

# Polypyrrole/multiwall carbon nanotube nanocomposites electropolymerized on copper substrate

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## Abstract

Polypyrrole/multiwall carbon nanotube (PPy/MWCNT) nanocomposites were successfully synthesized by electropolymerization of MWCNT-dispersed pyrrole solution on the surface of copper electrodes. The obtained nanocomposites were characterized with scanning electron microscopy (SEM), linear sweep voltammetry (LSV) and thermal gravimetric analysis (TGA). Polypyrrole structures which embraced the MWCNTs led to the formation of nanocomposite striated parallel walls. MWCNTs acted as appropriate substrates for electrodeposition of polypyrrole particulate structures and high yield synthesis of PPy was observed on them. Smooth PPy/MWCNT nanocomposite films were obtained on Cu electrodes by decreasing the potential scan rate. Thermogravimetric analysis showed that MWCNTs increased the thermal stability of polypyrrole.

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## 1. Introduction

Desirable electrical, optical and chemical properties of polypyrrole (PPy) as an interesting conductive polymer make it an appropriate material for many biological applications [1,2], electronic noses [3] sensors and actuators [4,5], cathode and anode materials in lithium batteries [6,7]. However, low mechanical properties are drawbacks of this polymer [8]. To solve this problem and to enhance its physical properties, PPy based composites were developed [9].

Polymer/carbon nanotube nanocomposites have attracted much attention, since they were introduced by pioneers like Ajayan et al. [10]. Various researchers have investigated polypyrrole/carbon nanotube (PPy/CNT) composites and reported the improvement of the mechanical and physical properties of polypyrrole [11,12] due to the weird characteristics of CNTs [13]. PPy/CNT composites have superior electrical capacitance [14], magnetic properties and thermal stability [9].

Pyrrole oxidation has been performed via various processes such as electrochemical, chemical, photonic and catalytic polymerization in the monomer solution. Adherent coatings can be obtained merely from the electropolymerization techniques [15]. Inert materials (i.e. Pt, Au or glassy carbon) have been extensively used as appropriate substrates for pyrrole electropolymerization. Utilization of the metallic substrates for pyrrole electropolymerization leads to develop polymer based devices and laminates [16]. Recently, several investigations have been devoted to pyrrole electropolymerization on oxidisable surfaces such as Al [17], Zn [18] and Cu [19].

There is no report on electropolymerization of PPy/MWCNT nanocomposites on copper substrates. In this study we state a facile electropolymerization technique for synthesis of PPy/multiwall carbon nanotube nanocomposites on Cu electrodes and investigate its characteristics morphologically and electrochemically.

## 2. Experimental

The electrolyte contained 0.5 M pyrrole (98%,  $M=67.09$  g mol<sup>-1</sup>, Merck, Germany) in an aqueous solution of 0.1 M

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$\text{Na}_2\text{SO}_4$  (99.99%,  $M=142.04 \text{ g mol}^{-1}$ , Merck, Germany) in which sodium hydroxide ( $\text{NaOH}$ , 99%,  $M=40 \text{ g mol}^{-1}$ , Merck, Germany) solution was used to set the pH to 12. The copper electrodes (99%, Abhar Wire and Cable Co., Iran) were carefully polished and cleaned before the experiments. Multiwall carbon nanotubes (diameter range=60–110) were prepared via a chemical vapor deposition (CVD) method precisely described in [20]. Ultrasonic irradiation was carried out to disperse CNTs in the precursor solution. All the electropolymerization processes were carried out in an Autolab PGSTAT30 potentiostat/galvanostat equipment using a standard three-electrode cell. The experiments were performed with the given scan rates and potential ranges. Electrochemical potentials were recorded versus an  $\text{Ag}/\text{AgCl}$  reference electrode. The morphology of the nanocomposites was studied using a scanning electron micro-

