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THERMAL DECOMPOSITION OF THE CARBON NANOTUBE/SiO_2 PRECURSOR POWDERS
Thermal analysis coupled with mass spectrometry

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TG-DSC-MS (thermogravimetry-differential scanning calorimetry-mass spectrometry) coupling techniques were used to make a simultaneous characterizing study for the thermal decomposition process of the carbon nanotube (CNT)/SiO_2 precursor powders prepared by rapid sol–gel method. The thermal stability of the CNT and the SiO_2 pure gel were investigated by TG-DSC. The results showed that the oxidation of CNT began from 530 and combusted at about 678°C at the heating rate of 10°C min^{-1} in air. Moreover, the faster the heating rate, the higher the temperature of CNT combustion. The appropriate calcinations temperature of the CNT/SiO_2 precursor powders should be held for 1 h at 500°C.

Keywords: *carbon nanotube(CNT), CNT/SiO_2 precursor powders, SiO_2 pure gel, sol–gel, TG-DSC-MS, thermal decomposition*

Introduction

In recent years, scientists have paid more attention to study the carbon nanotube (CNT). CNT is a new form of carbon reported by Iijima in 1991 for the first time when he discovered multi-walled carbon nanotubes (MWNT) in carbon-soot made by an arc-discharge method [1]. Due to its fascinating electronic and mechanical properties [2], CNT has been used to reinforce many kinds of materials including polymer, metal and ceramic [3–6]. SiO_2 is one kind of excellent dielectric materials [7]. Guo *et al.* developed continuous carbon fiber (C_f)/SiO_2 composites successfully in 1970's. The results indicated that there are good physical and chemical compatibility between C_f and SiO_2 [8]. Considering the comparability between the CNT and carbon fiber, CNT has been used to reinforce the SiO_2. Seeger *et al.* reported a novel route to nanocomposites consisting of multi-walled carbon nanotube embedded in amorphous SiO_x [9]. TG studies demonstrate that the coated nanotubes are extremely resistant to oxidation, remaining intact after heating in air up to 1200°C. Ning *et al.* reported the fabrication and properties of the carbon nanotube-reinforced SiO_2 matrix composites by rapid sol–gel process. In the experimental, firstly the CNT/SiO_2 precursor powders were prepared by rapid sol–gel process without C_{16}TMAB surfactant. Then the CNT/SiO_2 precursor calcined in air and removed the structural water and got the CNT/SiO_2 mixture powders. Finally the CNT/SiO_2 mixture powders were sintered by hot pressing (25 MPa at 1300°C for 0.5 h) in pure N_2 atmosphere and got the CNT-reinforced SiO_2 matrix composites. The CNT-reinforce SiO_2 composites were characterized by X-ray diffraction (XRD) and transmission electronmicroscopy (TEM) and high resolution electronmicroscopy (HREM) [10–14].

However, the research of thermal decomposition process of the CNT/SiO_2 precursor powders was seldom seen in literature. The SiO_2 gel in the CNT/SiO_2 precursor powders contained many –OH and –C_2H_5O groups. In order to form the SiO_2 glass powders, the SiO_2 gel was needed to calcine in air and to remove the structural water. It was obvious that the calcination temperature of the CNT/SiO_2 precursor powders must not be higher than the temperature of the CNT oxidation. Therefore, the determination of CNT oxidation temperature and calcination temperature were very important for the preparation of the CNT/SiO_2 precursor powders. In our work, TG-DSC-MS techniques [15–18] are used to characterize the mass losses, the thermal effects caused by the chemical reactions or physical processes and the evolved gaseous components of the CNT/SiO_2 precursor powders. The thermal stability of CNT and the SiO_2 pure gel as well as the thermal decomposition process of the CNT/SiO_2 precursor powders were investigated in this work. Finally, the calcination temperature of the CNT/SiO_2 precursor powders was also determined.

