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In situ probing of acidic groups on acid-treated carbon nanofibers using 1-aminopyrene

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Abstract

Acidic functional groups produced on the surface of acid-treated carbon nanofibers (CNFs) were characterized by fluorescence measurements using 1-aminopyrene (1-AP) as an in situ probe molecule. The 1-AP molecules only slightly interacted with the untreated CNF surface, whereas the 1-AP cation-like bands were observed on the HNO_3-treated and HNO_3/H_2SO_4 treated CNF surfaces. These results indicate that 1-AP was tightly immobilized by the hydrogen bonding interaction between its amino group and the Brönsted-acidic groups on the CNF surface. A stronger acid treatment (with HNO_3/H_2SO_4 mixture) caused the chemical modification to generate higher amounts of the acidic functional groups on the CNF surface.

Keywords: Carbon nanofibers; 1-Aminopyrene; Adsorption; Fluorescence; Acidic functional groups

1. Introduction

Developing the technology to control the structure of materials on a nanosize scale is necessary in order to obtain certain physical and chemical properties of the nanomaterials. Carbon nanofibers (CNFs) [1–3] are very large multi-walled carbon nanotubes and are technologically easier and economically more favorable to produce than individual single- or double-walled carbon nanotubes [4,5]. The CNFs are valuable materials for electronic, mechanical, and optical devices because of their unique structural and quantum characteristics that are similar to small-sized carbon nanotubes [1–3,6–9]. For practical use, such carbon nanomaterials need to be well dispersed throughout other raw materials. An example of this is the incorporation of carbon nanomaterials into plastics or ceramics, which provide practical materials with well-defined shape and increased strength. Composites of matrices with dispersed carbon nanotubes have been prepared by the polymerization of a polyimide under sonification [10] and by the sol–gel reaction of a system containing a relatively large amount of *N*,*N*′-dimethylformamide as the starting material [11]. However, carbon nanomaterials have a high specific surface area and easily aggregate. Surface functionalization of the carbon nanomaterials is an effective method to disperse them throughout various media for producing new functional materials, which utilize their unique characteristics [12–14]. In order to functionalize these carbon nanomaterials one must treat their surface with acids or other chemicals. Treatment of the carbon nanomaterials with nitric acid and sulfuric acid leads to the oxidation of their surface that forms oxidized groups such as –COOH and –C=O within the graphene sheet [15–17]. Generally, the surface functional groups of the modified CNFs are characterized by IR or Raman spectroscopy. It is, however, difficult to obtain quantitative information of the chemical species existing in a monolayer or only a few layers of the oxidized surface of the CNFs using these analyses.

We have previously shown that observing the fluorescence spectra of 1-naphthol (1-NP) is a useful probe on a molecular level for studying the physicochemical properties of the surrounding environment around the 1-NP [18–23]. In situ fluorescence measurements of non-treated and acid-treated CNFs using 1-NP as a physicochemical probe revealed two types of adsorption onto the surface of the CNFs when they were dispersed in solvents and the sol–gel reaction systems of silicon alkoxide. One is generated by the π–π interaction between 1-

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NP and the graphene sheet and the other is the hydrogen-bonding interaction between 1-NP and proton-accepting groups such as –COOH (–COO^-) and –C=O [21–23]. Our unique procedure to create a highly disperse system of CNFs throughout solvents allowed these observations even though the fluorescence of aromatic molecules adsorbed on carbon materials has scarcely been observed due to strong quenching.

1-Aminopyrene (1-AP) is a Brönsted base and is expected to interact with acidic groups on a solid surface [24,25]. In this study, oxygen-containing functional groups produced on the surface of the acid-treated CNFs, especially acidic groups such as –COOH [26,27], are characterized by UV–vis spectroscopy and the fluorescence measurements using 1-AP as a molecular probe. 1-AP is suitable as a fluorescence probe since its spectrum drastically changes with the acid–base equilibrium compared with those of aminonaphthalene or aminoanthracene.

