



# Acidified multi-wall carbon nanotubes/polyaniline composites with high negative permittivity



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## ABSTRACT

Acidified multi-wall carbon nanotubes (MWCNTs-COOH) have been synthesized using mixed acid acidification, and then acidified multi-wall carbon nanotubes (MWCNTs-COOH)/polyaniline (PANI) composites with negative permittivity have been successfully synthesized by in situ polymerization. At the same time, the effects of composition and structure on the permittivity of MWCNTs-COOH/PANI composites have been systematically studied. The effects of MWCNTs-COOH content on the generation and variation of negative permittivity are illuminated by the structure model of “nano wires”. XRD analysis indicates that MWCNTs-COOH becomes the crystal nucleus and affects the crystallinity of the MWCNTs-COOH/PANI composites. SEM results indicate that different contents of MWCNTs-COOH cause various dispersion states of MWCNTs-COOH, thus lead to different morphologies of MWCNTs-COOH/PANI composites and variation of permittivity.

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## 1. Introduction

Carbon nanotubes (CNTs) has been concerned by researchers in the area of chemistry, physics and materials for its unique properties and quasi one dimensional tubular structure since discovered by Iijima in 1991 [1]. In the rapid development of metamaterials today, multi walled carbon nanotubes (MWCNTs) were also tried to apply in metamaterials. Zhu et al. [2,3] found negative permittivity in graphene/polyaniline composites or multi-walled carbon nanotubes (MWCNTs)/polyaniline composite. MWCNTs caused an excellent amplification effect on the negative permittivity of polyaniline (PANI) and the negative permittivity reached  $-2 \times 10^4$  when the content of MWCNTs is only 5 wt% in PANI. Qian et al. [4] found negative permittivity in MWCNTs/phenolic resin composites, and the negative permittivity increased with the increase of MWCNTs content in the range 10 M~1 GHz and it reached  $-4 \times 10^3$  when the content of MWCNTs got 37 wt%. In 1994, Green et al. [5] found that carbon nanotubes could be cut into short tubes and got open ends handled by strong acid. Later in following works, Green [6] found that the carbon nanotubes with open ends contained a number of active groups such as hydroxyl, carboxyl, etc. Both HNO<sub>3</sub>

and H<sub>2</sub>SO<sub>4</sub> (volume ratio 1:3) were used to treat carbon nanotubes and achieved fine effects in works of Liu [7], Kuznetsova [8], Chen [9]. The surface of MWCNTs contains a number of active groups after acidification, and the dispersion and stability of MWCNTs in the water are improved. Moreover the active groups produced by acidification will react with aniline matrix to form an integrated system. The electronic conductivity of the whole composite is improved to a certain extent, and thus enhances the negative permittivity of composites.

Zhong et al. [10] reported that CNFs/PI composites had negative permittivity. It was considered that CNFs/PI composites with determinant structure were equivalent to the fine wires in the study of Pendry. Therefore, they believed the determinant structure was essential for the realization of negative permittivity of nanocomposites. In studies of our group, the generation mechanism of negative permittivity in MWCNTs/PANI composites and oxide crystal/PANI composites is illuminated by the structure model of “nano wires” [11,12], and the transition frequency of permittivity from negative to positive moves to higher frequency with the increase of MWCNTs content [11]. In this paper, MWCNTs-COOH/PANI composites with negative permittivity are prepared by in situ polymerization on basis of the original study of MWCNTs/PANI composites with negative permittivity. The generation mechanism of negative permittivity is illuminated by the structure model of “nano wires” and the high negative permittivity is considered to be

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produced by rod-structures.

## 2. Experimental

### 2.1. Chemicals

Aniline, ammonium persulfate (APS) and p-toluene sulfonic acid (PTSA), nitric acid and sulfuric acid are purchased from Sinopharm Chemical Reagent Co. Ltd. China. Multi-walled carbon nanotubes were purchased from Cheap Tubes. All the chemicals were used as received without any further treatment.

### 2.2. Fabrication of MWCNTs-COOH

Firstly, 120 ml of concentrated sulfuric acid and 40 ml of concentrated nitric acid were mixed with 2 g MWCNTs and placed in 500 ml round bottom flask. The round bottom flask was placed in heating oil bath about 0 °C under a magnetic stirring with 500r/min speed for 2 h. After 2 h of acidification, the acid solution was diluted, filtered and rinsed repeatedly with deionized water. Then MWCNTs-COOH was obtained after 48 h of drying in an air blast oven at 100 °C.

### 2.3. Fabrication of MWCNTs-COOH/PANI nanocomposites with low resistivity

Firstly, PTSA (proton acid, 5.167 g), APS (oxidant, 4.108 g) and different contents of MWCNTs-COOH were dispersed in 300 ml distilled water with ultrasonic for 40min (power 320 W). The resultant dispersion was placed into a crystallizing dish containing a mixture of ice and water. Next, An (3.35 g) in 60 ml water was added dropwise into the dispersion solution under a magnetic stirring with 1000r/min speed for 10min when temperature of the dispersion solution about 0 °C. This dispersion with An was treated with ultrasonic for 6 h (320 W) in the ice/water mixture. Finally, the product solution was filtrated in a sand core funnel and washed with deionized water and ethanol until the supernatant was transparent. MWCNTs-COOH/PPy composites were obtained after drying for 6 h in an air blast oven at 80 °C. The mole ratio of PTSA: APS: An was 5:3:6. The sum quality of the filler and An was 3.35 g.