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Experimental

Sample preparation

The multi-walled CNT provided by Shenzhen NANO Tech. Port. Co. Ltd (China) and TEOS ($Si(C_2H_5O)_4$ A. R.) were used as the raw materials. Firstly, the CNTs were added into the water solution of TEOS and dispersed by ultrasonic. Then the hydrochloric acid (1.16M HCl) was dropped into the mixture solution and stirred by the magnetic mixer for 2 h. Next, the ammonia solution $NH_3{\cdot}H_2O$ (A. R.) was dropped into the solution to make it gel rapidly. Finally, the gel was washed with distilled water and alcohol and dried in the furnace at 100°C. The dried lumps were crushed, passed through a 200 mesh plastic sieve and got the CNT/SiO_2 precursor powders. In addition, the same process was used to prepare the SiO_2 pure gel without adding the CNT.

TG-DSC measurement

The Netzsch STA 449C TG-DSC thermal analyzer was used in the experiments. The mass of CNT for each experiment with the heating rate of 5, 10 and 20°C min^{-1} was 3.8, 5.0 and 3.3 mg, respectively. The argon with a flow speed of 5 mL min^{-1} was used for the protective gas of TG-DSC furnace. The air with a flow speed of 20 mL min^{-1} was used as the carrying gas. The temperature region of TG-DSC was from room temperature to 900°C. The heating rate was 10°C min^{-1}.

TG-DSC-MS measurement

The Netzsch STA 449C TG-DSC thermoanalyzer coupled with Balzers Thermostar Quadrupole Mass Spectrometer was used in the experiments. The quartz capillary was used as the interface between thermoanalyzer and the quadrupole MS. The mass of the SiO_2 pure gel was 4.4 mg. The mass of the CNT/SiO_2 precursor powders was 3.0 mg. The vacuum for the system of quadrupole MS was 10^{-4} Pa. The multiple ion detector (MID) mode was used for the MS measurement. In each channels, the different *m*/*z* mass numbers were proposed (the zero channel was proposed for symbolizing temperature; the other mass to charge (*m*/*z*) propositions in other channels can be seen from Table 1). The mass filtering time was 1 s. The mass resolution was 50. The mass scanning speed was 1 s. The channel-tron was used to record the positive ion mass spectra signals.

Table 1 Mass numbers propositions[a]

m/*z*	Expected positive ion mass spectra	*m*/*z*	Expected positive ion mass spectra
12	C^+	27	$C_2H_3^+$
16	NH_2^+	28	CO^+/N_2^+
17	NH_3^+/OH^+	44	CO_2^+
18	H_2O^+	45	$C_2H_5O^+$

[a] The intensities of the positive ion mass spectra mentioned above were proposed automatically

The calculations and data treatment were carried out in progress after completing the proposed programs.

XRD measurement

The X-ray diffraction (XRD Model D/max 2550 V, Japan) was used to identify the phase compositions of the SiO_2 glass powder and the CNT/SiO_2 composite powders. The CuK$_\alpha$ radiation (λ=0.15406 nm) was used. The SiO_2 glass powder and the CNT/SiO_2 composite powders were prepared by the SiO_2 pure gel and the CNT/SiO_2 precursor powders calcined at 500°C holding for 1 h in air, respectively.

Results and discussion

TG-DSC results for the CNT measured at the different heating rate

The TG and DSC curves of CNT measured at the heating rate of 5, 10 and 20°C min^{-1} are shown in the Figs 1 and 2. In Fig. 1, the TG curves at the heating rate of 5, 10 and 20°C min^{-1} show a mass loss from about 530 to 680, 530 to 750 and 530 to 820 separately. In Fig. 2, the corresponding DSC curves appear the three exothermic peaks at 659, 738 and 805°C, respectively. It indicates that with the increasing of the heating rate, the temperature of the DSC exothermic peaks move towards to the higher temperature. As a result, the oxidation of CNT began from 530°C in air and combusted at about 659, 738 and 805°C separately. Thus the calcination temperature of the CNT/SiO_2 precursor powders must be lower than the temperature of the CNT oxidation in air.