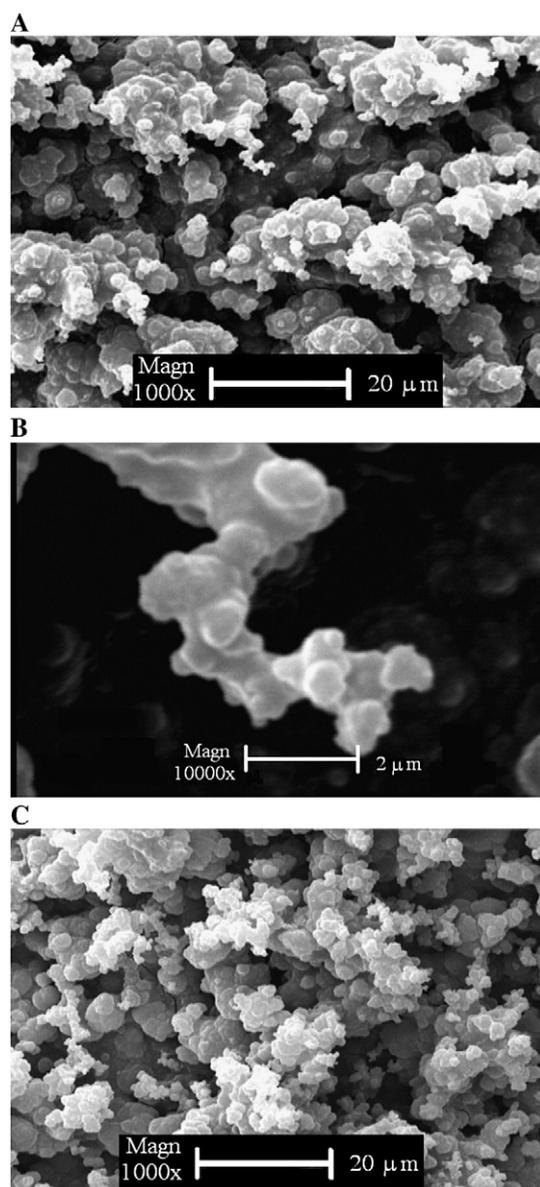


Fig. 1. SEM images of PPy deposited on the Cu electrode with scanning rate of 10 mV/s and potential range of 0.8–0.9 V vs.  $\text{Ag}/\text{AgCl}$ , (A), (B) with MWCNTs and (C) without MWCNTs.

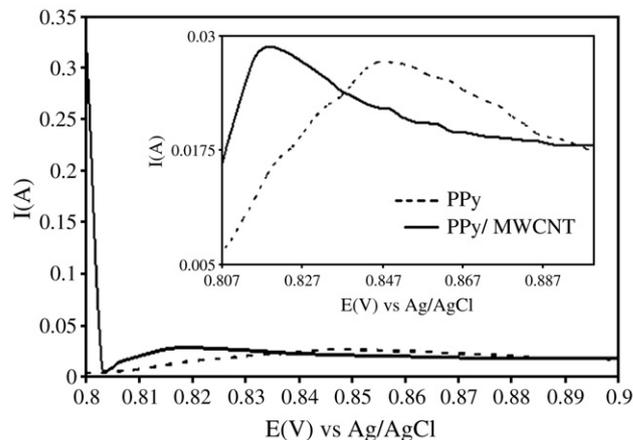


Fig. 2. Linear voltammograms of the potentiodynamic synthesis of PPy, PPy/MWCNT, at a potential range of 0.8–0.9 V vs.  $\text{Ag}/\text{AgCl}$  and scanning rate of 10 mV/s. The magnified area of the peaks is shown inset.

copy (SEM, Philips XL30). Thermal gravimetric analysis was carried out with a DTA/TG equipment (Shimadzu DTA-50) up to 800 °C using a heating rate of 10 °C/min.

