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In situ polymerization and characterizations of polyaniline on MWCNT powders and aligned MWCNT films

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ABSTRACT

Polyaniline/CNT composites have been synthesized by means of in situ polymerization on two different macroscopic structures of CNTs, namely non-ordered CNT powders and aligned CNT films supported on Ti foils. SEM, TEM images illustrated that a rather uniform layer of PANI with a thickness of 5–8 nm has been successfully coated on the aligned CNTs. The molecular structure and the degree of protonation of PANI have been studied by means of Raman spectroscopy. The alignment of CNT film on the foils favors the formation of uniformly distributed layer of the protonated PANI on each CNT, which is possibly a result of controlled diffusion in the pseudo 1D channel and a confinement in the space between CNTs in the aligned CNT films. Furthermore, the reaction temperature has a more pronounced effect on the degree of protonation of PANI on the CNT powders than on the aligned CNT films.

1. Introduction

Among the applications of carbon nanotubes, energy related fields such as solar cells, fuel cells and supercapacitors have become more and more important nowadays [1–3]. Composites made of CNTs and conducting polymers have been extensively studied due to their superior performance resulted from the significant synergy of them. CNTs have many interesting properties such as high conductivity, large surface area, good corrosion resistance, high temperature stability, percolated pore structure, and relatively easy functionalization for manipulating their surface properties for specific applications [4–6]. Conducting polymers such as polypyrrole (PPy), polythiophene (PTs) and polyaniline (PANI) have an ability of protonization and an excellent capacity for energy storage (350 $\mathrm{F\,g^{-1}}$ for polypyrrole, 250 $\mathrm{F\,g^{-1}}$ for polythiophene and 428 $\mathrm{F\,g^{-1}}$ for polyaniline), but relatively poor charge and discharge kinetics and very poor cyclic stability [7–9]. Outstanding capacitance and good stability have been obtained from the electrodes prepared from CNT/conducting polymer (e.g. 606 $\mathrm{F\,g^{-1}}$ for CNT/polyaniline) [10]. The common method for making such electrodes is to deposit or synthesize conducting polymers on CNTs and brush or compress the composite onto a metal plate. However, this manufacturing process of the electrodes seems to be a little complex and the interface between the composite layer and the metal surface is far from optimized. This work aims at simplifying the electrode manufacturing step by employing a simple approach and desirable conditions for in situ polymerization of protonated PANI (or PANI salt which is conducing form) on the aligned CNT arrays supported on Ti foils with a better control of the coating layer and degree of the protonation of PANI. A comparative study of in situ polymerization on CNT powders and aligned CNT films on Ti foil was performed to gain a better understanding of the effects of the CNT alignment on the properties of the PANI coating layer. The influence of the reaction conditions on the composition of the CNT powder composites and the possible interaction between PANIs and CNTs will be discussed. The present work reports a simple and scalable method for large-scale production of PANI/CNT film on metallic foils.

2. Experimental

All the polymerization took place in an aqueous acidic media, using ammonium peroxydisulfate as the oxidizing agent and HCl as the acid. A classic reaction condition described by Chiang and MacDiarmid was selected to produce polyemeraldine [11]. The chemical reaction route is shown in Fig. 1 [12].

2.1. Preparation of CNT on foils

Carbon nanotubes array was synthesized on Ti foils (Alfa Aesar) using CVD method and ferrocene (Avocado) as a catalyst precursor.

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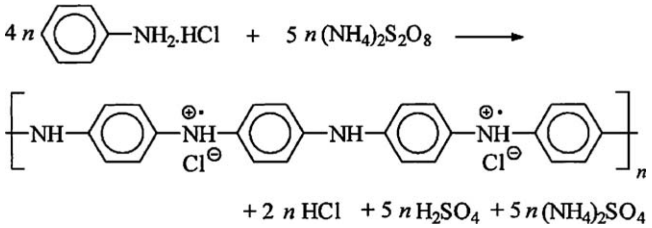

Fig. 1. Aniline hydrochloride oxidized by ammonium peroxydisulfate to yield polyemeraldine (quoted from Ref. [13]).