2. Experimental

1-AP (Wako Pure Chemicals, S grade) was recrystallized three times from water. Concentrated nitric acid and sulfuric acid (Wako Pure Chemicals, S grade) were used as received. All water used was ion-exchanged and distilled. The CNFs (VGCF, vapor grown carbon fiber) having a diameter ca. 200 nm, a length of ca. 10–20 μm, and a surface area of ca. 15 $m^2\ g^{-1}$, were provided by Showa Denko Co., Ltd. [3]. Functionalization of the CNF surfaces was carried out in two ways with liquid acid, as reported in the literature [15–17,21,22]. The first was by refluxing the CNFs in concentrated nitric acid at 393 K for 24 h followed by rinsing them with copious amounts of water and allowing them to dry at room temperature under vacuum. For a stronger treatment procedure, the CNFs were sonicated in a concentrated H_2SO_4/HNO_3 mixture (3/1 in volume) at 313 K for 24 h. They were then refluxed in a mixture of concentrated sulfuric acid and 30% aqueous hydrogen peroxide (4/1 in volume) at 343 K for 24 h and were refluxed in concentrated nitric acid at 393 K for 24 h. They were then rinsed with copious amounts of water until the washings were confirmed neutral using a pH test paper and allowed to dry at room temperature under vacuum. Untreated CNF sample was also used. Designation is held throughout this paper as the following: Untreated CNFs (N-CNF); CNFs treated solely with nitric acid (A-CNF); CNFs treated with both sulfuric and nitric acids (AA-CNF).

The surface structures of the three CNF samples were hardly distinguished by their TEM images. These images are not shown here because they agreed with previously reported results [28,29]. The SEM images and IR spectra of these samples have been described elsewhere [23].

The N-, A-, and AA-CNFs were individually dispersed in the 1-AP solutions containing water and ethanol (4/1 in volume) at 1.0×10^{-4} mol dm^{-3} by ultrasonic irradiation for 1–18 days. The resulting suspensions were centrifuged to remove any precipitates. The UV–vis absorption, fluorescence, and fluorescence excitation spectra of the resulting supernatant suspensions were measured. The UV–vis absorption spectra were measured using a Shimadzu UV-3150 spectrophotometer, and the fluorescence and excitation spectra were measured using a Shimadzu RF-5300 spectrofluorophotometer. The excitation wavelength for the fluorescence spectra was 350 nm, and the emission wavelength for the excitation spectra was 420 nm. The UV–vis absorption spectra of the supernatant suspensions after the centrifugation confirmed that a certain amount of CNFs was dispersed there. The suspensions contained slightly amounts of acids and were almost neutral.

3. Results and discussion

3.1. Changes in UV–vis absorption spectra of CNF suspensions

The adsorption of 1-AP on the CNFs and the dispersion of the CNFs into the liquid phase were examined by UV–vis absorption of the CNF suspensions. In the N-CNF suspension, only slight temporal changes in the spectrum are observed. This suggests that 1-AP was not adsorbed on the N-CNF surface as readily as 1-NP [21,22]. Our experiments revealed that the N-CNF adsorbed pyrene much better than 1-AP though the results are not shown here. This adsorption property indicates that the polar amino group prevents the π–π interaction between the pyrene ring and graphene sheet even though pyrene molecules are adsorbed onto the carbon nanotubes by this interaction [30,31]. Fig. 1 shows the absorption spectra of the AA-CNF suspension containing 1-AP observed immediately after the preparation, and after the ultrasonic irradiation for 4–11 days. In the AA-CNF and A-CNF suspensions, the absorbance gradually decreases with time. We conclude from these data that there is an interaction between 1-AP and the acid-treated CNFs.

Fig. 2 displays the changes in the absorbance of each CNF suspension at 350 and 500 nm versus the ultrasonic irradiation time. The absorbance at 350 nm indicates the amount of 1-AP existing in the liquid phase. 1-AP was hardly adsorbed on the N-CNF, but was adsorbed on both the A-CNF and the AA-CNF. The AA-CNF was seen to adsorb the 1-AP at a faster rate than the A-CNF. The absorbance at 500 nm corresponds to the degree of CNF dispersion according to a good correlation

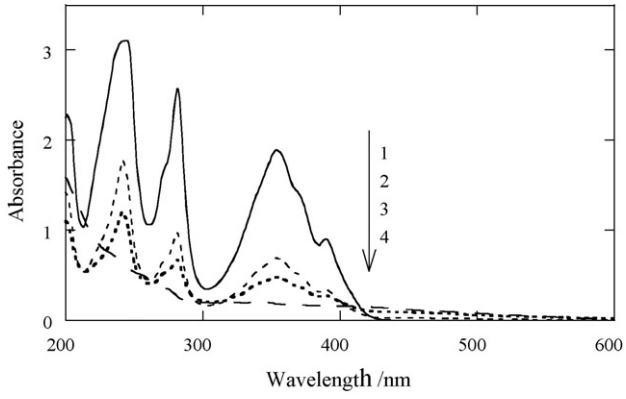

Fig. 1. Absorption spectra of AA-CNF suspensions containing 1-AP observed (1) just after the preparation and after ultrasonic irradiation of (2) 4 days, (3) 7 days, and (4) 11 days.

