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Surface Modification of Ag Nano Composites Polymer Membranes by Glow Discharge Plasma

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Abstract

Nano particles of silver has been synthesized by Mangifera indica (mango) plant extract and characterized using UV-Vis spectrophotometer, FTIR (Fourier Transform Infrared Spectroscopy), XRD (X-ray Diffraction) and SEM (Scanning electron microscope). These nanoparticles were used as nano composites for polymer membranes. Using solution casting and spin coating method, Ag nano composite polymeric membranes in the range of 20–40 micron were prepared. Helium ion glow discharge plasma treatment was done for the membranes. Surface modifications for membranes were characterized before and after plasma to make comparative study by different technique such as optical microscopy, SEM- Scanning electron microscope. Results are discussed in this paper.

Introduction

Metallic nanoparticles synthesized traditionally by wet chemical synthesis where the chemicals used are often toxic and flammable[1]. Noble metal nanoparticles are widely used in many biological applications[2]. So, there is a growing need to develop environmentally friendly processes for nanoparticle synthesis without using toxic chemicals. Biological methods of nanoparticle synthesis using micro-organisms, plants including algae, fungi, bryophyte, pteridophyta etc. have been suggested as possible ecofriendly alternatives to chemical methods [3]. Among the various inorganic metal nanoparticles, silver nanoparticles have received substantial attention for various reasons – like magnetic and optical property, electrical conductivity, catalysis, antimicrobial activities[4-6]. The use of silver metal ions for their sustained antifungal and antibacterial effects has been practiced [7-10]. In the present study Ag NPs were synthesized using Mangifera indica (mango) plant extract and characterized by UV-Vis spectrophotometer, FTIR, XRD and SEM.

Surface properties of polymers membranes not allow permanent bonding, coating, printing, etc., so it is very difficult to use on many polymers without surface pre-treatment in many applications[11].Also after the surface treatment of polymers these have significant benefits in the field specific requirements of surface properties while retaining bulk mechanical properties unaltered[12]. The complex nature of plasma due to presence of ions, neutrals and radiation in the discharge makes low-temperature plasmas widely used in a growing number of materials fabrication processes including the etching of complex patterns and surface modifications of polymeric membranes[13-14].

Plasma surface treatment usually refers to a plasma reaction that either results in modification of the molecular structure of the surface, or atomic substitution. Plasma treatment is a useful tool in modification of surface properties[15]. The accelerated electrons from the plasma have sufficient energy to induce cleavage of the chemical bonds in the membrane structure and to form macromolecule radicals, which subsequently initiate graft copolymerization[16]. The use of low pressure plasma enables the modification of polymer materials. Various plasma components such as electrons, ions, radical etc. are involved in this process. These components react with the exposed surfaces. Since some parts of the surface are exposed to energies higher than the characteristic bond energy of polymers, these parts undergo scission reactions and form new bonding configurations on the surface[17]. Plasma treatment of polymer surface causes not only a modification during the plasma exposure, but also leaves active sites on the surfaces which are subjected to post-reaction[18-19].

Experimental

The plant material were collected from university campus and washed with sterile distilled water. The plant extract was prepared by taking 25 g of thoroughly washed plant material in a 250-mL Erlenmeyer flask with 100 mL of distilled water, and then boiling the mixture for 10 min in a water bath. The leaf broth was then cooled and filtered through Whatman No.1 filter paper (pore size 25 µm). 10 mL of the prepared plant extract was added to 90 ml of 1mM silver nitrate solution and incubated in a rotary shaker for 2 h. The color of the solution changed from light yellow to brown indicating the formation of silver nanoparticles.

The reduction of pure Ag+ ions was monitored by measuring the UV-Vis spectrum of the reaction medium at 2 hours after diluting a small aliquot of the sample into distilled water. UV Vis spectral analysis was done by using UV-Vis spectrophotometer (Shimadzu). After the complete reduction of Ag+ ions by the plant extract, it was analyzed by FTIR spectrophotometer (IR Affinity-1 Shimadzu) in the range of 4000- 400 cm-1 for knowing the possible functional groups responsible for the formation of silver nanoparticles. The dried mixture of silver nanoparticles was analyzed by an X' Pert Pro x-ray diffractometer (PAN alytical BV,

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The Netherlands) operated at a voltage of 40 kV and a current of 30 mA with Cu Kα radiation in a θ-2θ configurations. Scanning Electron Microscopic (SEM) analysis was done using Hitachi S-4500 SEM machine. Thin films of the sample were prepared on a carbon coated copper grid by just dropping a very small amount of the sample on the grid and then the film on the SEM grid was allowed to dry.

