

Electrodeposition of Precursor Polymer Dispersed Carbon Nanotubes CPN Nanocomposite Films for Nanopatterning Application

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Abstract

In this work, the preparation of poly (*N*-vinyl carbazole) (PVK) and carbon nanotubes (CNTs) or PVK/CNTs CPN nanocomposites film was carried out by an electrochemical approach. Solutions of the CNTs or multi-walled carbon nanotubes (MWNTs) with the PVK were prepared using mixed solvents aided by sonication which resulted in exfoliation and deaggregation of the MWNTs into the PVK polymer matrix. Cyclic voltammetry (CV) was carried out from spin-coated films of this homogeneous dispersion which resulted in the formation of a conjugated polymer network (CPN) nanocomposite film. The spectroscopic, electrochemical, and interfacial charge-transfer behaviour of the nanocomposites films were also analyzed using CV, UV-vis and fluorescence spectroscopy and spectroelectrochemical measurements. The use of polymers in making inverse opals is advantageous since they have unique mechanical, optical, and electrochemical properties. These properties are highly enhanced with the incorporation of CNT, which are known to have inherent electrochemical, electrical and mechanical properties.

Keywords

Carbon Nanotubes, CPN, Nanopatterning, Electrodeposition

1. Introduction

Polymer nanocomposites containing carbon nanotubes (CNTs) have received high interest due to its unique properties, such as adjustable electrical conductivity, robust thermo-mechanical properties, and the potential to create new materials with improved characteristics coupled with a good chemical stability [1]. This includes both single-walled nanotubes (SWNT)s and multi-walled nanotubes (MWNT)s, the latter being commercially relevant. However, effective utilization of the excellent properties of CNTs composites depends on the quality of their dispersion and the level of polymer-CNTs interfacial bonding through covalent or non-covalent interactions. CNTs provide a tailored structure to interact with π -conjugated polymers by means of π - π electronic interactions [2].

The formation of a homogeneous film made of polymer solubilizing CNTs by “wrapping” on the outer surfaces of CNTs has remained a great challenge because of the easy agglomeration of CNTs [3]. As the processing of CNTs is generally blocked by their insolubility in most common organic solvents, only low weight/weight (w/w) or weight/volume (w/v) concentrations are usually obtained. It is necessary to obtain a homogeneous dispersion of CNTs in an organic solvent for film preparation. A convenient and facile route by solution mixing methods of a dispersant polymer and CNTs is desirable. One approach that has been commonly employed is the direct grafting of small molecules or polymers on the surface of the CNT, e.g. surface initiated polymerization (SIP), but with a reduction in the electro-optical properties of the CNT [4-5]. Another involves the use of non-covalently adsorbed initiators or end-grafted polymers

on the surface of the CNT without disrupting the π -conjugation of the aromatic rings on the CNT [6].

One interesting application of the CNT and PVK nanocomposite is to make a robust and conducting patterned surface of 2D arrays (called inverse opals) via facile approach called colloidal template assisted electropolymerization. Recently, inverse opals have become a significant interest due to myriad applications such as photonic crystals, diffraction gratings, biosensors, and surface-enhanced Raman scattering (SERS) [7]. The use of polymers in making inverse opals is advantageous since they have unique mechanical, optical, and electrochemical properties. These properties are highly enhanced with the incorporation of CNT, which are known to have inherent electrochemical, electrical and mechanical properties [8]. To date, CNTs have been applied to nanoelectronic devices, composite materials, field-emission devices, atomic force microscope probes, gas and chemical sensors, lithium ion storage, 3D electrode, etc. [9] Previously, single walled carbon nanotubes (SWNTs) have been reported to have a great potential for the reinforcement of polymer matrix composites because of their high strength, outstanding thermal property and good electrical conductivity [10].

2. Materials and Methods

2.1. Materials

The MWNTs (purity $\geq 95\%$) used in this study were obtained commercially as Baytubes (C150 P). The prepared MWNTs from Baytubes were produced in a high-yield catalytic process based on chemical vapour deposition (CVD). The outer and inner diameter, length, and density of the MWNTs were 13 nm, 4 nm, 1 μm and 130-150 kg/m^3 respectively. The obtained MWNTs were further purified by heating at 200°C for 6 hours prior to use. The poly (N-vinyl carbazole) (PVK) was purchased from Sigma-Aldrich Chemicals (USA) (ca MW= 25,000-50,000 g/mol). All solvents were of analytical grade and used without further purification [11].