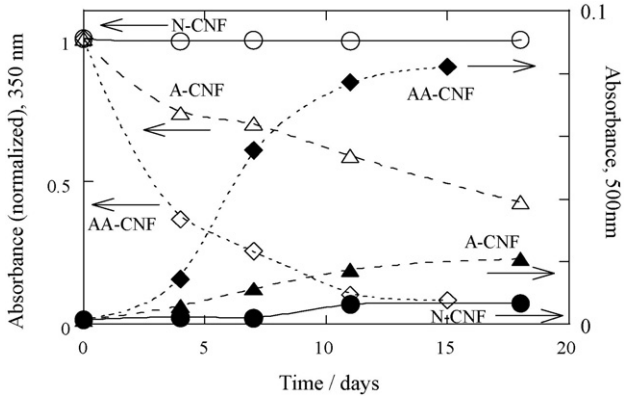

Fig. 2. Changes in absorbance vs. ultrasonic irradiation time monitored at 350 (open dots) and 500 nm (closed dots) in N-CNF, A-CNF, and AA-CNF suspensions.

between the concentration and the absorbance of the carbon nanotubes in a solvent [32]. Such nanocarbon materials exhibit the broad absorption spectra over a wide range of UV–vis-IR due to the superposition of various electric structures originating from many species [33,34]. The wavelength of 500 nm was selected to observe the dispersion because 1-AP have no absorption at longer wavelength than around 450 nm and the CNFs have higher absorption at shorter wavelength. The absorbance increased with the ultrasonic irradiation time until reaching saturation. These results indicate that the degree of CNF dispersion of each sample is ordered in this way; AA-CNF, A-CNF, N-CNF, with AA-CNF being most highly dispersed. This order is closely correlated to the amount of adsorbed 1-AP. In addition to the surface modification by the acid treatment the adsorption of aromatic molecules should also play an important role in the CNF dispersion [22].

3.2. Changes in fluorescence and fluorescence excitation spectra of CNF suspensions

1-AP exhibits a protonation equilibrium; the original species is called AP, and the protonated species is called APH^+. The proton dissociation equilibrium constant of the ground state (pK_a) and the excited state (pK_a^*) are 2.8 and −1.2, respectively [35]. Therefore, in moderately low-pH solutions, 1-AP exists as APH^+ in the ground state, deprotonates to form AP in the excited state, and then emits fluorescence.

Fig. 3 shows the fluorescence and fluorescence excitation spectra of 1-AP in the AA-CNF suspension immediately after preparation and after ultrasonic irradiation for 4–11 days. The broad bands of fluorescence around 440 nm and fluorescence excitation around 350–400 nm are assigned to AP in the liquid phase of the suspension since they coincide with the spectra of 1-AP in neutral polar solvents [24,25]. The shape of this excitation spectral band is also similar to that of the absorption spectra of 1-AP shown in Fig. 1. The fluorescence spectral bands around 360–400 nm and fluorescence excitation spectra around 300–360 nm are similar to those of APH^+ in the acidic solution. Their relative intensities increased with ultrasonic irradiation time. The spectra of APH^+ are

