

Study on the preparation of carbon nanotubes by iron modified phenolic resin pyrolysis

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Abstract: An iron modified phenolic resin was synthesized by grafting ferric ions into a phenolic resin structure through a coordination reaction. Carbon nanotubes were prepared by high temperature pyrolysis of phenolic resin under the protection of argon gas. The CNTs were characterized by SEM, Raman and TEM. The effects of iron content, temperature and time on the formation of carbon nanotubes were studied. The results show that when the content of iron is 0.005, the yield of carbon nanotubes in the pyrolytic carbon is the highest, and the optimal time and temperature for the pyrolysis of iron modified phenolic resin to generate carbon nanotubes are 3h and 1000°C, respectively. The process of high temperature pyrolysis of iron modified phenolic resin to produce carbon nanotubes follows the "melting carbon-carbon precipitation" mechanism, generating a tube diameter of 80 to 100 nm, a length of several tens of micrometers and a complete structure with about 20 layers of wall thickness multi-walled carbon nanotubes.

1. Introduction

Carbon nanotubes (CNTs) are one-dimensional carbon nanomaterials with nanometer diameter and micron length and sealed at both ends of the tube. Owing to their excellent mechanical, electrical and optical properties, carbon nanotubes are widely used in composite materials, integrated circuits, photocatalysis and other fields^[1-4]. There are many methods for preparing carbon nanotubes. The most common synthetic carbon nanotube technologies are chemical vapor deposition (CVD), arcing, and laser ablation^[5], in which the CVD growth process is very flexible, but in the production process the widely use of flammable gaseous carbon sources is dangerous, and the structure of the prepared carbon nanotubes is incomplete, and the catalyst particles are likely to remain in the carbon nanotubes, affecting the properties of the carbon nanotubes. Using phenolic resin as a solid carbon source to pyrolyze carbon nanotubes is safer and easier for mass production which has broad application prospects^[6-7].

2. Experimental part

2.1. Preparation of iron modified phenolic resin

Phenol, formaldehyde and sodium hydroxide with a ratio of 1: 1.5: 0.1 were added into a four-necked



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flask equipped with a thermometer, a stirrer and a reflux condenser. After reflux heating at 65°C for 60 min, the temperature was increased to 90°C and kept for 120 min. The chelating agent (the ratio to phenol amount was 0.03: 1) was added and stirred for 10 min. Then the mixture was cooled to 55°C, and the pH was adjusted to 7 by adding hydrochloric acid. Modifier was added with the ratio of ferric chloride to phenol substance of 0.003-0.0008. The temperature was hold at 55°C for 30 min. The obtained mixture was distilled in the vacuum under the condition of 0.09-0.1 MPa, while the discharge temperature was 75°C. Finally ethylene glycol was added to adjust the viscosity of the resin to obtain the iron modified phenolic resin. Iron modified phenolic resins are named PF-Fe0.003, PF-Fe0.005 and PF-Fe0.008 depending on the iron contents.

2.2. Preparation of iron-modified phenolic resin pyrolytic carbon

The iron modified phenolic resin was put into the clean small porcelain boat, and the phenolic resin was cured after curing in the vacuum drying oven at 205°C for 2h. The cured phenolic resin is placed in a rotary tubular resistance furnace, after a certain process conditions pyrolysis carbonization under the protection of high-purity argon gas, high temperature pyrolysis of phenolic resins are obtained.

3. Results and discussion

3.1. Analysis of SEM test results

Figure 1 is SEM images of the pyrocarbon of carbonized phenolic resins with different iron contents at 1000°C for 3 hours. As can be seen from the figures, there are many pores on the surface of ordinary pyrolysis resin pyrolysis charcoal because pyrolysis of phenolic resin will decompose small molecules such as CH₄, CO and H₂. The surface of the iron modified phenolic resin pyrolysis charcoal also generates similar pore structures, but CNTs are attached to the pores, and a small amount of coarse and uneven carbon nanotubes are generated in the pyrolytic carbon pores of the sample PF-Fe0.003. The quantity of CNTs in the pores increases as the content of iron increased to 0.005. It can be seen from figure 1(e) that the diameters of the CNTs are evenly distributed, between 80 and 100 nm, and the length reaches dozens of micron. When the iron content increased to 0.008, iron tends to agglomerate due to excess iron, and no carbon nanotubes are generated in the pyrolytic carbon. From the EDS diagram, it can be seen that the CNTs produced by the PF-Fe0.005 pyrolysis are relatively pure, only contain a small amount of iron, and have no other impurities attached to the CNTs.

