

An Efficient Synthesis of Polypyrrole/carbon Fiber Composite Nano-thin Films

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Polypyrrole(PPy) thin films were deposited on vapor grown carbon fibers(VGCF). Formation of PPy on VGCF was carried out by using an in-situ chemical polymerization of the monomer in presence of FeCl₃ oxidant. An ultrasonic cavitation stream was used during polymerization of pyrrole, to enable the deposition of uniformly thin (*ca.7nm*) PPy films onto the surface of VGCF. The PPy/VGCF composite was characterized by FTIR spectroscopy. The surface morphology of the polymer films were characterized by using scanning electron microscopy (SEM) and scanning transmission emission microscopy (TEM).

Keywords: Nano-composite films, polymerization, polypyrrole, SEM, TEM

1. INTRODUCTION

Conjugated polymers have been intensively studied in the fields of fundamental and applied researches, because of their one-dimensional intrinsic properties and their potential for commercial applications [1]. They have relatively high conductivity, are light in weight, inexpensive, flexible, air-stable, etc. The conjugated polymers, most notably polypyrrole (PPy), polythiophene (PT), polyaniline (PAN), poly(3,4-ethylenedioxythiophene) (PEDOT), and poly(*p*-phenylenevinylene) (PPV) have been synthesized, in free-standing film and bulky powder form, through the electrochemical or chemical polymerization methods [2]. They are easy to prepare in the form of extended surface thin films, and can store the charge throughout their entire volume [3,4]. In the form of thin and plastic films polypyrrole has many potential applications in electrochemical capacitors [4,5], electrochromic devices [6], batteries [7], actuators [8] and sensors [9]. With the development of Si-based nanotechnology, conjugated organic materials have been applied to many nanoscale devices and

microelectronic devices [10,11], electrochemical devices, single electron transistors [12], nanotips in field emission displays (FED) [13], etc. Recently, many attempts have been devoted to the use of electronically conducting polymers (ECPs) as electrode materials in electrochemical capacitors, often called supercapacitors [14]. The increasing interest in such polymers is stimulated by the demand of active materials with high specific capacitance, for maximum specific energy and specific power of the device. Especially polyaniline (PANI) and polypyrrole (PPy) have been considered as the most promising materials for this application due to their excellent capacity for energy storage, easy synthesis, higher conductivity and lower cost than many other conducting polymers [15]. However, the long-term stability during cycling is a major demand for an industrial application of ECPs. Degradation of the electrode during cycling occurs because of the volume change of the polymer due to the insertion/deinsertion of counter ions. Thus, the mechanical stress in the polymer film relates directly with the cycle life of polymer-based capacitors. This has been overcome to some extent by the use of composite structures [16,17]. The conductivity of the composite materials is lower than in the pristine ECP. Rather high energy and power densities have been reported when ECPs are deposited as a thin coating on some supporting substrate such as carbon paper and cloth [18,19]. Different kinds of nanotubes and their composites have been already proposed as electrode materials for supercapacitors [20-28].

In this paper, we would like to report synthesis of a composite electrode material, with nano-thin films of PPy coated on vapor grown carbon fibers (VGCF) by using a simple method of in-situ chemical polymerization.

2. EXPERIMENTAL PART

2.1. Materials

Pyrrole (Aldrich, 99%) was used as received. All other reagents and solvents obtained from commercial sources were reagent grade purity and used as received. Solutions were prepared using de-ionized water. All reactions were conducted at room temperature ($20 \pm 2^\circ\text{C}$).

2.2. Synthesis of Composite Nano-thin Films

For preparing the nanocomposite materials, we used VGCF having diameter 200nm and average length 2 μm were dispersed in 20% aqueous methanol solution.

The well stirred solution containing VGCF was subjected to ultrasonic cavitation stream for 30 minutes. After the addition of 0.02, 0.05, 0.1, 0.2, 0.5 and 0.75 moles of pyrrole monomer and 0.2 moles of sodium toluene sulfonate, ultrasonication was again done for 10 minutes so that the monomer is uniformly adsorbed on the surface of the carbon nanofiber. One molar solution of FeCl_3 , dissolved separately in water, was then added to the above solution drop by drop in 15 minutes duration. After continuous stirring for 6 h at room temperature, the oxidized monomers were considered to polymerize on the VGCF surface leading to the formation of VGCF/PPY (hereinafter,

PV) composite films. The VGCF/PPy powder formed was separated by suction filtration. The product was washed with copious amounts of deionized (DI) water and several times with ethanol to remove the residual oxidant. At the end, the prepared PV composites were washed with acetone and dried under vacuum at 60° for 24h. Fig. 1 represents the schematic of the synthesis of the nano-thin composite films.

