give only ill-defined products containing residual fluorine [5]. Second, our film grows on an ideally flat surface of a liquid amalgam, and its thickness is defined (Eqs. 3a,b). This allows growth of precise films down to nanometer-scale thickness.

The prepared carbon films were extracted by toluene (Aldrich, HPLC grade) in a Soxhlet extractor for ca. 20 - 40 hours. Alternatively, the product was first extracted by water (to remove MF and MOH) and then by toluene. The toluene extracts were analyzed for fullerenes by HPLC, UV-Vis and mass spectroscopy. The analyses revealed a small amount of fullerene, C_{60} in defluorinated perfluorocyclopentene, perfluorodecalin and perfluoronaphthalene. Hence, the model reactions (cf. Eq. 2 and discussion thereof) seem to occur. However, the yield of C_{60} was usually below 0.1%, referred the total amount of carbon produced (Eq. 4). The best yield of C_{60} was 0.36% in one batch from C_5F_8/Li-amalgam, but it was not reproducible. Although the carbonization (Eq. 4) was always perfect, the yield of C_{60} usually decreased, when the same portion of precursor was repeatedly exposed to fresh amalgams. In some cases, even no fullerene was detectable.

The rest after toluene extraction was ground in an agate mortar, dispersed in acetone and evaporated on a collodion grid for transmission electron microscopy (TEM). The microscopic and electron-diffraction studies revealed graphitic carbon nanotubes, both straight and curly (Fig. 1). The straight nanotubes appeared preferentially in carbons from C_5F_8; they were typically about 15 nm in diameter and 100-200 nm long.

The yield of carbon nanotubes was ca. 1-2 % in the best samples. Spheroidal graphitic carbon grains of about 20 - 100 nm size were also occasionally detected (Fig 1A); they are similar to onion-like particles. To the best of our knowledge, this is a first indication that carbon nanoparticles can be prepared by "soft chemistry" at room temperature.

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Semi-continuous synthesis of single-walled carbon nanotubes by a hydrogen arc discharge method

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Since the discovery of single-walled carbon nanotubes (SWNTs) in 1993 [1,2], significant progress has been made in their synthesis techniques. Three methods, including laser-ablation [3], catalytically decomposition of hydrocarbons [4] and electric arc discharge [5], have been reported to be able to prepare SWNTs on a large scale. In this letter, we report a hydrogen arc discharge method by