In summary, when the iron content is 0.005, the effect of pyrolysis of the modified phenolic resin to generate CNTs is the best.

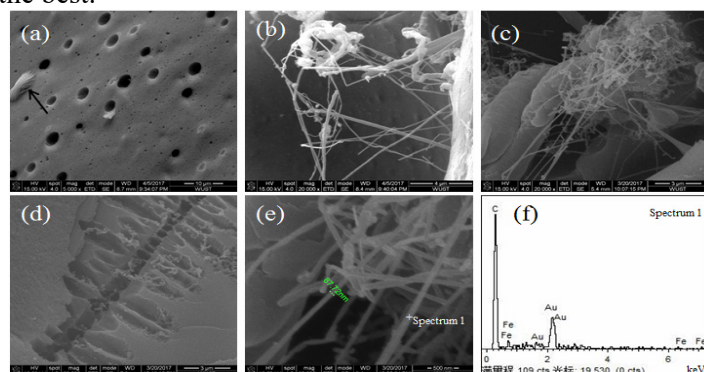


Figure 1. The SEM images of pyrolytic carbon with different iron content of PF: (a) Ordinary PF; (b) PF-Fe0.003; (c) PF-Fe0.005; (d) PF-Fe0.008; (e) CNTs diameter; (f) EDS spectra of point 1 in (e).

Figure 2 is the SEM images of CNTs produced by pyrolysis of sample PF-Fe0.005 at different temperatures for 3h. As can be seen from the figures, at a temperature of 900°C, no CNTs are formed

in the pores of the pyrolytic carbon, because the carbon atoms are hardly melted or cannot be melted into the metallic iron during pyrolysis of the phenolic resin at a relatively low temperature. It is impossible to generate CNTs when the temperature is lowered. When the temperature is 1100°C , the quantity of CNTs in the pores is much less than that produced at 1000°C , and the structure is not complete. It may be because the temperature is too high, carbon atoms precipitate too quickly on metallic iron, easy to accumulate, which is not conducive to the formation of structural integrity of CNTs, then leading to the block structure shown in figure 2(c). In summary, the optimal temperature for the pyrolysis of the sample PF-Fe0.005 to generate CNTs is 1000°C .

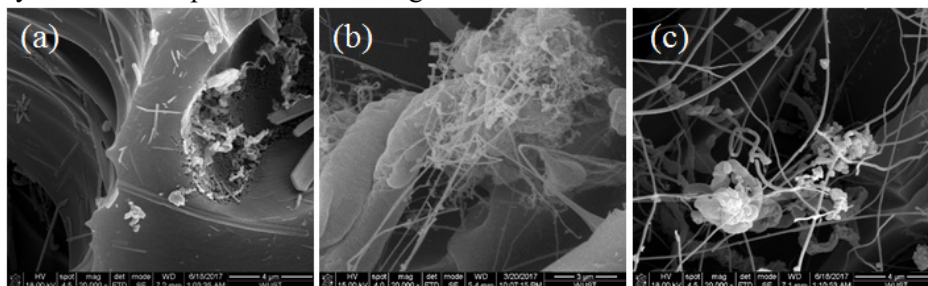


Figure 2. The SEM images of CNTs produced by pyrolysis of PF-Fe0.005 at different temperatures: (a) 900°C ; (b) 1000°C ; (c) 1100°C

Figure 3 is the SEM images of CNTs generated by pyrolysis of the sample PF-Fe0.005 at 1000°C for different times. It can be found that when the carbonization time is 2h, the quantity of CNTs generated in the pores on the pyrolytic carbon surface is small, and the structure is incomplete, and the CNTs also have agglomerate phenomenon. When the carbonization time is 4 hours, although the quantity of CNTs has increased, but it is far less than the quantity of CNTs produced when the carbonized time is 3 hours. The structure is also not complete, and there are also serious agglomeration phenomena. Considering synthetically, the optimal time for pyrolysis of CNTs produced by the sample PF-Fe0.005 is 3 h. With this carbonization time, the quantity and the structure completeness of CNTs is the best.

