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The Mossbauer spectra of carbon nanotubes synthesized using ferrite catalyst

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Abstract: The ferrite powder with honeycombed structure obtained by chemical combustion was used as catalyst to synthesize multi-walled carbon nanotubes by chemical vapor deposition. The magnetic components and characters of the carbon nanotubes synthesized were investigated by X-ray diffraction (XRD), Mossbauer spectra and vibrating-sample magnetometer (VSM). The ferric components of the carbon nanotubes samples can be identified by Mossbauer spectra. The Mossbauer spectra of carbon nanotubes sample after purification contains two ferromagnetic sextet components corresponding to $\alpha$-Fe species and Fe$_3$C (cementite) species. While the Mossbauer spectra of the carbon nanotubes sample before purification contains three ferromagnetic sextet components corresponding to $\alpha$-Fe species, Fe$_3$C species and $\gamma$-Fe$_2$O$_3$. The saturation magnetization intensity $M_s$ of carbon nanotubes sample after purification is decreased from 46.61 to 2.94 emu/g, but the coercive force increased and reached 328Oe.

Keywords: multi-walled carbon nanotubes, Mossbauer spectra, ferrite powder

1. Introduction
Due to their fascinating physical and chemical properties, carbon nanotubes may be used for nanoscale devices [1-6]. At present, chemical vapor deposition (CVD) process [7-10], in which carbon nanotube was synthesized in large-scale and high quality, make this application practicable. However, for all these device applications of CVD carbon nanotubes, it is important to further understand the magnetic properties of the carbon nanotubes sample synthesized in order that controllable growth for carbon nanotubes given magnetism. Previous studies[11-13] about magnetic properties of the carbon nanotubes focused on electron spin resonance (ESR) spectra of purified and unpurified carbon nanotubes.
nanotubes. Other studies about the magnetic properties of the carbon nanotubes of purified and unpurified are few.

In this paper, we have prepared a pure ferrite powder with honeycombed structure by chemical combustion using ferric nitrate and citric acid as raw material. By using the ferrite powder with honeycombed structure as a catalyst, we also have prepared multi-walled carbon nanotubes by chemical vapor deposition. The multi-walled carbon nanotubes prepared may be used as a kind of good electromagnetical wave absorbent. We tried to study the magnetic component and especial magnetic properties of these carbon nanotubes sample synthesized using magnetic ferrite powder as a catalyst by Mossbauer spectra and vibrating-sample magnetometer (VSM).

2. Experimental
2.1 Preparation of ferrite catalyst
Fe(NO$_3$)$_3$·6H$_2$O and citric acid were dissolved in the adding de-ionized water at 1:1 mol ratio, and then PH value of the solution was adjusted to seven by ammonia. The prepared solution was baked in 120°C, and a red-brown xerogel was gained. A russety and fleecy ferrite is obtained by burning the gel in the air at about 200°C. The ignition point was examined by the thermogravimetric analyses (TGA). TGA experiments were performed at a heating rate 20 °C/min from room temperature to 350°C under dry-air atmosphere. The surface morphology of the ferrite was observed by scanning electron microscope (SEM).

2.2 Preparation of carbon nanotubes
The ferrite with nanometer pores was used as catalyst and was loaded on a quartz reactor. First, nitrogen gas with a flow rate of 50ml/min was introduced until the furnace temperature up to 550°C and then hydrogen gas with a flow of 50ml/min was introduced. When the temperature was up to 850°C, acetylene was introduced at a flow rate of 100 ml/min. After 30 minutes reaction, hydrogen and acetylene gas were closed and nitrogen gas was introduced until the equipment cooled down to room temperature. Then multi-walled carbon nanotubes were obtained. The prepared carbon nanotubes are purified by heating reflux with 98% strong nitric acid for an hour. Transition electronic microscope (TEM) and SEM were employed to observe the carbon nanotubes samples. XRD was employed to test the composition and structure of the samples. The Mossbauer spectra of samples are measured by Mossbauer spectrometer using $^{57}$Co (Pd) source at room temperature. All isomer shifts are given relative to that of α-Fe. The vibrating-sample magnetometer (VSM) experiments of the samples were also performed at room temperature.