Ferrocene ($C_{32}H_{16}FeN$, 9%) was purchased from Avocado Company and used directly without further purification. Ferrocene was stationed at the inlet of the reactor where the temperature was above its sublimation temperature about 175 °C. The Ti foils with a thickness of 0.037 mm were provided by Alfa Aesar Company. The plates were cut into pieces with a size of 1 cm × 2 cm and were cleaned with acetone in the ultrasonic bath for 10 min. After the cleaning step, the plates were directly used and placed in the middle of the reactor. Each synthesis started with the CVD reactor under N_2 atmosphere. CVD growth of CNTs was carried out at 750 °C with the flow rates of ethane, hydrogen and nitrogen at 40, 15 and 140 mL min^{-1}, respectively. This flow of the mixture was maintained for the entire growth period between 60 and 120 min. After the reaction, only the nitrogen flow was maintained during the cooling process.

2.2. In situ polymerization of PANI on CNT powders

Multiwall CNT powder (Chengdu Organic Chemicals Co., Ltd.) was functionalized by concentrated HNO_3 for 6 h. After washing, they were dispersed in ethanol (20 mL) following sonication for 1 h. A nominal loading of PANI of 70% was selected as the probe system in the present work. Aniline hydrochloride (0.72 g, 5.4 mmol), as the monomer, was added into the dispersion and stirred. Ammonium peroxydisulfate (1.57 g, 6.75 mmol), dissolved in the solution of distilled water (16 mL) and hydrochloric acid (37%, 4 mL), was drop-wisely added into the mixture. The reaction mixture was maintained at 0 °C at pH around 1. After 4 h, the product was washed with 0.2 M hydrochloric acid and acetone and dried in vacuum oven at room temperature for 24 h. In addition, in situ polymerizations at this monomer concentration were also tried at ambient temperature 20 °C for either 2 or 4 h.

To estimate the yield of polymerization (η), the following equation was used according to the reaction route in Fig. 1:

$$\eta = \frac{(m(\text{composite}) - m(\text{CNT}))}{m(\text{anilinehydrochloride})} \quad (1)$$

The fraction, C, of PANI in the composites is calculated using the equation below:

$$C = \frac{(m(\text{composite}) - m(\text{CNT}))}{m(\text{composite})} \quad (2)$$

2.3. In situ polymerization of PANI on the CNT arrays grown on foils

As described above, this type of composite contains vertically aligned CNT array on either one or both sides of foils. Reagents for polymerization were the same as those used on powders. A foil was immerged into a solution of aniline hydrochloride (0.72 g, 5.4 mmol) and ethanol (20 mL). Ammonium peroxydisulfate (1.57 g, 6.75 mmol), dissolved in solution of distilled water (16 mL) and hydrochloric acid (37%, 4 mL), was drop-wisely added into the mixture with stirring. The reaction took place at ambient temperature 20 °C and the pH value was around 1. After 2 h, the foil was washed with 0.2 M hydrochloric acid and acetone and dried in vacuum oven at room temperature for 24 h.

2.4. Characterization

Electron scanning microscopy (SEM) images were taken on a Zeiss Ultra 55 microscope, transmission electron microscopy (TEM) investigations on a JEOL JEM-2010 microscope.

Thermogravimetric analysis (TGA) was performed in air flow (25 cm^3 min^{-1}) at a heating rate of 10 °C min^{-1} from 30 to 850 °C, with a NETZSCH STA 449 C Thermogravimetric Analyzer.

Raman spectra were recorded on a Horiba Jobin Yvon LabRAM HR800 UV spectrometer, with an excitation of HeNe 633 nm laser using a 100× objective. A filter was systematically used to prevent degradation of the polymer. Powder samples were crashed into finer grains in a mortar to reduce static electricity; composite supported on Ti foils was removed from the foils and ground.

3. Results and discussions

Polyaniline has generally three states as shown in Fig. 2, namely pernigraniline, emeraldine and leucoemeraldine, which has a color of blue/violet green/blue and white/clear, respectively. The structure of the PANI depends on the ratio of the reduced and the oxidized repeat units of the molecule [13]. Polyemeraldine, whose reduced and oxidized repeat units are quantitatively equal, has been intensely studied. Because of protonation, polyemeraldine can be transferred from its base form (nonconducting) to the protonated form (conducting). To obtain conducting PANI, pH value is one of the critical parameters in polymerization.