2.2. PS Particle Layering

The layering of PS microbeads (or formation of colloidal crystals) is accomplished using a similar procedure described earlier by Grady and co-workers [7]. The method is called Langmuir-Blodgett (LB)-like technique for it forms a monolayer of PS particles onto flat surfaces without using the conventional LB set-up that employs floating barriers. Briefly, the substrate is attached into the dipper motor via Teflon clip and is dipped into an aqueous solution containing PS particles (1 wt.%) and SDS (34.7 mM) as spreading agent. Note that a higher concentration of anionic surfactant (SDS) will result to multiple layers of highly disordered latex spheres while a lower concentration will not formed a full coverage in hexagonal array.

Then the substrate is withdrawn vertically from the solution at a lift-up rate between 0.1 to 0.3 mm/min. Finally, the substrate is dried by suspending it in air for a few minutes. The monolayer ordering of the microsphere particles has been reported to be dependent on the LB-like technique and the concentration of the particles and surfactant (sodium *n*-dodecyl sulfate or SDS) in solution. The addition of surfactant has been explained to increase the ionic strength of the solution, and thus creating a driving force for the migration of particles from the bulk solution to the air-liquid interface. Also, the surfactant molecules at the air-liquid interface has been reported to slow down the evaporation rate of the latex-surfactant solution with respect to the latex solution, giving more time for the particles to rearrange and form a highly ordered arrays on the substrate as the liquid film evaporates [12]. The other roles of surfactant towards the formation of well-ordered arrays of latex spheres have been explained elsewhere [13].

2.3. Electropolymerization.

The electropolymerization of the monomer is done using cyclic voltammetric (CV) and chronoamperometric techniques using an Autolab PGSTAT 12 potentiostat (Brinkmann Instruments now MetroOhm Inc) in a standard three electrode measuring cell (fabricated electrochemical cell with a diameter of 1.0 cm and 0.785 cm^3 , Teflon made) with platinum wire as the counter electrode, Ag/AgCl wire as the reference electrode, and the bare Au or PS coated Au substrate as the working electrode (Figure 1). The potential is scanned between 0 V to 1.5 V at varying scan rate and cycles. After the electrodeposition, the resulting film is washed in ACN (for 3 times), and a monomer free scan is performed by using exactly the same experimental parameters but for 1 CV cycle only. Then the electropolymerized substrate is dried with nitrogen gas. The PS microspheres are removed from the surface after electropolymerization by dipping the PS coated substrate in THF for 30 minutes (2 times) to create the inverse colloidal crystals of composite films. The THF removes the PS particles only and not the electropolymerized composite film. Then the substrate is allowed to dry naturally under ambient condition [14].

3. Results and Discussion

To illustrate the patterning, the nanocomposite is electrodeposited via cyclic voltammetry (CV) around a sacrificial template layer of PS particles (500 nm size) thru PVK, which has a carbazole moiety that is an electropolymerizable unit. The use of CV technique endows several advantages – ease in control of thickness and lateral dimension of the pattern, site-directed patterning, and deposition over large surface areas onto various conducting substrates. After electropolymerization using cyclic voltammetric technique, the layer of PS particles is removed from the surface by solvent washing (2x, 30 mins) using THF, dichloromethane, or toluene. The fabrication scheme is summarized in Figure 1.

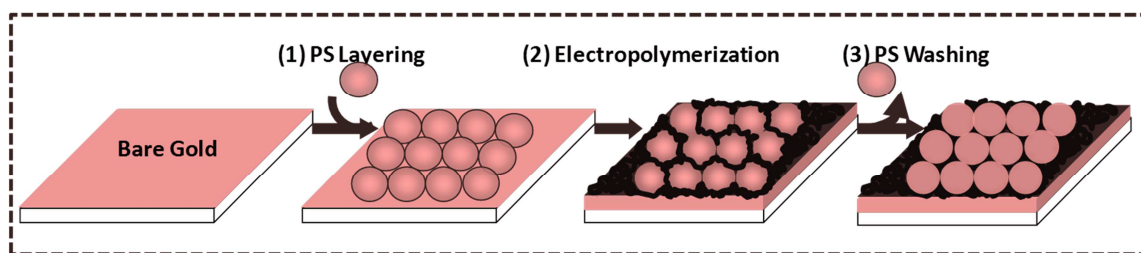


Figure 1. Fabrication scheme of 2D patterned arrays (called inverse opals) using the composite solutions.