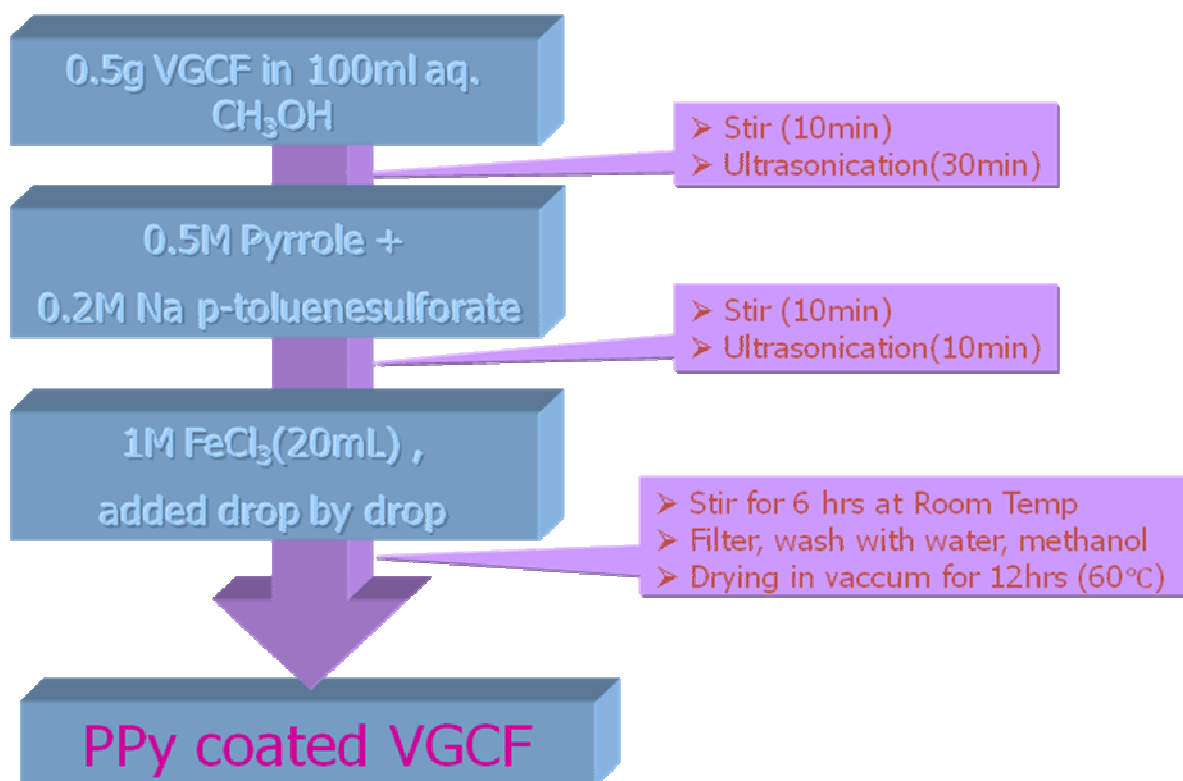


Figure 1. Schematic of the synthesis of the nano-thin composite films.

2.3. Morphological Characteristics

Infrared spectrum (KBr pellet) was recorded by using Fourier transform infrared spectrophotometer (Shimadzu model 8900) to identify the chemical structure of the prepared PV. The infrared spectrum of the PPy samples utilized in this study was compared with that reported in the literature. The scanning electron microscopy (SEM, Hitachi S-4700) and scanning transmission electron microscopy (TEM, JEOL - J200CX @ accelerating voltage 200kv) was used to examine the surface morphology and the thickness of the PPy film layers for differently prepared PV powders. Princeton, USA).