It has been reported that high conductivity can only be achieved by polymerization at pH lower than 2 [13]. The HCl concentration of 1 M was used in the present work to get pH value around 1.

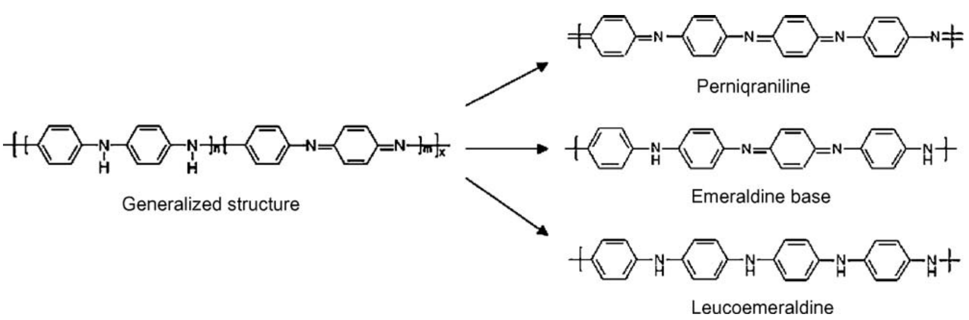

Fig. 2. Molecular structure of polyaniline.

Moreover, in the preliminary experiments, different concentrations of aniline hydrochloride were used to synthesize PANI. No difference in Raman spectra was observed for all the products. This implies that the monomer concentration has no effect on the PANI state.

A series of in situ polymerizations of PANI on CNT powders were performed in an aqueous medium to understand the effects of the reaction time and temperature on the yield of the polymerization. The yield is calculated by Eq. (1). It was found that with the existence of the same amount of CNT, polymerization yielded 79.4% PANI at 0 °C after 4 h, 78.1% at 20 °C after 2 h and 76.1% at 20 °C after 4 h. The corresponding fractions of PANI in these composites are 65.6%, 65.2% and 64.6%, calculated by Eq. (2). It was found that the yield was slightly higher when polymerizations were carried out at the lower temperature but it decreased with the increasing reaction time at 20 °C. They are in good agreement with the observations reported in the literature [12,13]. Considering the better yield and the possibility of destruction of the composite layer on the foil, the reaction conditions of 20 °C and 2 h have been chosen for the in situ polymerization of PANI on the aligned CNT array on foil.

SEM images were taken on the composites made of PANI and CNT powder and those made of PANI and aligned CNTs. Fig. 3 shows the overview of the composites structures and the polymer coating morphology. For the PANI and CNT powder composites, two reaction temperatures 0 and 20 °C and reaction time 4 and 2 h were tried. The original morphology of the CNT can be hardly seen after being coated by PANI in situ polymerized at 0 °C after 4 h (a). It appears that the polymer coating is very thick and the resulting composite is easily compacted into pellets. When the reaction temperature changes to 20 °C (b and c), the tube structure becomes clearer. Its surface is homogeneously covered by a polymer layer. The difference in the morphology (b and c) caused by the reaction time is not obvious.

For the composite supported on the Ti foils, it can be seen that the polymer has been successfully synthesized among aligned CNTs, either on one side (Fig. 4a and b) or two sides (Fig. 4c and d) on the Ti foils; the diameter of the tubes is rather uniform, although the tubes are not perfectly straight.

TEM images provide not only a sound proof of the existence of the polymer coating on CNT, but also the nanostructure of the tubes and the morphology, distribution and the thickness of the coating. In Fig. 5, two types of composites made under the same reaction condition (monomer concentration, temperature, pH value and reaction time) are compared. Among these images, Fig. 5a and b clearly shows the different graphene sheets typically from multiwall structure and the open end of CNT, which is 50 nm in diameter. The thickness of the coating layer varies significantly from 5 to 40 nm along the tube. As concerned with the composites supported on the Ti foil, images c and d illustrate the neat multiwalled CNT whose diameter is around 30 nm and the uniform thickness of the polymer layer, from 5 to 8 nm. Many images of PANI/CNT have been taken on both samples, and it was found that the images presented in Fig. 5 are very representative. This result brings the probability of obtaining a better control of the polymer coating thickness on the vertically aligned CNT film. The difference in the coating morphology is possibly caused by the following factors. The pseudo 1D channel among the CNTs in the aligned film on Ti foil is possibly favorable for the controlled supply of the monomers by means of diffusion, which might control the rate of in situ polymerization, while monomers can react more freely without limitation of the supply on the CNT powders. The more defined and dense space among the aligned CNTs forces the reagents to enter the "channels" among CNTs and adsorb on each tube at a slower rate which determines the rate propagation of polymer chain, hence the growth of the polymer. As a result, the polymer coating is evenly distributed along each tube in the vertically aligned CNT film.