Figure 2 shows the 2D patterned surface on ITO composed of CNT and PVK nanocomposites. The AFM topography 2D image with 3D image on inset (Figure 2a) revealed highly ordered triangular objects or simply inverse colloidal monolayer crystal arrays with cavity lateral dimension about the size of the PS particle (500 nm). The 2D patterned surface is also evident in the AFM phase image (Figure 2b). The height of the wall cavity is determined from the AFM line profile analysis of the topography image, which is between 30-35 nm. As a control, the same solution of the CNT and PVK composites was electropolymerized onto bare

ITO using the same CV parameters. As expected, no pattern is formed on the surface but rather a layer of CNT/PVK film is adsorbed (Figure 2d) as later confirmed by UV-Vis and FTIR spectroscopy measurements. The phase image (Figure 2e) illustrates nanometer scale granular features atop the ITO substrate (as shown to be a flaky surface), which is typical for a polymer electrodeposition. The AFM cross sectional analysis (Figure 2f) presents a random profile (-2 to +2 nm) of the polymer film deposition unlike in the patterned surface that shows a high regularity of the line profile.

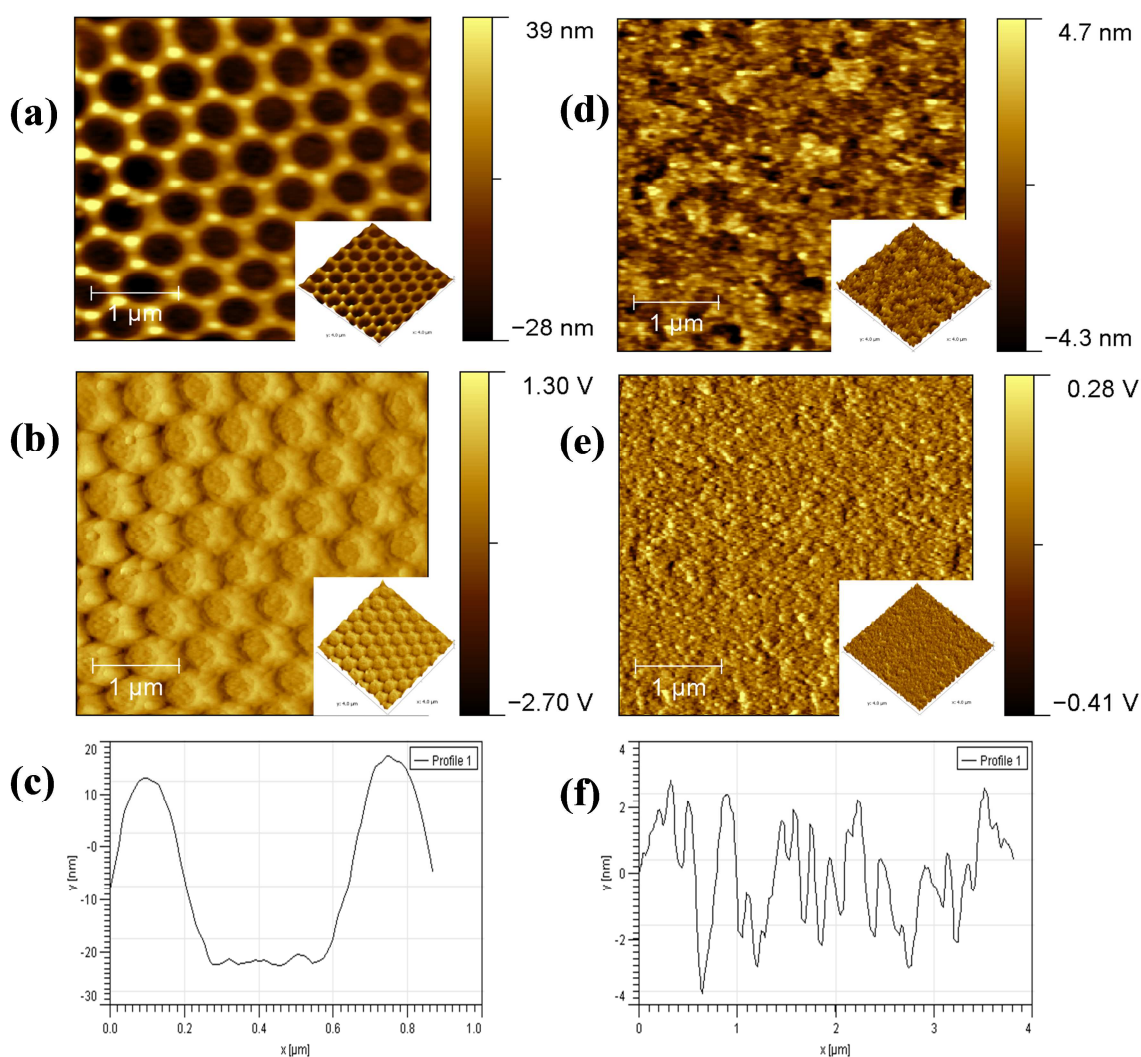


Figure 2. AFM (a, d) topography, (b, e) phase and (c, f) line profile measurements of CNT+PVK (a, b, c) patterned (using 500 nm PS particles) and (d, e, f) unpatterned surfaces. Note: CV deposition at 0V -1.5V, 10 mV/s, 10 cycles.

By simply varying the conditions for the CV electropolymerizations, the pattern on the surface can be easily modified. For instance, by increasing the number of cycles and scan rate, a thicker cavity wall is formed (Figure 3a). This finding is seen clearly in the AFM phase image (Figure 3b) and also observed in the line profile analysis (Figure 3c). Still, the pattern is present on the surface. Furthermore, with these electropolymerization conditions, the composite film starts to form on the inside cavity as observed in the topography and phase images. More compelling evidence is the result of the line profile, which shows a decrease in the peak-to-base distance (as compared

to Figure 2c). Similarly, the same solution of the CNT and PVK composites was electropolymerized onto bare ITO using these parameters. Again, a random deposition of the composite film is observed on the surface (Figure 3d) with the same granular features depicted on the phase image (Figure 3e). Like the earlier control experiment, a random profile (Figure 3f) is seen in the cross sectional analysis but the height has increased (-4 to +4 nm). Note that the size of the pattern can be changed by varying the size of the PS masks. Moreover, the cavity wall and cavity dimensions can also be modified by electrodeposition of a thicker polymer composite.

