Surface fractal dimension of single-walled carbon nanotubes

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Isolated single-walled carbon nanotubes (SWNTs), SWNT bundles, and ropes (or strands) show a structural self-similar characteristic. By calculating the Hausdorff dimension, it was found that their self-similar organization leads to surface fractality and the value of the surface dimension (D_s) depends on self-similar patterns. Experimentally, D_s obtained by nitrogen adsorption measurements at 77.3 K and by the small-angle x-ray scattering technique in our study proved our calculation that the surface dimension of SWNTs is nonintegral, $2 < D_s < 3$, which indicates that the surface of SWNTs is fractal. According to our calculation and analysis, the fractality is determined by the self-similar arrangement of SWNTs, but the value of D_s is also influenced by the effect of finite length and irregular aggregation of real SWNT samples.

I. INTRODUCTION

It is well known that single-walled carbon nanotubes (SWNTs) are apt to form into bundles and bundles may form into ropes.[1–5] Ebbesen *et al.* noticed the fractal-like growth pattern of multiwalled carbon nanotube arrays and figured out a schematic diagram of the fractal-like organization of carbon nanotubes, from the largest bundles down to individual carbon nanotubes.[6,7] And recently Pipes and Hubert[8] reported the self-similar organization of SWNTs: that is, carbon nanotubes form into bundles, bundles into wires, and wires into microfiber. However, whether the self-similarity organization of SWNTs leads to a fractal surface remains unknown. Generally, a perfectly smooth surface has a surface dimension $D_s = 2$, a fractal surface has $2 < D_s \leq 3$, and for a highly rough surface, $D_s = 3$.[9,10] Experimentally, the fractal dimension of solid surfaces can be determined with a variety of techniques, such as small-angle x-ray scattering (SAXS) analysis[11] and adsorption measurements.[10,12] Using the fractal analysis approach, extensive studies have revealed that, carbonaceous materials, such as carbon blacks [$D_s = 2.25 \pm 0.09$ (Ref. 13)], activated carbon [$D_s = 2.315$ (Ref. 14)], and carbon fibers [$D_s = 2.38 – 2.70$ (Ref. 10)], possess surfaces with fractality. As far as we know, however, the self-similar organization of SWNTs and the surface dimension of SWNTs have not been quantitatively calculated and characterized. However, the exploration of the application of carbon nanotubes, such as gas storage, requires knowledge of surface roughness and irregularity, which can be expressed by the surface dimension.[10,13]

In the present paper, the Hausdorff dimension[15] of SWNTs is calculated based on a self-similar organization model and the surface dimension of SWNTs is measured by the liquid nitrogen adsorption method and SAXS technique. Our experimental results proved our calculation that the surface dimension of SWNTs is nonintegral, indicating that the surface is a fractal surface. And according to our calculation and analysis, the fractality is determined by the self-similar arrangement of SWNTs, but the value of D_s is influenced by the effect of finite length and irregular aggregation of SWNTs.

II. MODELING AND CALCULATION

Figure 1 is a model used in our calculation based on the schematic diagram[7,8] of the self-similar organization of SWNTs, and every circle represents a unit (not necessarily a SWNT) with infinite length. And adjacent units are tangent. In Fig. 1, n is the times of similar transformations; ε, the yardstick, is the radius of the subunit after similar transformations for n times, and $\varepsilon = (1/3)^n$; N is the number of the smallest units in the structure and it is a function of n, $N = m^n$, and m is the number of subunits in one unit. For the organization in Fig. 1, $m = 7$. Figure 1(a) is the biggest unit with a radius of 1, Fig. 1(b) describes that the biggest unit is divided into 7 subunits ($m = 7$), and this can be sought as the first similar transformation, and Fig. 1(c) is the second similar transformation of the biggest unit. In the cross-sectional space, the Hausdorff dimension[15] can be calculated based on the relationship of N and ε by

$$D = \lim_{\varepsilon \to 0} \frac{\ln N(\varepsilon)}{\ln(1/\varepsilon)}. \tag{1}$$

For this type of self-organization in Fig. 1, $\varepsilon = (1/3)^n$ and $N = 7^n$, so $D = 1.77$.