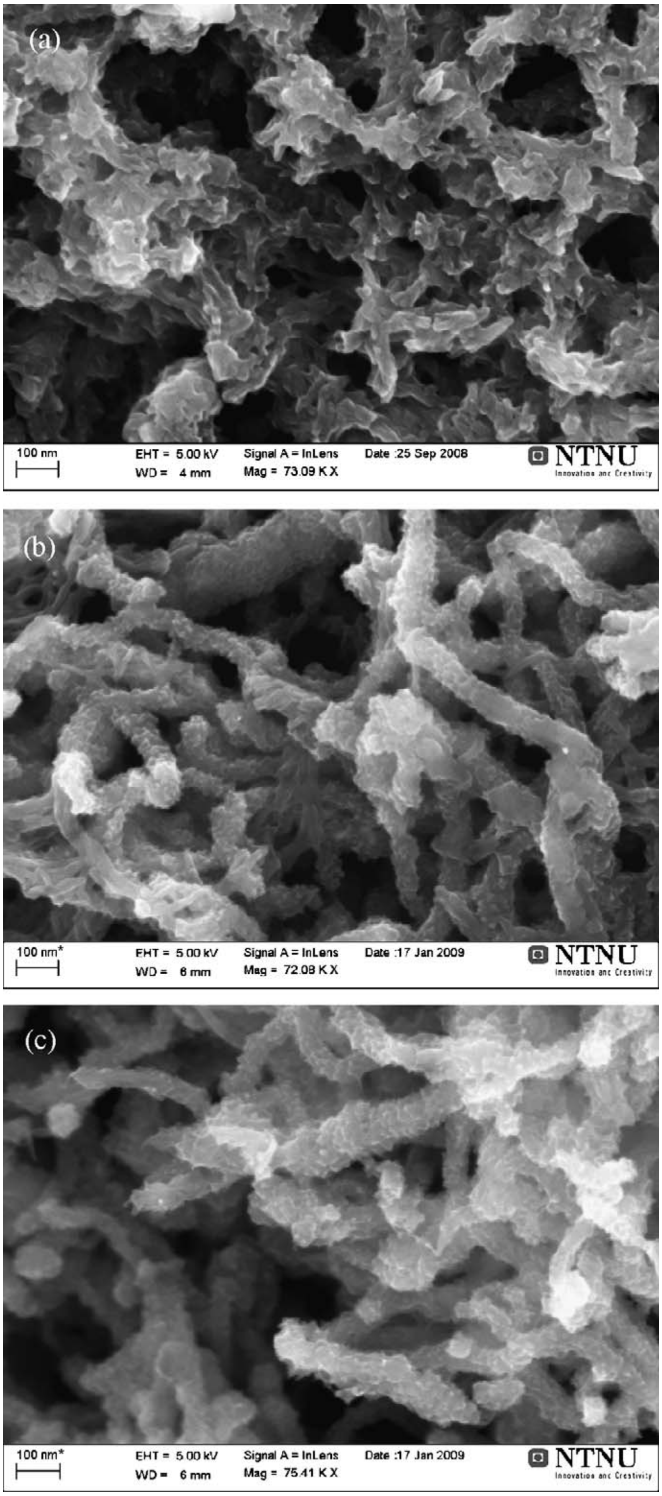

Fig. 3. SEM images of PANI coated on CNT powders at reaction conditions: (a) 0 °C, 4 h, pH 1; (b) 20 °C, 4 h, pH 1; (c) 20 °C, 2 h, pH 1.