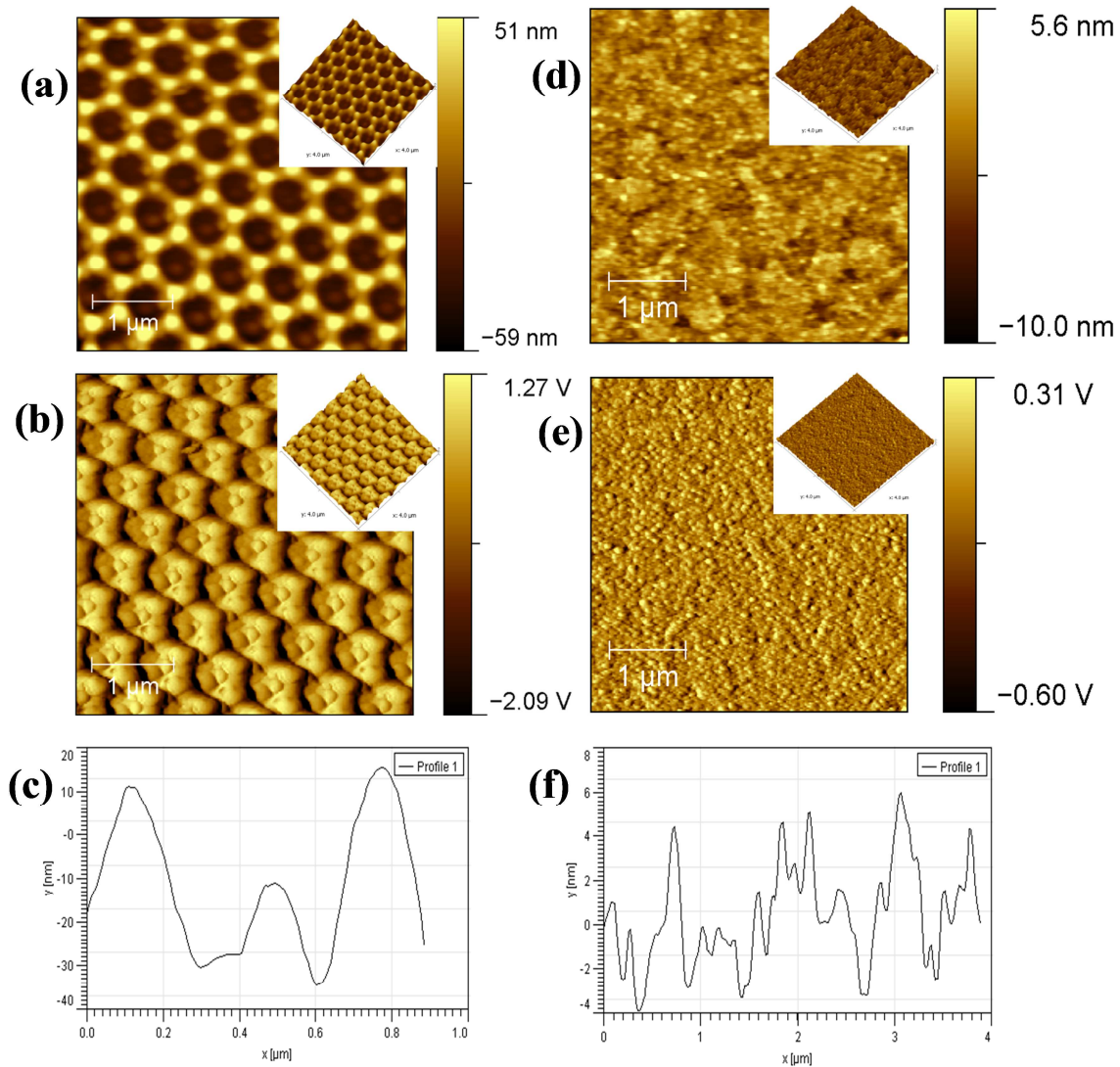


Figure 3. AFM (a, d) topography, (b, e) phase and (c, f) line profile measurements of CNT+PVK (a, b, c) patterned (using 500 nm PS particles) and (d, e, f) unpatterned surfaces. Note: CV deposition at 0V -1.5V, 25 mV/s, 25 cycles.

Chronoamperometric technique (constant potential deposition alternative to CV deposition) was also exploited in the electrodeposition of the composite film. An oxidation potential of 1.5 V was used for the electropolymerization (1000 sec) of the PVK. After etching the sacrificial template layer, a patterned surface is also seen but not as defined and

ordered as the CV electrodeposition (Figure 4a and 4b). Also, the inside cavity is slightly backfilled with the composite film. The formation of the patterned surface is also evident in the AFM line profile (Figure 4c). With the longer deposition time at 2000 seconds, a thicker cavity wall (Figure 4d and 4e) is formed that almost covered the inside hole (Figure 4f). At

this condition, the PS templated-pattern almost disappeared. Previously, we have compared the CV versus constant potential deposition of poly (3,4-ethylenedioxythiophene) on conducting substrate. The film formation was monitored in-situ by combination of electrochemistry, surface Plasmon resonance spectroscopy, and atomic force microscopy called EC-SPR-AFM technique. Results showed that CV deposition is more reproducible and homogenous than the constant potential. Both techniques have been explained to exhibit different electrodeposition mechanisms. For constant potential, an induction period for the build-up of charge is required, which will eventually cause nucleation and gradual

deposition of the film to the substrate. At the start, a slow initial stage occurs that is related to the nucleation on bare substrate involving a double layer charging effect. The next stage involves the rapid deposition of the polymer film corresponding to autocatalytic growth. In the case of CV, the formation of radical cation via oxidation process occurs simultaneously with electrodeposition of the film onto the substrate. This is probably the reason why the CV deposition demonstrated a more ordered and periodic pattern on ITO. It is also believed that the formation of patterned film via constant potential can be improved by further optimization of the parameters.