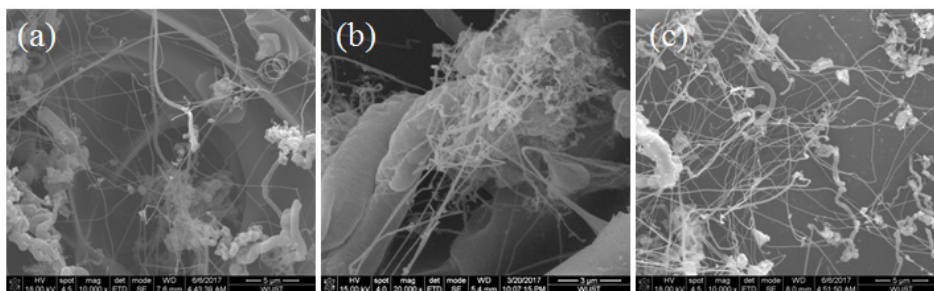


Figure 3. The SEM images of CNTs produced by pyrolysis of PF-Fe0.005 at different carbonization times: (a) 2h; (b) 3h; (c) 4h

3.2. Analysis of Raman test results

Figure 4 is the Raman spectrograms of the CNTs produced by PF-Fe0.005 under 1000°C . As can be seen from Figure 4, the CNTs are generated in the sample PF-Fe0.005 pyrolysis 2-4h, but the R value are all close to 1.3. This indicates that the sample PF-Fe0.005 produced multi-walled carbon nanotubes (MWCNTs) under these three pyrolysis times. Some of the iron ions are embedded in the carbon crystal lattice, making the carbon nanotubes have crystal defects, which makes the D peak obvious. This is consistent with the results of EDS analysis[8-9]. When the pyrolysis time is 2h, the 2D peak is 2675 cm^{-1} and the peak is weak. The 2D peak in the Raman spectrum is 2700 cm^{-1} with carbonizing 3h and 4h. Because the time of pyrolysis is too short and the reaction is not sufficient, some iron ions are combined in the carbon tube. There is a charge transfer between carbon and iron, which makes the 2D peak shift. The 2D peak of carbonizing 4h is weaker than carbonizing 3h,

indicating that the CNTs content is lower in the pyrolysis carbon of 4h.

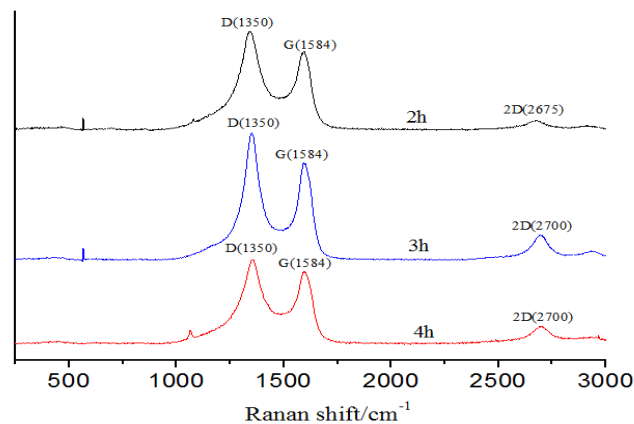


Figure 4. The Raman images of CNTs produced by pyrolysis of PF-Fe0.005 at different carbonization times

3.3. Analysis of TEM test results

Figure 5 shows the TEM image of CNTs prepared by the sample PF-Fe0.005 in 1000°C carbonization time 3h and the CNTs purchased commercially. It can be seen from Figure 5 that the CNTs prepared by the PF-Fe0.005 pyrolysis with a diameter of about 100 nm and the length of more than 10 microns are larger, which is consistent with the SEM test results. As can be seen from figure 5(b), the CNTs prepared by resin pyrolysis are uniform and straight, clean and free of impurities in the carbon pipe, and the wall is thin. However, the CNTs purchased commercially are uneven and distorted, contain catalyst residues and the wall is too thick. Therefore, the CNTs prepared by the sample PF-Fe0.005 pyrolysis are larger and purer, and the structure is more complete. As can be seen from figure 5(c), the number of tube wall layers of CNTs is about 20, which represents MWCNTs. It is meeting to the Raman test results.