3. RESULTS AND DISCUSSION

The infrared spectrum of the vapor grown carbon fiber and PPy/VGCF (PV) composite show all the bands of PPy (conjugated double bond: 1548 cm^{-1} , amines: 1172 cm^{-1} , etc.) are present in the spectrum of the composite electrode [11] indicating that polypyrrole had deposited on VGCF.

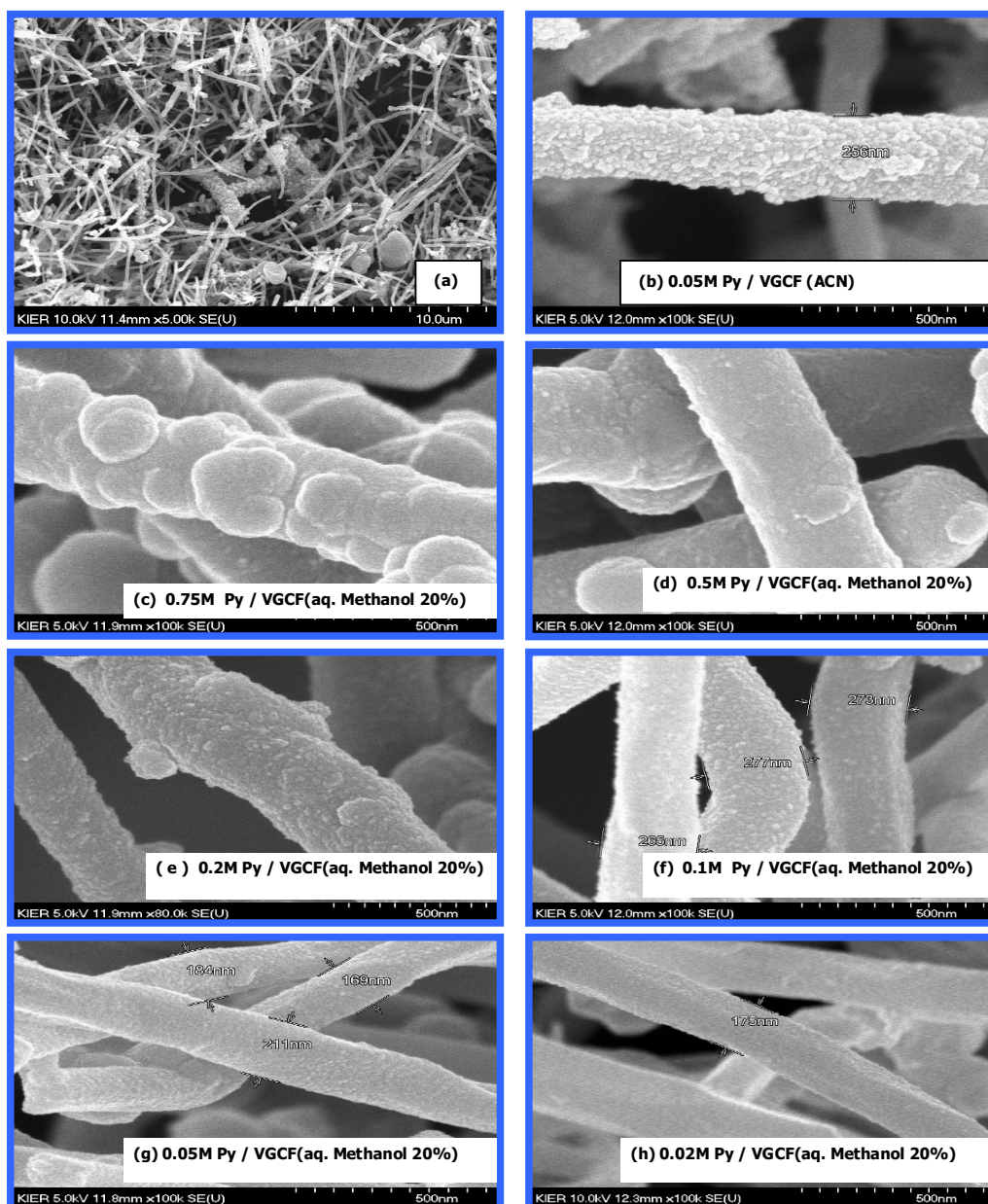


Figure 2. SEM pictures of PPy coated VGCF (a) in water without ultrasonication (b) in ACN solvent (c) to (h) in 20% aqueous methanol using different monomer content. The mole contents are marked in the images.

