



## Research Paper

## Electrodeposition of polypyrrole/functionalized-multiwalled carbon nanotubes composite and its application in supercapacitors

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## ABSTRACT

In this study, we fabricate polypyrrole(PPy)/functionalized-multiwalled carbon nanotubes (FM) composites (PPy/FM) by cyclic voltammetry onto the stainless steel mesh (MS) which is modified by FM before use. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) results show that MS-PPy/FM composites form core (MWCNTs)-shell (PPy) structures via hydrogen bond. The electrochemical performances were investigated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectrum (EIS). Electrochemical tests demonstrate that, at the current density of  $5 \text{ mA cm}^{-2}$ , MS-PPy/FM composites show a larger specific capacitance of  $1269 \text{ F g}^{-1}$  when the addition amount of FM is 0.8%, and the capacitance retention of MS-PPy/FM is 88.1% after 1000 cycles. All the electrochemical properties of the composites are better than those of PPy.

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## 1. Introduction

Recently, Electrochemical Supercapacitors (ES), which possess both high power density and high energy density, have been widely researched due to their high energy density, long cyclic life and good environmental friendliness [1,2]. As we know, the properties of ES mainly depend on the electrode materials. At present, carbon-based materials, redox metal oxides and conducting polymer are often applied as electrode materials owing to their various advantages [3]. Considering the high pseudocapacitance performances and low production cost, PPy, which is a kind of conducting polymer, have been received more and more attention [4]. However, during doping/dedoping process, the volume of PPy changed. The poor mechanical properties of PPy lead to an electrochemical performance decline, which limits its application as individual electrode material. In order to overcome these defects, different materials with large mechanical strength have been employed to fabricate PPy-based composites [5].

Since carbon nanotubes (CNTs) were discovered in 1991, many scientists have been devoted to researching their properties in many fields [6]. Commonly, CNTs are considered as an ideal nano-

reinforcing candidate thanks to their excellent properties, such as good mechanical characteristics, nanometer size, high conductivity, and high surface area [7]. As we know, there are single walled (SWCNT) and multiwalled carbon nanotubes (MWCNTs) [8]. It is well known that  $\pi$ - $\pi$  non-covalent bonds can be formed between conducting polymer and MWCNTs because of their delocalized  $\pi$  electrons [9]. Therefore, for PPy, it has been demonstrated that to cooperate with MWCNTs is a good idea, which helps to increase the electrode's surface area and facilitate electron transfer [10]. Nevertheless, the major problem when MWCNTs added to PPy is their low dispersibility (commonly called "solubility") in common solvents, which derives from abundant van der Waals interactions between individual nanotubes. Usually, functionalization with carboxylic acid groups (designated as FM) is a good method to prevent MWCNTs self-aggregation. It was also used to enhance the properties of PPy/MWCNTs composites and allow for tuning their physicochemical properties and surface morphology [11].

There are usually three methods to prepare PPy/MWCNTs composites: (i) chemical synthesis [12], (ii) electropolymerization of PPy on the MWCNTs electrode [13] and (iii) electrochemical co-deposition [14]. Among them, the second method has been envisioned to provide the deposition of polymer coatings with high levels of conductivity and chemical stability [15]. Du et al. [16] synthesized PPy/CNT composites with a specific capacitance (SC) of  $154.5 \text{ F g}^{-1}$ . Jurewicz et al. [5] fabricated PPy/MWCNT composites

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by electrochemical polymerization techniques and the maximum SC of the composites is  $163 \text{ F g}^{-1}$  at a  $2 \text{ mV s}^{-1}$  scan rate. Paul et al. [17] assembled full cells with the PPy/MWCNT composite electrodes deliver initial SC ranging from 146.3 to  $167.2 \text{ F g}^{-1}$  at  $0.5 \text{ mA cm}^{-2}$ . Sun et al. [18] prepared the composite of PPy and functionalized MWCNTs, which obtained a SC of about  $243 \text{ F g}^{-1}$  at a scan rate of  $10 \text{ mV s}^{-1}$ . PPy/MWCNT composites with SC of  $427 \text{ F g}^{-1}$  has been achieved using 5-s electrodeposition pulses, reported by Fang et al. [19]. Lin and Xu [20] reported PPy/MWCNT composites have a porous 3D nanostructure, with high SC of  $890 \text{ F g}^{-1}$  calculated from CV at  $2 \text{ mV s}^{-1}$  in  $1.0 \text{ mol dm}^{-3}$  KCl.

In this work, in order to improve the SC and cycle stability of the PPy electrode, we fabricated polypyrrole/functionalized-multiwalled carbon nanotubes (PPy/FM) composites by cyclic voltammetry (CV) on low cost substrates: (1) stainless steel wire mesh (SS) (2) stainless steel wire mesh modified by FM before use (MS). The structure and electrochemical properties of the composites were further systematically studied. We illustrated that the composites combined with FM possess a high SC and excellent cycle stability in contrast to PPy, especially MS-PPy/FM composites. These traits suggest that PPy/FM composites may become a promising electrode of supercapacitor in the future.

## 2. Experimental

### 2.1. Reagents and materials

Pyrrole was purified before use.  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  were analytical grade and used without further purification. MWCNTs powder was purchased from Institute of Chemical Physics (Chengdu, China). Solutions were prepared with distilled water.