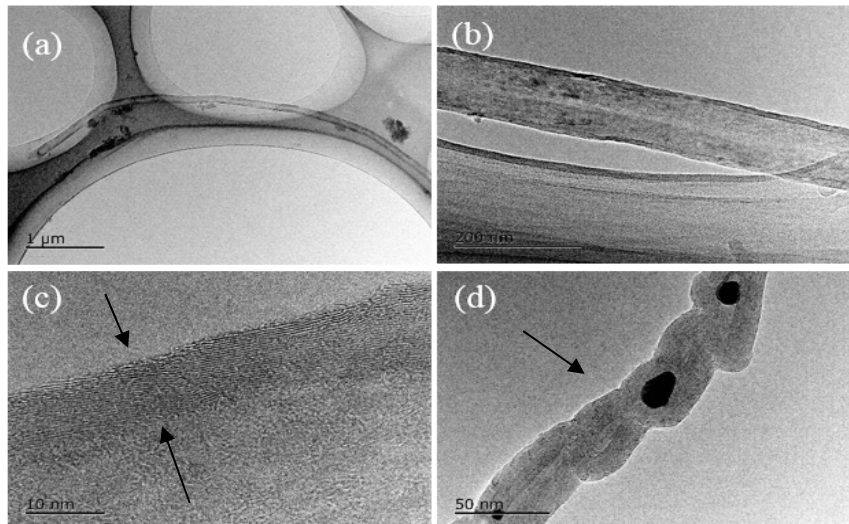


Figure 5. The TEM images of CNTs: (a~c) CNTs prepared by pyrolysis of PF-Fe0.005; (d) Commercialized graphene.

3.4. Carbon nanotubes formation mechanism

In the formation of CNTs, the catalyst ferric chloride is surrounded by a carbon layer to form a globular structure. At high temperatures, iron and carbon form cementite (Fe_3C). When the temperature is lowered, carbon in Fe_3C precipitates to form a curved surface of carbon atoms, as

shown in figure 6(a). CNTs are gradually formed by using cementite as the core.

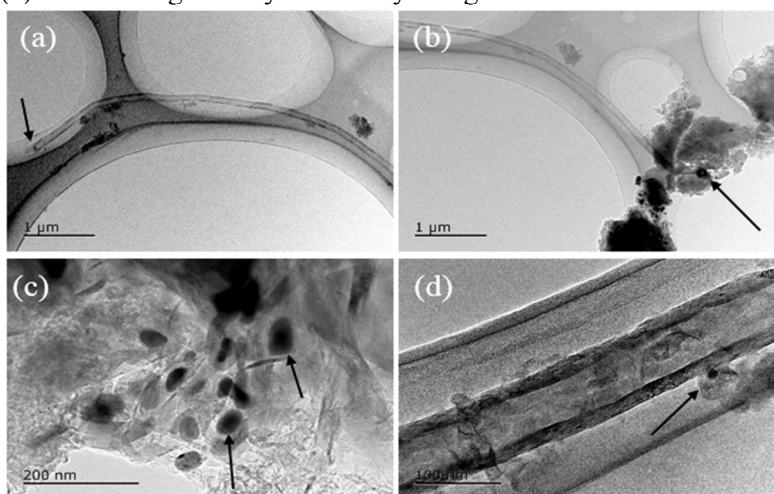


Figure 6. The TEM images of different parts of CNTs

With the growth of carbon nanotubes, Fe₃C gradually reacts with carbon to form Fe₅C₂, which loses catalytic activity and the growth of CNTs is terminated[10], therefore, there will be catalyst residues at the tail end of the CNTs, as shown in figure 6(b), and a small amount of iron ions are not involved in the catalytic pyrolysis reaction and adhere to the carbon nanotubes. The internal catalyst size is much larger than the original size, as shown in figure 6(c). In that case, the diameter of the generated CNTs is relatively large, around 80 to 100 nm. During the formation of CNTs, part of the catalyst escaped from the defect and formed an onion-like nano-carbon structure as shown in figure 6(d).

4. Conclusions

The iron modified phenolic resin was used as a solid carbon source to produce CNTs by high temperature pyrolysis under the protection of argon gas. The best experimental parameters for producing CNTs was proven as follows: the content of iron was 0.005, the carbonization temperature was 1000 °C and the carbonization time was 3h. The process of high temperature pyrolysis of iron-modified phenolic resin to produce CNTs follows the "melting carbon-carbon precipitation" mechanism, generating a tube diameter of 80 to 100 nm, a length of dozens of micrometers and a complete structure with about 20 layers of wall thickness MWCNTs.

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