Research Article

Nanocomposite Materials of Alternately Stacked C₆₀ Monolayer and Graphene

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We synthesized the novel nanocomposite consisting alternately of a stacked single graphene sheet and a C₆₀ monolayer by using the graphite intercalation technique in which alkylamine molecules help intercalate large C₆₀ molecules into the graphite. Moreover, it is found that the intercalated C₆₀ molecules can rotate in between single graphene sheets by using ¹³C NMR measurements. This preparation method provides a general way for intercalating huge fullerene molecules into graphite, which will lead to promising materials with novel mechanical, physical, and electrical properties.

1. Introduction

C₆₀ intercalated graphite has previously been designed, and the electronic properties and stabilities have been studied theoretically [1]. It is also reported that the C₆₀ intercalated graphite may possess potential applications in semiconductor [2] and hydrogen storage device [3]. On the other hand, fullerene molecules, especially, C₆₀, also have unique lubrication effects, and they have been treated as a lubricant due to their spherical shape [4–6]. Up to now, we have studied C₆₀ monolayers confined by graphite flakes [7] and C₆₀ monolayers included among graphite [8–10], which, interestingly, exhibit ultralow friction, because quasi-freely rotating C₆₀ molecules act as molecular bearings. However, it is quite difficult to perform a mass production for intercalating C₆₀ molecules into graphite and to provide nanomaterials with a perfectly alternate stacking of C₆₀ monolayer and graphene in previous studies.

Here we show nanocomposite materials consisting alternately of a stacked single graphene sheet, by the graphite intercalation technique in which alkylamine molecules help intercalate large C₆₀ molecules into the graphite.

2. Experimental

First, graphite oxide (GO) was synthesized from graphite powder with an average size of 500 μm (Nippon Carbon Co., Ltd.) in accordance with the Hummers method [12] with some modifications, and the intercalation of octylamine into graphite (GO-OA) was performed as described previously in [13, 14]. Next, octylamine-intercalated graphite oxide (GO-OA) was added to fullerene solution (100 mg of C₆₀ dissolved in 100 mL toluene), and after that, the toluene used was evaporated at room temperature, leaving behind in the products (GO-OA-C₆₀). The C₆₀ fullerene used in this experiment was purchased from Frontier Carbon Co., Ltd, in

FIGURE 1: XRD intensity from as-prepared samples. (a) XRD intensity from graphite oxide (GO) and alkylamine-intercalated graphite oxides (GO-amine) with different chain lengths ($C_nH_{2n+1}NH_2$) ($n = 3$ – 8). The peaks of GO and GO-amine are indicated by the arrows in the figure. (b) XRD intensity from GO-amine with different chain lengths in C_{60} solution ($n = 3$ – 8).

FIGURE 2: XRD intensity from the specimens heated for 80 minutes at 600°C under a high vacuum of 10^{-6} Torr for the GO- C_{60} specimens of Figure 1(b).

Japan. The products of GO-OA- C_{60} were treated with 0.1 N hydrochloric acid solution at room temperature for at least 30 minutes and dried in air at 80°C overnight to remove the octylamine, resulting in the C_{60} -intercalated graphite oxide (GO- C_{60}). Finally, in order to remove C_{60} powders that are not intercalated into the graphite, and moreover, to remove octylamines that are intercalated into the graphite, GO- C_{60} was heated for at least 80 minutes at 600°C under a high

FIGURE 3: XRD intensity from the specimens heated for 80 minutes at 600°C under high vacuum of 10^{-6} Torr for alkylamine-intercalated graphite oxide (GO-amine).

vacuum of 10^{-6} Torr, which results in the nanocomposite consisting alternately of a stacked single graphene sheet and a C_{60} monolayer. All specimens were analyzed by using X-ray diffraction (Rigaku RINT 2200/PC diffractometer: CuK α radiation at 40 kV and 30 mA), FT-IR spectroscopy (FTIR: JASCO 480 Plus FT-IR spectrometer: the samples in KBr pellets), NMR (our original 7.1 T spectrometer with a Tecmag Apollo spectrometer and a Doty SuperSonic MAS

FIGURE 4: FT-IR spectra from the specimens of Figure 2. The C_{60} intermolecular IR-active (F_{1u}) modes are indicated in the inset of the figure.