### 2.2. Preparation of FM

FM was prepared from MWCNTs through the following method. Firstly, certain quality (0.2 g) of pristine MWCNTs (PM) were added into 30 mL  $\text{H}_2\text{SO}_4$ , and then the mixture was stirred for 6 h and treated under ultrasonic condition for 4 h. Secondly, 10 mL  $\text{HNO}_3$  was added into the above solution and was stirred for 30 min. After that, the reaction mixture was refluxed at  $140^\circ\text{C}$  for different time. Finally, after rinsing and pumping filtration with distilled water and drying in a vacuum at  $60^\circ\text{C}$  for 24 h, the FM was obtained. For comparison, according to the reflux time, the samples were named FM-0.5h, FM-1h and FM-2h.

### 2.3. Synthesis of MS-PPy/FM composite

Before use, the stainless steel wire mesh (304 type,  $1 \times 2.5 \text{ cm}$ , designated as SS) was immersed into the mixture of 25 mg FM and 5 mL N,N-dimethyl formamide (DMF) for 24 h, and ensured the area in solution was  $1 \text{ cm}^2$ . Then the modified SS (MS) were dried at  $60^\circ\text{C}$  for 12 h.

MS-PPy/FM composite was electrodeposited on stainless steel mesh substrates by cyclic voltammetric method on CHI660D electrochemical work station, using  $0.1 \text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$ ,  $0.1 \text{ mol dm}^{-3}$   $\text{CuSO}_4$ ,  $0.1 \text{ mol dm}^{-3}$  pyrrole monomer and 0.8% FM. The electrochemical cell for deposition contained a standard calomel electrode (SCE), SS (304 type,  $1 \times 2.5 \text{ cm}$ ) and MS, employed as reference, counter and working electrode, respectively. The cyclic voltammetry (CV) curves were recorded at a scanning rate of  $5 \text{ mV s}^{-1}$  by scanning the potential from  $-0.2$  to  $0.9 \text{ V}$  for 31 segments. After deposition, the product was rinsed with  $0.1 \text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  and distilled water to remove soluble monomeric species, and then dried at  $60^\circ\text{C}$  for 12 h to obtain the MS-PPy/FM-0.8%. Keeping other experimental conditions unchanged, in terms of the additive

amount of FM, the composites were named MS-PPy/FM-0.2%, MS-PPy/FM-0.4%, MS-PPy/FM-1.2% and MS-PPy/FM-1.6%, respectively. Additionally, we also prepared PPy (without FM, SS is working electrode) and SS-PPy/FM (the mass ratio of FM and Py was same to MS-PPy/FM-0.8%, just MS was replaced by SS) composites for comparison.

### 2.4. Structure and morphological characterization

All tests used samples scraped from stainless steel mesh substrates. The morphology of the composites was characterized by scanning electron microscopy (SEM: J EOL JSM-6701F) and transmission electron microscopy (TEM: JEM-1200EX). The structure of samples was characterized by FT-IR (Nicolet, type210, America) which was recorded between  $4000$  and  $500 \text{ cm}^{-1}$ . The XRD patterns were characterized by D/MAX-2400X X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.154056 \text{ nm}$ ), employing a scanning rate of  $10^\circ \text{ min}^{-1}$  in the  $2\theta$  range of  $10$ – $90^\circ$ . The XPS data were obtained by a V.G. ESCA Laboratory 210 photoelectron spectrometer with Mg K $\alpha$  source, the spectra were acquired with  $30 \text{ eV}$  pass energy.

### 2.5. Electrochemical tests

Electrochemical measurements were performed using  $1.0 \text{ mol dm}^{-3}$   $\text{HNO}_3$  aqueous solution. The stainless steel mesh, impregnated with as-prepared samples, was used as working electrode. A SCE electrode ( $E^\theta = 0.268 \text{ vs NHE}$ ) and a platinum sheet were employed as the reference electrode and the counter electrode. Cyclic voltammograms (CV) and galvanostatic charge–discharge (GCD) curves were recorded in the potential window of  $-0.3$  to  $0.7 \text{ V}$ . Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from  $10^5$  to  $10^{-2} \text{ Hz}$  at open circuit potential with the amplitude of  $5 \text{ mV}$ .

## 3. Results and discussion

### 3.1. Structure characterization of FM

Fig. 1A depicts the FTIR spectra of the PM and FM. The spectrum for FM shows there is an intense O-H peak at  $3428 \text{ cm}^{-1}$  compared with PM, suggesting re-introduction of some O-H after acid treatment. The peaks of  $2924$  and  $2856 \text{ cm}^{-1}$  correspond to the CH and  $\text{CH}_2$  stretching vibration [21]; the peaks at  $1727$  and  $1543 \text{ cm}^{-1}$  are assigned to different C=O (COOH and  $\text{COO}^-$ ) stretching vibration, which may be caused by the ionization of COOH [22,12]; the peaks near  $1285$  and  $1047 \text{ cm}^{-1}$  are ascribed to the C-C-O and C-O stretching vibration [21], respectively. In summary, the spectrum of FM illustrates that some functional groups such as hydroxyl and carboxyl are successfully introduced on the surface of FM after PM treated with mixed acid.

XRD patterns of PM and FM are shown in Fig. 1B. The peaks at  $25.2^\circ$  and  $45.3^\circ$  are described to the typical (002) and (100) reflections of MWCNTs [23]. One can observe from the patterns that the peak intensity of FM is obviously decreased compared with PM. It is suggested the orderly  $sp^2$  hybridized carbon atom on the sidewalls of MWCNTs turned into the  $sp^3$  hybridized carbon atom after functionalization [24]. Fig. 2 is SEM images of PM and FM, in comparison with the PM, we can find that FM exhibits a well-ordered tubes after treated by mixed acid.

### 3.2. Structure characterization of composites

Compared the morphology of SS and MS in Fig. 3A and B, it can be obviously observed that MWCNTs chains uniformly distributed

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