Polycarbonate granules were used to prepare flat sheet membranes by solution cast method. They were obtained as commercial grade from Loxim Polymers, Jaipur. Dichloromethane of extra pure grade was used as a solvent for preparing 10% polymer solution. Solution-casting method was used for preparation of polycarbonate membranes (both doped and pristine). Polycarbonate granules are weighed and dissolved in dichloromethane (CH_2Cl_2) to prepare a 10% solution. Agitation of the solution is important, since the solvent penetration is very slow for high molecular weight polymers and a viscous coating is usually formed over each particle. The solution is stirred by magnetic stirrer to ensure the uniform dissolution and to enhance the rate of dissolution[20-21]. The process is carried out at room temperature for around 2-3 hours till a clear solution is formed. The solution was then put into flat-bottomed Petri-dishes floating on mercury to ensure a uniform structure of the membranes. The solvent was allowed to evaporate slowly over a period of 10 –12 h. The films so obtained were peeled off using forceps. For 3 % Ag nano composites membrane; Ag nanoparticles were dispersed in the solvent dichloromethane using ultra-sonicator. This dispersed solution was then added to the polycarbonate solution and stirred for around 30 minutes.

Plasma treatment consists of a source chamber with the complete power supply, connected to a vacuum system. The magnet is positioned to get a magnetic field inside the source chamber. The helium gas used for containing plasma is admitted into source chamber using a flow controller and applying DC power between two electrodes in magnetic field. The confined plasma in the chamber is used for surface modification. In this study we have used He plasma. The plasma is almost homogenous in a low-pressure glow discharge. The reaction chamber is evacuated and then refilled with low-pressure He gas to create glow discharge plasma. The gas is then energized by direct current. The energetic species in plasma include ions, radicals, electrons and meta-stable photons in short-wave UV range.

Results and Discussion

UV-Visible absorption spectrum shows characteristic surface plasmon resonance (SPR) peak of Ag NPs at 412 nm (Figure 1), indicating reduction of silver nitrate and formation of Ag nanoparticles. Absorption bands obtained using FTIR are classified as (A) stretching vibration of Ag NPs at 763 cm-1, (B) C=C unsaturated at 1285 cm-1, (C) C=O stretching vibration at 1712 cm-1, (D) C-H stretching vibration 3579 cm-1 of aromatic compounds (Figure 2). Biosynthesized silver nanoparticles were further confirmed by the characteristic peaks observed in XRD profile and morphological and structural view under the scanning electron microscope. The XRD study indicates the formation of silver (Ag) nanoparticles which show four intense peaks (Figure 3) and SEM image of silver nanoparticles show average particle size of 40-60 nm (Figure 4). This indicates that the sample contained mixed phase, cubic (44.5 º and 77º) and hexagonal structures (peaks at 38 º and 64.1 º 2θ angle, after comparing form GCPDF data base) of silver nanoparticles. UV-Visible absorption spectrum shows characteristic surface plasmon resonance (SPR) peak of Ag NPs at 412 nm (Figure 1), indicating reduction of silver nitrate and formation of Ag nanoparticles. Absorption bands obtained using FTIR are classified as (A) stretching vibration of Ag NPs at 763 cm-1, (B) C=C unsaturated at 1285 cm-1, (C) C=O stretching vibration at 1712 cm-1, (D) C-H stretching vibration 3579 cm-1 of aromatic compounds (Figure 2). Biosynthesized silver nanoparticles were further confirmed by the characteristic peaks observed in XRD profile and morphological and structural view under the scanning electron microscope. The XRD study indicates the formation of silver (Ag) nanoparticles which show four intense peaks (Figure 3) and SEM image of silver nanoparticles show average particle size of 40-60 nm (Figure 4). This indicates that the sample contained mixed phase, cubic (44.5 º and 77º) and hexagonal structures (peaks at 38 º and 64.1 º 2θ angle, after comparing form GCPDF data base) of silver nanoparticles.

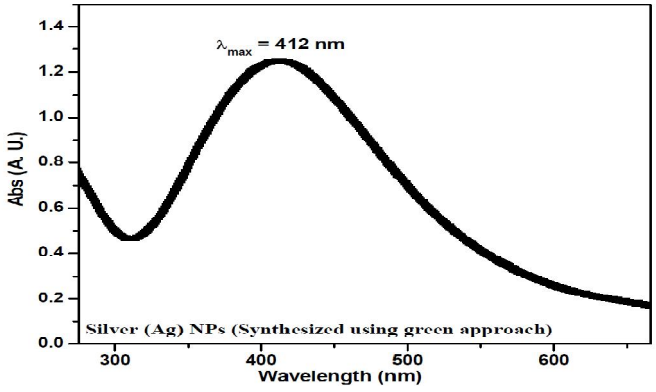

Figure 1: UV-Vis absorption spectrum of silver nanoparticles.