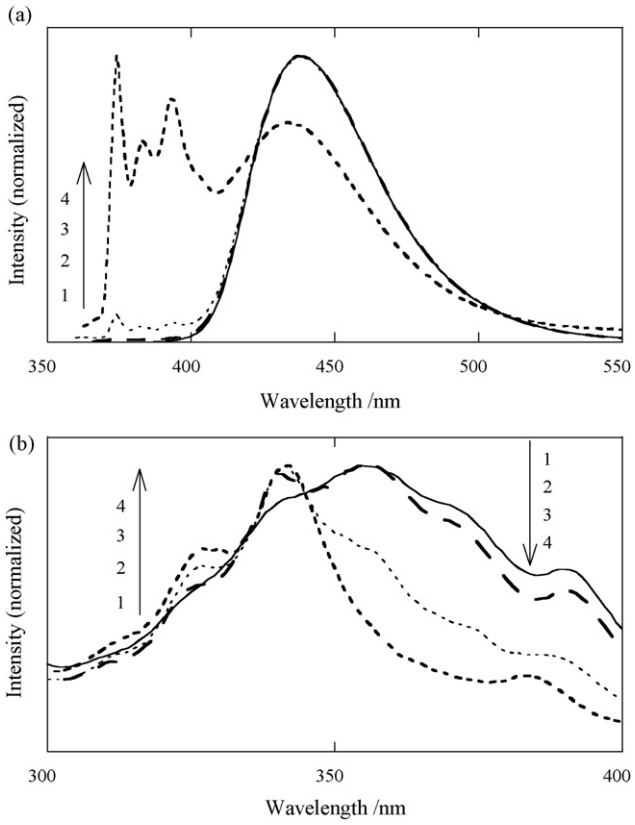

Fig. 3. (a) Fluorescence and (b) excitation spectra of 1-AP in AA-CNF suspension observed (1) just after the preparation and after ultrasonic irradiation of (2) 4 days, (3) 7 days, and (4) 11 days.

structurally similar to those of pyrene because the interaction between the free electron pair of nitrogen and the π-electrons in the pyrene ring is blocked by protonation of the amino group [24,25]. These results of the fluorescence indicate that 1-AP is adsorbed on the CNF surface to form APH^+-like species.

In a previous study, the ^1L_b fluorescence of 1-NP, which is observed in nonpolar environments, was seen on the CNFs due to π–π interaction between 1-NP and the graphene sheet [21–23]. The N-CNF cannot readily adsorb 1-AP molecules due to its low dispersibility throughout the solvent (Fig. 2(b)). Some amount of 1-AP should be adsorbed onto the graphene sheet of the acid-treated CNFs because they are better dispersed throughout the liquid phase [28,29]. Unlike the 1-NP species, fluorescence was not observed, however, from the 1-AP species adsorbed through π–π interaction onto the CNFs. This is due to quenching that occurs in the more strongly interacting 1-AP/CNF systems.

Fig. 4 shows the changes in the fluorescence intensities of 1-AP in the CNF suspensions as a function of the ultrasonic irradiation time. The fluorescence intensities of each CNF suspension at 375 nm per unit dispersed-CNF amount are plotted versus time. These values were obtained by dividing the original fluorescence intensities by the absorbance at 500 nm for each sample. The N-CNF did not adsorb 1-AP whereas the AA-CNF readily adsorbed 1-AP as the APH^+-like species. The A-CNF adsorbed 1-AP at an intermediate rate. The order of the adsorp-

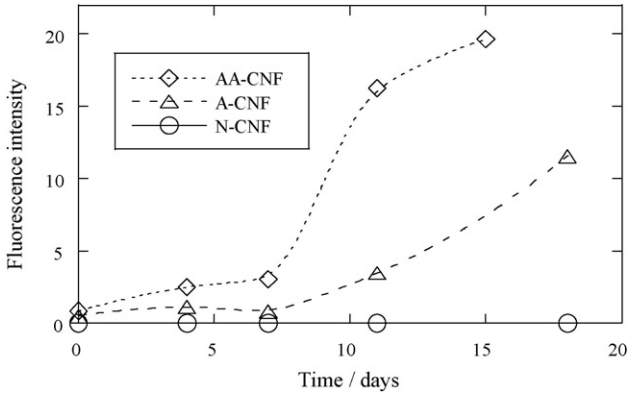

Fig. 4. Changes in fluorescence intensities of 1-AP per unit dispersed-CNF amount vs. ultrasonic irradiation time monitored at 375 nm in N-CNF (◯), A-CNF (△), and AA-CNF (◊) suspensions. The values were obtained by dividing the original fluorescence intensities by the absorbance at 500 nm for each sample.

tion ability of the CNF samples agreed with that estimated from the UV–vis absorption spectra depending on the CNF dispersion into the solvent.

It was previously reported that the ion-pair fluorescence of 1-NP was generated by the relatively strong hydrogen-bonding between 1-NP and the oxidized groups, such as –COOH, –C=O, and –OH [21,22]. As a Brönsted base, 1-AP is expected to interact with the acidic oxygen-containing groups and selectively detected the acidic groups such as –COOH. It is suggested that 1-AP was immobilized by the hydrogen bonding between its amino group and the Brönsted-acidic groups on the CNF surface, leading to the formation of APH^+-like species. This behavior agrees with previously reported results that the carboxyl group on the carbon nanotube surface is modified by amines forming the ionic bond of $–COO^- {}^+H_3N–$ [26,27]. The fluorescence intensities per unit dispersed-CNF amount for each CNF sample indicate that its adsorption ability depends on not only the CNF dispersion into the solvent but also the amounts of the acidic groups on the CNFs.