3. Result and discussion
Ferric nitrate and citric acid were reacted according to the chemical equation as follows:

$$2\text{Fe(NO}_3\text{)}_3 + C_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O} + 2\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 6\text{NO}_2 + 6\text{CO}_2 + \text{H}_2\text{O}$$

Fig.1 is the SEM image of the ferrite after combustion reaction, from which we can see that ferrite presents a honeycombed structure, and there are many pores with the diameter from tens to hundreds nanometer. When using as a catalyst, this kind of structure with very large specific surface area can contact reacting gas fully in chemical vapor deposition processes of preparing carbon nanotubes.

Fig.2 shows the thermogravimetric (TG) curve of xerogel prepared by citric acid and ferric nitric,
from which we can see the sample's weight decrease slowly when the temperature varies from 30°C to 210°C. This is because the crystalline water in the ferric nitrate and citric acid are removed. The sample's weight sharply decreases when the temperature rises up to 210°C, which is the ignition point of xerogel and the sample starts to be decomposed. When the temperature rises to 250 °C, the sample is decomposed completely and hybrid metals oxide is formed, so the sample's weight no longer changes when the temperature continues to go up. Due to the strong oxidizing property of nitrate ion (NO₃⁻), the xerogel occurs oxidation-deoxidization reaction above 100°C until it is burned entirely. The ferrite having nanometer pores is formed, with high activity and uniform pore size distribution.

Fig.1 The SEM image of ferric oxide sample

Fig.2 TG curves of the gel prepared by ferric nitrate and citric acid

Fig.3 and Fig.4 show that the SEM and TEM image of the multi-walled carbon nanotubes prepared by using ferrite with nanometer pores as catalyst, and we can see the diameter of carbon nanotubes is between 20-30 nm, and the length of carbon nanotubes is above 20 μm. The diameter of carbon nanotubes prepared is uniform. The growth process of carbon nanotube is probably as follows: In the hydrogen atmosphere, the ferrite is deoxidized, then carbon nanotubes are formed when acetylene is decompounded on the ferrite surface.

Fig.3 The SEM image of carbon nanotubes
XRD spectra of the carbon nanotubes before and after purification are shown as Fig.5, and we can see that the main components of the sample are carbon, $\alpha$-Fe and a small quantity Fe$_3$C. The catalyst is removed from the sample by nitric acid heating reflux. XRD spectra of the carbon nanotubes after purification are shown in fig.6, the main components in the purified sample are carbon, a small quantity of $\alpha$-Fe and Fe$_3$C. The relative content of carbon and $\alpha$-Fe is much larger than before purification from the X-ray diffraction, but the peak of $\alpha$-Fe is still higher because $\alpha$-Fe is crystal even of a little content, so its peak of X-ray diffraction is still stronger than that of carbon.

Because of its high energy distinguish ability, Mossbauer spectra can be used to test sensitively most tiny energy variety occurred around the atomic nucleus, and it is a effective way to investigate the composition of nanomaterials. There are two samples tested in our experiments: one is carbon nanotubes before purification (named sample A), the other is carbon nanotubes after purification (named sample B). The Mossbauer spectra of carbon nanotubes (sample A and sample B) are shown in
Fig.7. Mossbauer parameters obtained by fitting the curves in Fig.7 are shown in Table 1 and Table 2. Because Mossbauer spectra are only used to check the content of magnetic composition of elements and compound in samples, the magnetic elements and compound containing iron in carbon nanotubes samples can be checked by using Mossbauer spectra, except large numbers of carbon.

Table 1 Mossbauer parameters of sample A

| Component | IS (δ) (mm/s) | QS (△) (mm/s) | Hyperfine field (A/m) | WHM (half width of half height) | Relative area(%) |
|-----------|---------------|---------------|-----------------------|-------------------------------|-----------------|
| α-Fe      | 0.01±0        | -0.01±0       | 330.0±0.1             | 0.16±0                        | 29.7%           |
| Fe3C      | 0.20±0        | 0             | 209.7±0.1             | 0.20±0                        | 65.5%           |
| γ-Fe2O3   | 0.28±0.03     | -0.06±0.06    | 485.9±2               | 0.27±0.02                     | 4.8%            |