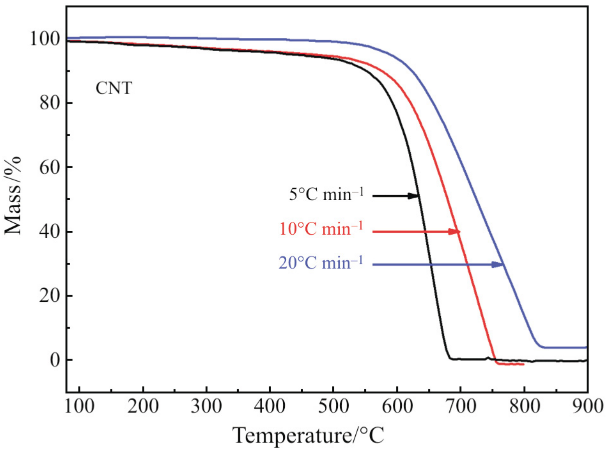

Fig. 1 TG curves of CNT (heating rate: 5, 10, 20°C min^{-1})

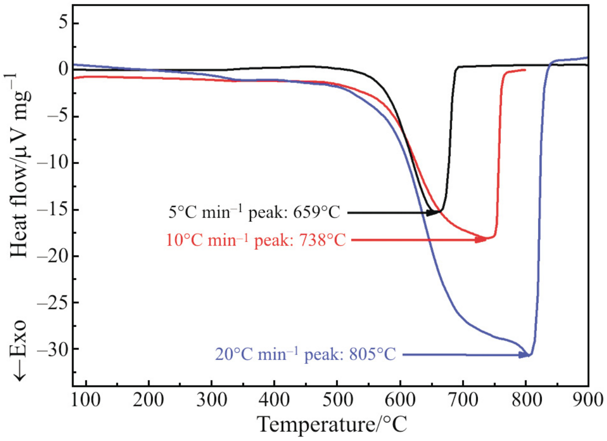

Fig. 2 DSC curve of CNT (heating rate: 5, 10, 20°C min^{-1})

TG-DSC results for the SiO_2 pure gel

The TG-DSC results of the SiO_2 pure gel from room temperature to 500°C and then holding at 500°C for 1 h at the heating rate of 10°C min^{-1} are shown in Fig. 3. The results show that the thermal decomposition for the SiO_2 pure gel completed in two steps. The total mass losses are 11.25%. The DSC curve appears a small endothermic peak at 77.7°C. It can be inferred that the endothermic peak at 77.7°C is the vaporization and desorption of the adsorbed water and the part solvents on the surface of the SiO_2 gel. It is worth to point out that the DSC curve tend to level and there was no obvious enthalpy at about 200–800°C, but the TG curve has mass losses. It can be concluded that the dehydration of the SiO_2 gel was very slow during the process of condensation at about 200–500°C. The TG curve shows no mass losses during the holding temperature stage at 500°C and indicates that the net-like structure of SiO_2 was formed. It means that the SiO_2 pure gel was changed to the amorphous SiO_2 glass powder [19].

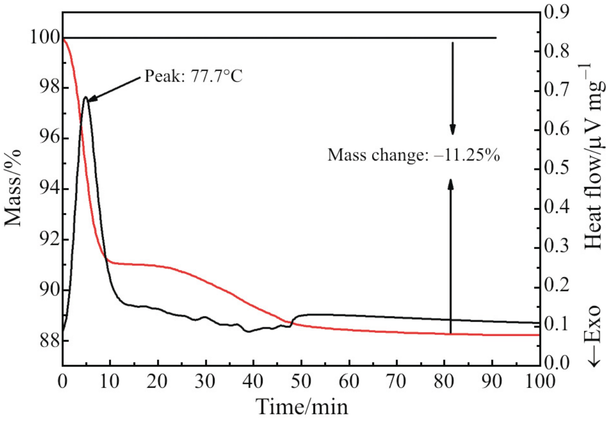

Fig. 3 TG-DSC curve of the SiO_2 pure gel (heating rate: 10°C min^{-1} from room temperature to 500°C and then holding at 500°C for 1 h)

