

Ion Implantation of Silver Nanoparticles on Electrodeposited Polycarbazole Via Plasma Sputter Type Negative Ion Sources

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Abstract. The discovery of conducting polymer has brought tremendous advancement in developing various polymeric materials, Carbazole pendants of poly(ethyl methacrylate) was cross-linked via an electrochemical route. The obtained film of poly(carbazole ethyl methacrylate) electrodeposited on the surface of indium tin oxide (ITO) was modified by implanting silver nanoparticles on its surface. This was done using Plasma Sputter-type Negative Ion Sources (PSTNIS) The modified and unmodified films of polycarbazole were characterized to assess its properties. Implanting silver nanoparticles on the surface of the cross-linked polymer abruptly changed its surface roughness, absorbance in the visible region and its current-voltage characteristic. A more pronounced diode-like characteristic was observed with a turn-on voltage of $\sim 0.4V$. Investigation and tailoring the properties of electropolymerized carbazole attached to poly (ethyl methacrylate) backbone with implanted silver nanoparticles could lead to important materials with impact in optoelectronic devices.

1. Introduction

The increasing demand for advanced technologies resulted researchers to develop new techniques in synthesizing or modifying nanostructured materials. Conducting polymers are one of the most interesting materials with semiconducting properties. Since the discovery of this group of materials by Heeger and coworkers, numerous researches have been devoted to conductive polymers [1, 3]. Among the numerous conducting polymers prepared to date, polycarbazole is by far one of the most extensively studied. As a result of its good intrinsic properties, polycarbazole could be a promising material for several applications including, electrochemical biosensors, conductive textiles and fabrics and optoelectronic devices. One useful and viable technique in depositing conducting polymer on a suitable substrate is electrodeposition. This is an advantageous process since the polymer is formed and deposited on the surface of the working electrode in just one process. The chemical and physical properties of the film can then be controlled by adjusting synthesis parameters such as current density, monomer concentration, electrolyte type, electrolyte concentration, pH and number of cycles [2, 3]. The intrinsic properties of electrodeposited polycarbazole are highly dependent on electropolymerization conditions. With the advent of surface modification techniques, plasma modification through ion implantation emerged as the most promising one since it allows reaching a high metal filing factor beyond the limit of metal solubility. In addition this technique allows easier



control on the dosage of ions that one would want to implant [4, 5, 6]. In this study, Ag nanoparticles were implanted using negative ion sources of plasma and the effect of this implantation on the optical, morphological and electrical properties of the conducting polymer film were observed.

2. Methodology

2.1 Materials

An indium tin oxide (ITO) coated glass slide purchased from Ossila Ltd. With sheet resistivity of $30\Omega\text{-m}$ was used as the substrate. 2-(9H-carbazol-9-yl)ethanol, methacrylic acid, 4-(*N,N*-dimethylamino)pyridine, *N,N'*-dicyclohexylcarbodiimide, dichloromethane and chloroform were all purchased at Sigma-Aldrich. All reagents were used as received without further purification.

2.2 Electropolymerization of Polycarbazole

The substrate was prepared and cleaned by following the conventional procedure of cleaning ITO coated glass slide. Briefly, the ITO coated glass slide was washed in a detergent solution (Hellmanex, Ossila Ltd) then ultrasonicated in acetone, ethanol, propanol and deionized water for five minutes in particular order. The ITO was dried at 110C and blown with dry nitrogen prior to its use. Polycarbazole was electrodeposited using the following parameters: 1mg/mL precursor material concentration, 0.1M of TBAPF6 as supporting electrolyte in chloroform, ITO as working electrode, platinum rod as counter electrode and Ag/AgCl as reference electrode, cycled for 15 times at 25mV/s. After the electrodeposition, the film was washed with chloroform and dried at 60C for 5-10 minutes and vacuum dried for another 30 minutes.

