Shaping Carbon Nanotubes with Chemistry

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Abstract

As-grown, string-shaped single-walled carbon nanotubes were transformed into other shapes by applications of organic chemistry. Cutting carbon nanotubes in strong acids affords oxygen-containing groups at both ends of the open tubes. These groups were utilized for ring-closure reactions in very dilute conditions. Atomic force microscopy reveals ring-shaped nanotubes with a mean diameter of 540 nm as products. Also, the end groups were used to react with the surface amine groups of PAMAM dendrimer. It gave star-shaped structures in which straight nanotubes are radiating from dendrimer centers. These experiments clearly demonstrate that covalent chemistry is useful for construction of super-structured carbon nanotubes.

Introduction

A single-walled carbon nanotube (SWNT) has a structure of a single sheet of graphite rolled to a few nm in diameter and over microns in length [1]. Ever since their discovery in 1991 [2], SWNTs have attracted the attention of researchers for their excellent physical properties. So far, all fundamental studies and applications have been based on their native string-like form, simply because this is the only shape that the present growth methods afford [1, 3]. Unlike thin wires made of ordinary metals, SWNTs possess one-dimensional electronic character and ballistic transport. Thus, it is of great interest to have SWNTs in various other shapes for the development of new quantum devices. In this paper, we demonstrate that chemical modification is useful for transforming its shape or constructing larger-scaled structures with string-shaped SWNTs by introducing two examples: formations of rings and stars.

Organic reactions typically proceed in solution. Despite their importance, hardly anything is known about the behaviors of SWNTs in solution. We begin by briefly describing dispersing properties of acid-treated SWNTs in various solvents. The modification studies further help to gain deeper insight into physical properties of SWNTs in solution.

Dispersions

In order to perform common chemical reactions, it is necessary to disperse SWNTs in solution. Pristine SWNTs, however, do not disperse in any solvent to significant amounts suitable for reactions. Although addition of surfactant molecules helps them to disperse, these additives may interfere
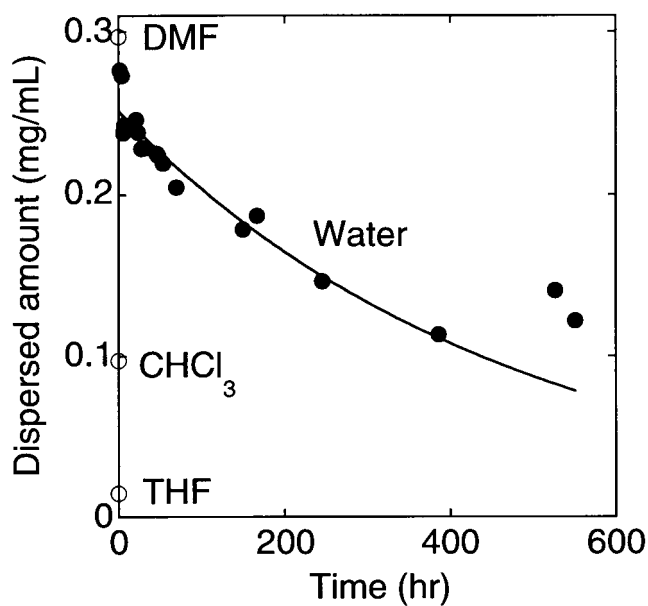

Figure 1. The dispersed amount in various solvents. A temporal change was also followed in 10 mM NaOH. The solid curve is an exponential function with a time constant of 470 hr.

with chemical reactions and are difficult to separate during purification. Another way to improve dispersibility is to cut SWNTs into short pieces by ultrasonicating in strong acids [4]. This inevitably damages SWNTs and introduces various chemical groups at defect sites as well as open ends [5]. The damage extends so far that pristine hydrophobic tubes become strongly hydrophilic. Nevertheless, we can take this damage as an advantage for chemical modifications. Cut SWNTs are then etched with H_2O_2/H_2SO_4. Etching introduces oxygen-containing groups, such as carboxylic acids and phenolic hydroxides, to the damaged sites, which can be used for further modifications [4, 6, 7].
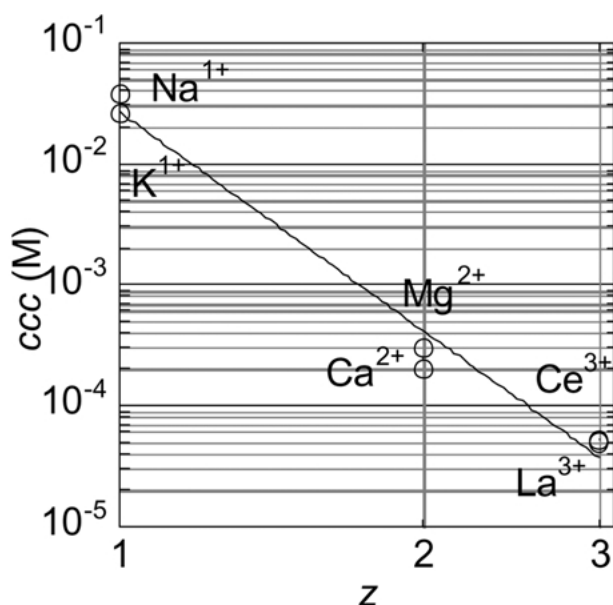
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Figure 1 shows the dispersed amounts of the acid-treated SWNTs in various solvents [8]. The dispersed amount is defined here as the concentration of SWNTs in a supernatant solution after being centrifuged at 3500 g. Although the absolute values depend on the strength of centrifugal forces, the relative amounts can be taken as a measure of dispersing ability. SWNTs are dispersed relatively well in water and DMF, but only poorly in THF and chloroform. In all cases, several SWNTs bundle together to form a rope. Ropes coagulate even in water, although the process is slow with a time constant of 470 hr. Experimentally, we have found that once SWNTs are brought into poor dispersing solvents, they do not re-disperse even when the solvent is exchanged for a better one.

