and then washed with acetone to remove organic particles on the surface and then rinsed thoroughly with distilled water. A solution containing PVA (1.5 gm) in 50ml of ethanol is added with synthesized CuO nano powder. Then mixture was stirring constantly for 2hrs. Film deposition was carried out in air at room temperature and 323K for 30mins by the dip coating method. The films were prepared and allowed to dried at 70°C in an air oven. A well dispersed film of CuO nano doped with PVA was obtained.

2.3 Plasma Exposure

The coated CuO nano PVA films were exposed to DC glow discharge plasma of low –pressure was generated in a stainless steel chamber 50cm length and 30cm internal diameter. Vacuum of 10^{-3}mbar was maintained inside the chamber using a vacuum pump. Required vacuum was maintained of fine control gas needle valve. Pirani gauge was used for pressure measurement. Circular shaped electrodes made of aluminium with a diameter of 6cm were fixed inside the chamber. The electrodes were separated by a distance of 3cm. High tension DC power supply 1.5Kv was

used. The films were placed perpendicular to the discharge axis between the parallel electrodes using a holder. After the plasma treatment the treated film was analyzed. The operating parameters influence the surface modification of the film. The operating parameters are listed in Table.

| | |
|----------------------|-------------------|
| Discharge potential | 400v |
| Pressure | 0.3mbar |
| Exposure time | 5mins |
| Electrode separation | 3cm |
| Samples | Nano CuO/PVA film |

3.Results and Discussion

3.1 Structural Analysis

X-Ray Diffraction

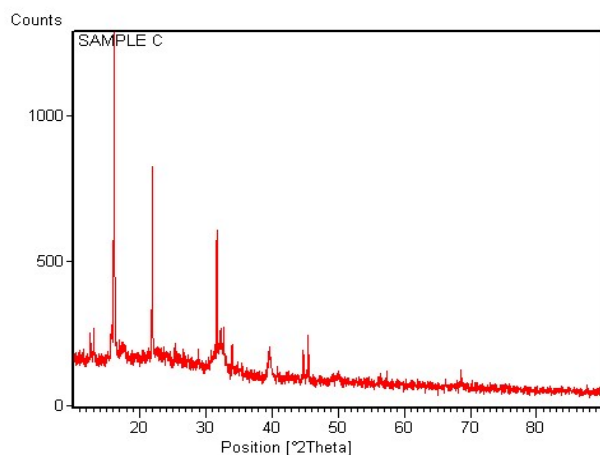


Figure 3.1: (a) XRD pattern of the plasma untreated CuO nano / PVA film

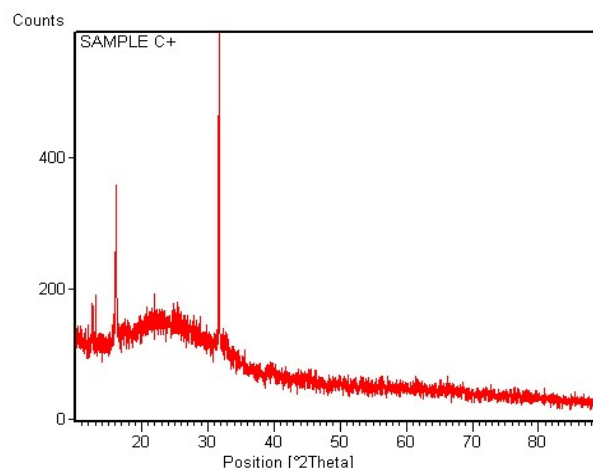


Figure 3.1: (b) XRD pattern of the plasma treated CuO nano / PVA film

Figure 1(a) and 1(b) shows the characteristic diffraction peaks of CuO nano particles doped with PVA films for plasma treated and untreated. These x-ray diffraction patterns indicate the formation of monoclinic structure of CuO. In figure 6(a) and 6(b) a series of peak $2\theta = 16^\circ$ represents semicrystalline peak of PVA. While a characteristic peak 31° (110) corresponding to CuO and they agreed very well with the literature for both plasma treated and untreated films. However full width half maximum progressively increased in the treated film compare to untreated film. The XRD pattern corresponds to monoclinic copper oxide phases which are in very good agreement with reported values in the literature JCPDS 89-5895. No characteristic peaks of impurity and intermediate products were observed.