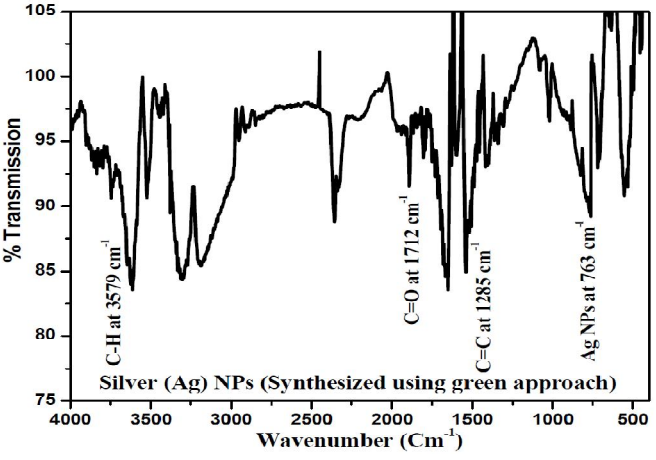

Figure 2: FTIR spectra of vacuum dried powder of silver nanoparticles

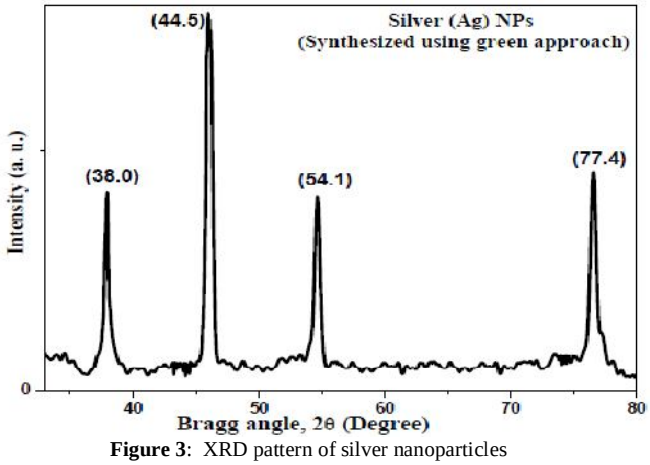

Figure 3: XRD pattern of silver nanoparticles

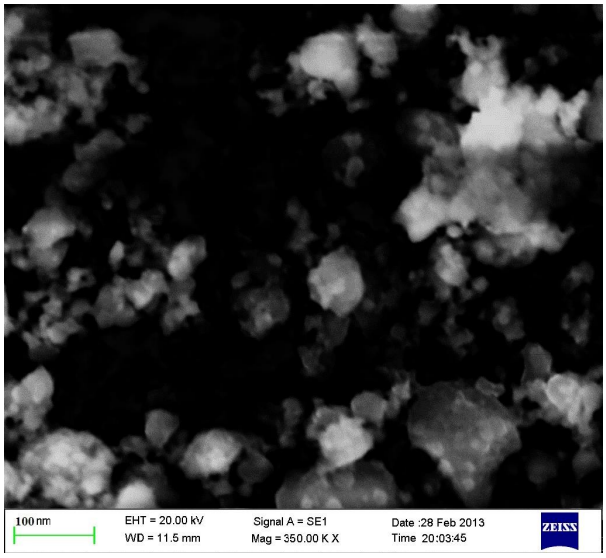

Figure 4: SEM image of silver nanoparticles

Surface modifications for membranes were characterized before and after plasma to make comparative study by different technique such as optical microscopy, SEM- Scanning electron microscope. Optical microscope is the fundamental tool to study surface structures. It magnifies an image by sending a beam of light through the object. The eye-piece further magnifies the magnified image formed by the objective lens. An eyepiece does little to the primary image other than making it visible to the eye. LABOMED microscope is used for recording optical images. The micrographs are stored in computer through CCD camera which is attached to the computer with standard Pixel View software. Images shows that pristine membrane have very smooth surface but plasma treatment increase its roughness. Nano composite membrane is comparatively having high porosity but plasma treatment again increases its roughness (Fig. 5).

Surface morphologies of pristine polycarbonate membranes were investigated before and after plasma treatment and Ag Nano composite polycarbonate membran after plasma treatment using SEM. The SEM images of films are shown in Figure 6. We can easily say after looking the plasma treated membrane that it drastically change the surface property, this shows that plasma treatment techniques applied here have shown considerable improvement in surface morphology and flux. Plasma treatment has helped in increasing flux whereas doping has modified the surface properties (Figure 6).