2.3 Ion Implantation of Silver Nanoparticles

The PSTNIS was first evacuated using a rotary pump and turbomolecular pump to reach a base pressure of 4×10^{-5} torr. The chiller is then switched on and set to 140 °C before applying current to the tungsten filament. Then the argon gas was allowed to flow inside the chamber with a flow rate of 5sccm. Next, the valve was throttled to control the pressure inside the chamber after introducing gas into it. The operating pressure was kept around 1mtorr. Steady state plasma was finally produced by applying a current of 9A to the tungsten filament. A discharge voltage of 50V was also applied to ignite the plasma. The target potential used for deposition were -300V, -400V, and -500V.

3. Results and Discussion

3.1 Electrodeposition

The cyclic voltammograms obtained with poly(carbazole ethyl methacrylate) on the surface of the ITO coated glass slide electrode is depicted in Figure 1A. The voltammetric curves are indicative of oxidation proceeding on every surface under consideration in two stages. The anodic peak observed at positive potentials is particularly intense in the anodic branch of the first spinning cycle and can be attributed to the initial monomer oxidation. The succeeding cycles of cycling the potential led to the formation of dimers and eventually to oligomers and/or polymers. The dimer of carbazole is proposed to be formed by the loss of an electron (e^-) and of a proton for every carbazole molecule.

3.2 Characterization

3.2.1 FTIR and XRD. The FTIR spectrum of the monomer, poly(carbazole ethyl methacrylate) (PCzEMA) and electrodeposited poly(carbazole ethyl methacrylate) (ePCzEMA) is shown in Figure 1C. While band centered at 832cm^{-1} in ePCzEMA only, it can also be observed in the spectra of 9H carbazole and PCzEMA the presence of peaks ranging from $730\text{-}750\text{cm}^{-1}$ indicating vibrational modes of 1: 2 disubstituted benzene rings of carbazole species. However, upon electrodeposition this peak suddenly disappeared and the presence of a new band centered at 833cm^{-1} is observed. This peak

is mainly attributed to the crosslinking of the carbazole units due to the polymerization of benzene rings along the polymer backbone. The band centered at 1708 in PCzEMA and ePCzEMA is attributed to C=O, a characteristic peak of ethyl methacrylate.

Shown in Figure 1B is the x-ray diffractogram of the ePCzEMA with Ag. It can be seen from this diffractogram the presence of the broad peak from 2 values of 15-35 which is mainly attributed to the amorphous nature of ePCzEMA. On the other hand sharp peaks for the (111) of Ag was observed signifying the presence of Ag on the polymer. Peaks for the ITO substrate were also evident in the diffractogram, a result that is inevitable since the deposited ePCzEMA forms only a thin layer on top of the ITO.

