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# Effect of Hydrogen on Polymerizing the Fullerene Molecules in the Single-wall Carbon Nanotubes

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Forming rate of inner tubes via the heating of $C_{60}$ encased single-wall carbon nanotubes (peapods) can be controlled by the pre-heating in hydrogen gas. Once the peapods were heated in the hydrogen at 1100 °C, polymerization of $C_{60}$ molecules drastically suppressed and this effect remains for a while even after exhausting the hydrogen gas. Then, the polymerization rate gradually recovered. This phenomenon reminds that the hydrogen gas effectively controls the chemical reaction in such a confined nano-space without destructing the original features.

Polymerization between the $C_{60}$ molecules proceeds under irradiation of ultraviolet rays to the $C_{60}$ film[1] and to the peapods.[2] Energy of the ultraviolet rays is in the range of 3–4 eV, and the magnitude of the C–C interaction in the $sp^2$ bonded carbon network is known to be ca. 3 eV.[3] This energetic consistency is considered to be a principle in the polymerization. On the other hand, $C_{60}$ polymerization in the nanotube is taken place gradually at the temperature of ca. 1000 °C in vacuum.[4] This temperature corresponds to the energy of ca. 0.1 eV and is considerably lower than that of ultraviolet ray. Recently, the enhancement of $C_{60}$ polymerization in the nanotube was found in the inert gas environments.[5] For instance, by the heating in He, the polymerization rate was increased by ca. 9 times as compared with that in vacuum. Mechanism of this enhancement is not clear, but it is of interest in the aspect of controlling the reaction rate. Here, we report the effect of hydrogen gas on the $C_{60}$ polymerization in the nanotube that indicates considerable suppression on the polymerization, and this suppression remains rather long time. Such opposite feature against the enhancement observed for the inert gas suggests that the polymerization rate can be controlled by inletting or exhausting the hydrogen gas during the heat treatment. In this paper, we describe the details of hydrogen effect on the polymerization and discuss the facts in connection with the chemical reactivity of hydrogen.

Peapods were prepared by the vapor-phase reaction of paper-formed SWNTs and $C_{60}$ molecules in the vacuum-sealed glass ampoule at 400 °C. Although the details of the preparation procedure can be found in the literature already published,[4] it should be noted here that the most important process in the preparation is to clean up the tube surface and to open the tube-end or sidewall of the tubes, which were achieved by conducting the heat treatment in the flux of dry air at 480 °C. After exposing the $C_{60}$ vapor to the SWNTs for 2 days, peapod sample was taken out from the ampoule and used in this study.

High-temperature heat treatments of the peapods were carried out in the following instruments: one is the thermogravimetric analyzer of Q600 made by a TA Instruments, and the other is the vacuum tight tube furnace. Experiments by using Q600 were conducted in a 50 sccm of mixture flux of Ar (99.999%) and $H_2$ (99.99999%) at 760 Torr with the ramp rate of 5 °C/min to 1200 °C, where the $H_2$ flux was introduced just in front of the sample pan. Concentrations of hydrogen were changed between 0 and 10%. Experiments by using the tube furnace were executed in a 100 Torr of Ar flux (100 sccm) at 1100 °C.

Raman spectra were recorded at room temperature by using a Bruker RFS100 spectrometer with the laser excitation of 1064 nm. Diameter of the laser beam on the sample was ca. 100 µm, and the laser output was selected at 20 mW in order to avoid heating the sample.

Although the formation of inner tubes can be directly observed by the transmission electron microscopy,[4] it is rather difficult to evaluate quantitatively the yield of inner tubes due to artificial selection. Instead of direct observation, the formation of inner tubes can be also understood from the radial breathing mode (RBM) Raman signals in the range between 250 and 450 $cm^{-1}$; especially the bands at ca. 340 and ca. 360 $cm^{-1}$ (see the peaks on the dotted lines in Figure 1), which associate with the inner tubes. In vacuum, these peaks gradually grow and it takes more than 24 h at 1200 °C until the Raman intensities saturate.[5] On the other hand, in Ar environment, it takes only 4 h.[6] In Figure 1, this condition consists with the case for 0%

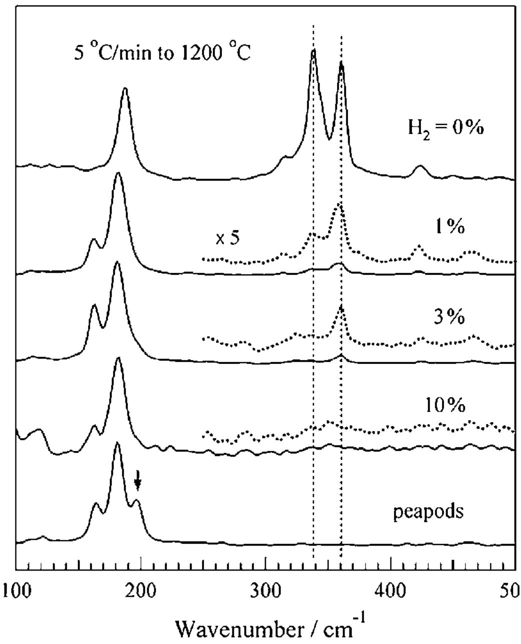

**Figure 1.** Raman spectra recorded in the RBM region. The bottom spectrum is from pristine peapods, and other spectra are from the heated samples in various concentrations of $H_2$. The peak at ca. 180 $cm^{-1}$ was used for normalization. Excitation wavelength is 1064 nm.

