Preparation and thermal properties of carbon Nanotubes/5-Amino-1H-Tetrazole energetic composites

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Abstract. Carbon nanotubes were prepared in large quantities by fluidized bed method and nitrogen-doped carbon nanotubes were prepared by chemical vapor deposition method. Carbon nanotubes/5-amino-1H-tetrazole composites were prepared by ultrasonic resonance method. The appearance characteristics and thermal properties of composites were analyzed by scanning electron microscope (SEM), transmission electron microscope (TEM), thermogravimetry (TG) and differential scanning calorimeter (DSC).

Keywords: Carbon nanotubes; Nitrogen-doped carbon nanotubes; 5-Amino-1H-tetrazole; Energetic composite

1. Introduction
In 1991, Iijima [1] discovered carbon nanotubes by using an electron microscope to observe the products of graphite-dc discharge. Carbon nanotubes are generally small in diameter, the outside diameter is generally several nanometers to several tens nanometers and inner diameter is just a few nanometers. Carbon nanotubes have excellent properties in physics and chemistry, especially the excellent mechanical and electrical properties [2].

The nanotube network in the nitrogen-doped carbon nanotubes has many structural defects due to the effect of the nitrogen doping. These structural defects include carbon vacancies and/or the inclusion of pentagons or heptagons within the carbon hexagonal network. The chemical environment of nitrogen atoms in the nanotubes were suggested that one nitrogen atom bonded to two carbon atoms, which were arranged as “pyridine-like” structures [3]; or one nitrogen atom bonded to three carbon atoms, which were arranged as “graphite-like” structures [4]. And the most common types of the nitrogen-dopants in the nitrogen-doped carbon nanotubes are substituted or accompanied by the incomplete-bonding defects [5-6]. Therefore, the existent of the large number of defects and reactive sites leads to a higher density and dispersion of functional groups on the surface of nitrogen-doped carbon nanotubes [7].

Composed with carbon nanotubes make energetic materials to achieve nano-level dispersion in the composites [8]. In addition, good thermal conductivity of carbon nanotubes can improve the heat transfer rate greatly in the reaction process of energetic materials [9].

In this paper, Nitrogen-doped carbon nanotubes, carbon nanotubes and 5-amino-1H-tetrazole composites were prepared by simple physical mixing and ultrasonic resonance methods [10]. Through
the control experiment, the effects of carbon nanotubes mass fraction on the thermal decomposition of the composites were studied.

2. Experimental

2.1. Materials and equipment

Materials: Carbon nanotubes were prepared according to literature [11-12] and nitrogen-doped carbon nanotubes were prepared according to literature [13-14]; 5-Amino-1-H-tetrazolium (5-ATz, A) and other chemical reagents and solvents were purchased and used as supplied without further purification. Analytical equipment: Scanning Electron Microscope (SU8010; Tokyo, Japan); Transmission Electron Microscope (JEM-2010; JEOL); Thermogravimetric analyzer (Netzsch STA 449 C; Selb, Germany); Differential Scanning Calorimeter (DSC Q2000; New Castle, USA).

2.2. The preparation of nanotubes/energetic composites

5-Amino-1H-tetrazole (A, 1.02 g, 12 mmol) was dissolved in 25 mL ethanol. Stirring for 20 min, the precipitate residue was removed by filtration and the saturated solution of A was obtained at room temperature. Then carbon nanotubes were added (mass fraction 10%), stirring for 10 min, ultrasonic resonance for 30 min, then solvent was evaporated to give the solid power (B). By the same method, we obtained the composites of A and nitrogen-doped carbon nanotubes with the mass fraction 5% (E). The composite materials of carbon tube mass fraction of 5% (C), 10% (D) were obtained by physical mixing method.

3. Results and discussion

3.1. SEM/TEM

The SEM image of nitrogen-doped carbon nanotubes (N-CNT) is shown in Figure 1; the TEM image of carbon nanotubes (CNT) is shown in Figure 2 and the TEM image of CNT/5-ATz is shown in Figure 3.

From Figure 2 and 3, the outer diameter of the non-loaded carbon nanotubes is about 3 nm, the TEM is clear and bright. The composite pipe diameter is thickened, about 6 nm, the tube is dark, and the local tube has granular solids.

**Figure 1.** SEM image of N-CNT. **Figure 2.** TEM image of CNT.
3.2. Thermogravimetric analysis

The TG and DSC curves of A, B, C, D and E under Ar atmosphere are shown in Figure 4. The DSC curves show that the thermal decompositions of all samples involved a single exothermic process. At the same time, the TG curves provided insight into the total weight losses from the 5-ATz (A) associated with this process [15]. Characteristic temperatures in the TG-DSC curves of the samples are shown in Table 1.

![Figure 3. TEM image of CNT/5-ATz composites.](image)

**Figure 4.** TG traces of the samples (L) and DSC traces of the samples (R).

|       | A  | B   | C   | D   | E   |
|-------|----|-----|-----|-----|-----|
| \(T_0/°C\) | 203.82 | 181.03 | 185.34 | 189.35 | 174.32 |
| \(T_P/°C\) | 207.69 | 206.96 | 206.13 | 205.68 | 203.39 |

*\(T_0\) is the initial temperature of the TG curves; \(T_P\) is the peak temperature of the DSC curves.

From TG data, it can be seen that the initial decomposition temperature of weightlessness process for A is 203.82 °C, for B is 181.03 °C, for C is 185.34 °C, for D is 189.35 °C, and for E is 174.32 °C, respectively. Comparing the data of B and C, compared with the sample, which were prepared by grinding the mixture of A and carbon nanotubes, the initial thermal decomposition temperature of the
composites obtained by ultrasonic resonance method is about 4 °C lower. Comparing the data of C and D, the initial thermal decomposition temperature for the sample obtained by grinding the mixture of A and 5% carbon nanotubes is lower than the mixture of A and 10% carbon nanotubes about 4 °C. For E, the composite of A and nitrogen-doped carbon nanotubes, the thermal decomposition temperature was obviously lower than A 30 °C; compared with B it also decreased by 7 °C. Through the above analysis, the following conclusion were drawn: the excellent heat conductivity of carbon nanotubes reduces the thermal decomposition temperature of A in the composite materials; the presence of nitrogen in the nitrogen-doped carbon nanotubes makes it better for conducting thermal conductivity. Therefore, the reduction of the thermal decomposition temperature of A after forming the composite is more obvious. This result is consistent with other reports [16-18].

From DSC data, it can be seen that compared with A, the maximum peak temperatures of heat decomposition for B, C and D were not obviously changed; the exothermic peak temperature of thermal decomposition process for nitrogen-doped carbon nanotubes composites is about 4 °C in advance compared with the else. Compared the DSC exothermic data with the other groups of carbon nanotube composites, the nitrogen-doped carbon nanotubes have greatly increased on the release of heat because of containing nitrogen.

4. Conclusions
The thermal conductivity of carbon nanotubes reduces the thermal decomposition temperature of 5-amino-1H-tetrazole. Compared with the carbon nanotubes, the nitrogen-doped carbon nanotubes have much better conductance about thermal conductivity due to nitrogen element in the carbon nanotubes, make the thermal decomposition temperature of the 5-amino-1H-tetrazole, which in composites, decreases more obviously and the heat of the decomposition was improved greatly. In addition, compared with the composites formed by physical mixing, the composites formed by ultrasonic resonance make the thermal decomposition temperature of 5-amino-1H-tetrazole much lower.

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