As a result, the result of TG-DSC shows the vaporization and desorption of water and the part solvents adsorbed on the surface of the SiO_2 pure gel at about RT–200°C. As the increasing of temperature, the $–C_2H_5O$ groups in the gel was gradually replaced by the –OH groups and transformed to the $Si_nO_n(OH)_{4-n}$. Finally, through the dehydration and condensation further, the amorphous $SiO_{4/2}$=SiO_2 was formed. The appropriate calcinations temperature of the CNT/SiO_2 precursor powders should be held for 1 h at 500°C.

XRD results for the SiO_2 glass powder and the CNT/SiO_2 composite powders

Figure 4 is the XRD patterns of the SiO_2 glass powder and the CNT/SiO_2 composite powders. Curve a showed that the amorphous SiO_2 had formed after the SiO_2 pure gel calcined at 500°C for 1 h. Curve b showed that the peak of the CNT could be observed in the CNT/SiO_2 composite powders except the amorphous SiO_2. It indicates that the structure of the CNT has not changed and the amorphous SiO_2 had formed after the CNT/SiO_2 precursor powders calcined at 500°C for 1 h. These results were corresponded to the TG-DSC results.

TG-DSC-MS results for the CNT/SiO_2 precursor powders

Figures 5–7 are the TG-DSC-MS curves of the CNT/SiO_2 precursor powders. The results show that the TG curve has three mass losses: 7.03% (room temperature–200°C), 8.12% (200–500°C) and 13.34% (500–800°C). There are no mass losses appearing over 730°C basically. The DSC curve appears a small endothermic peak at 98.4°C, a big exothermic peak at 677.5°C. Corresponding to the DSC curve, the MS

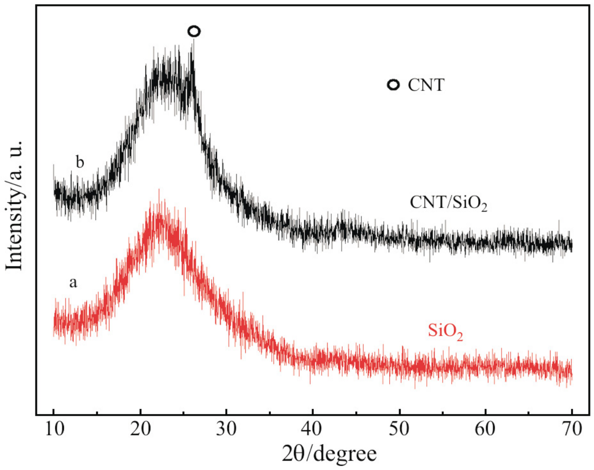

Fig. 4 XRD patterns of the a – SiO_2 glass powder and b – the CNT/SiO_2 composite powder