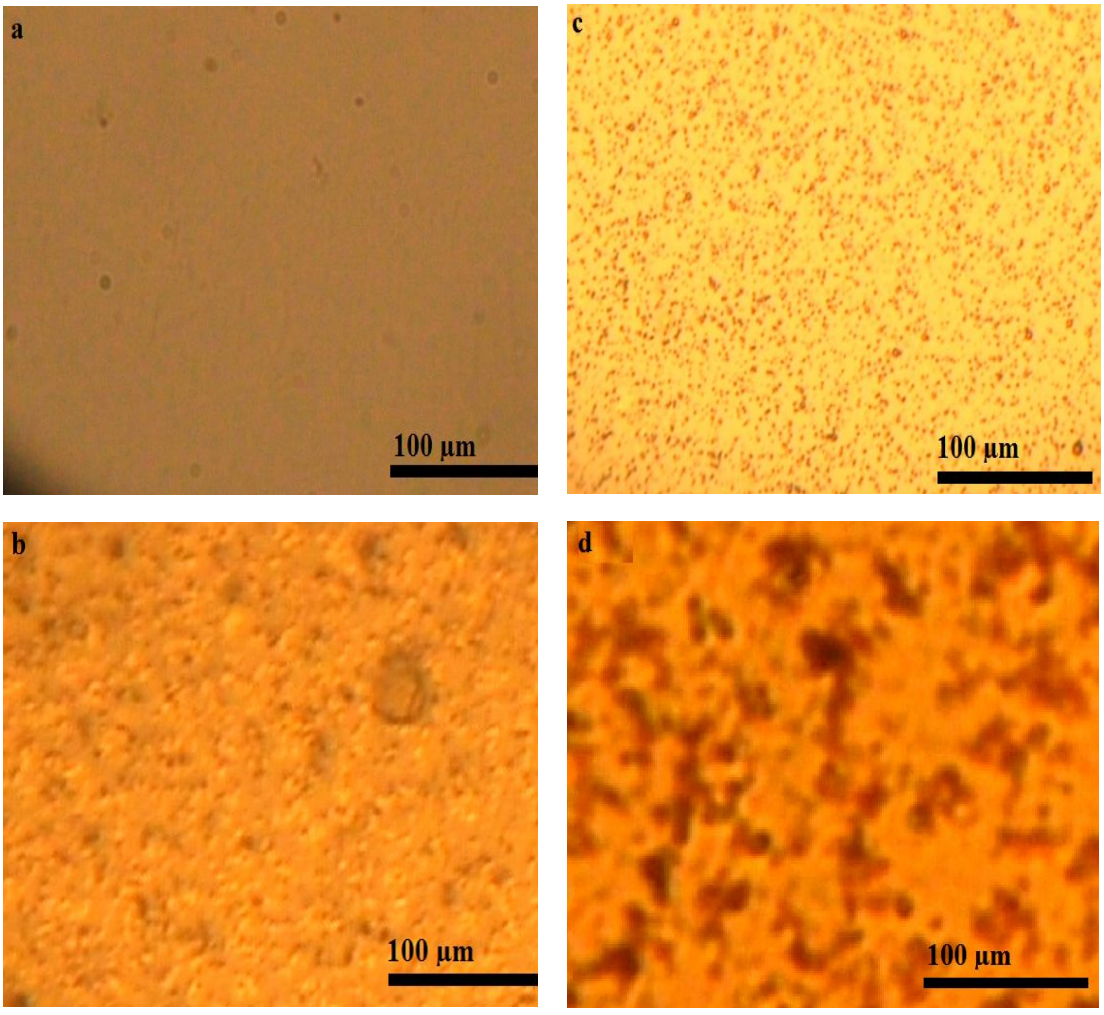

Figure 5: Optical microscope images of pristine and Ag nano composite both plasma treated and untreated (a) Pristine membrane, (b) 3% Ag Nano composite membrane, (c) Plasma treatment pristine membrane, (d) Plasma Treated 3 % Ag Nano Composite Membrane.