The samples were further tested by means of temperature programmed oxidation (TPO) in TGA. In principle, TPO experiments can provide the information of the polymer loading and the interaction of polymer and CNTs. The TPO results of neat CNT and PANI and PANI/CNT composite are summarized in Fig. 6. It can be

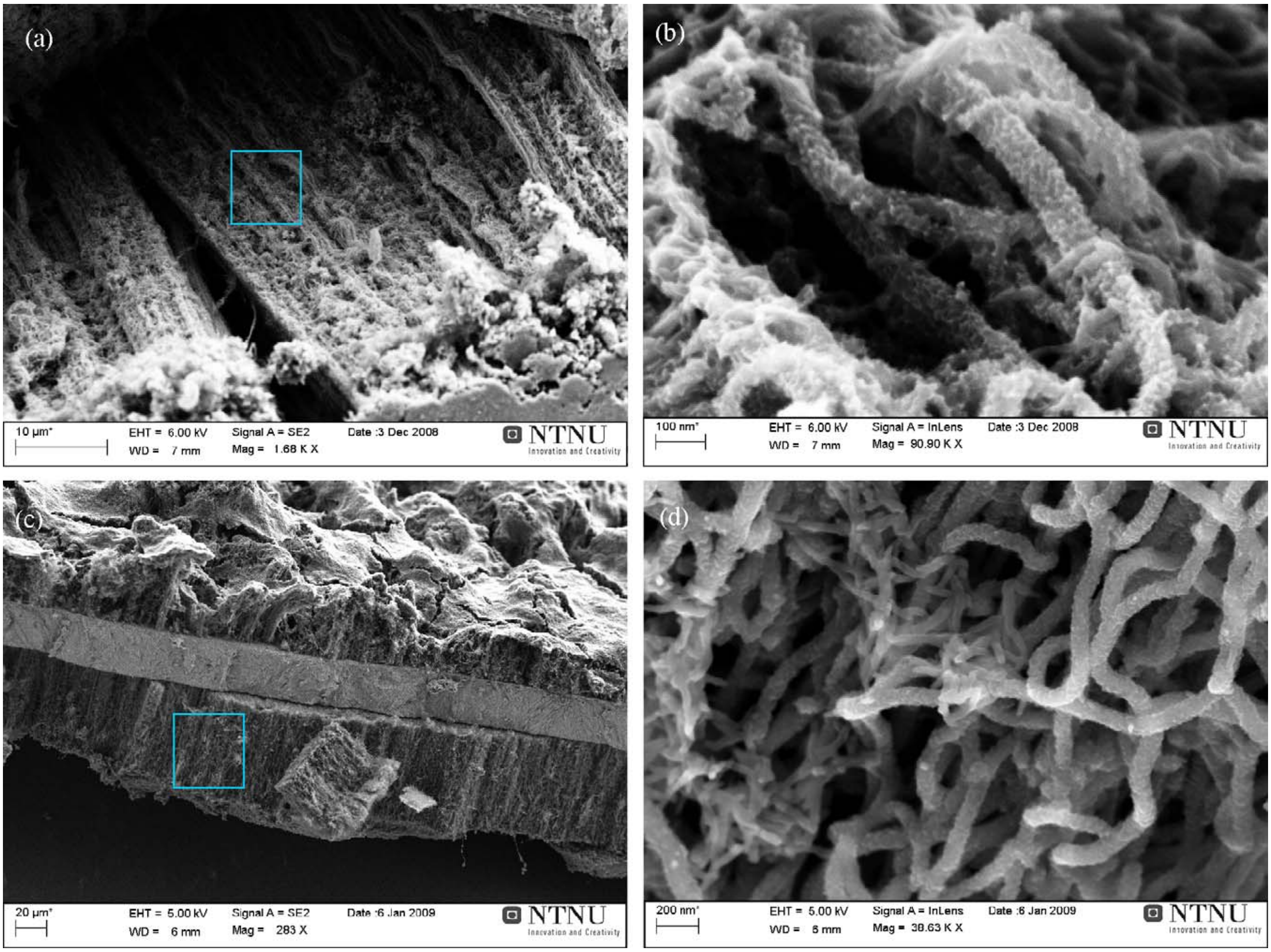

Fig. 4. SEM images of PANI coated on aligned CNT on the Ti foil with low (a and c) and high resolution (b and d) at reaction conditions: (a and b) 20 °C, 2 h, pH 1, (c and d) 20 °C, 2 h, pH 1.

