THE EFFECT OF SULFUR ON THE SYNTHESIS OF SINGLE-WALLED CARBON NANOTUBES BY ELECTRIC ARC METHOD

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1. Introduction

An improved plasma electric arc method by which single-walled carbon nanotubes (SWNTs) can be semi-continuouslly synthesized in a large scale was recently developed [1]. In the synthesis process, we found that the addition of a sulfur-containing growth promoter was critical, i.e. only crumbly soot in which little SWNTs exist can be obtained with sulfur absent, while we obtained large-scale high-quality SWNTs when suitable sulfur-containing compounds was added. The promoting effect of several kinds of sulfur-containing growth promoters, including FeS, CdS, PbS, and pure sulfur, was further investigated. Moreover, the working mechanism of sulfur was proposed.

2. Experimental

2.1. Method

The electric arc was operated in a cylinder-shaped chamber with a diameter of 600mm and a height of 400mm. The cathode is a graphite rod (10mm in diameter), and the anode is a graphite cylinder (120mm in diameter and 35mm in height), on whose upper surface several holes (15mm in diameter, 10mm in depth) were drilled. Nickel (2.6 at. %), cobalt (0.7 at. %) and iron (0.7 at. %) served as co-catalyst. The mixture of graphite powders, catalysts and sulfur-containing growth promoter was then filled into the holes for co-vaporizing. Rather than expensive helium gas which is usually used in the conventional electric-arc method [2,3], argon and hydrogen gases were selected as buffer gases. The electric arc was typically operated by a dc of 150A under the atmosphere of 250 torr Ar and 150 torr H_2.

2.2. The addition of different sulfide

The promoting effects of FeS, CdS, PbS and pure sulfur were investigated by adding them into the mixture for co-vaporizing, respectively. The amount added was 0.75 in atomic percentage, and a blank experiment (no sulfur-containing growth promoter added) was done for contrast.

3. Results and discussions

3.1. The characterization of the products

In Table 1, we show the existing forms of the products prepared by adding different sulfur-containing growth promoters. As we can see, only crumbly soot can be obtained with sulfur-containing growth promoter absent. Observed by TEM, the crumbly soot was mainly comprised of amorphous carbon and some nanoparticles, little SWNTs can be found. In contrast, when FeS or pure sulfur was introduced, we obtained rubbery soot and web-like substance, which contain SWNTs in abundance. A TEM image of the as-prepared FeS-promoted rubbery soot is shown in Figure 1. The volume percentage of SWNT is estimated to be ~70%. The Raman spectrum of the product (not shown) also showed a high quality of the SWNTs.

The experimental results show that the promoting effect of CdS and PbS is not as notable as that of FeS and pure sulfur. At high temperature (~2000K), Fes decomposes into Fe and sulfur. While CdS and PbS would have sublimated before their decomposition, thus the sulfur concentration near the arc column is very low. This fact implies it is sulfur that promotes the synthesis of SWNTs.

Table 1. The existing forms and SWNT content of the products promoted by different sulfides.

Promoter	None	S	FeS	CdS	PbS
Product forms	Crumbly soot	Rubber soot and web-like structures	Rubbery soot and web-like structures	Crumbly soot	Crumbly soot
Volume percentage of SWNTs (%)	0	70	70	5	5

3.2. The promoting mechanism of sulfur

The addition of sulfur in synthesizing SWNTs has been mentioned in some previous reports [5,6], while there is not a convincing interpretation of the novel roles that sulfur plays yet, since the detailed growth mechanism of SWNTs also remains unclear. Here we propose a SWNT growth process under our experimental conditions, and based on the proposal, the role of sulfur will be discussed. The growth process of SWNTs may be:

i. In the scope near to the arc column, the temperature is high enough to gasify the mixture powders, carbon and catalysts exist as gas state.

ii. Blown by the plasma, the gas comprising carbon and catalyst atoms flows to a lower temperature range, where catalyst liquid drops form.

iii. With the decrease of temperature, some tiny crystalline grains, based on which carbon nanotubes grow, separate out from the drops. And the carbon atoms dissolved in the liquid drops act as the carbon source for constructing SWNTs.

iv. When the drop coagulates entirely, the growth process terminates, leaving catalyst particles beside the nanotube bundles (as seen in Figure 1).

In above process we ignored some details, such as the way that carbon atoms rearrange in constructing carbon nanotubes. We consider that the form and existence of tiny catalyst liquid drops is an essential step in the synthesis process. Seen from phase diagrams [7], the addition of sulfur will broaden the temperature range in which catalyst liquid drops can exist. Namely, the scope that is suitable for nanotube growth in the reactor chamber is enlarged. Supposing the plasma flow velocity as a constant, the growth time is also prolonged. It is above effect of sulfur that promotes the growth of SWNTs.

4. Conclusions

(1) The addition of a suitable sulfur-containing growth promoter is critical in synthesizing SWNTs by our improved electric arc method.

(2) The addition of sulfur may broaden the temperature range in which catalyst liquid drops can exist, and hence promote the growth of SWNTs

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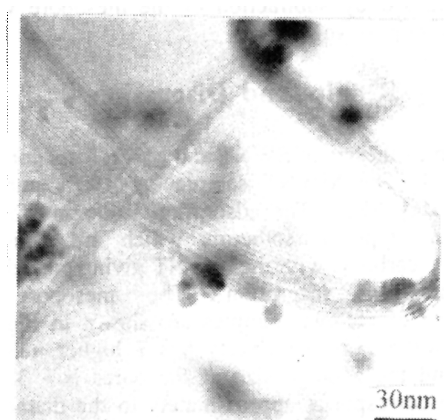

Figure 1. TEM image of the FeS-promoted SWNT