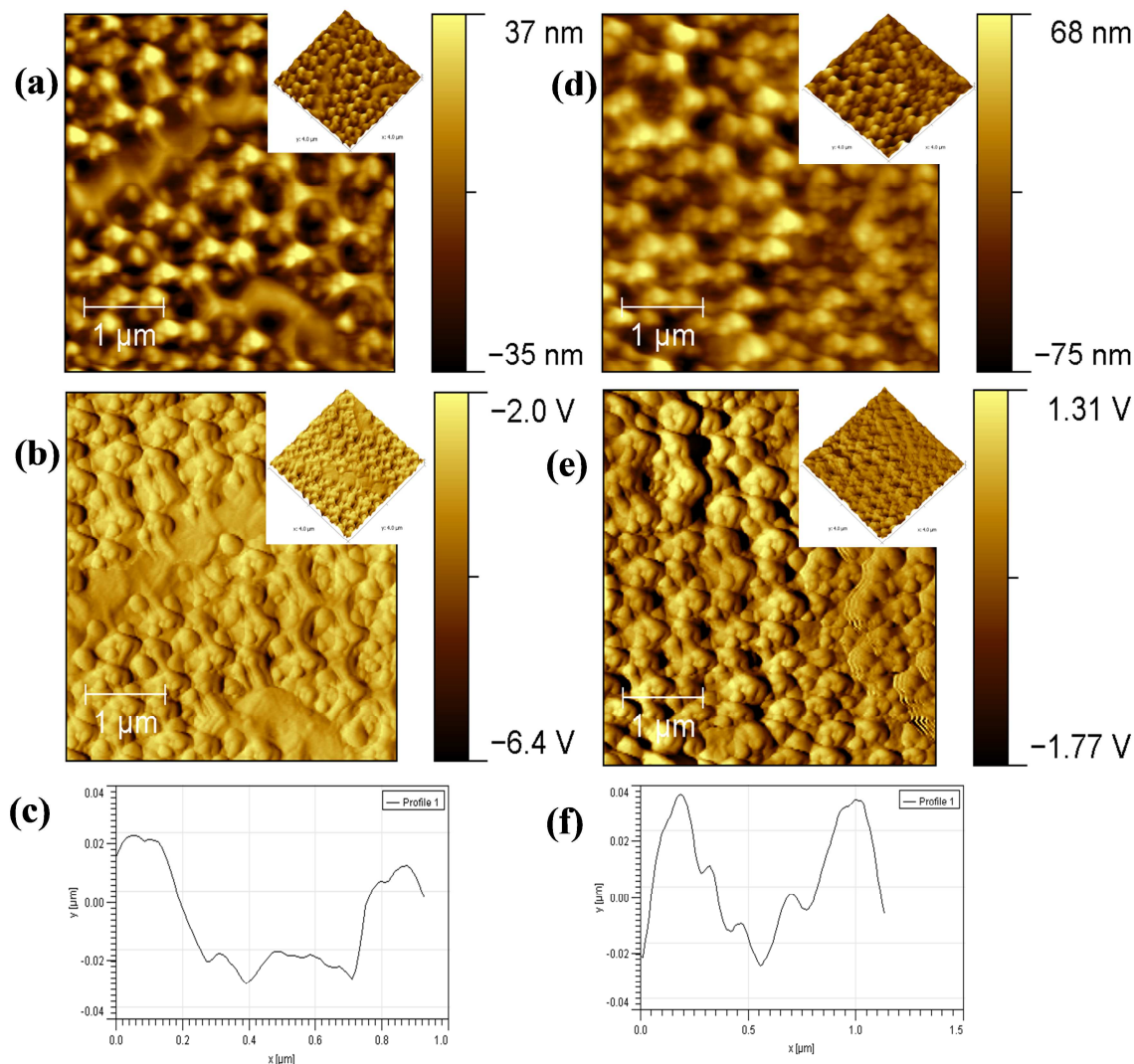


Figure 4. AFM (a, d) topography, (b, e) phase and (c, f) line profile measurements of CNT+PVK patterned surfaces (using 500 nm PS particles) prepared using constant potential growth (at 1.5 V) for (a, b, c) 1000 sec and (d, e, f) 2000 sec.

4. Conclusions

This work has shown that the PVK/CNTs nanocomposites can be electrochemically cross-linked and deposited on ITO glass substrate resulting in the formation of conjugated polymer networks without decomposing the polymer backbone. The electrochemical cross-linking response of PVK/MWNTs nanocomposites showed the doping role in the

charge-transfer interaction of MWNTs in PVK/MWNTs nanocomposites. The redox peaks observed at 0.9-1.0 V for PVK vs Ag/AgCl as confirmed by CV measurements were due to the carbazole electroactive species. The disappearance of the oxidation peak for the pure PVK could be due to the addition of CNTs in PVK/CNTs CPN nanocomposite films in which the CNTs acting as electron acceptor and PVK act as electron donor. These results emphasize that the PVK/CNTs

nanocomposite films is feasible for the electropolymerization of PVK/CNTs CPN films without affecting the polymer backbone. The said deposition method resulted in PVK/CNTs characteristics in a single film. This was further confirmed using spectroelectrochemical measurements.

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