seen that neat MWCNT are stable up to 500 °C and oxidized completely above 700 °C. The residue of 2 wt% verifies the existence of metal catalyst used to prepare CNT. The mass of the neat PANI starts to decrease at a relatively low temperature region under 150 °C. This might be the result of deprotonation of PANI salts. Neat PANI is completely oxidized at about 660 °C. The thermal stability of PANI in the composite appears to be better than the neat PANI and it starts oxidation at a relatively higher temperature. The composite is completely oxidized at a similar temperature to neat PANI. However, it is impossible to extract the exact amount of polymer form the TPO curve, since the oxidation of PANI and CNT are overlapped. It seems that PANI or the iron catalyst catalyzed the oxidation of CNT. The TPO results suggest that there is a good interaction between PANI and CNT and that all the CNT surfaces seem to be covered by PANI. The results support the SEM and TEM observation as shown in Figs. 3 and 4. In addition, it was found that the BET surface area decreased significantly from 130 m^2/g of neat CNTs to 40 m^2/g of PANI/CNT powder composite. It is possibly a result of blockage of inner pores of tubes by PANI.

The sample of PANI/aligned CNT was prepared by mechanically removing from the Ti foil. It was found that complete oxidation occurred at a much lower temperature than the powder composite, and a large amount of residue was found to be the iron catalyst used for CNT growth. Therefore, the data is not directly comparable with the data of powdered composites, since iron can catalyze the oxidation of the composite. The TPO curve of PANI/aligned CNT composite is not presented here.

The color of the composites can briefly tell in which state the polyaniline is. The greenish color of the composites indicates the existence of polyemeraldine salt (protonated partially or completely), since other states such as pernigraniline is violet and leucoemeraldine is white. The PANI/CNT composites were further studied by Raman spectroscopy, where the vibrational frequencies provide detailed information about polymer composition. The spectra of PANI and PANI/CNT composites shown in Fig. 7 are typically corresponded to polyemeraldine [14]. Fig. 7 f illustrates two bands at 1331 and 1586–1618 cm^{-1} denoted D and G band of CNT, respectively. D band is related to the defects and the presence of amorphous carbon and G band to the C–C stretching in the graphene plane. However, it can be found that some of PANI bands overlap with CNT bands at these positions by comparing to the spectra of pure PANI in Fig. 7b). The bands at 810, 1169, and 1592–1618 cm^{-1} are assigned to the ring symmetric stretching, CH in-plane bending and ring stretching in PANI molecules, respectively. More importantly, the difference in polyemeraldine doping (protonation) state can be seen from bands at 1221 and 1251 cm^{-1}, both of which represent the CN stretching band. The shift of the band from 1221 to 1251 cm^{-1} results from the doping of the unit ($-NH-C_6H_4-$) to its salt form ($-NH_2^+Cl^-C_6H_4-$)