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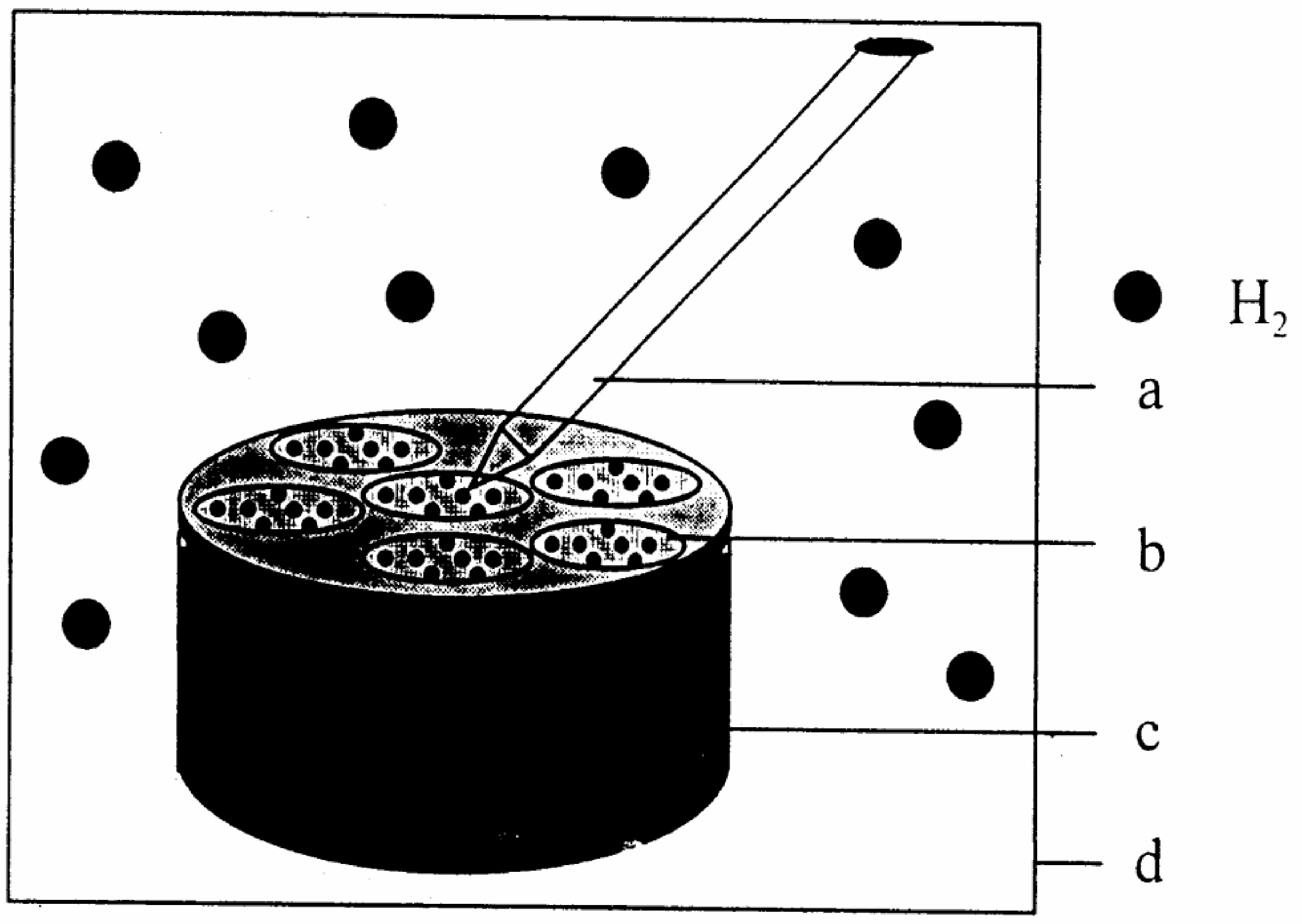

Fig. 1 Schematic diagram of the apparatus used for synthesizing SWNTs by our semi-continuous hydrogen arc discharge method. a, graphite cathode; b, mixture of graphite powder and catalysts; c, graphite anode; and d, chamber wall. As we can see, the two electrodes make an oblique angle, and this point is different from the conventional apparatus, in which the cathode and the anode are vertically opposite [1, 2, 5]. Moreover, the graphite anode can be rotated and has many holes filled with mixed powders of graphite and catalysts, which makes our synthesis process a semi-continuous one.

which large-scale high-quality SWNTs can be semi-continuously synthesized at low cost, since we employed H_2 rather than expensive He as the buffer gas, designed a novel reactor, and introduced a sulfur-containing SWNT-growth promoter. Our method may be promising for the commercial-scale synthesis of SWNTs. Moreover, based on the resonant Raman measurements, the SWNTs we obtained have a wider diameter distribution and larger mean diameter in comparison to previous reports [1,3,5].

A high vacuum apparatus that can produce a plasma electric arc within a big reactor chamber was employed in this study (Fig. 1), which is much different from the conventional electric arc reactors used for the synthesis of fullerenes and carbon nanotubes [1,2,5]. The cylinder-shaped reactor chamber has a diameter of 600 mm and height of 400 mm. The cathode is a graphite rod (10 mm in diameter) and the anode is a big rotatable graphite cylinder (~400 mm in diameter, 35 mm in height), on whose upper surface many holes (10 mm in diameter, 15 mm in depth) were drilled. The mixture of graphite powders and catalysts was then filled into the holes.