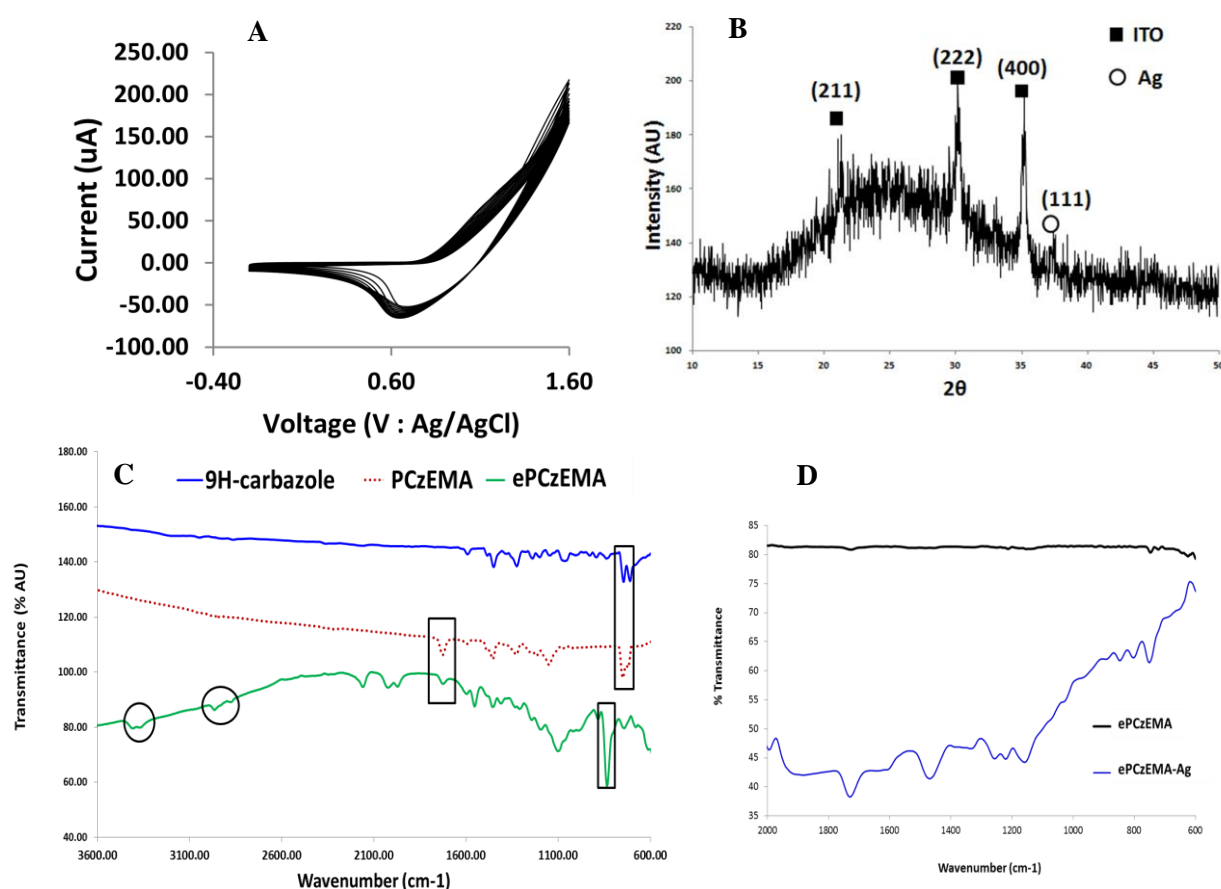


Figure 1 A) Cyclic voltammogram of ePCzEMA deposition, B) XRD diffractogram and C) FTIR of monomer, prepolymer and ePCzEMA, and D) FTIR of ePCzEMA-Ag on ITO

3.2.2 AFM and SEM. The surface morphology and topography of the electrodeposited film were observed using SEM and AFM. Figure 2 shows the AFM images for the substrate, Ag nanoparticles deposited on the substrate, pristine ePCzEMA and Ag implanted ePCzEMA. From this image the surface roughness were obtained and found that the ITO substrate has an rms value of ~ 2.5 nm, the Ag implanted ITO with rms value of 9.5nm, pristine ePCzEMA ~ 6 nm and Ag-ePCzEMA ~ 7.6 nm. These results corroborate with the SEM images depicted in Figure 2E and 2F showing the surface morphology of pristine ePCzEMA and Ag-ePCzEMA. From these images it is evident that the implantation of Ag led to a rougher texture with areas that appear to be bright and protruded relative to the surface.

To observe the effect of the target potential to the topography and roughness of the film, 300V, 400V and 500V were applied. Figure 3 shows the AFM images with varying target potential. Increasing the target potential led to a rougher surface since it was believed that the ions have more energy that could mechanically impact the surface of ePCzEMA upon landing.