3.2 FTIR Analysis

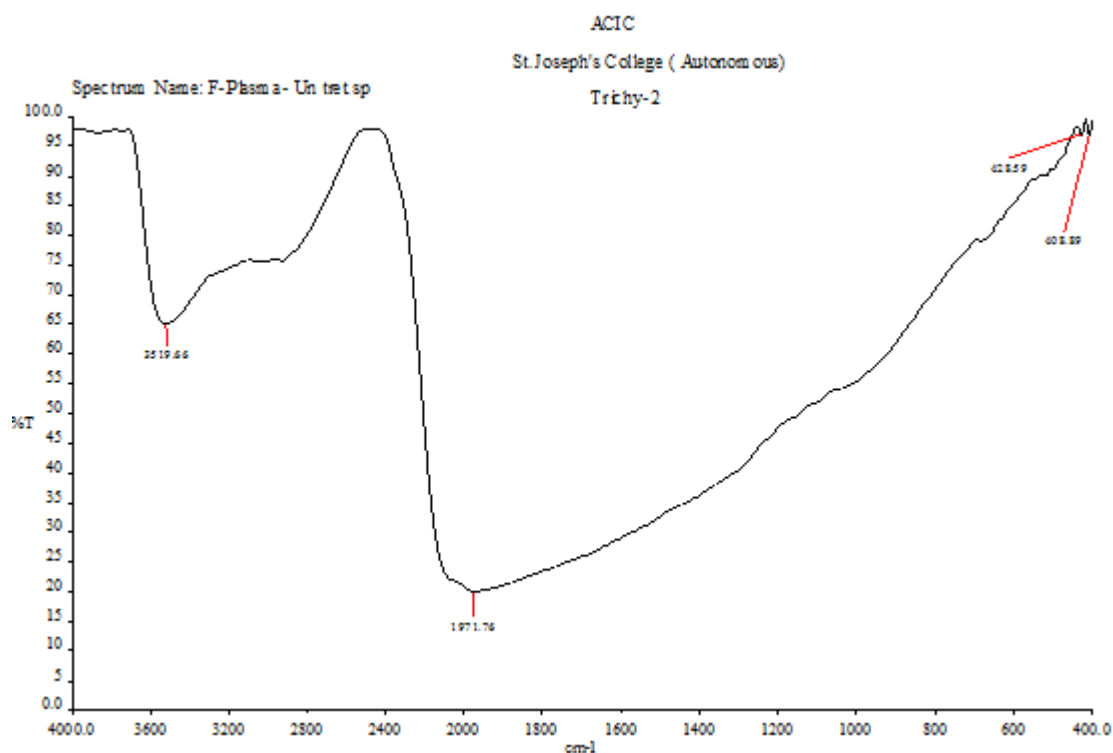


Figure 3.2: (a) FTIR spectrum of plasma untreated CuO nano / PVA film

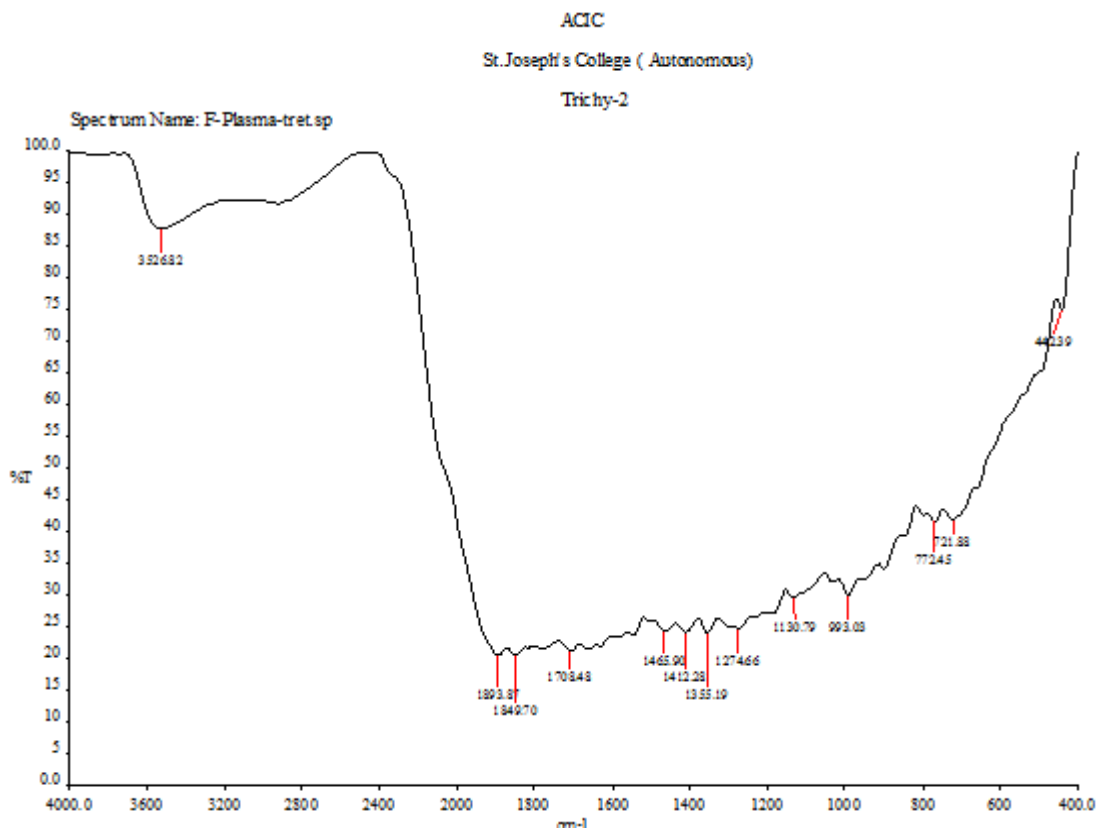


Figure 3.2: (b) FTIR spectrum of plasma treated CuO nano / PVA film

Infrared spectroscopy is used to determine presence of particular functional group. The interaction between the CuO nano particles and the PVA matrix is observed from the infrared spectra. FT-IR spectra of the films were obtained at room temperature by using FT-IR spectrometer in the range 4000-400 cm^{-1} for plasma treated and untreated films. Figure 7.1(a) and 7.2(b) shows the FT-IR spectrum of plasma treated and untreated films. The absorption band at 1893 cm^{-1} and 1971 cm^{-1} in both plasma treated and untreated film is assigned to the transition metal carbonyls. A broad band at 3519 cm^{-1} and 3526 cm^{-1} corresponds to stretching mode of OH group. This result supported the suggestion that, The plasma exposure does not change the basic functional groups

of the films. In turn, The bonds at 1708 cm^{-1} , 1465 cm^{-1} , 1355 cm^{-1} , 1130 cm^{-1} , 1274 cm^{-1} , 772 cm^{-1} can be assigned to the stretching and bending of ketone, -C, C-O-C, O-O-H, C-H groups. The carbonyl bond at 1412 cm^{-1} of PVA can be assigned to the vinyl C-H in plane bend. The surface of the CuO nano/PVA film activated during plasma treatment, which brings existing groups on the surface of the film and created new polar functional groups.