Usually, helium serves as a buffer gas when synthesizing SWNTs by the conventional electric arc method [2,5]. In our method, hydrogen gas, which is much cheaper than He, was introduced into the reactor chamber as a buffer gas. Due to its high thermal conductivity, hydrogen is able to quench the plasma flow efficiently and produce a temperature gradient, which may be critical for the growth of SWNTs. Moreover, hydrogen can promote the vaporization of catalyst metals and keep the exposed catalyst surface clean from encapsulating carbons that will deactivate it [6]; hence hydrogen is beneficial to the synthesis of SWNTs. Hydrogen can also selectively etch the impurity of amorphous carbon by forming hydrocarbons and then improve the quality of our SWNTs [7].

Another characteristic of our SWNT synthesis method is the addition of a sulfur-containing growth promoter (FeS typically). With FeS absent, only crumbly soot, in which hardly any SWNTs exist, is obtained. By contrast, we obtained large-scale high quality SWNTs when a suitable amount of FeS was added. This result indicates that sulfur plays an important role in synthesizing SWNTs by our hydrogen arc discharge method, although the detailed mechanism remains unclear.

The electric arc was typically operated in a dc mode using 150A and an atmosphere of 200 torr H_2, with a distance of ~2 mm maintained between the two electrodes. Transition metals, including iron, nickel and cobalt were selected as co-catalysts. A mixture of 2.6 at.% Ni, 0.7 at.% Fe, 0.7 at.% Co, 0.75 at.% FeS and graphite powders gave the best result, with a yield of more than 100 mg SWNTs within 3 minutes of synthesis. Furthermore, since the positions of the two electrodes are both adjustable, when the mixture in one hole (drilled on the upper surface of the anode) was consumed, we can rotate the anode so that another hole filled with raw materials can be shifted to a suitable position for continuous synthesis. After the replacement of buffer gases, the electric arc was operated again. Thus, our synthesis process is semi-continuous. With the big rotatable anode and the large volume of the reactor chamber, SWNTs can be semi-continuously synthesized at a rate of 1.0 gram per hour.

There are mainly two kinds of products obtained: (i) web-like substances hanging between the cathode and the upper chamber wall; (ii) thin films form on the upper chamber wall, which can be peeled off in large slices (~200 cm^2), and is self-fluttering, self-adhering to hands and vessels. The existing change in the form of the products (in comparison to the previous reports [1, 2, 5]) may be attributed to the different opposite orientations of the electrodes, which lead to different ways that the plasma flows.

The microstructures of the as-prepared products were observed by Scanning Electron Microscopy (JSM 6301F, SEM) and Transmission Electron Microscopy (Philips EM420, TEM). The results show that the obtained products contain SWNTs in abundance (estimated >70% in volume percentage).

In Figure 2, we show an SEM image of the as-prepared web-like products collected between the upper chamber wall and the cathode (the sample was prepared by adhering the web-like substance onto a piece of silicon chip). Curled or circled SWNT bundles (~20 nm in diameter) can be observed in the image. It is difficult to measure the length of the bundles accurately, which is estimated to be several, or even up to tens of microns.

