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Synthesis of high-quality single-walled carbon nanotubes by catalytic decomposition of C_2H_2

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High-quality single-walled carbon nanotubes free of defects and amorphous carbon coating have been produced by catalytic decomposition of C_2H_2 over Fe–Mo/Al_2O_3 catalyst.

Single-walled carbon nanotubes (SWNTs) exhibit unique mechanical and electronic properties that have promise in various applications. High-quality SWNTs are necessary for both fundamental research and technological applications. Today, SWNTs are synthesized by three main methods: arc discharge,[1] laser vaporization,[2] and catalytic chemical vapor deposition (CCVD).[3–14] Among them, catalytic decomposition of carbon-containing molecules over a metal catalyst (in general, the supported Fe, Ni, Co, Mo or their mixtures), represents the benefit for large-scale production of high-quality SWNTs.

For the synthesis of multiwalled carbon nanotubes, the catalytic decomposition of C_2H_2 has mainly been used. However, there were a few reports for the synthesis of SWNTs using C_2H_2 carbon source. Rao *et al.*[3] and Xie *et al.*[11] demonstrated the synthesis of SWNTs by the pyrolysis of C_2H_2 on the floating catalyst, but in their experimental results, SWNTs suffer from poor quality or small quantity. Moreover, there was no report for the synthesis of SWNTs over supported metal catalyst using C_2H_2 as carbon feedstock.

In this communication, we report synthesis of high-quality SWNTs by catalytic decomposition of C_2H_2 over an alumina-supported Fe–Mo bimetallic catalyst. Our results demonstrate that C_2H_2 can be used as ideal carbon feedstock to realize the synthesis of high-quality SWNTs.

The synthesis of SWNTs was carried out by catalytic reaction of C_2H_2 and Fe–Mo catalyst. A mixture of $Fe(NO_3)_3{\cdot}9H_2O$ (99%, Aldrich) and Mo solution (9.8 mg ml^{-1} of Mo in H_2O) was dissolved in DI water for 1 h. In order to embed the Fe–Mo bimetallic catalyst onto the Al_2O_3 powder, the mixed Fe–Mo solution was introduced to the solution of Al_2O_3 powder and DI water followed by sonication for 1 h. In our experiment, the molar ratio of catalyst was $Fe:Mo:Al_2O_3 = 1:0.1:13$. After drying, the material was baked at 150 °C for 15 h in vacuum ambient and then ground in mortar to break the chunks into powder. For each synthesis, ~50 mg catalyst was placed in the quartz boat that was inserted into the center of a quartz tube (i.d.: 20 mm, length: 500 mm). The quartz tube mounted in an electrical tube furnace was then heated to 950 °C in Ar ambient. Subsequently, the mixture of Ar/C_2H_2 at a flow rate of 570 sccm (Ar/C_2H_2, 500:70) was introduced into the quartz tube for production of SWNTs. The flow rate of Ar/C_2H_2 was maintained for 10 min before the furnace was cooled to room temperature in Ar atmosphere.

The morphologies and microscopic structure of carbon nanotubes were characterized by the scanning electron microscopy (SEM) (Hitachi S-4700), high-resolution transmission electron microscopy (HRTEM) (JEOL, JEM-3011, 300 kV), and Raman spectrometer (Bruker RFS-100/S, excitation beam wavelength: 1064 nm).

Fig. 1(a) shows the SEM image of as-synthesized product, which indicates large amounts of entangled carbon filaments.

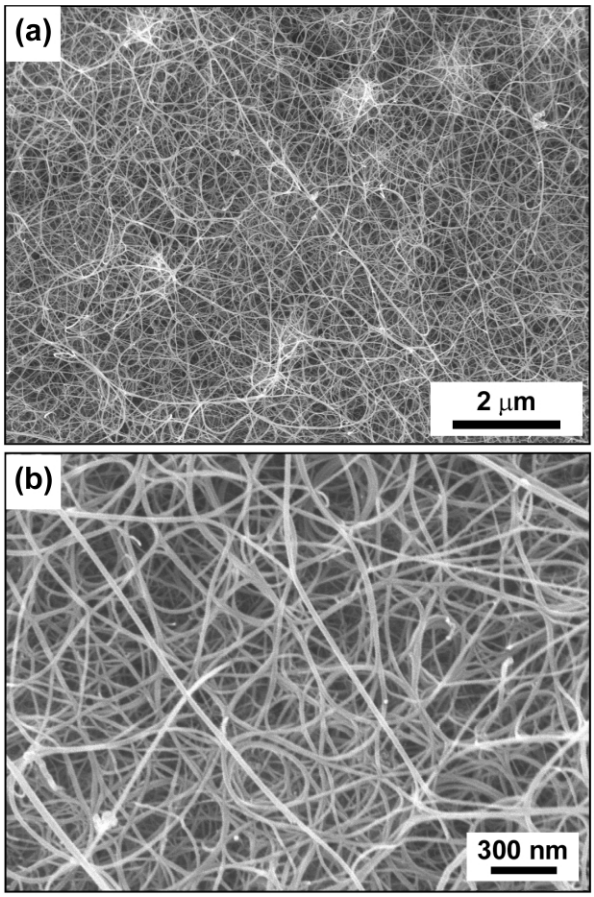

Fig. 1 SEM images of as-synthesized carbon nanotubes material by catalytic decomposition of C_2H_2 at 950 °C over Fe–Mo/Al_2O_3. (a) Low magnification SEM image, (b) higher magnification SEM image.