3.3 Optical Analysis

UV- VISIBLE ABSORPTION STUDY OF CuO NANO / PVA FILMS

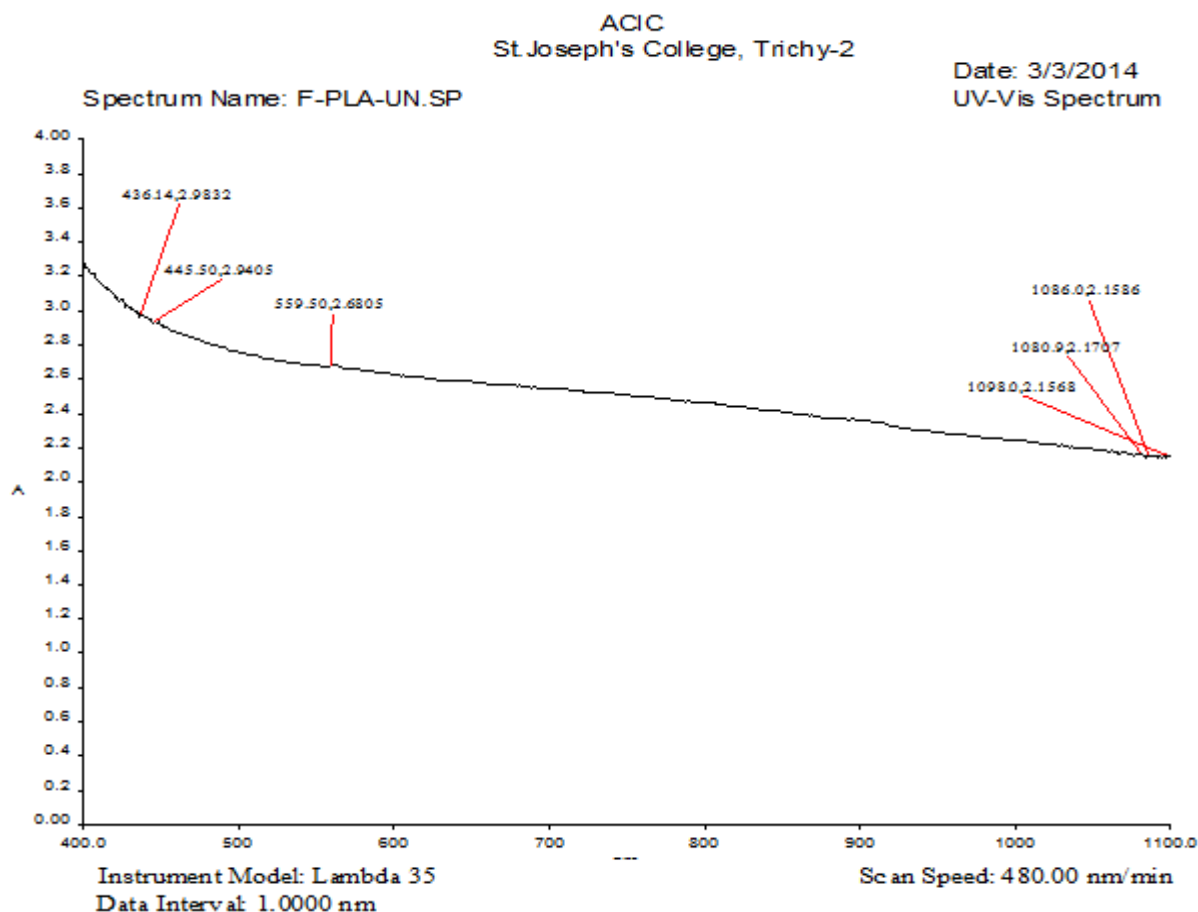


Figure 3.3: (a) UV- Visible absorption study of plasma untreated CuO nano / PVA film