Figure 2 describes different sizes of units. One big unit is made of 19, 37, and 61 subunits in Figs. 2(a), 2(b), and 2(c), respectively. Based on Fig. 2, the general expressions of $N, s,$ and m for this similar structure can be obtained, $m = 3s^2 - 3s + 1$, where s is a positive integer, $N(n) = (3s^2 - 3s$
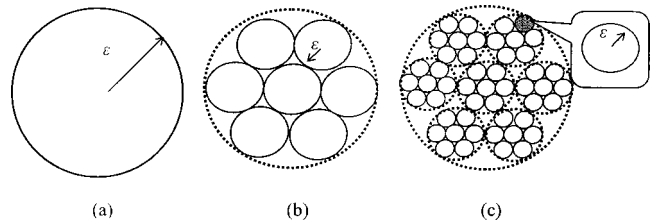

FIG. 1. The schematic diagram of the similar transformation and every unit is divided into 7 subunits by one time of similar transformation: (a) $n = 0$, $\varepsilon = 1$, $N = 1$; (b) $n = 1$, $\varepsilon = (1/3)^1$, $N = 7^1$; (c) $n = 2$, $\varepsilon = (1/3)^2$, $N = 7^2$.
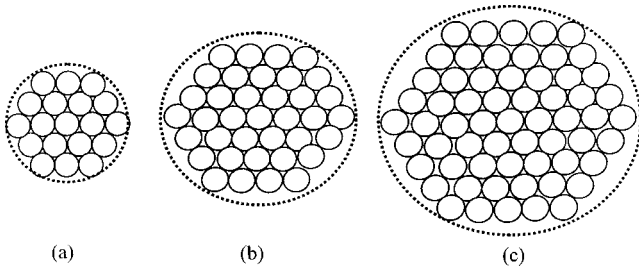
FIG. 2. The schematic diagram of the self-similar patterns and every unit is divided into m subunits by one time similar transformation: (a) $m=19$, $\varepsilon=(1/5)^n$, $N=19^n$, $D=1.83$; (b) $m=37$, $\varepsilon=(1/7)^n$, $N=37^n$, $D=1.86$; (c) $m=61$, $\varepsilon=(1/9)^n$, $N=61^n$, $D=1.87$.

$+1)^n$, and $\varepsilon=(1/r)^n$, where r is an odd number, $r=2s-1$. In Fig. 1, $s=2$, $m=7$, $\varepsilon=(1/3)^n$, and $N=7^n$. In Figs. 2(a), 2(b), and 2(c), $s=3$, 4, and 5, respectively. N, m, r, and ε can be obtained based on the values of s according to the general expressions above, and the values of D have been calculated according to Eq. (1), $D=1.83$, 1.86, and 1.87 for Figs. 2(a), 2(b), and 2(c). For the two limits, $m=1$ ($s=1$) and $m=\infty$, $D=1.5$ and 2, respectively. Therefore, for all values of m ($m=3s^2-3s+1$, $s=1,2,3,...$), the Hausdorff dimension exists and D is in the range of 1.5–2. So this self-similar organization leads to fractality in the cross-sectional space. In our model, all units have infinite length, so the dimension along the axis direction is 1. In this case, the fractal dimension in the three-dimensional space is $(D+1)$ without considering the effect of finite length.

III. EXPERIMENTS, RESULTS, AND DISCUSSION

To confirm our calculation, the surface dimension of SWNTs was measured by nitrogen adsorption measurements at 77.3 K and the SAXS technique in our study. The SWNTs used in this investigation were produced by a hydrogen-arc discharge method[16] and were purified according to the method of Hou *et al.*[17] With this procedure, SWNTs with a purity of above 90 wt % were achieved.