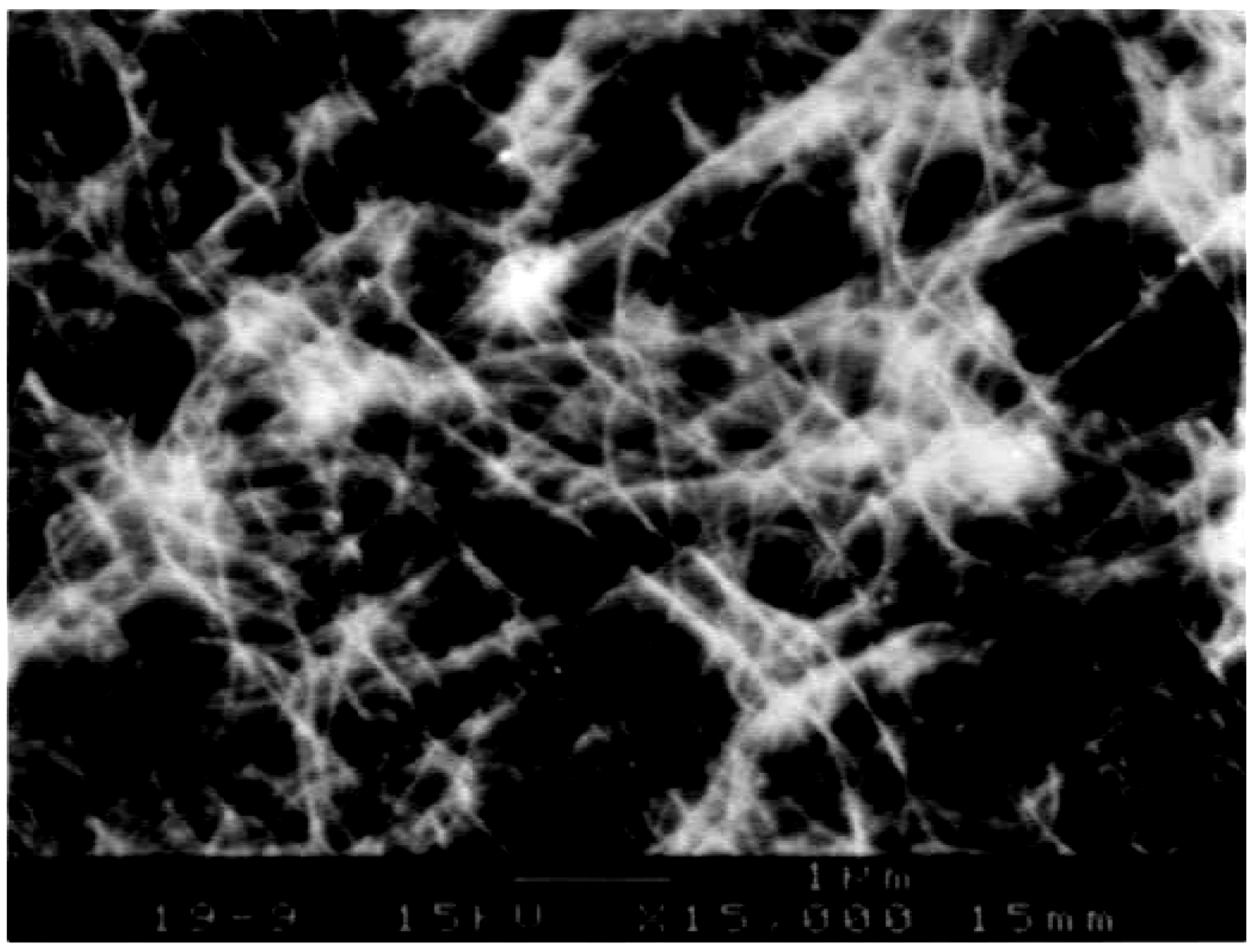

Fig. 2 SEM image of the as-prepared web-like substance. The entangled SWNT bundles are usually curved or circled. Scale bar, 1μm.

After mounting on a holey copper grid, the as-prepared thin film substance was observed by TEM, as shown in Figure 3. We can see two SWNT bundles, one curled and the other straight. The two bundles are both comprised of tens of packed SWNTs, whose axes are roughly parallel. We note that in comparison to the SWNTs synthesized by the conventional electric arc method, our products contain less amorphous carbon, which may be attributed to the etching effect of hydrogen [7].

