Adsorption characteristics of heat-treated fullerene nano-whiskers

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Abstract. Fullerene nanowhiskers (FNWs) were synthesized by the liquid-liquid interfacial precipitation method and the adsorption properties of their heat-treated samples were characterized. It was found that vacuum-annealed FNWs at a high temperature are of microporous materials and, especially, ultramicropores are highly developed in these materials. Porosities even remain in samples after heat treatment at a temperature higher than 2273 K. The presence of ultramicroporosity is indicative of the molecular sieving properties of the vacuum-annealed FNW materials, suggesting the possibilities of their application as new materials for gas separation and gas storage.

1. Introduction

Fullerene (or C₆₀ molecule) has attracted a great deal of concerns since its finding in 1985 [1] from both fundamental and industrial fields, because of its unique structure and properties, and hopeful applications as superhard materials, lubricants, composite components, solar cell materials, and so forth. It is well-known that solid fullerene forms molecular crystal via van der Waals-type interaction among fullerene molecules. The fullerene crystal is generally of a face-centered cubic (fcc) structure with a lattice constant of 1.417 nm and C₆₀-C₆₀ distance of 1.002 nm, sublimates at a lower temperature (523~573 K) [2, 3], and is of semiconductor property with a band gap of 1.7 eV [4]. Sometimes the morphology of fullerene crystal can be controlled by controlling the crystalline growth conditions. Michaud and Céolin have found that needle-like fullerene crystals can be obtained by slow evaporation of solvents from the fullerene solutions in dichloromethane, n-hexane, etc [5, 6]. However, these needle-like crystals generally have big (20 to 100 μm in diameter) and long (0.2 to 20 mm in length) sizes.

Recently, Miyazawa et al have found that fullerene nanowhisker (FNW) and nanotube (FNT) consisting of C₆₀ molecules with nanosized diameter and high aspect ratio can be simply obtained by liquid-liquid interfacial precipitation method [7-9]. In this method, a poor solvent of C₆₀ molecules is contacted with a good solvent of C₆₀ molecules and the interfacial surface between the two solvents serves as the nucleation sites for fibrous crystal growth of C₆₀ molecules which are previously
dissolved in the good solvent. While the FNW and FNT materials are of attractive structures and properties, the heat-treated FNWs show unusual light-emitting property [10] and are expected as a new group of functional materials. In this study, we applied gas/vapor adsorption techniques to investigate the structural (porous) and surface properties of the heat-treated FNWs.

2. Experimental

2.1. Materials
Isopropyl alcohol (IPA) and toluene were used, respectively, as the poor and good solvents of C\textsubscript{60} for synthesizing the FNW samples. C\textsubscript{60} with purity of 99.5% purchased from MTR Ltd. (Cleveland, OH) was first dissolved into toluene to form a saturated solution containing 0.3 mass% C\textsubscript{60} molecules and IPA was gently layered on the solution to form a liquid-liquid interface. The solutions were kept still at 278 K for 7 days. The obtained needle-like C\textsubscript{60} crystals, i.e., fullerene nanowhiskers (FNW) were dried at room temperature (RT).

The FNW powders were evacuated at RT in a quartz cell, which was sealed by an oxyhydrogen flame in a vacuum with a pressure less than 10\textsuperscript{-5} Pa. The vacuum-sealed FNW powders were first heat-treated in a muffle furnace at 1173 K for 1 h. The collected 1173 K-treated samples were further treated in a carbon furnace under argon atmosphere at 2273 and 2773 K for 1 h. The obtained samples are denoted as FNW-T where T stands for the heat treated temperature.

2.2. Characterization and adsorption
The microscopic structures of samples were examined using a field-emission scanning electron microscope (SEM, JEOL JSM-6700F) and a high-resolution transmission electron microscope (HRTEM, JEM-4010, JEOL).

Adsorptions on samples were measured at 77 K for N\textsubscript{2} and 298 K for H\textsubscript{2}O and C\textsubscript{6}H\textsubscript{14} by a commercial volumetric apparatus (BELSORP 18A). The equilibrium time for each adsorption point was maintained at 10 min. Before N\textsubscript{2} adsorption, samples were pre-evacuated under 1 mPa for removing impurities. Any strong specific interaction between FNW-T samples and N\textsubscript{2}, H\textsubscript{2}O, or hexane molecule is hardly considered, since the FNW-T samples contain almost no surface functional sites. Hence, the FNW-T powders after N\textsubscript{2} adsorption were reused for H\textsubscript{2}O adsorption and those for H\textsubscript{2}O adsorption reused for hexane adsorption. The used FNW-T samples were evacuated again at 393 K for 2 h before reusing for the next run adsorption.