Nitrogen adsorption measurements at 77.35 K were carried out using a volumetric adsorption apparatus (ASAP 2010 M, Micrometritics Instrument). The fractality of many carbonaceous materials has been revealed through adsorption studies and the surface dimension D_s was often determined by the equation[10]

$$\ln\left(\frac{V}{V_m}\right)=\text{const}\times\tan t+(D_s-3)\left[\ln\ln\left(\frac{P_0}{P}\right)\right], \quad (2)$$
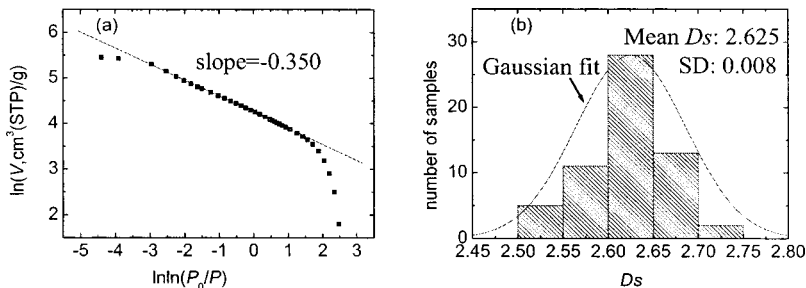
where V_m is the volume of adsorbed molecules in a monolayer at the standard temperature and pressure (STP), V is the volume adsorbed at equilibrium pressure P, D_s is the fractal dimension, and P_0 is the saturation pressure of the adsorbate. So by analyzing the relation between $\ln(V/V_m)$ and $\ln\ln(P_0/P)$, the fractal dimension D_s can be obtained by

$$D_s=S+3, \quad (3)$$

where

$$S=d[\ln(V/V_m)]/d[\ln\ln(P_0/P)]. \quad (4)$$

Figure 3(a) shows the nitrogen adsorption isotherm of SWNTs expressed as the relation between $\ln V$ and $\ln\ln(P_0/P)$. From Fig. 3(a), it is clear that Eq. (2) is applicable over a certain range of P/P_0 and it exhibits linearity with slope$=-0.350\pm0.002$ over a wide range. Conversion of the slope into a D_s value yields $D_s=2.650\pm0.002$ according to Eq. (3). Apparently, the value of D_s was nonintegral. The D_s distribution of 61 SWNT samples under investigation (including the data of two samples reported by Fujiwara *et al.*[18]) is shown in Fig. 3(b) with a Gaussian mean value of 2.625 ± 0.008. Two samples of Fujiwara *et al.*[18] have $D_s=2.698$ and 2.729, respectively.

SAXS is another common technique to measure the fractal dimension of porous materials. To confirm the values of D_s obtained from the above adsorption method, the SAXS technique was carried out using a PW1700 x-ray diffractometer (Philips Inc., Holand) with Kratky small-angle scattering accessory by Cu $K\alpha$ radiation. Generally, the analysis of the data of SAXS is based on Bale and Schmidt's theory,[11] and the intensity of radiation scattered on a fractal surface is often proportional to a negative power of the wave vector k:

$$I\propto k^{-\alpha}, \quad (5)$$

where

$$D_s=6-\alpha. \quad (6)$$

Usually this dependence is observed only when k satisfies the inequality $k\,\xi\gg1$, where ξ is the characteristic length of the structure producing the scattering. From the value of α one can determine the fractal nature of the system under investigation. For system with fractal surfaces, the exponent α varies between 3 and 4.