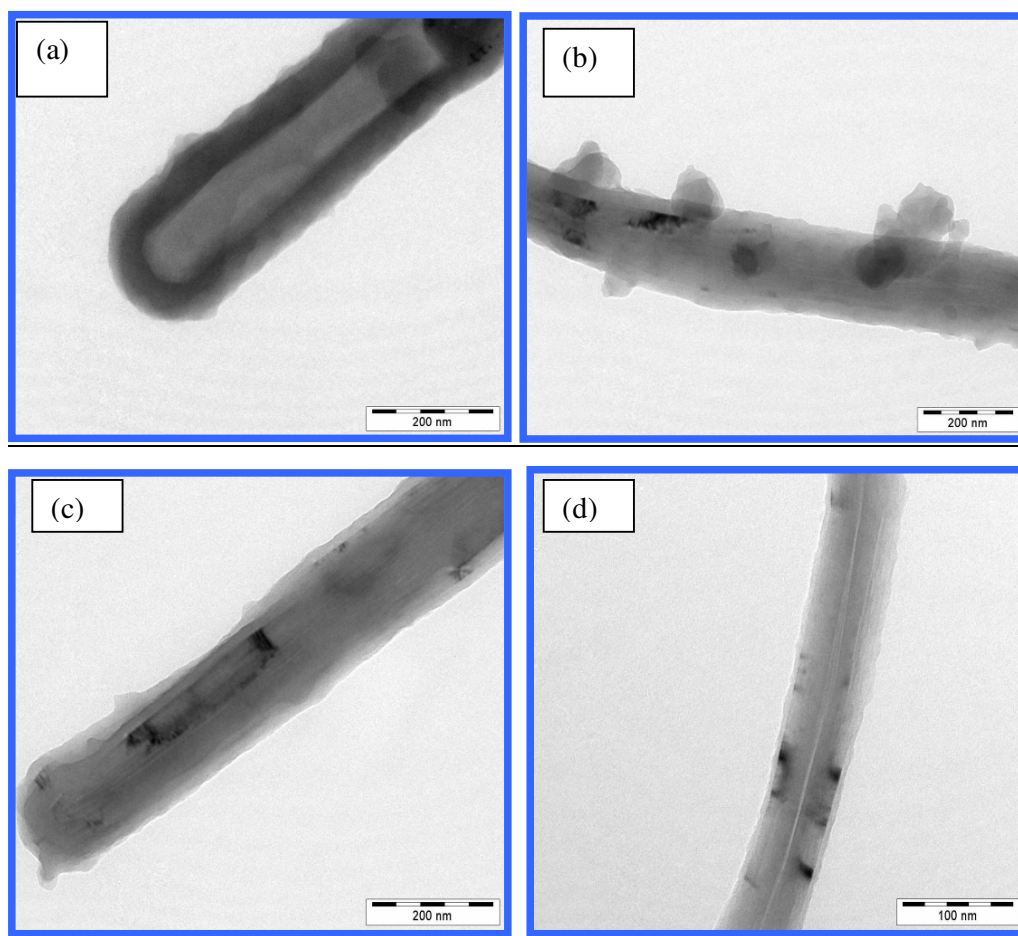


Figure 3. TEM pictures of PPy coated VGCF having different monomer content (a) 0.2M (b) 0.1M (c) 0.05M and (d) 0.02M Pyrrole/VGCF in aq. methanol (20%) in the initial polymerization solution.

Figs.3 and 4 represent the selected views of scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) for the surfaces of various PV composites. Typical SEM images of polymer powder composites resulting from the solutions having 0.75M, 0.5M, 0.2M, 0.1M, 0.05M and 0.02M of pyrrole monomer content respectively, in the initial polymerization solution are given in Fig. 2(c-h) and TEM images of composites obtained from 0.2M, 0.1M, 0.05M and 0.02M monomer solutions respectively in Fig.3(a-d).