These filaments seem to be layer networks which are similar to purified SWNTs.[15] It is worth mentioning that the SEM image shown here is of as-synthesized samples and no-purification was conducted before the imaging. This suggests that a high yield of carbon filaments is obtained by C_2H_2 decomposition over the alumina supported Fe–Mo bimetallic catalyst. Fig. 1(b) is the magnified SEM image of as-synthesized carbon filaments. It clearly shows that the diameters of these carbon filaments are in the range 15–50 nm. From this image, one can clearly see that the overall catalyst surface is fully covered with carbon filament material.

The HRTEM image of as-synthesized samples is shown in Fig. 2, which provides structure details of the sample. It shows that carbon filaments observed in the SEM picture are bundles of SWNTs. The diameters of the SWNTs measured from the HRTEM observation are in the range 1.0–2.5 nm. Occasionally, we could find isolated SWNTs beside bundles of SWNTs. In general, the isolated SWNTs have a larger diameter compared with the individual SWNTs within the bundle.

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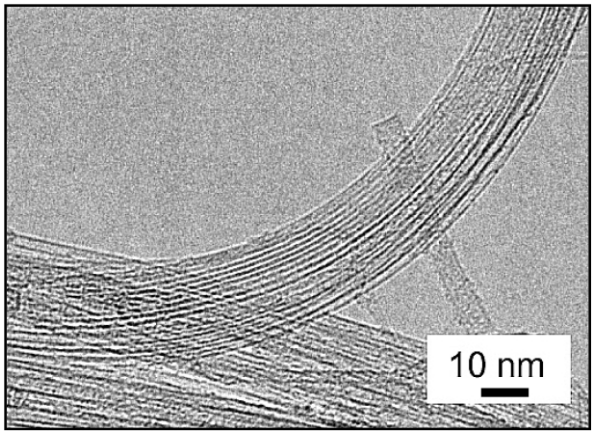

Fig. 2 HRTEM image of as-synthesized single-walled carbon nanotubes by catalytic decomposition of C_2H_2 at 950 °C over Fe–Mo/Al_2O_3.

Fig. 3 shows the Raman spectrum of the SWNTs materials. It reveals the characteristic narrow G-band at 1591.1 cm^{-1}, which has been assigned to the E_{2g} (stretching) mode of graphite. The strongest peak of G-band in the spectrum indicates a good arrangement of the hexagonal lattice of graphite. Whereas, the D-band at 1275 cm^{-1} indicates the level of disordered carbon. The weak D-band in the spectrum reveals the high purity of as-synthesized SWNTs. The spectrum obtained in low frequency domain shows eight components at 96.7, 109, 120.3, 133.3, 146.5, 162.8, 173.6, and 262.8 cm^{-1}. This frequency is related to the curvature of the nanotubes and therefore to the diameter of nanotubes. Generally, van der Waals interaction between the tubes appears because individual SWNTs are packed into bundles in the sample. In this case, the diameters of nanotubes can be calculated by the expression of w (cm^{-1}) = 6.5 + 223.75/d (nm)[16] (2.48 , 2.18 , 1.97 , 1.76 , 1.60 , 1.43 , 1.34 and 0.87 nm, respectively). The average diameter of SWNTs is about 1.70 nm. This value is in agreement with that from HRTEM images.

SWNTs prepared from C_2H_2 often suffer from amorphous carbon coating due to their self-pyrolysis at elevated temperature.[3] However, in this work, we see no amorphous carbon deposit on the surface of nanotubes. It is suggested that high-quality SWNTs result from the optimized C_2H_2 partial pressure. It has been shown that the growth rate of SWNTs prepared from catalytic decomposition of C_2H_4 and CO on the supported catalyst is limited by the supply of carbon to the catalyst particles.[7] We tried to investigate the effect of partial pressure on the synthesis of SWNTs. The results showed that increasing (Ar/C_2H_2, 500 sccm/100 sccm) or decreasing (Ar/C_2H_2, 500 sccm/40 sccm) of C_2H_2 partial pressure resulted in a lower yield of SWNTs. With the partial pressure in excess of 12443 Pa (Ar/C_2H_2, 500 sccm/70 sccm), more self-pyrolysis carbon was produced, which may induce inactivation of the catalyst particles, therefore decreasing the yield of SWNTs. These results suggest that the partial pressure of C_2H_2 is an important parameter for the synthesis of SWNTs. The above experimental results also indicate that the rate-limiting step is the carbon supply to the catalyst, which is affected by the partial pressure of C_2H_2.

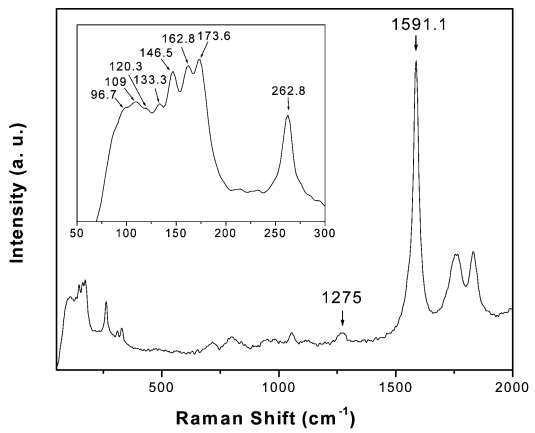

Fig. 3 Raman spectrum of as-synthesized single-walled carbon nanotubes by catalytic decomposition of C_2H_2 at 950 °C over Fe–Mo/Al_2O_3.

In summary, high-quality SWNTs have been produced by catalytic decomposition of C_2H_2 at 950 °C over Fe–Mo/Al_2O_3 catalyst. The synthesized SWNTs have a diameter in the range 0.87–2.48 nm. The average diameter of SWNTs is 1.70 nm. Our result demonstrates that C_2H_2 can be an ideal carbon feedstock to produce high-quality SWNTs over alumina supported Fe–Mo bimetallic catalyst.

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