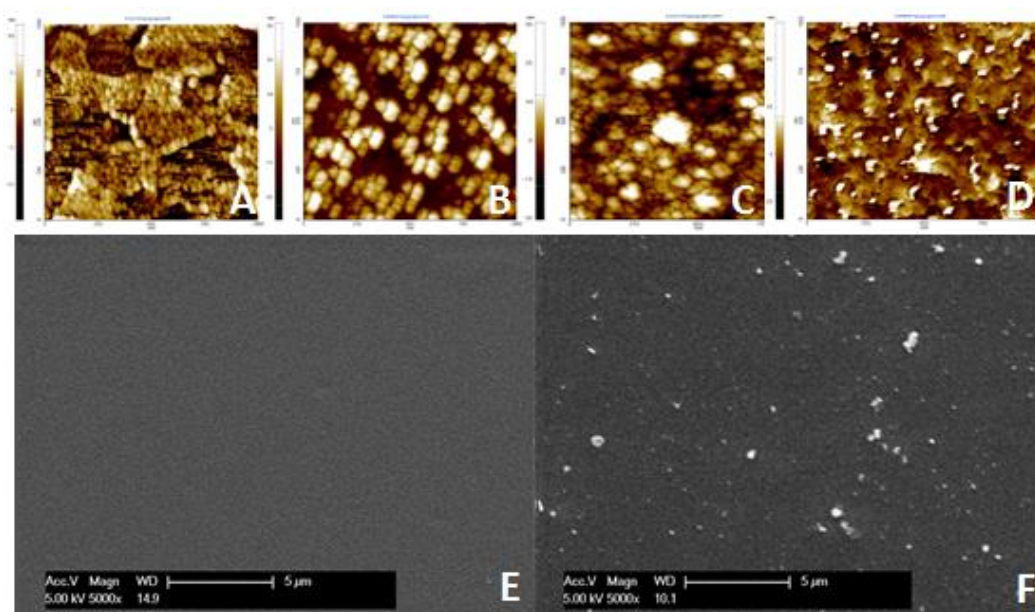


Figure 2. Atomic Force micrographs of a) pristine ITO coated glass slide, b) Ag on ITO c) ePCzEMA on ITO, d) Ag-ePCzEMA on ITO e) SEM of ePCzEMA on ITO, and f) SEM of Ag-ePCzEMA on ITO

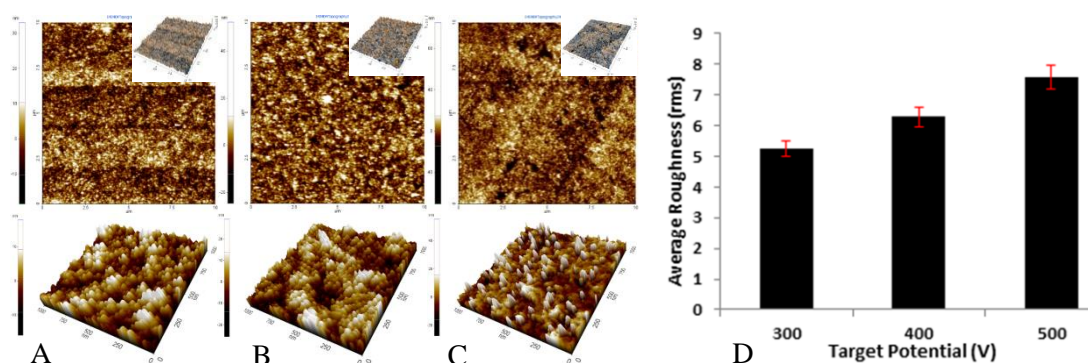


Figure 3. Atomic Force Micrographs of ePCzEMA with implanted Ag at different target potentials A) 300V B) 400V C) 500V and D) root mean squared value for each film

3.2.3 UV-Vis and I-V Curve. As can be seen from Fig. 4A, the UV-visible spectrum of ePCzEMA shows strong and sharp absorption peaks at 325 which may be derived from the $\pi-\pi^*$ transition of the short conjugated chain. Furthermore optical band gap was calculated based on the absorbance spectra of the polymers. The band gap of the polymer was estimated using the relation.