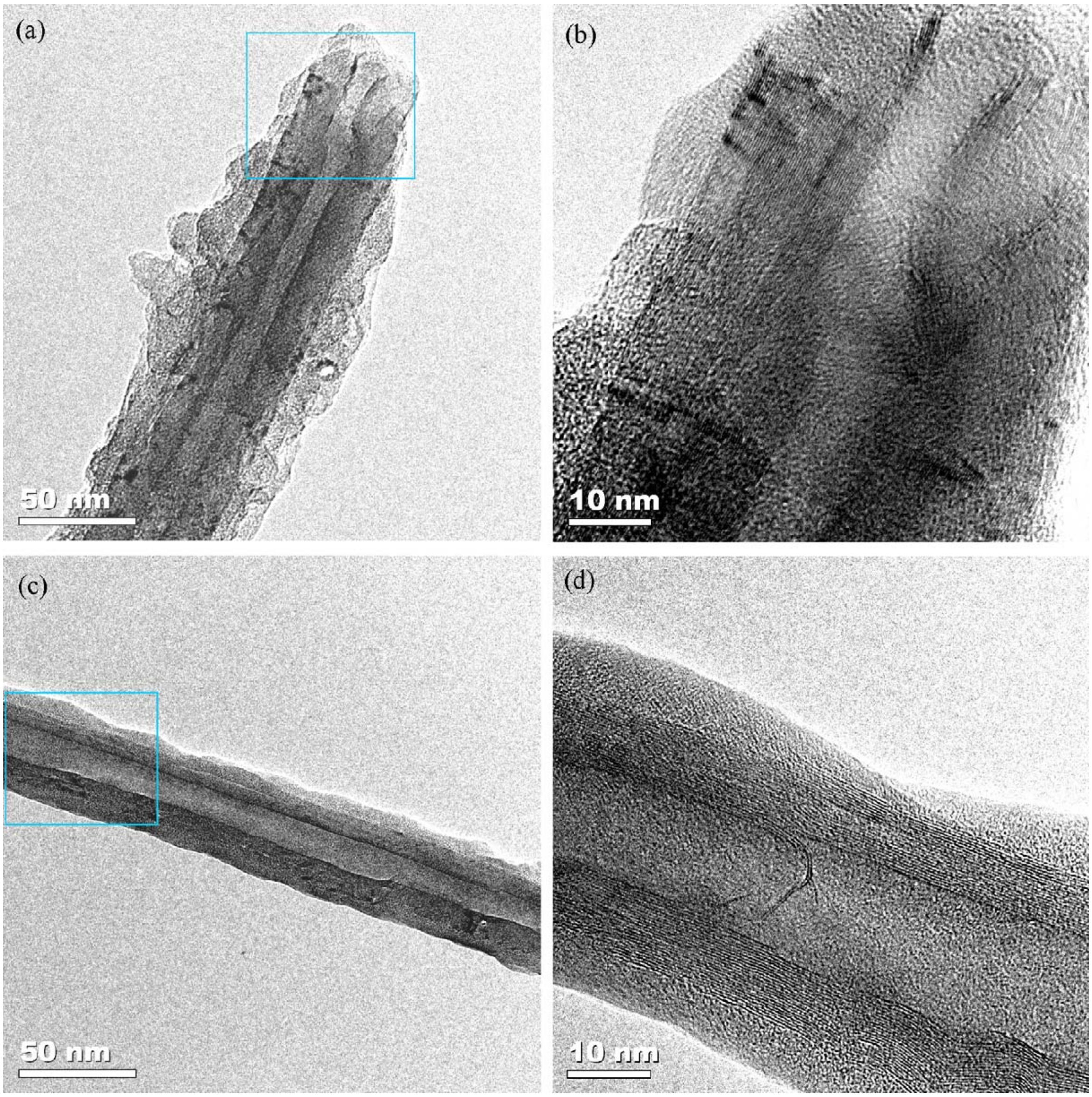

Fig. 5. TEM images of PANI coated on (a and b) PANI synthesized on purchased CNT powder at 20 °C for 2 h, pH 1; (c and d) PANI synthesized on CNT aligned on the Ti foil at 20 °C for 2 h, pH 1. (b) and (d) are the high resolution images of (a) and (c), respectively.

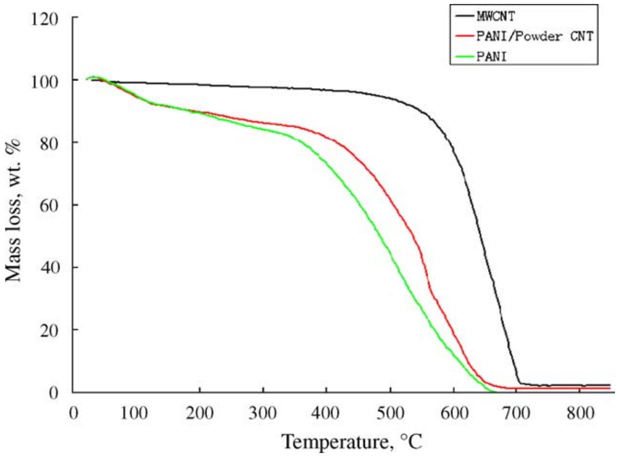

Fig. 6. TG analysis in air flow (25 $cm^3\ min^{-1}$) at a heating rate of 10 $°C\ min^{-1}$ from 30 to 850 °C.