3. Results and Discussion

3.1. Microscopic structures
Miyazawa et al. has reported that structure and size of needle-like C\textsubscript{60} crystals can be controlled by changing the kind and volume ratio of solvents. While pyridine solvent leads to formation of fibrous fullerene crystals with tubular structure, toluene and \textit{m}-xylene solvents give rise to solid fullerene nanowhiskers [8, 9, 11]. Figure 1 shows the FE-SEM and TEM images of FNWs synthesized in this work. Coinciding with the previous reports, FNWs consist of large number of needle-like particles with a diameter ranging from 300 through 700 nm and a length generally surpassing 5 \textmu m. The TEM image clearly confirms that the needle-like particles are of solid property rather than tubular structure. The previous research reported the powder of pristine C\textsubscript{60} with a very small specific surface area (~20 m\textsuperscript{2}/g), despite that pores are directly detected on the surface of the FNWs prepared by use of benzene and IPA [12]. The solvent-wetted FNWs are of a hexagonal structure but transformed to the face-centered cubic (fcc) structure when completely dried, which is similar to that of the bulk C\textsubscript{60} powders, however, containing lots of lattice defects [13].
On the other hand, the morphologies of the heat-treated FNWs are not greatly changed as compared to the pristine FNWs (microscopic data omitted for simplicity). High-resolution TEM observation indicates that the fullerene crystal structure is completely destroyed by heat treatment above 1173 K and glassy carbon-like structures are formed, with the stacking carbon hexagon layers increasing with the increase of heat treatment temperature [14].

3.2. Nitrogen adsorption

Figure 2 shows the $N_2$ adsorption isotherms at 77 K on FNW-T. The $N_2$ adsorption on FNW-1173 presents a sharp uprising at very small relative pressure ($P/P_0$) ranges, followed by a gradual increase at higher $P/P_0$ ranges, indicating that the material possibly contains micropores and possesses comparatively a large part of external surface [15]. Hysteresis phenomenon is observed for this material (from the desorption branch of the isotherm), which is extended to very low $P/P_0$ ranges (<0.2). Since chemisorption or any kind of strong specific adsorption is not possible for $N_2$ adsorption, and structural changes such as swelling or shrinking of the material are hardly realized due to $N_2$ adsorption, the low pressure adsorption hysteresis of $N_2$ adsorption in this case can most possibly be attributed to the existence of pores or pore apertures with smaller
or competitive sizes as compared to nitrogen molecules.

\( \text{N}_2 \) adsorption gradually decreases with the increase in the heat treatment temperature. However, the adsorption isotherm on FNT-2273 is still of a typical type IV shape [15], indicative of formation of mesoporosity in this material. Thus, porosities in FNW-T are very tolerant to high temperature. On the contrary, the adsorption isotherm on FNT-2773 changes to a typical type III shape, manifesting the formation of low affinity surface toward \( \text{N}_2 \) molecules and almost disappearance of porosity.

For relative comparison among the heat-treated FNW samples, the following well-known Brunauer-Emmett-Teller (BET) equation was applied to obtain the pore parameters of the samples (though it is argument to use it for pore analysis of microporous materials):

\[
n = \frac{n_m C x}{(1-x)/(1-x+C x)}
\]

where \( n \) is the adsorption amount at \( x = P / P_0 \), \( n_m \) is the monolayer capacity of adsorption from which specific surface area, \( a_{\text{BET}} \), can be calculated, and \( C \) is a constant reflecting the interaction energy between adsorbate molecules and adsorbent surface. Table 1 shows the values of \( a_{\text{BET}} \) and \( C \) for the three samples from \( \text{N}_2 \) adsorption. The \( a_{\text{BET}} \) values of the FNW-T samples are much greater than that of the pristine FNW (around 20 m\(^2\)/g). Especially, the greatest \( a_{\text{BET}} \) value of FNW-1173 implies the evolution of a great amount of pores by vacuum annealing of FNW, lots of which are even retained after heat treatment at 2273 K. The greatest \( C \) value of this sample relates to the sharper uprising in \( \text{N}_2 \) adsorption at small \( P / P_0 \) ranges, which comes from a strong adsorbate-adsorbent interaction. The porosity of FNW-1173 may have some relationship with the destruction or partial destruction of fullerene cages, by which pore openings with molecular sizes are possibly formed.