$$\alpha h\nu = B(h\nu - E_g)^n \quad (1)$$

where α is the absorption coefficient, $h\nu$ is the energy of absorbed light, $n = 1/2$ for direct allowed transition and B is proportionality constant. Energy gap (E_g) was obtained by plotting $(\alpha h\nu)^2$ vs. $h\nu$ and extrapolating the linear portion of $(\alpha h\nu)^2$ vs. $h\nu$ to zero. Employing the method stated above yields an estimated 3.7 eV optical bandgap for ePCzEMA. It can be noted from this result that the signal for the UV-Vis spectrum of the pristine ePCzEMA was increased upon the implantation of Ag on it. The presence of Ag nanoparticles on the polymer matrix could provide more excitation of carriers due to plasmon resonance effect as observed in systems with small metallic nanoparticles. The I-V curve of the device with ePCzEMA-Ag sandwiched to ITO and thermally evaporated Al had been obtained and

is presented in Figure 4B. Applied potential from -0.2 V – 1.0 V was used to observed the electrical properties of pristine ePCzEMA and ePCzEMA-Ag. Both I-V curves exhibit a nonlinear trend and exhibit more of a diode like characteristic. The shape of this I-V curve is attributed to the Schottky contact formed between the ITO and the polymer, together with an ohmic contact that could formed between the Al and some silver nanoparticles. The rectifying behavior is more prominent to that of the sample with Ag primarily because of the enhanced contacts between the ITO and Ag as well as the improved charge excitation offered by the Ag nanoparticles on the ePCzEMA matrix.

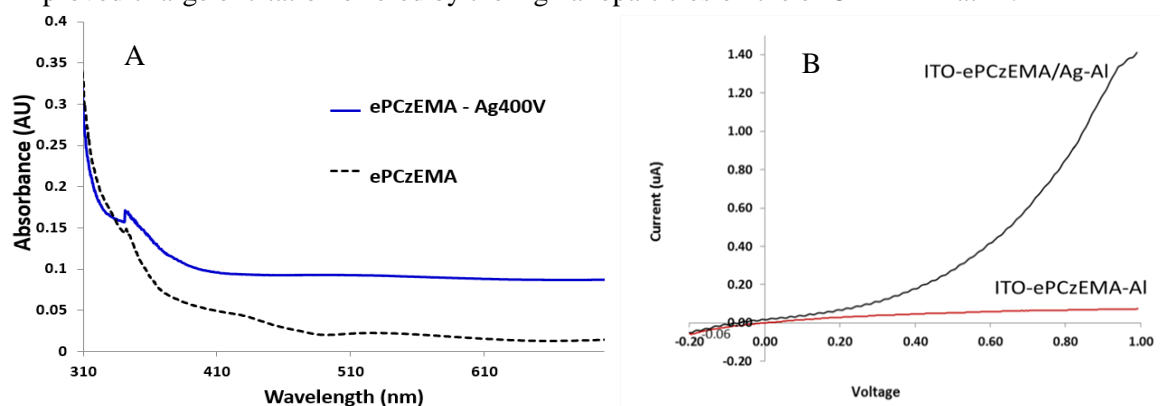


Figure 4. A) UV-Vis spectra and B) I-V curve of ePCzEMA, with and without implanted Ag

4. Conclusion

Silver nanoparticles have been deposited on the surface PCzEMA via plasma sputter type negative ion sources. Characterization results based on FTIR, XRD and UV-Vis showed that structures and optical property of the carbazole pendants have been intensified but preserved. The increased in target potential for plasma deposition altered the morphology and topography of the electropolymerized carbazole. Lower voltage of 300V produced a smoother surface compared to 500V target potential. The optical and electrical characteristics Ag modified ePCzEMA were enhanced and this could wave to the development of functional materials necessary for applications in optoelectronics field.

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