In aqueous solution, the acid-treated SWNTs possess an anionic charge. Upon addition of counter ions, SWNTs coagulate critically at concentrations that depend on the ionic valency [9]. Critical coagulation concentrations follow the Schulze-Hardy rule [10, 11] as shown in Figure 2. This means that SWNTs in electrolytes behave as kinetically stable colloids. In the case that chemical reactions occur in aqueous conditions, it is important to keep cation concentrations low so that SWNTs stay dispersed.

Rings

Ring-closure of SWNTs can be achieved by coupling the oxygen-containing groups by suitable reagents, such as 1,3-dicyclohexylcarbodiimide, under very dilute conditions in DMF [12]. It is extremely important to keep SWNTs as dispersed as possible throughout all procedures. Once coagulated, it is difficult to re-disperse bundles using mild methods. Bimolecular reactions are suppressed by maintaining the SW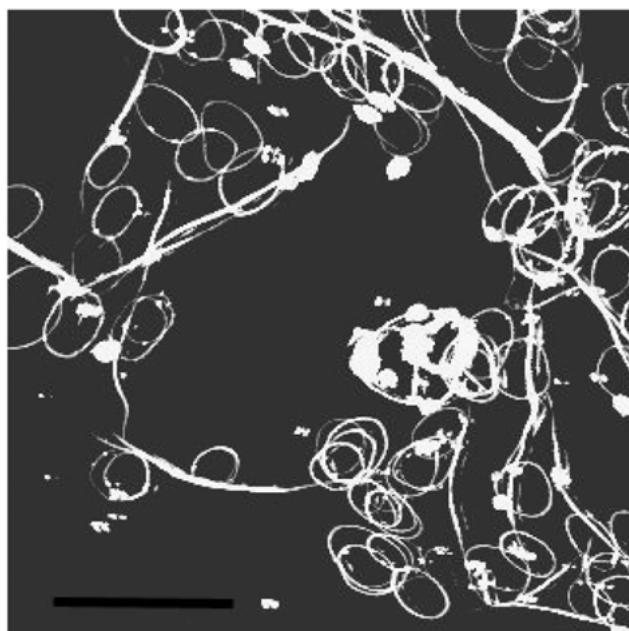NT concentration very low. Since the absolute amount of dispersed SWNTs in DMF is not so large and the concentration must be low to make coagulation as slow as possible, this requirement is automatically fulfilled. We have removed very long SWNTs by centrifugation.