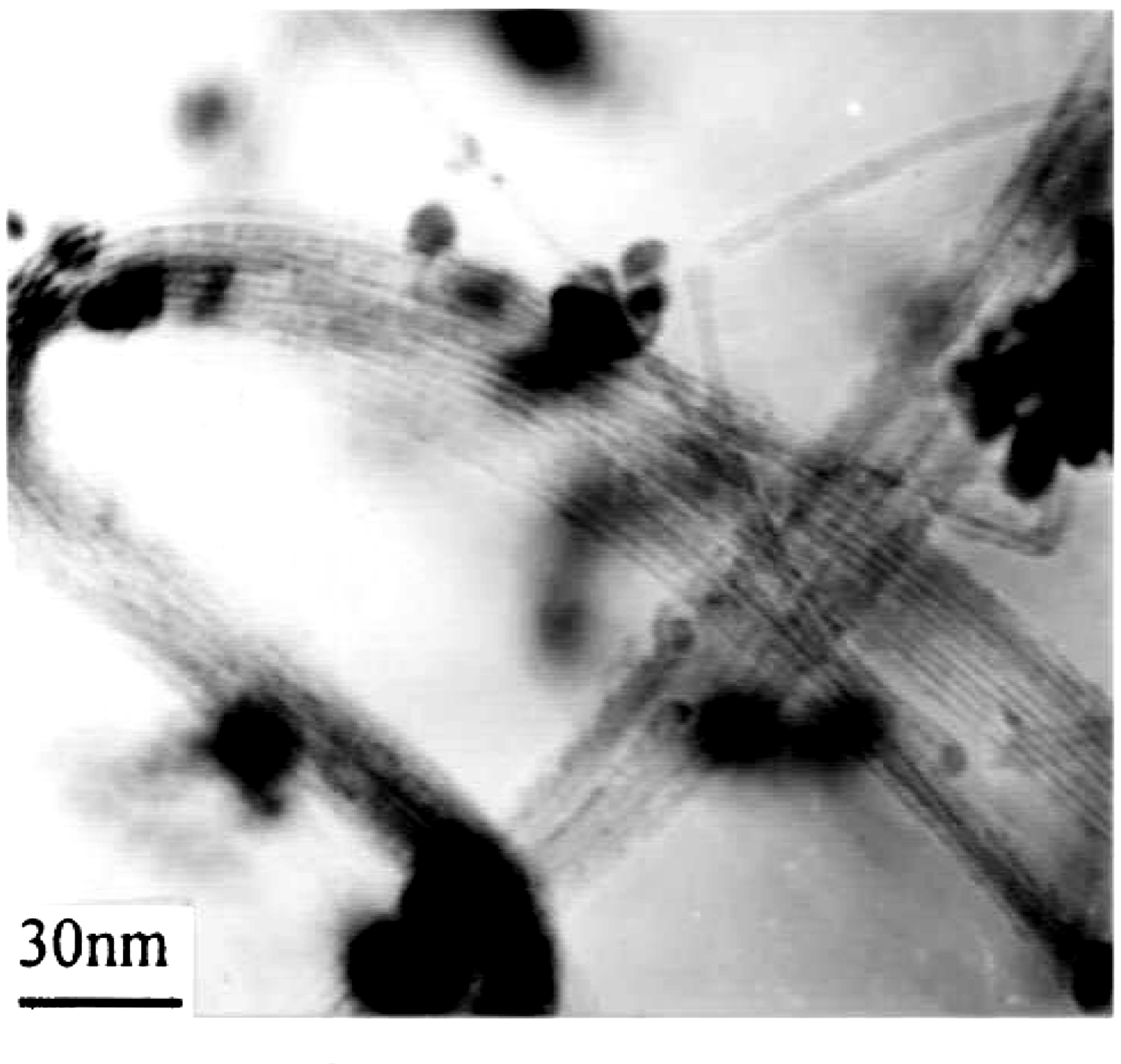

Fig. 3 TEM image of the as-prepared thin film substance. Two SWNT bundles comprising tens of packed SWNTs can be seen.