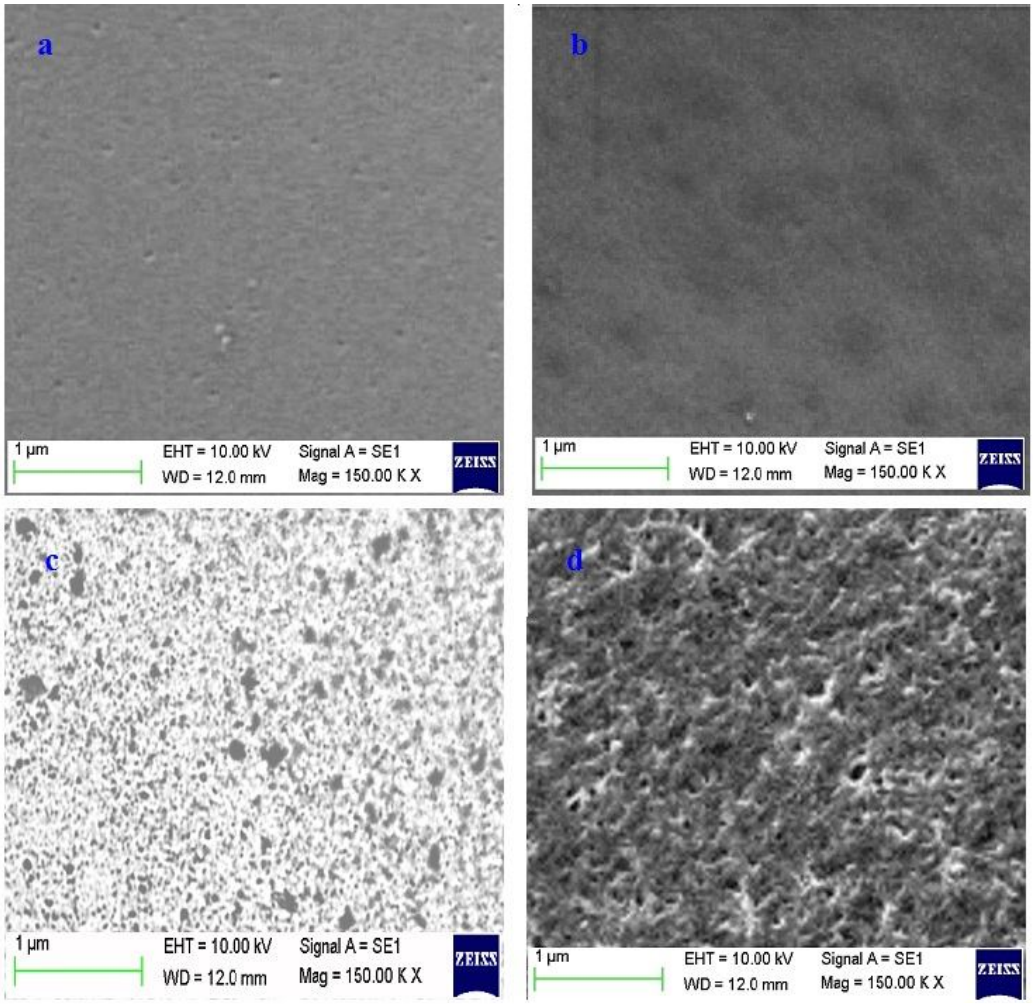

Figure 6: SEM images of pristine and Ag nano composite polymer membranes before and after plasma treatment (a) Pristine membrane, (b) 3% Ag Nano composite membrane, (c) Plasma treatment pristine membrane, (d) Plasma Treated 3 % Ag Nano Composite Membrane.

Conclusions

There was a visible color change from green to brownish as the plant extract was mixed in the aqueous solution of the silver ion complex which indicated formation of silver nanoparticles. Silver NPs formation was further confirmed by UV-Visible spectrophotometer by obtaining a spectrum in visible range of 300nm to 800nm. A typical absorbance peak at 412 nm of silver nanoparticles was obtained due to the surface Plasmon vibrations of silver nanoparticles. Biosynthesized silver nanoparticles were further confirmed by the characteristic peaks observed in XRD profile and morphological and structural view under the scanning electron microscope. The XRD study indicates the formation of silver (Ag) nanoparticles which show four intense peaks and SEM image of silver nanoparticles show average particle size of 40-60 nm. This indicates that the sample contained a mixed phase, cubic and hexagonal structures of silver nanoparticles. FTIR measurement carried out to identify the possible interaction between biomolecule and SNPs.

Pristine polycarbonate membranes and polycarbonate membrane doped with Ag nanoparticles were prepared by solution cast method. These membranes were subjected to surface modification techniques by He plasma treatment. Plasma treatment techniques applied here have shown considerable improvement in surface morphology and flux. Plasma treatment has helped in increasing flux whereas doping has modified the surface properties. As polycarbonate membrane is prepared without the help of any support, it can be concluded that polycarbonate has considerable strength as compared to other polymeric materials like polyamide which cannot be prepared without the help of support. An increase in surface roughness has been observed after plasma treatment by SEM and optical microscope images.

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