of $H_2$ (see the top spectrum). Raman spectrum of pristine peapods is indicated in the bottom of Figure 1. In this spectrum, any peaks associated with the inner tubes were not recorded. Characteristic Raman peak for the highly filled peapods can be seen at ca. $200\,cm^{-1}$ (see the down-pointed arrow peak). We temporary assigned this peak to the $C_{60}$ filled stiffened RBM band of original tubes with the diameter of ca. 1.4 nm,[6] and this band can be easily weakened by annealing in vacuum at ca. 800 °C without changing the spherical shape of encased $C_{60}$ molecules.[4] When we mix 10% of $H_2$ in Ar flux and conduct the high-temperature treatment, no Raman peak associated with the inner tubes can be recognized but a drastic decrease of ca. $200\,cm^{-1}$ band was observed as shown in the spectrum denoted as 10% of Figure 1. These facts mean that the $H_2$ gas certainly suppressed the polymerization between $C_{60}$ molecules but some structural relaxation occurred due to high-temperature treatment. Suppression of polymerization due to $H_2$ can be also recognized in the case for 1% of $H_2$. In 1 and 3% of $H_2$, weak Raman signal associated with the smaller diameter inner tubes (peak at ca. $360\,cm^{-1}$ that corresponds to the diameter of ca. 0.69 nm) was dominated rather than the signal at ca. $340\,cm^{-1}$ (corresponding to ca. 0.73 nm in diameter), and the intensity is slightly stronger for 1% sample (see the signals on the dotted lines in Figure 1). Since the small diameter tubes, whose diameters are almost the same as that of $C_{60}$, are grown at the initial stage of $C_{60}$ polymerization and next the diameter transformation is taken place in order to match up the layer spacing with the van der Waals distance, observed phenomena of growing ca. $360\,cm^{-1}$ band indicate that the polymerization rate is strongly suppressed by $H_2$ gas and is dependent on the small concentration of $H_2$.

Yield of the inner tubes was estimated by the following way: the Raman spectra were normalized with the peak intensity of ca. $180\,cm^{-1}$ band. Next the Raman signals were integrated between 300 and $400\,cm^{-1}$, and the yield of inner tubes was evaluated by using this magnitude. Results are in Figure 2, where the data of pristine peapods (solid circles) and $H_2$ treated peapods (open circles) are indicated as a function of the heating time in Ar flux. The latter sample of $H_2$-treated peapods means that the pristine sample was in advance heated in a 100% of $H_2$ flux at 1100 °C for 1 h in the tube furnace, and then used for this experiment. According to Figure 2, yield of inner tubes for pristine peapods was first rapidly increased in an hour treatment and then indicated a gentle slope. On the other hand, $H_2$-treated peapods did not show such a rapid increase on the yield, but indicating gradual increase until ca. 5 h, and then the increasing rate became almost the same with that of pristine peapods. That is, the suppression of polymerization due to $H_2$ remains rather long time even after exchanging the environment gas to Ar. This means that the hydrogen molecules should have some interaction with $C_{60}$ molecules, and therefore may cause slight modification on the electronic structure of peapods via the electron doping or chemical reaction.

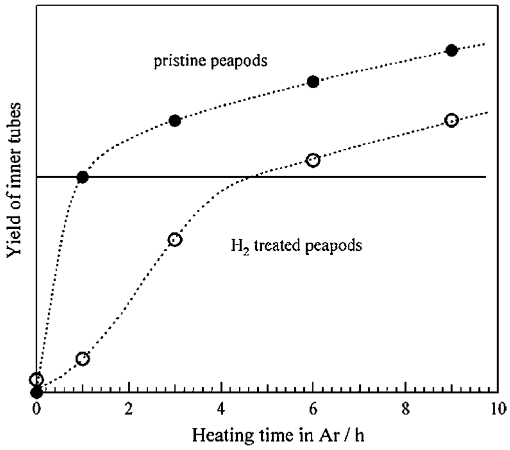

**Figure 2.** Formation yields of inner tubes as a function of heating time in Ar. Heating temperature was kept at 1100 °C. Formation yields were estimated by the Raman intensities of $300–400\,cm^{-1}$ band. The dashed lines are for eye guide. For $H_2$-treated peapods, forming rate of inner tubes resumes after ca. 5 h heating as indicated with the curves above the solid line.

Present experimental results clearly showed that the $H_2$ gas effectively suppressed the polymerization of $C_{60}$, and this effect remained rather long time even at 1100 °C and gradually recovered. We therefore consider that the $H_2$ molecules keep remaining around the $C_{60}$ molecules of peapods at room temperature like as a stable compound and prevent the reaction of polymerization. When the temperature is elevated, such $H_2$ molecules are gradually released from the peapod without destruction of $C_{60}$ and tube structures. Then, the reaction for forming the inner tubes proceeds like as to resume the polymerization in the pristine peapods. That is, the hydrogen acts as like a pinning material on the fusing process of $C_{60}$ molecules. Such chemical feature is useful for controlling the reaction rate, and it may be possible to perform detailed investigation of intermediates that will be formed in the tube.

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