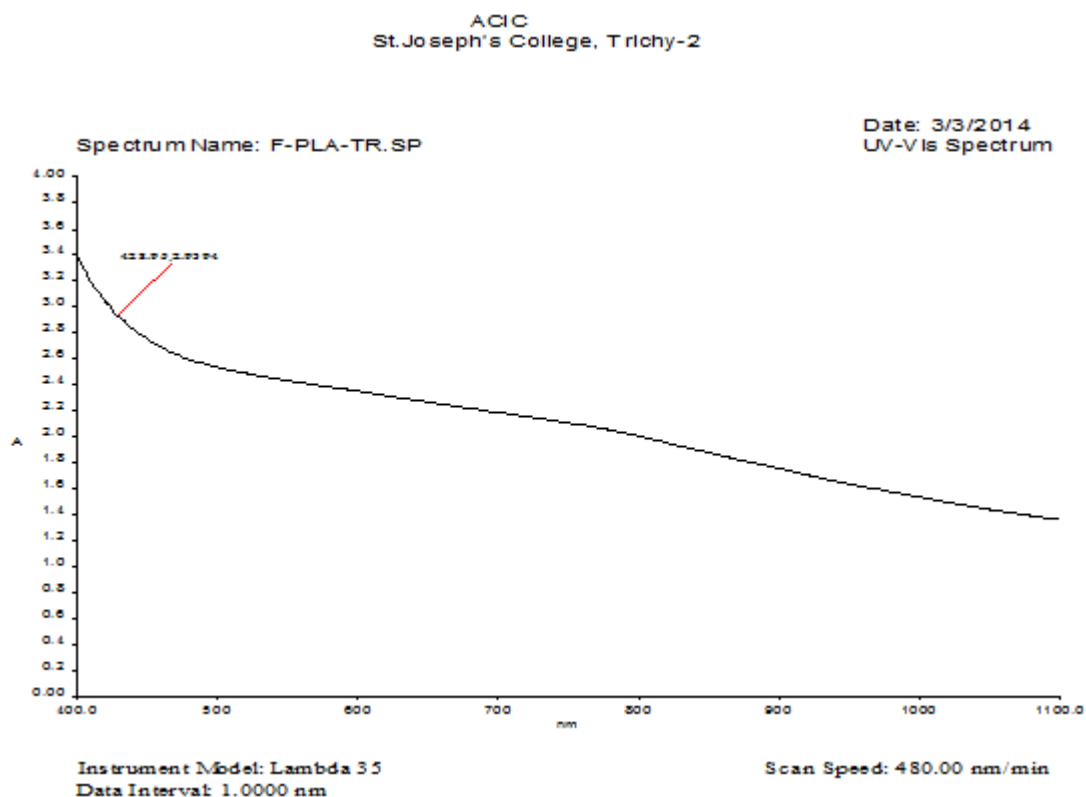


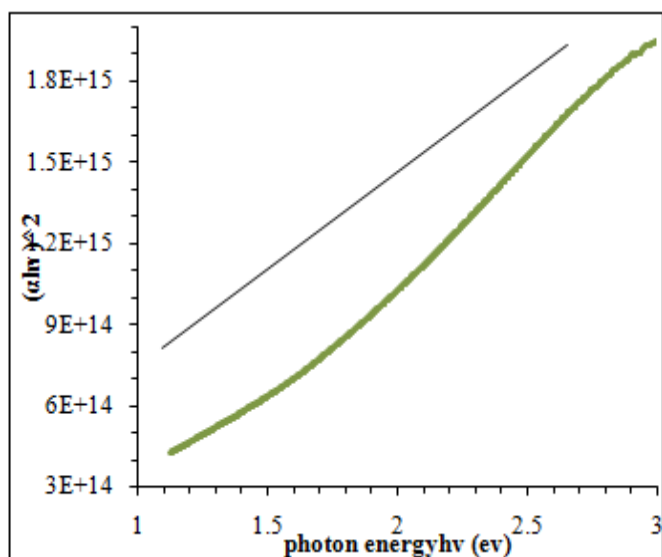
Figure 3.3: (b) UV- Visible absorption study of plasma treated CuO nano / PVA Film

The optical absorption spectrum of CuO nano /PVA film was recorded in the wave length region from 400to1100nm for plasma treated and untreated film is shown figure (a) and (b).The uv absorption edge for the CuO nano /PVA film was