Figure 4 is the scattering curve of our SWNTs. For a wide interval of k, the curves exhibit linearity. By fitting the experimental data in the linear region, the values of the slope of $\log_{10}I$ versus $\log_{10}k$ were obtained, and $\alpha=3.400$

FIG. 3. (a) Nitrogen adsorption isotherms of SWNTs at 77.3 K expressed as the relation between $\ln V$ and $\ln\ln(P_0/P)$. (b) D_s distribution of 61 SWNT samples under investigation using data obtained from adsorption measurements.
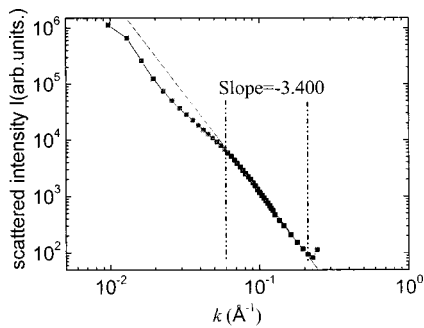
FIG. 4. Small-angle x-ray scattering pattern for SWNTs.

± 0.040 over the range of $0.051 \text{ Å}^{-1} < k < 0.210 \text{ Å}^{-1}$, so $D_s = 2.600 \pm 0.040$ according to Eq. (6). The values of D_s obtained from the SAXS technique ($D_s = 2.600 \pm 0.040$) and from adsorption measurements are quite consistent though not identical. The small deviation is due to the different physical background of the two methods. However, all results indicate that the surface dimension of SWNTs is non-integral, $2 < D_s < 3$.

Comparing with our calculated results above, the values of D_s obtained from experimental measurements are smaller. This is considered to be due to two deviations: the finite-length effect and the irregular aggregation of SWNTs. In our calculation, it is assumed that SWNTs are infinitely long and the dimension along the axis direction is 1. However, for real samples, especially the shortened ones by purification, SWNTs are finitely long and the dimension along the axis direction is less than 1. In addition to the finite-length effect, the real SWNTs are irregularly aggregated, much looser than closely packed SWNTs as described in Fig. 1 because there are many aggregated pores.[19] Therefore, the value of D_s may further decrease because of this irregular aggregation. Though the quantitative relationship between those deviations and the surface dimension remains unknown, the finite effect and the irregular aggregation must have influence on the surface fractality of SWNTs. Except the two deviations above, the impurity of amorphous carbon or other carbonaceous materials present in the sample may take an error as well.

Comparing with carbon blacks and activated carbon,[13,14] SWNTs have a higher fractal dimension value. We thought that it is attributed to the high aspect radio (length/diameter)

and the self-similar array of SWNTs. Pfeifer *et al.* observed high values of fractal dimension ($D = 2.85 - 3.0$) in activated carbon[20] and found that those samples with high values of fractal dimension exhibit volume fractal characteristics.[20,21] In our investigation of SAXS, SWNTs exhibit surface fractal dimension, different from those activated carbon samples with high values of fractal dimension reported by Pfeifer *et al.*[20] Ismail and Pfeifer[10] also measured the surface dimension of carbon fibers obtained from different precursors and found that their values of D_s changed in a wide range of $2.38 - 2.70$. Scanning tunneling micrographs for carbon fibers at the atomic level showed that the sample with the highest fractal dimension consisted of almost entirely nongraphitic, amorphous regions in the surface, which have not been observed in the SWNT samples in our investigation. Therefore we consider that the high value of D_s of SWNTs is not a volume fractal according to our SAXS experiments: moreover, it does not come from amorphous carbon regions in the surface, but it is determined by the self-similar array of SWNTs, as we calculated.

IV. SUMMARY

In summary, our calculation shows that SWNTs have fractal surfaces and the fractality is determined by the self-similar arrangement of SWNTs, but for real SWNT samples, the values of D_s, $D_s = 2.625$ and 2.600 from adsorption and SAXS measurements, respectively, decrease because of the effect of finite length and irregular aggregation of SWNTs compared with the calculated results ($D_s = 2.77$, 2.83, 2.86, 2.87). The value of fractal dimension denotes the surface roughness and irregularity of SWNTs, which may be helpful for an understanding of gas adsorption in SWNTs. Moreover, the concept of fractality can be introduced into the analysis of the specific surface area of SWNTs with different adsorbate gases.

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