[15]. The coexistence of the bands 1221 and 1251 cm^{-1} (spectra b, c and d) illustrates some extent of doping, no matter if the polyaniline is synthesized with CNT (as shown in spectra c and d) or without CNT (as shown in spectrum b). Consequently spectra b, c and d exclude the effect from CNT on the doping of the unit (–NH–C_6H_4–).

The single band 1251 cm^{-1} (spectra a and e) states the complete doping of –NH–C_6H_4–. The shift of these two bands from spectrum a to that in c reveals reaction temperature of 0 °C being a better choice for obtaining doped PANI with non-aligned CNT. The interesting finding is that doped PANI can be obtained at 20 °C on vertically aligned CNT film on the Ti foil.

Change from spectrum d to e explains that aligned CNT film facilitates doping. It is probably because the volatile doping agent HCl is more easily confined and stabilized among compact and well-aligned CNT films. It is worth mentioning that the product was treated the same way after each reaction. So it seems that the reaction temperature and the alignment of CNT can influence the molecular structure of PANI.

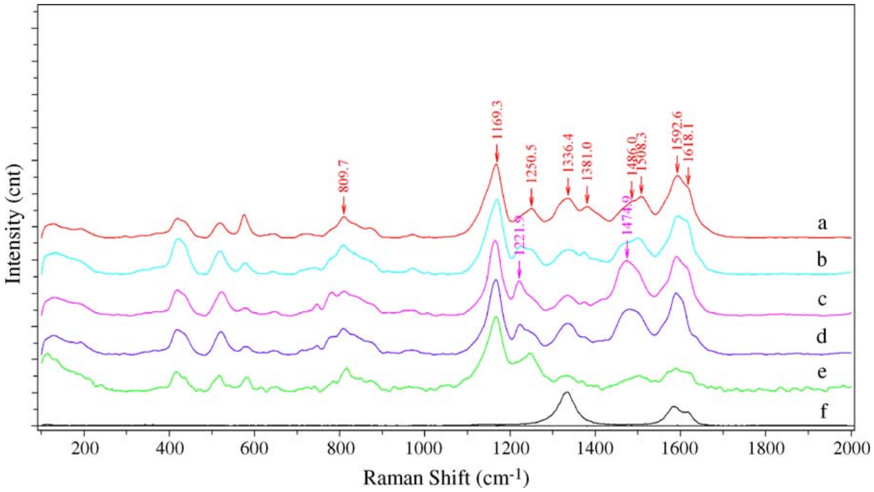

Fig. 7. Raman spectra taken at 632.8 nm, (a) PANI in situ synthesized on CNT powders at 0 °C for 4 h, pH 1; (b) PANI synthesized at 20 °C for 4 h, pH 1; PANI in situ synthesized on CNT powders at (c) 20 °C for 4 h, pH 1; (d) 20 °C for 2 h, pH 1. (e) PANI in situ synthesized on CNT aligned on Ti foil at 20 °C for 2 h, pH 1, (f) CNT powder purified by concentrated HNO_3.

4. Conclusions

The goal of our work is to simplify the electrode manufacturing process. It is achieved by employing a simple and efficient approach, namely in situ polymerization of PANI on CNTs array substrate. Doped polyemeraldine was produced at 20 °C, 2 h and pH around 1. No control of temperature is needed and the reaction time is reduced compared with in situ polymerization of PANI on CNT powders.

The different architectures of CNT can cause changes in morphology of PANI coating. The alignment of CNT film on the foils favors the even distribution of the polymer coating. Furthermore, the choice of reaction temperature is important for obtaining doped sample. For aligned CNT films, however, the influence from temperature seems to be less pronounced on doping. In conclusion, proper diffusion in the pseudo 1D channel and the space confinement between CNTs in the aligned CNT film result in enhanced formation of uniformly distributed layer of the doped PANI on each CNT. It is believed that this simple in situ polymerization method is in general scalable for large-scale production of the composites of conductive polymers on aligned CNT films. This composite made of PANI and other conductive polymers integrated with CNT–foil structure will be examined as a potential candidate for supercapacitors and photovoltaic cells.

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