### 2.4. Characterizations

Fourier transform infrared spectra (FT-IR) of the samples were recorded with a EQUINOXSS/HYPER FT-IR infrared spectrometer in the range of 4000–576  $\text{cm}^{-1}$ . X-ray diffraction (XRD) analysis of the samples was by D/MAX 2550VB3+/PC under the test condition of diffraction angle 10–75°, continuous scanning 5°/min, tube voltage 40 KV and current 35 mA. Thermogravimetric analysis was by NETZSCH(TG-DTA/DSC) under 30–500 °C with temperature rise rate of 10 °C/min. Scanning electron microscope (SEM) images were taken on a Quanta FEG 250 field emission scanning electron microscopy. Dielectrical properties were investigated by an LCR meter (Agilent, E4991A) equipped with a dielectric detector (Agilent, 16454A) at the frequency of 20 Hz to  $2 \times 10^6$  Hz at room temperature. The sample was a wafer with the diameter of 10 mm and thickness of 1–3 mm prepared by moulding composite powder in 8.0 MPa pressure. The wafer was coated with conductive silver paste on top and bottom surface and dried in vacuum at 80 °C for 4 h in order to form two electrodes before testing. Resistivity was tested by electrochemical work station CHI660E in the frequency range of 1– $1 \times 10^5$  Hz.

## 3. Results and discussion

### 3.1. MWCNTs-COOH analysis

Fig. 1 shows the ATR curves of MWCNTs and MWCNTs-COOH. The absorption peaks at 1512  $\text{cm}^{-1}$  and 1063  $\text{cm}^{-1}$  are caused by C=C and C–C stretching vibration in benzene rings of MWCNTs in curve (1). In curve (2), the peak at 1674  $\text{cm}^{-1}$  is attributed to C=O of carboxyl. The absorption peaks at 1506  $\text{cm}^{-1}$  is caused by C=C stretching vibration in benzene rings. The peak at 1390  $\text{cm}^{-1}$  is attributed to C–O stretching vibration of carboxyl, while the peak at 1099  $\text{cm}^{-1}$  is attributed to C–C stretching vibration of benzene rings [13,14]. The peak at 999  $\text{cm}^{-1}$  is attributed to bending vibration of O–H. From above it can be shown that MWCNTs-COOH is successfully prepared compared curve (1) with curve (2).

Fig. 2 shows TG curves of MWCNTs-COOH and MWCNTs-COOH/PANI composites. MWCNTs has stable structures which will not change significantly under high temperature, merely having a small decrease in weight. The carboxyl group on the surface of MWCNTs-COOH is easy to break off at high temperature and obvious decrease of weight occurs. It also can be seen that the weight loss of MWCNTs is significantly increased after treated by mixed acid. MWCNTs-COOH produces more weight loss than MWCNTs at 450 °C due to the decomposition of –COOH.

### 3.2. MWCNTs-COOH/PANI composites analysis

Fig. 3 shows the ATR curves of MWCNTs-COOH/PANI composites. The absorption peaks at 1562  $\text{cm}^{-1}$  and 1483  $\text{cm}^{-1}$  are caused by C=O and C=C stretching vibration. The peak at 1298  $\text{cm}^{-1}$  is attributed to C–N stretching vibration of aromatic amines [15–17]. The peak at 1115  $\text{cm}^{-1}$  represents stretching vibration of –SO–O– bonds in the PANI molecular chains because of the presence of PTSA. The peak at 796  $\text{cm}^{-1}$  shows bending vibration of C–H on benzene rings. The peak at 677  $\text{cm}^{-1}$  is caused by the presence of C–S bonds in the PANI molecular chains after doping with PTSA. No chemical bond between MWCNTs-COOH and PANI can be found.

Fig. 4 gives the XRD curves of MWCNTs-COOH, PANI and MWCNTs-COOH/PANI composites. There are two prominent peaks of MWCNTs-COOH presenting crystal surface (002) and (100). The characteristic peak of MWCNTs-COOH at 42.88° gradually appears in curves of MWCNTs-COOH/PANI composites with the content of MWCNTs-COOH up to 10 wt%. PANI has two weak and broad crystallization peaks in 20.38° and 25.08°, respectively present

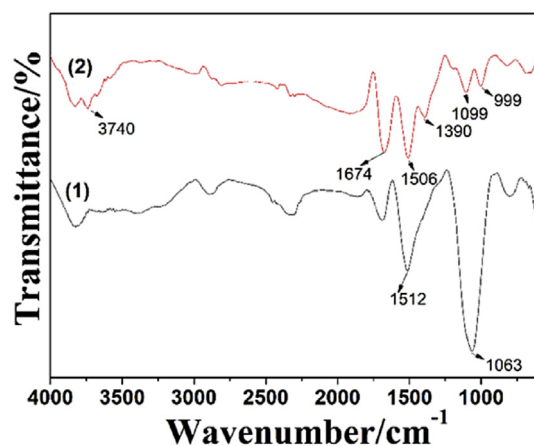


Fig. 1. ATR curves of MWCNTs-COOH/PANI composites and MWCNTs/PANI composites (1)MWCNTs (2)MWCNTs-COOH.

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