Atomic force microscopy (AFM) reveals ring-shaped nanotubes in the reaction mixture, as displayed in Figure 3. The average ring diameter is 540 nm. Figure 4a shows a histogram of SWNT contour length prior to the reaction as measured directly from AFM images of cast films. It has a maximum below 1 μm and a decaying tail to several mm. In contrast the rings have a narrow contour distribution centered at 1.7 μm (Figure 4b). Thus, only a part of string-shaped SWNTs was converted to rings. To understand this result, we note that pristine SWNTs in vacuum are stiff and straight. In order for a chain of finite stiffness to close itself, the chain must be long enough so that thermal fluctuation can bring its two ends together. What is not known is the chain stiffness in solution. So, we have taken the above result to find out the stiffness in solution, assuming that elastic property is the limiting factor for ring-closure. A statistical polymer model has been developed to give the ring-closure probability of a stiff chain with a persistence length p as a function of contour length L [13, 14]. The theory predicts that the probability remains nearly zero until L = $2p$, then increases sharply and stays roughly the same for longer L. The narrow ring size distribution results from this sharp rise of closure probability at $2p$ and a smaller number of the longer SWNTs in the starting solution. The least-squares fit of the measured ring contour distribution with the theory gives p = 0.8 μm. In other words, SWNTs shorter than 0.8 μm behave stiff and straight, whereas those longer than $2p$ = 1.6 μm are semi-flexible. The value of 0.8 μm is comparable to the stiffest organic polymers, such as cellulose derivatives, but is rather small if we consider that SWNTs have a Young modulus of 1 GPa in vacuum [15].
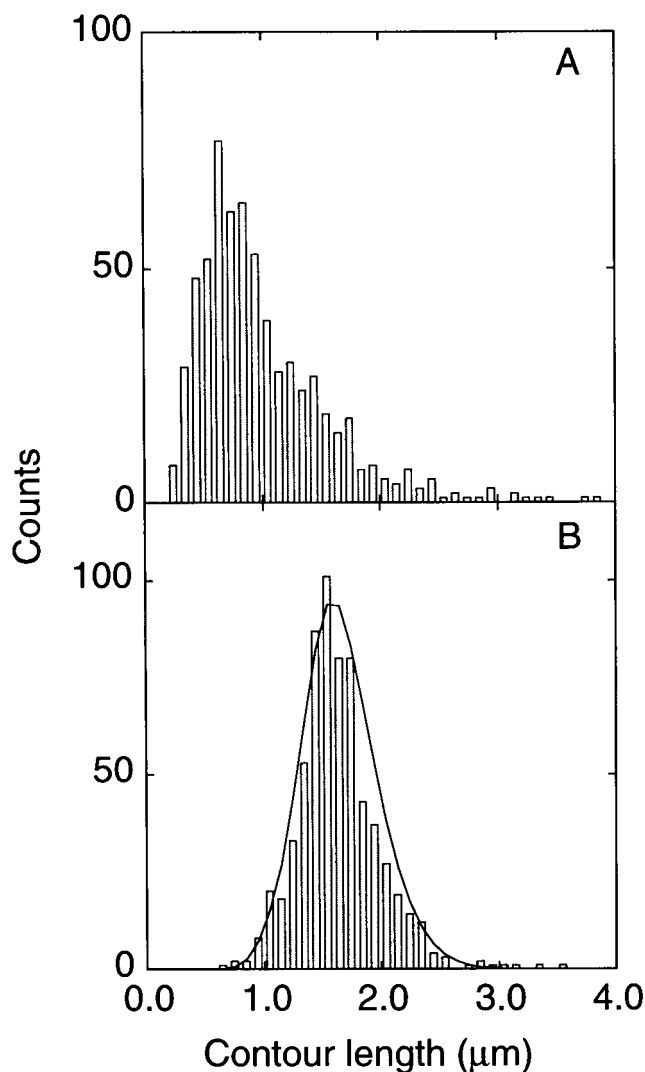
Figure 4. Histograms of contour length measured directly from AFM images of cast films for (A) SWNTs before reactions and (B) the rings. The solid curve represents a theoretical polymer model with a persistence length of 0.82 μm.

Figure 5. SEM image of nanotube stars on mica. Pt-Pd coated.

recognized in a reaction mixture when it included shorter tubes.

Conclusions

We have demonstrated that, by properly controlling solution behaviors, it is possible to construct super-structures of SWNTs using common organic chemistry. Both examples resulted in modifications of open ends. This suggests that the acid groups on the ends are more reactive than those on the side walls. Investigating the reactivity of other functional groups will be the next step toward the development of a general procedure for constructing super-structures.

Stars

As the previous example shows, SWNTs after the acid treatments have broad size distributions. The mole fractions of short tubes are usually much larger than those of longer tubes. As far as intermolecular reactions are concerned, the dependence of reactivity on size becomes an essential factor in constructing large-scale structures with SWNTs. Especially, if the reactivity of short tubes is high, the normally larger diffusion of small objects implies that all reactive sites may be used up by short tubes before longer tubes have a chance to attack. We have tested this idea by reacting SWNTs with dendrimers.

Using centrifugation, acid-treated SWNTs with roughly 1 μm length were collected. Carboxylic acid groups were converted to acid chlorides by refluxing SWNTs in thionyl chloride. It was then reacted with amine-terminated generation 10 PAMAM dendrimers. The SEM image of Figure 5 shows star-shaped structures in which many straight SWNTs radiate from a dendrimer at the center [16]. Stars were not
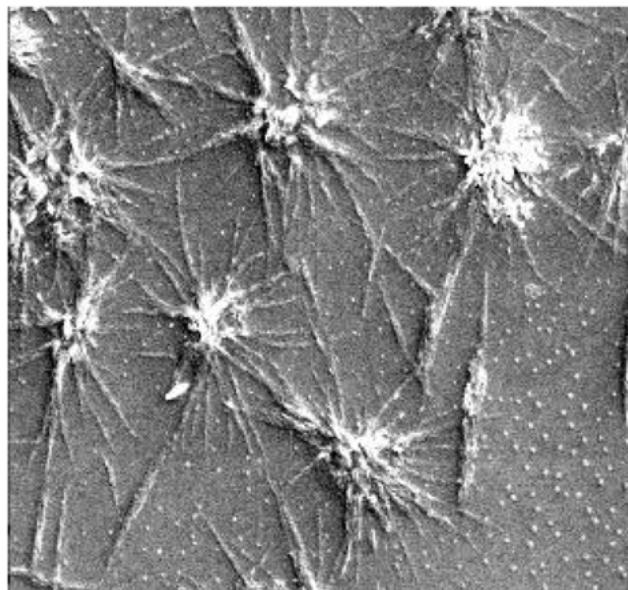
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