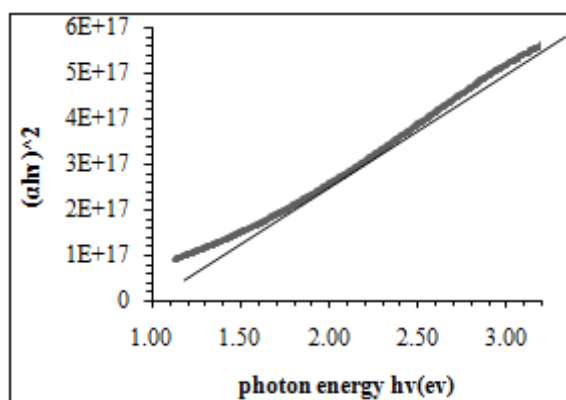
observed to be around 400nmfor plasma treated and untreated film .It is expected that the nano particles in polymer matrix could be used as uv filters in optical materials. The absorption of the plasma treated film was

increases when compared to the untreated film. The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of electrons.

3.3.1 UV-VISIBLE BAND GAP STUDY OF CuO NANO / PVA FILMS



3.3.1 (a) Band gap energy of CuO nano/ PVA for plasma untreated film



3.3.1 (b) Band gap energy of CuO nano/ PVA for plasma treated film

The optical band gaps were calculated from the absorbance spectrum by plotting $(\alpha h\nu)^2$ versus $h\nu$ and extrapolating the linear portion of the curve to $(\alpha h\nu)^2 = 0$, where α is the absorption coefficient and $h\nu$ is the photon energy as shown in figure 6.2.3 (a) for plasma treated CuO nano /PVA films. The relation between the absorption co-efficient (α) and photon energy ($h\nu$) for direct allowed transition is

$$\alpha h\nu = (h\nu - E_g)^n$$

Where

α is Absorption co-efficient

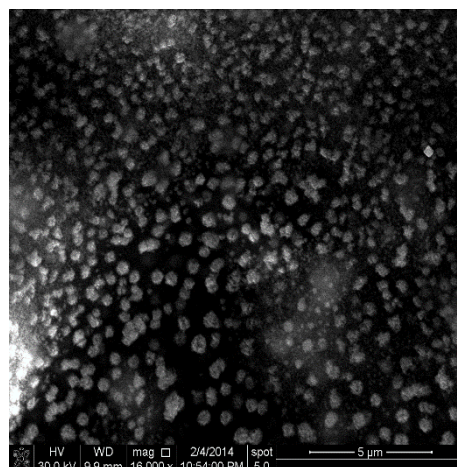
$h\nu$ is photon energy

E_g is Energy gap

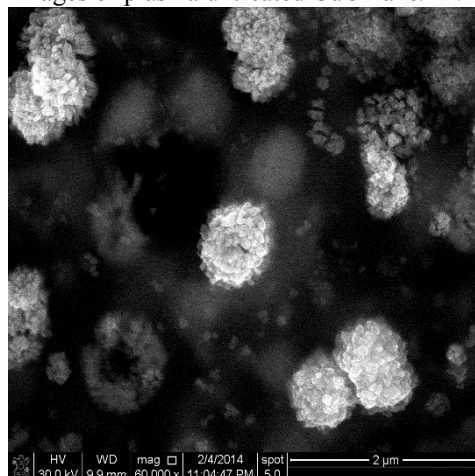
n is an interger depending on the nature of electronic transition, for the direct allowed transition, n has a value of $\frac{1}{2}$ while for indirect allowed transition $n=2$. The direct – band gaps of films were calculated for untreated and plasma

treated film in the range 1.2 eV and 1 eV. This tendency is attributed to the combination of factors including composition, change in crystalline size, and surface reconstruction during plasma treatment.