FIGURE 5: The ^{13}C NMR spectra for the specimens of Figure 2 at room temperature. Only one sharp line with a peak position of 144 ppm [11] was observed.

7 mm probe head), and high-resolution electron microscopy (JEM3100FEF: a lattice resolution of 0.1 nm when it is operated at an acceleration voltage of 300 kV).

3. Results and Discussion

Figure 1(a) shows the X-ray diffraction (XRD) intensity from graphite oxide (GO) and alkylamine-intercalated graphite oxide (GO-amine) with different alkyl chain lengths ($\text{C}_n\text{H}_{2n+1}\text{NH}_2$) ($n = 3$ to 8). The appearance of a peak in the GO of Figure 1(a) shows that the spacing between graphite oxide sheets is approximately 8 Å, which is identical to the published data [12]. It is found that the spacing between graphite oxide sheets in the case of the GO-amine ($n = 3$ to 8) increases with the increase in the length of the alkyl chain incorporated in the interlayer space of the GO. Figure 1(b) shows the XRD intensity from the GO-amine ($n = 3$ to 8) in C_{60} solution, which we call the C_{60} -intercalated graphite oxide (GO- C_{60}). It should be noted that there appear drastic changes in the XRD intensity between $n = 5$ and $n = 6$ in Figure 1(b), which indicates that C_{60} molecules are intercalated in the interlayer space of the GO by the driving force of alkylamine situated at between the graphene oxide sheets when the interlayer space is sufficiently larger than the C_{60} molecule. However, there exist many C_{60} powders which are not intercalated into the GO in these GO- C_{60} specimens because the stronger peaks, (111), (220), (311), (222), (331), (420), (422), and (511), of XRD intensity from C_{60} powders (JCPDS file No.44-0558) appear in the spectra of Figure 1(b). In order to remove C_{60} powders that are not intercalated into the GO, and moreover, to expel the alkylamines which are intercalated into the graphite, the GO- C_{60} specimens of Figure 1(b) were heated for 80 minutes at 600°C under a high vacuum of 10^{-6} Torr, as shown in Figure 2. It should be noted that $n = 6$, $n = 7$, and $n = 8$ have broad peaks of A and B corresponding to d -spacings of 9 Å and 4.6 Å, respectively, in addition to a broad peak of $d = 3.3$ Å corresponding to the spacing of graphite layers, although $n = 3$, $n = 4$, and $n = 5$ have only a single broad peak of $d = 3.3$ Å. Since the GO-amine reverts to the graphite layers when alkylamines leaves the GO-amine host after heating at up to 600°C, as shown in the XRD intensity of Figure 3, the graphene oxide layers in

FIGURE 6: High-resolution electron microscope (HR-TEM) image and structure model of alternately stacked graphene sheets and C_{60} monolayers. (a) High-resolution electron microscope (HR-TEM) image from the nanoribbon of the specimens of Figure 2. Graphene layers (area: A) and C_{60} molecules between graphene sheets (area: B) are shown. (b) Structure model of alternately stacked graphene sheets and C_{60} monolayers, where C_{60} molecules can rotate between graphene sheets.

the GO- C_{60} , which do not include C_{60} molecules, also revert to the graphite layers when alkylamines go out from it after heating. It is expected that the peaks of A and B ($n = 6$ to 8) in Figure 2 are due to the d -spacing between the graphenes intercalating the C_{60} monolayer and their stacking faults (the disorder of the stacking) [15], respectively. However, since peak A is also widely distributed, the d -spacings between the graphenes intercalating the C_{60} monolayer are considered to be widely distributed.