### 3.3. \( \text{H}_2\text{O} \) and hexane adsorption

Figure 3 shows the \( \text{H}_2\text{O} \) adsorption isotherms at 298 K on FNW-T samples. While the adsorption amounts of \( \text{H}_2\text{O} \) on the three samples are the same sequence as those of \( \text{N}_2 \) adsorption (Figure 2), the adsorption isotherm of \( \text{H}_2\text{O} \) on FNW-1173 presents an unusual shape. It was known that \( \text{H}_2\text{O} \) adsorption on porous carbonaceous materials is generally very low at low \( P / P_0 \) ranges because of the hydrophobic carbon surface, and suddenly increases when \( P / P_0 \) surpasses a medium value (above ~0.4) [15]. An S-shaped isotherm of \( \text{H}_2\text{O} \), characteristic of an evident uprising in \( \text{H}_2\text{O} \) adsorption from the low \( P / P_0 \) ranges, can be observed on ultramicroporous materials due to the enhanced potential fields from the opposite walls of the ultrafine pores [15]. Although the specific surface area of FNW-1173 is much smaller as compared to the ordinary porous carbons of high specific surface area such as activated carbons, the \( \text{H}_2\text{O} \) adsorption on this material is sufficiently high at the low \( P / P_0 \) ranges so that the S-shape of the isotherms rather becomes evident at the low \( P / P_0 \) ranges. This result strongly suggests the existence of ultramicropores in the material which induces stronger interaction between pore walls and small molecules such as \( \text{H}_2\text{O} \).

To the contrast, the \( \text{H}_2\text{O} \) adsorption on FNW-2273 is very low at \( P / P_0 < 0.5 \),
characteristic of typical carbonaceous materials, with a broad hysteresis branch due to the mesoporosity. Because of less porosity, H₂O adsorption on FNW-2773 is very small in the whole P/P₀ range.

The values of BET specific surface area were calculated from H₂O adsorption isotherms and shown also in Table 1. Although the aBET values from H₂O adsorption are much smaller in comparison with that from N₂ adsorption for the FNW-2273 and -2773 samples because of the depressed H₂O adsorption at small P/P₀ ranges, that from H₂O adsorption is comparable with that from N₂ adsorption for the FNW-1173 sample, due to the enhanced H₂O adsorption at very small P/P₀ ranges.

Figure 4 shows the hexane adsorption isotherms at 298 K on FNW-T samples. All the isotherms exhibit a slight uprising at small P/P₀ ranges and, subsequently, a gradual increase at the higher P/P₀ ranges. The characteristics of isotherms on FNW-1173 and -2273 are the great low pressure hysteresis branches, indicating that both materials contain micropores with very small pore widths. Especially, the FNW-1173 material demonstrates a greater hysteresis; its hexane adsorption is comparable with that on FNW-2273 in the whole range despite that its N₂ and H₂O adsorptions are much higher. This result suggests that a part of pores in the material are hardly accessible to hexane molecules which have a larger molecular size as shown in Table 1. Therefore, the material presents molecular sieve property, containing ultramicropores excluding molecules with sizes greater than 0.43 nm. The vacuum-annealed FNW materials can thus possibly be a group of new material for the purposes of gas separation and gas storage.

| Adsorbate | Molecular size / nm | aBET / m²/g | FNW-1173 | FNW-2273 | FNW-2773 |
|-----------|---------------------|-------------|-----------|-----------|-----------|
| N₂        | 0.364               |             | 195       | 140       | 80        |
|           | C                   |             | 795       | 22        | 1.4       |
| H₂O       | 0.265               | aBET / m²/g |           |           |           |
|           | C                   |             | 155       | 3         | 2         |
| Hexane    | 0.43                | aBET / m²/g |           |           |           |
|           | C                   |             | 4         | 26        | 33        |

Figure 4. Hexane adsorption isotherms at 298 K on FNW-T samples.
4. Conclusion

Liquid-liquid interfacial precipitation using toluene and IPA solvents provides non-tubular FNWs with a diameter greater than 300 nm and a length longer than 5 μm. While the morphology of FNW is maintained by high temperature annealing, the fullerene structure is destroyed and changes to a glassy carbon-like structure. Adsorption measurements using probe molecules of different molecular sizes and of different polarities confirm that the vacuum-annealed FNW materials are highly porous and contain ultramicropores of molecular sizes, leading to molecular sieve properties. By optimizing the synthesis method and conditions, these materials can possibly become a group of new nanoporous materials for applications in gas separation and gas storage.

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