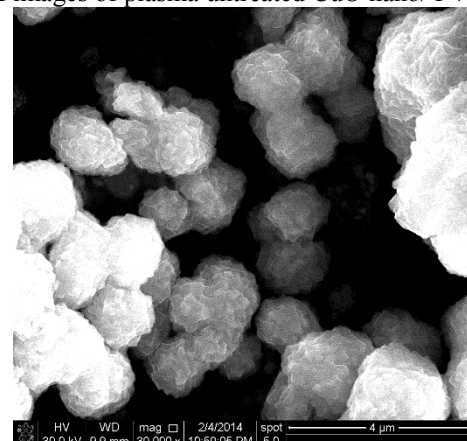
3.4 SEM Analysis



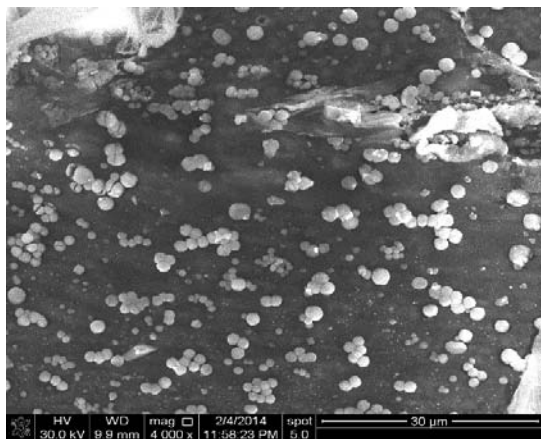
SEM images of plasma untreated CuO nano/ PVA film



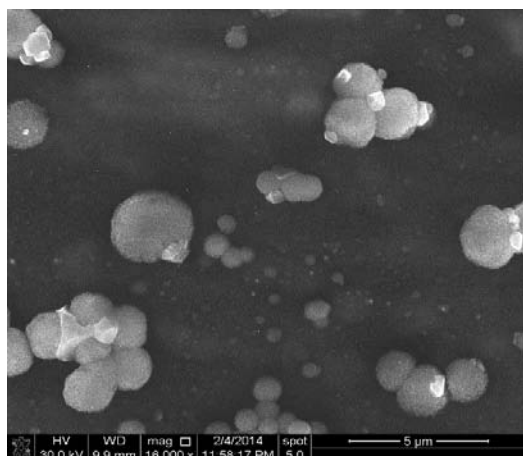
SEM images of plasma untreated CuO nano/ PVA film



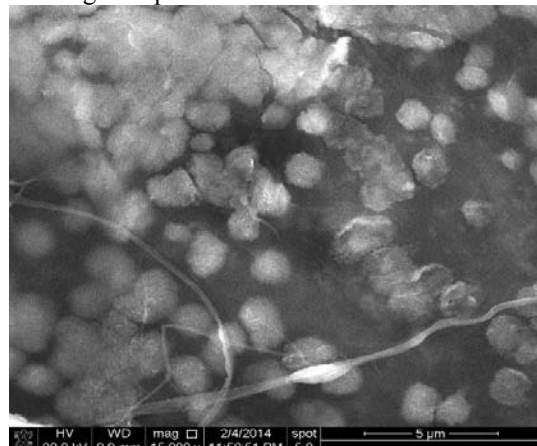
SEM images of plasma untreated CuO nano/ PVA film



SEM images of plasma treated CuO nano/ PVA film



SEM images of plasma treated CuO nano/ PVA film



SEM images of plasma treated CuO nano/ PVA film

The SEM is used to produce high –resolution imaginings of shapes of substances and to confirm spatial variations in chemical compositions. SEM images shows that of CuO nano/PVA film surfaces for plasma untreated and treated respectively. The surface morphology of both plasma untreated and treated films reveals that particles are spherical, regular in shape and films has flowers like structure in the form of clusters distributed over the entire surface.

4.Conclusion

We should that the preparation method used in this study, which is a combination of simple and well known techniques, can be used to successfully produce novel and promising materials. The results of XRD analysis of the

CuO nano/ PVA film confirmed that the plasma treatment does not modify the monoclinic structure of CuO nano particle on the film surface. The surface morphology of the film has been established by the inorganic surface modification of the CuO nano particles. From the UV-Visible analysis, found that the plasma treatment increase the band gap energy of the CuO nano/PVA film because new functional groups added, confirmed by FT-IR spectroscopy. Furthermore, it would be possible for us to construct an electrode for biosensor, applying this features using other metals which is much suitable for electrode.

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