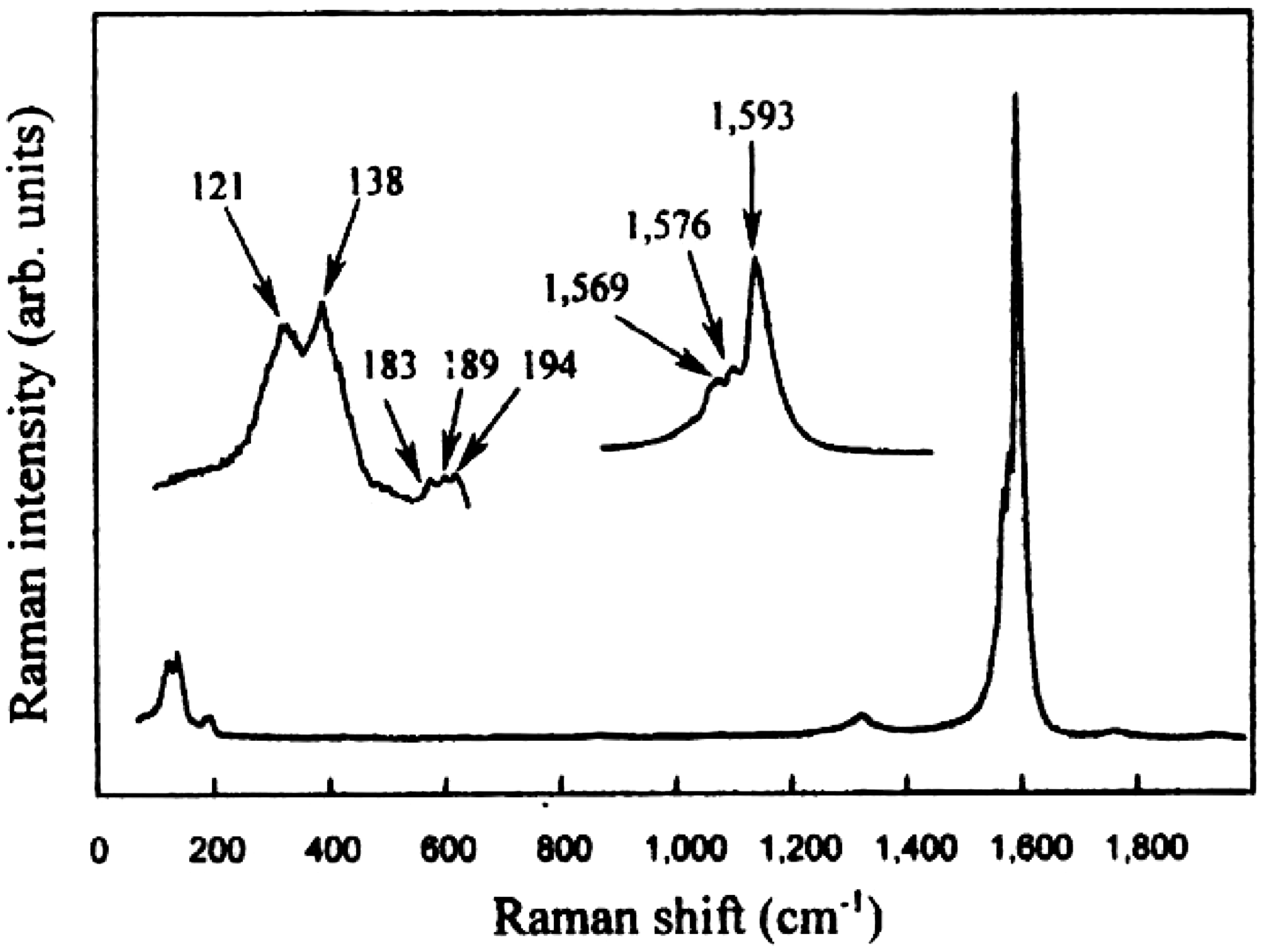

Fig. 4 Raman spectrum of the SWNTs with an excitation wavelength of 632.8 nm. Insets are the enlarged spectra in the range of 100~200 cm^{-1} and 1,500~1,650 cm^{-1}, respectively.