Figure 4 shows the FT-IR spectra from the specimens of Figure 2. This result is consistent with the conclusion based on Figure 2 that C_{60} molecules can be intercalated into the GO with alkylamine chains longer than that of $n = 5$ because the FT-IR spectra from $n = 6$, $n = 7$, and $n = 8$ in Figure 4 exhibit the C_{60} intermolecular IR-active (F_{1u}) modes [11] although those with the shorter alkylamine chains do not exhibit these modes. However, one mode of 526 cm^{-1} among IR-active (F_{1u}) modes only appears in these FT-IR spectra because the number of C_{60} molecules included in the specimens is rather small.

The rotational dynamics of C_{60} molecules between graphenes have been investigated by ^{13}C NMR in the temperature range from room temperature to -80°C . We prepared C_{60} materials 20–30% enriched in ^{13}C in order to increase the ^{13}C NMR signal. The present specimen was mixed with Na_2SO_4 in a weight ratio of 1:50 to avoid arcing in a NMR probe. The NMR experiments were performed at 75.4 MHz for ^{13}C in an external field of 7.1 T by the pulse inversion recovery method. ^{13}C NMR spectra were taken by Fourier transforming the signal following the $\pi/2$ pulse. The typical $\pi/2$ pulse width was 5.4 μs . It is well known that for C_{60} molecules in solid C_{60} at room temperature, large rotational motion averages out the chemical-shift anisotropy (CSA) and the ^{13}C NMR spectra show motional narrowing of 2.5 ppm in width. In contrast, spectra broaden at low temperature and develop the CSA power pattern with a CSA tensor with the principle values $\delta_{11} = 213\text{ ppm}$, $\delta_{22} = 182\text{ ppm}$, and $\delta_{33} = 33\text{ ppm}$ [11].

Figure 5 shows the ^{13}C NMR spectra for the specimens of Figure 2 at room temperature, where the ^{13}C NMR spectrum at room temperature is the same as that at the temperature of -80°C . Only one sharp line with a peak position of 144 ppm was observed, and its line shape is a Gaussian-like function with an FWHM value of 5 ppm. The positions are in good agreement with the average principle values for C_{60} molecules in solid C_{60} , and the linewidth is about one-twentieth narrower than that of the powder pattern [11]. These observations clearly demonstrate the lack of the polymerization [16] of C_{60} molecules in the present material. Furthermore, the observed Gaussian-like line shape means a motional narrowing and that C_{60} molecules rotate quasi-freely with a correlation time on the order of 10 ps. This correlation time is similar to that of the same case [17]. This means that no strong bonding such as chemical bonding between the graphenes and C_{60} molecules is made, and C_{60} molecules easily rotate for outer force.

It is possible that the specimens in the case of Figure 2 are broken into nanoribbons of nanometer thickness by ultrasonic vibration, which is analogous to the preparation method of the graphene nanoribbon. A high-resolution electron microscope (HR-TEM) image of the nanoribbon is shown in Figure 6(a). First, two parts of graphene layers (areas A) are shown in Figure 6(a). A missing rows of zigzag chains clearly appear in the graphene network, which indicates that the thickness of the specimen is on an atomic scale [18], and moreover, moiré patterns formed by graphenes also appear in area A. It is expected that the contrast of area B originates from the C_{60} molecules confined between graphene sheets, although we will discuss this contrast later in detail. Now we illustrate the structure model of C_{60} -intercalated graphite in Figure 6(b), that is, the nanocomposite consisting of alternately stacked graphene sheets and C_{60} monolayers in which C_{60} molecules can form a monolayer and rotate between graphene sheets.

4. Conclusion

At present, preliminary experiment indicates it is possible to intercalate huge fullerene molecules, such as C_{70} and $La@C_{82}$ larger than a C_{60} molecule into graphite. Hence it is expected that the unique structure comprising huge fullerene molecules intercalated into graphite will give rise to attractive novel applications such as superlubrication materials, variable nanocapacitance, nanoswitches, and hydrogen storage in the future. Moreover, since the tribological test of grease and oils with an additive of this nanocomposite powder exhibits excellent lubricating performance with an ultralow friction previously unattained, the structure and material properties are expected to be more attractive also from scientific and material points of view. These are examples of the application that shows the novel mechanical property, and the intercalated materials will lead to promising materials with novel mechanical, physical, and electrical properties.

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