3.3. Confirmation of formation of APH^+-like species

The desorption of 1-AP from the AA-CNF surface was examined by fluorescence measurements in order to confirm the adsorption of 1-AP on the CNFs as shown in Fig. 5. Fig. 5(a) shows the fluorescence spectra of 1-AP in the AA-CNF suspension observed before and after adding sodium hydroxide. The fluorescence of the APH^+-like species was seen in the original suspension even though the suspension is nearly neutral. After adding the basic NaOH, the structural band of the fluorescence spectra disappeared. This result indicates that the 1-AP molecules that were adsorbed onto the CNF surface as the APH^+-like species were desorbed from the surface into the liquid phase. The APH^+-like species and the acidic groups should be deprotonated and would then hardly interact with one another since the pH value in the suspension was greater than 13. The adsorption and desorption equilibrium was shifted to the desorption process under this condition.

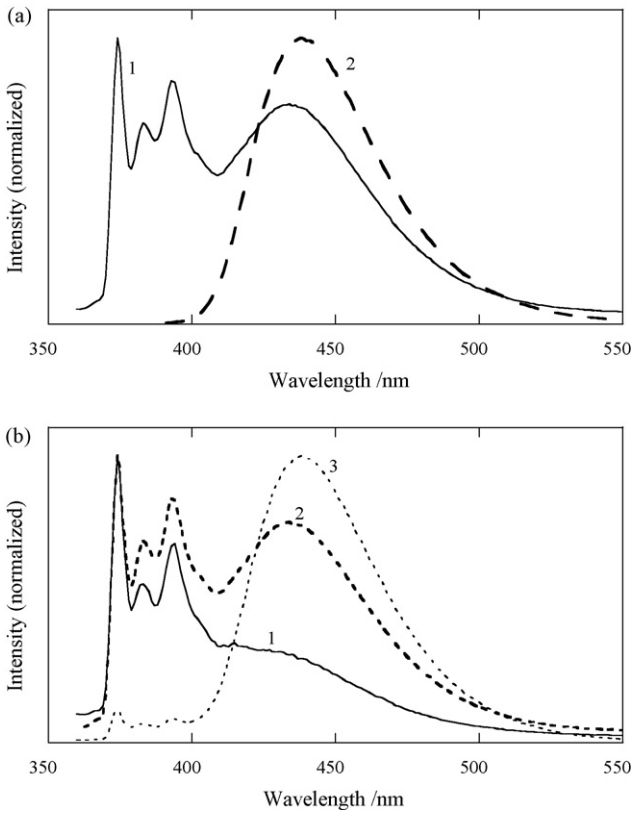

Fig. 5. Fluorescence spectra of 1-AP (a) in AA-CNF suspension observed before (1) and after (2) adding sodium hydroxide and (b) in suspension re-dispersing the 1-AP-adsorbing AA-CNF observed after ultrasonic irradiation of (1) 1 h, (2) 2 h, and (3) 5 h.

We examined the changes in the fluorescence spectra of the suspension re-dispersing the 1-APadsorbing AA-CNF as shown in Fig. 5(b). The suspension of the 1-AP-adsorbing AA-CNF was filtered, and then re-dispersed into pure water. The APH^+-like band intensity decreased with time while the AP band intensity increased with time. This result indicates that a portion of the 1-AP molecules that were adsorbed onto the CNF surface as an APH^+-like species were desorbed from the surface and then diffused into the liquid phase. The results shown in Fig. 5 support the adsorption of 1-AP onto the CNF surfaces as an APH^+-like species.

4. Conclusions

Brönsted-acidic functional groups produced on the acid-treated CNF surface were detected using 1-AP as a fluorescent probe. 1-AP was adsorbed onto the CNF surface by the hydrogen-bonding interaction between the amino group of 1-AP and the acidic functional group such as –COOH on the CNF surface to form APH^+-like species. A stronger acid treatment caused the chemical modification to generate higher amounts of the acidic functional groups on the CNF surface. For this reason the more strongly treated CNFs (AA-CNF) was better dispersed in the 1-AP solution and adsorbed a higher amount of 1-AP than the weakly treated CNFs (A-CNF). The quantitative analysis of the adsorption sites is now in progress and will be completed in the near future.

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