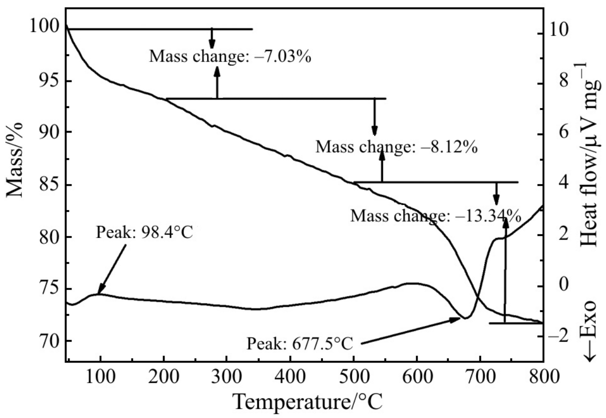

Fig. 5 TG-DSC curve of the CNT/SiO_2 precursor powders

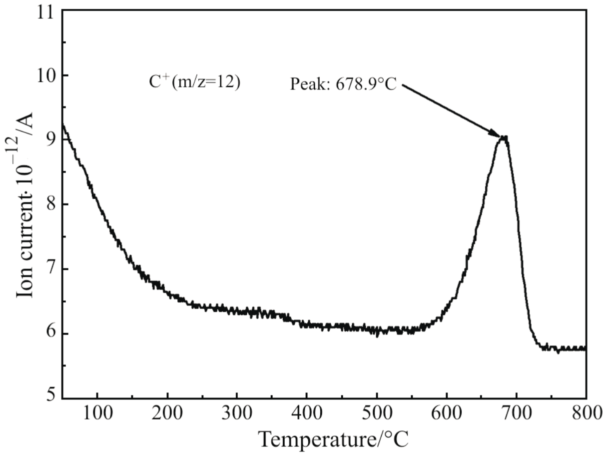

Fig. 6 MS spectra of the CNT/SiO_2 precursor powders C^+ (*m*/*z*=12)

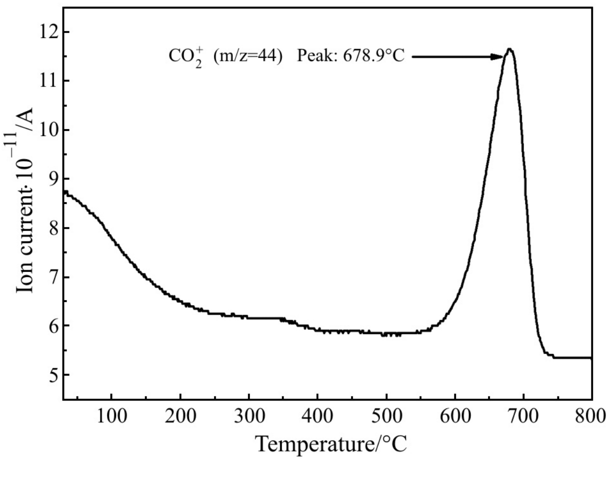

Fig. 7 MS spectra of the CNT/SiO_2 precursor powders CO_2^+ (*m*/*z*=44)

curves appear the positive ion mass spectra peaks of C^+ (*m*/*z*=12) and CO_2^+ (*m*/*z*=44) at 678.9°C.

Through the comparison, we can see that the thermal decomposition processes for the experimental results of the CNT/SiO_2 precursor powders and the SiO_2 pure gel from room temperature to 500°C have no differences. For the CNT/SiO_2 precursor powders, the TG curve shows the second obvious mass losses at about 680°C. The corresponding DSC curve shows obvious exothermic peak. Thus, it can be inferred that the thermal decomposition for the CNT/SiO_2 precursor powders completed in three steps. The first step shows the vaporization and desorption of the adsorbed water and the part solvents on the surface of the CNT/SiO_2 precursor powders at about room temperature–200°C. The second step shows the slow dehydration and polymerization of SiO_2 at 200–500°C and the third step shows the complete combustion of CNT at 500–850°C. The corresponding MS curves appear the positive ion mass spectra peaks of C^+ (*m*/*z*=12) and CO_2^+ (*m*/*z*=44) at 678.9°C (Figs 8, 9). It is related to the combustion of CNT.

Conclusions

According to the results measured by the TG-DSC-MS, the conclusions are the follows:

- The oxidation of CNT began from 530°C and combusted at 530–850°C in air. The faster the heating rate, the higher the combustion temperature of CNT.
- The appropriate calcinations temperature of the CNT/SiO_2 precursor powders should be held for 1 h at 500°C.
- The thermal decomposition for the CNT/SiO_2 precursor powders completed in three steps. The first step shows the vaporization and desorption of the adsorbed water and the part solvents on the surface of the CNT/SiO_2 precursor powders at about room temperature–200°C. The second step shows the slow dehydration and polymerization of SiO_2 at about 200–500°C and the third step shows the complete combustion of CNT at about 500–850°C.

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