Table 2. Mossbauer parameters of sample B

| Component | IS (δ) (mm/s) | QS (△) (mm/s) | Hyperfine field (A/m) | WHM (half width of half height) | Relative area(%) |
|-----------|---------------|---------------|-----------------------|-------------------------------|-----------------|
| α-Fe      | -0.02±0.01    | 0.05±0.03     | 332.6±1               | 0.13±0.01                     | 9.1%            |
| Fe3C      | 0.21±0        | 0.03±0.01     | 207.4±0.4             | 0.25±0                        | 90.9%           |

![Fig.7 Mossbauer of CNTs before purification (sample A) and CNTs after purification (sample B) at room temperature](image-url)
According to the Mossbauer spectra data, the composition of carbon nanotubes samples besides carbon can be identified. Mossbauer spectra of sample B were fitted to two ferromagnetic sextet components corresponding to $\alpha$-Fe species and Fe$_3$C (cementite) species. The Mossbauer spectra of sample A are fitted to three ferromagnetic sextet components corresponding to $\alpha$-Fe species, Fe$_3$C species and $\gamma$-Fe$_2$O$_3$. From Table 1 and Table 2, the components containing iron in the sample before purification include $\alpha$-Fe, Fe$_3$C and Fe$_2$O$_3$, however, only $\alpha$-Fe, Fe$_3$C after purification. So there is no ferric oxide in the carbon nanotubes sample after purification. On the other hand, the content of $\alpha$-Fe is less after purification than that before purification. In the high temperature of preparing carbon nanotubes, Fe$_3$C may form and not be eliminated in such purification way. XRD spectrum shows that the content of Fe$_3$C is much less than that of carbon. The $\alpha$-Fe content in the carbon nanotubes sample after purification is only 9% of Fe$_3$C by Mossbauer spectra data, so $\alpha$-Fe content can be neglected in the carbon nanotubes sample after purification.

Fig.8 shows that the hysteresis loop of carbon nanotubes before and after purification measured by using the vibrating-sample magnetometer (VSM). The carbon nanotubes represent soft magnetic property. Comparing the magnetism parameters of carbon nanotubes before and after purification (Table.3), and also compared with that of $\alpha$-Fe, the magnetism parameters of carbon nanotubes after purification is lower than that before purification. The residual magnetization intensity $M_r$ is about 0.53 emu/g and saturation magnetization intensity $M_s$ is about 2.94 emu/g. This is because a lot of $\alpha$-Fe and Fe$_2$O$_3$ are eliminated after purification. While the coercive force of the carbon nanotubes after purification is 328 Oe, close to that of iron. This shows that $\alpha$-Fe and Fe$_2$O$_3$ magnetic components in carbon nanotubes may decrease the coercive force of carbon nanotubes.

| CNTs | before purification | 46.61 | 3.84 | 113 | 0.0257 |
|------|---------------------|-------|------|-----|--------|
| CNTs | after purification  | 2.94  | 0.53 | 328 | 0.0204 |
| $\alpha$-Fe |                  | 113.69 | 16.71 | 344 | 0.0489 |

**Table.3** the magnetic parameters of carbon nanotubes before and after purification measured by the vibrating-sample magnetometer (VSM)

**Fig.8** The $M$ ($H$) loop curves of carbon nanotubes before purification (sample A) and after purification (sample B)
4. Conclusions
The ferrite powder with honeycombed structure can be synthesized by sol-gel process and chemical combustion method using ferric nitrate and citric acid as raw materials. This ferrite powder was used as a catalyst to synthesize successfully magnetic multi-walled carbon nanotubes by chemical vapor deposition. We have studied the magnetic components and characters of the carbon nanotubes synthesized by Mossbauer spectra, XRD spectra and vibrating-sample magnetometer (VSM). The main components of the samples with soft magnetic property are carbon nanotubes, α-Fe, Fe₃C and Fe₂O₃ before purification. After purification, Fe₂O₃ and the mass of α-Fe in the carbon nanotubes samples were eliminated, and the main components of the samples is carbon nanotubes and Fe₃C. The magnetism of the carbon nanotubes after purification is decreased and the saturation magnetization intensity Ms of carbon nanotubes sample is from 46.61 to 2.94 emu/g, but the coercive force of carbon nanotubes increases to 328 Oe, close to that of iron.

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