### 3. Results and discussion

The fundamental process in electrochemical reactions is the transfer of electrons between the working electrode surface and molecules in the interfacial region (either in solution or immobilized at the electrode surface). This heterogeneous process can be significantly affected by the microstructure and roughness of the electrode surface, the blocking of active sites on the electrode surface by adsorbed materials and the nature of the functional groups (e.g. oxides) present on the surface. Presence of MWCNTs affected the deposition of PPy and resulted in the formation of a striated structure made of parallel walls (Fig. 1A) which could be due to the surface adsorption of CNTs to high energy regions of the copper electrode and subsequent nucleation and electropolymerization of PPy on them. Therefore it could be concluded that CNTs adsorbed on the preferential sites on the surface of the Cu electrodes, and enhanced the nucleation and growth of polypyrrole chains on the mentioned high energy areas. Hence correlation between the fabrications of high performance aligned nanotube based polypyrrole composites and surface texture of the substrates should be taken into consideration. Such a novel microstructure would be of great interest for various applications in sensing/actuating devices.

Carbon nanotubes were encapsulated in polypyrrole and PPy nanoparticles were grown on the surface of MWCNTs (Fig. 1B). A large diameter of the selected area shown in this image (~700–1500 nm) illustrates high yield deposition of PPy on CNTs. EDAX analysis confirmed the presence of carbon nanotube in the mentioned structure. Roughly, it can be expressed that the high specific surface area of the CNTs provided a higher surface for the occurrence of the electropolymerization process and hence an elevated deposition rate was observed on MWCNTs. The nanoparticles formed on the carbon nanotubes demonstrate that MWCNTs could act as secondary electrodes to perform PPy electropolymerization [14]. Therefore carbon nanotubes not only increase PPy electrodeposition yield but also can act as a substrate to electrodeposit PPy protrusive structures (i.e. particles or micro containers in other conditions).

Comparing the linear sweep voltammograms shown in Fig. 2 reveals the influence of MWCNTs on the potentiodynamic electropolymerization of pyrrole at a potential range of 0.8–0.9 V vs.  $\text{Ag}/\text{AgCl}$  and

scanning rate of 10 mV/s. As it is observed, the general shapes of LSVs are similar which indicate that the electropolymerization pathway is not considerably altered. Some significant distinctions can be deduced in this analogy. As the peak current is higher (inset of Fig. 2), when the MWCNTs are dispersed within the electrolyte, the charge transferred through the cell is higher. Since this peak is associated with the polymerization of pyrrole, it can be inferred that a larger amount of the polymer has been electrodeposited on the copper electrode surface in the presence of carbon nanotubes. This phenomenon is due to the attachment of the MWCNTs on the electrode surface which provides an extended specific surface area and culminates in strengthening the electrochemical process. Therefore, larger amounts of the electro-active film can be deposited on the substrate. Another distinction can be concluded from the difference between the rates of the initial increase of the peaks. As the formation of the polymer film on the copper surface is more difficult than the subsequent film growth on the initial polymer layer, the preliminary increase of the peaks current is very significant. Carbon nanotubes provide better electrodeposition sites so that the rate of the peak growth increases with MWCNT addition.

Fig. 3 exhibits the influence of the potential scanning rate on the morphology of the electropolymerized polypyrrole/MWCNT nanocomposites. As it is observed in Fig. 3A, performing the potentiodynamic synthesis in the potential range of 1–2 V vs. Ag/AgCl and scan rate of 1 mV/s, smooth surfaces with flat edges and some protrusions have been deposited on the Cu electrode, while with increasing scan rate (i.e. 50 mV/s), an uneven structure was observed (Fig. 3B). With a linear potential ramp, the thickness of the diffusion layer which consists of the electro-active species accumulated in the vicinity of the electrode