Initial polymerization was carried out on VGCF in aqueous medium and without using ultrasonication. In Fig. 2a, VGCF clusters and polymer agglomerates on the surface of VGCF were observed, indicating that fibers are not well dispersed. This suggests that ultrasonication is required for the uniform dispersal of VGCF so that well ordered adsorption of PPy can take place on the carbon fiber. Keeping this in view ultrasonication was carried out as per details given in the experimental section. The use of acetonitrile (ACN) as solvent (fig. 2b) resulted in the granular agglomeration of PPy on the carbon fiber. PPy was also found to have relatively large

particle size with this solvent. On the other hand, the addition of methanol to aqueous dispersion resulted in decreased roughness of the deposited polymer layer as given in Fig.2(c-h), suggesting that morphological properties of PPy can also be controlled by the proper choice of the solvent [23]. The experiment was repeated with different methanol-water ratios and 20% aqueous methanol concentration was found to give the best results. By using different molar concentrations of pyrrole, composite films of varying thicknesses were synthesized. The thickness of the polymer layer on VGCF becomes smaller and smaller with the decreasing mole content of the pyrrole in the solution used for polymerization.

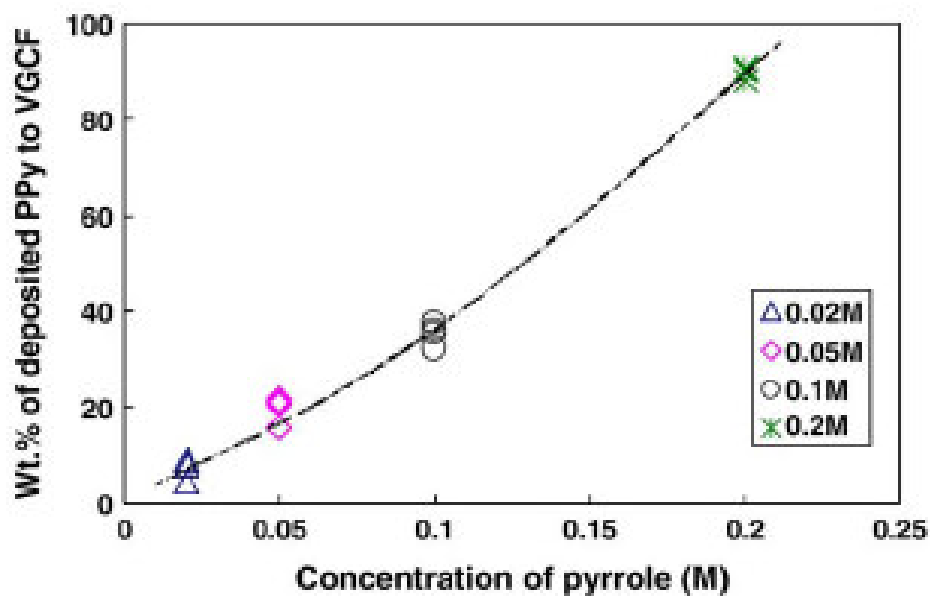


Figure 4. Weight percentage of PPy coated on VGCF as a function of mole content of the monomer.

Different monomer molar concentrations ranging from 0.75M to 0.02M were used in aqueous methanol solution to coat the carbon nanofibers with the polymer. It has been observed from the results that PPy has a tendency to grow on itself when higher pyrrole content is used for polymerization Fig.2(c-e). However the thinnest and smoothest composite polymer films were obtained by us by using 0.02 M of pyrrole, indicating lesser the molar content of the monomer during chemical polymerization, thinner is the polymer film on carbon fiber.

The average thickness of the polymer films on carbon fiber obtained using various mole contents of the monomer in the initial polymerization solution is represented below.

0.02M PV:	5~10nm
0.05M PV:	12~17nm
0.1M PV:	25~30nm
0.2 M PV:	55~60nm

It has been observed from fig. 4 that the quantity of Polypyrrole on VGCF is a linear function of mole content of pyrrole used for insitu polymerization. These results are also in agreement with that of SEM and TEM studies.

4. CONCLUSIONS

ECP/VGCF composites are fabricated by chemical oxidative polymerization of a monomer on the surface of VGCF in order to overcome the problems encountered with the electrochemical method. The electrochemical method is limited in terms of mass production of the materials and also it is not suitable for preparing composites with a large proportion of polymer. PPy films of various thicknesses were successfully coated on the carbon fiber by in-situ ultrasonic chemical polymerization using a common oxidant FeCl_3 . 0.02M pyrrole content in the initial polymerization solution was found to be the optimum concentration for deposition of thinnest layer (*ca.* 7nm).

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