Resonant Raman scattering measurements, which have been shown to be a powerful tool in characterizing SWNTs [8], were carried out in the range of 100~2,000cm^{-1} with the laser excitation wavelength of 632.8 nm. The Raman scattering spectra of our samples (mixture of the two kinds of products mentioned above, i.e., web-like substances and thin films) are shown in Figure 4. As we can see, the peaks are mainly distributed in two bands, namely 100~200 cm^{-1} and 1,500~1,600 cm^{-1}. Three well resolved peaks at 1,593 cm^{-1}, 1,576 cm^{-1} and 1,569 cm^{-1} are shown in the high frequency band of the spectrum (1,500~1,600 cm^{-1}), which can be assigned to a splitting of the E_{2g} mode of graphite and was considered to be characteristic of SWNTs [9]. In the low frequency band, two groups of peaks located in the range 180~200 cm^{-1} and 120~150 cm^{-1}, respectively, can be observed. In the range of 180~200 cm^{-1}, at least three peaks at 183 cm^{-1}, 189 cm^{-1} and 194 cm^{-1} were observed, consistent with the previous reports [3, 5, 8]. It is worth noting the appearance of the peaks at 121 cm^{-1} and 138 cm^{-1}, which have not been reported before. According to the theoretical calculations, the peaks in the range of 100~200 cm^{-1} are associated with the radial breathing mode (RBM) of SWNTs, and the peak frequency is diameter-dependent, the larger the diameter the lower the peak frequency [8, 10]. Thus, the appearance of the peaks at the lower frequency band indicates the existence of larger diameter SWNTs in the sample. In addition, the peaks in the range of 120~150 cm^{-1} are much stronger than those in the range 180~200 cm^{-1}. Thus we conclude that SWNTs with relatively larger diameters are more prevalent in our samples, which may be related to the introduction of sulfur or hydrogen. In fact, HRTEM observations showed a larger mean SWNT diameter of 1.85nm, which is consistent with the Raman measurements. These SWNTs with larger diameters will be more promising in gas-storage applications, such as the hydrogen-storage material for fuel-cell operated electric vehicles [11].

In summary, our semi-continuous hydrogen arc discharge method for synthesizing SWNTs is characterized by semi-continuity, low-cost, large-scale, high-quality and larger mean SWNT diameter. It shows a great possibility of engineering for mass production of SWNTs.

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Thermal shock resistance of C/C composites

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C/C composites are one of the most promising materials for structural applications at high temperature owing to their refractory property, lower density, and excellent mechanical properties. Whether C/C composites could suffer catastrophic failure by thermal stress when they subjected to an extremely severe environment is attracting considerable interest. The ability of a material to resist thermal shock damage is usually determined qualitatively by the concept of thermal shock resistance (TSR) [1-2]:

$$TSR = \sigma\kappa/E\alpha \qquad (1)$$

Where σ is the strength, κ the thermal conductivity, E the modulus and α the coefficient of thermal expansion. The higher the value of the TSR factor, the greater is the ability of a material to successfully withstand a thermal stress environment. TSR factors are extremely useful to qualitatively order materials for thermal shock resistance.

In the present paper, strength, conductivity, modulus and coefficient of thermal expansion of graphitized and non-graphitized carbon felt reinforced carbon matrix composites in the temperature range from 25 to 2500°C are measured. TSR factors of both composites at various temperatures are calculated using equation (1).

Carbon felt reinforced carbon matrix composites were fabricated to reach a density of $1.8 g/cm^3$ by chemical vapor infiltration (CVI) processing [3]. Heat treatment was carried out isothermally at 2800°C for some of the composites. Tensile tests were conducted on a high-temperature testing machine made here. The sample gauge size is $\Phi 4mm \times 50mm$. Young's modulus from 25 to 2500°C was measured by the acoustic frequency resonance method using rectangular beams of $10mm \times 5mm \times 202mm$. The non-steady state method and drop copper calorimeter method were employed to measure thermal diffusivity (α) and specific heat (C_p) in the temperature range from 25-2500°C respectively. Thermal conductivity κ was calculated by the expression $\kappa = \alpha C_p \rho$, where ρ is the bulk density of the materials. The coefficient of thermal expansion from 25 to 2500°C was observed directly by an optical comparator (projection comparator).

Table 1 presents strength, modulus, thermal diffusivity and coefficient of thermal expansion together with TSR data of graphitized and non-graphitized C/C composites at various temperatures.

It can be seen in table 1 that the tensile strength of C/C composites increases with temperature whether they are graphitized or non-graphitized, and the value at 2500°C is about 2 to 3 times that at room temperature. The thermal conductivity after heat treatment increases. The most significant difference between graphitized and non-graphitized materials is the values of the conductivity decrease for the former and increase slightly for the latter as temperature goes up. It is

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