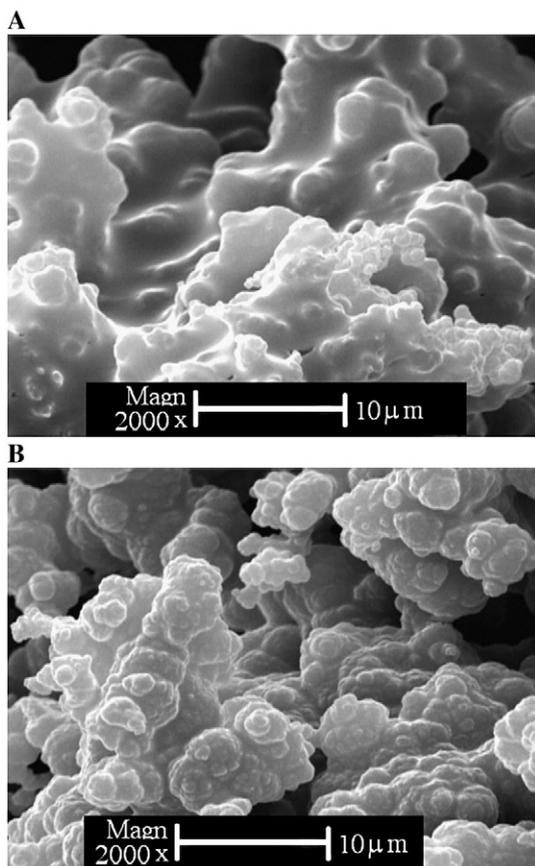


Fig. 3. SEM images of PPy/MWCNT deposited on the Cu electrode with potential range of 1–2 V vs. Ag/AgCl, (A), SR 1 mV/s, (B) SR 50 mV/s.

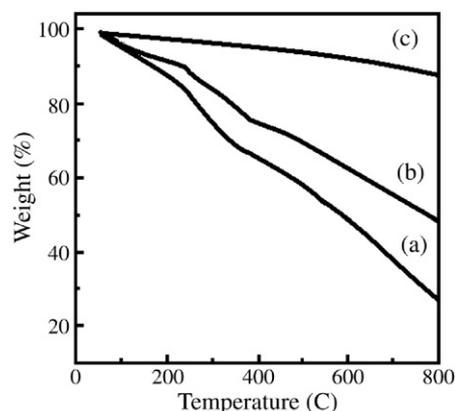


Fig. 4. TGA curve of (a) pure PPy, (b) PPy/MWCNT nanocomposite, (c) MWCNT.

surfaces varies with the voltage scan rate utilized during the process. In a slow voltage scan the diffusion layer will grow much further from the electrode in comparison to a fast scan. Consequently the flux to the electrode surface is considerably smaller at slow scan rates than it is at faster rates. As the faradaic current is proportional to the flux towards the electrode, the magnitude of the current will be lower at slow scan rates and higher at elevated rates. Such phenomenon led to the rising of the local temperature in the regions near the electrode surfaces at high scan rates and resulted in the increasing interaction between monomers together with monomers and MWCNTs so that the surface morphology of the PPy/MWCNT nanocomposite was roughened with increasing scan rate [21]. Therefore, low potential scanning rates are more appropriate for the formation of the smooth nanocomposite structures.

Thermogravimetric analysis (TGA) has been exhibited in Fig. 4. The pure MWCNTs are thermally stable up to 800 °C and small amount of weight loss occurred due to water or volatile impurities evaporation (Fig. 4c). Addition of MWCNTs to the PPy, increased the thermal stability of PPy between 0 and 800 °C around 20% (compare Fig. 4a and b).

#### 4. Conclusion

Polypyrrole/multiwall carbon nanotube nanocomposites were successfully electropolymerized on copper electrodes. It has been shown that MWCNTs led to preferential deposition of PPy chains on copper electrode and formation of striated parallel walls. High yield synthesis of PPy on the nanotubes was observed. MWCNTs acted as appropriate substrates for electrodeposition of polypyrrole particulate structures. Decreasing of the potential scan rate led to the formation of smooth PPy/MWCNT films on Cu electrodes. Thermogravimetric analysis showed that MWCNTs increase the thermal stability of polypyrrole.

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