Quantitative characterization of acidic groups on acid-treated multi-walled carbon nanotubes using 1-aminopyrene as a fluorescent probe

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Abstract

Acidic functional groups produced on the surface of acid-treated multi-walled carbon nanotubes (MWCNTs) were quantified by fluorescence measurements using 1-aminopyrene (1-AP) as an in-situ probe molecule.   The 1-AP cation-like bands were observed on the HNO_3/H_2SO_4 mixture-treated MWCNT surfaces because the 1-AP molecule was tightly immobilized by the hydrogen bonding interaction between its amino group and the Brönsted-acidic groups on the MWCNT surface.   The fluorescence measurement allowed us to confirm the Langmuir-type adsorption of 1-AP on the functional groups of the MWCNTs, and estimate their amount of the functional groups and adsorption equilibrium constant.   A longer acid treatment caused the chemical modification to generate higher amounts of the Brönsted-acidic functional groups and improve the adsorption ability on the MWCNT surface.   About 2% of carbon in the MWCNTs was oxidized by the 24-h acid treatment.   This value corresponded to 15−22% of carbon in the surface layer.

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1. Introduction

Advanced industry requires a nanotechnology to synthesize nanosized materials having a specific function. Carbon nanotubes (CNTs) are one of the most noteworthy materials for electronic, mechanical, and optical devices due to their unique structural and quantum characteristics [1–9]. Such carbon nanomaterials need to be functionalized on their surface in order to interact with other substances. For example, they should be well-dispersed in other raw materials, i.e., the incorporation of the carbon nanomaterials in plastics or ceramics provide practical materials with a certain shape and chemical and physical properties. Composites of matrices with dispersed CNTs were prepared, for example, by the sol−gel reaction of a system containing CNTs as the precursor chemical [10–12]. Surface functionalization of the carbon nanomaterials is an effective factor to allow them to easily interact and bond with various media for producing new functional materials utilizing their unique characteristics [13–15]. Therefore, CNTs can strongly interact with various matrices by pretreating their surface chemical structure with acids or other chemicals. The acid 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 in the graphene sheet [16–18]. Generally, the surface functional groups of the modified CNTs should be characterized by IR or Raman spectroscopy. However, it is difficult to obtain quantitative information about the chemical species existing in a monolayer or a few layers on the oxidized surface using these analyses. The quantification of the surface oxidized groups was performed by acid−base titration [19,20], XPS spectroscopy [20,21], and fluorescence measurement using fluorescent labeling [21−23]. The fluorescence measurement can more selectively and sensitively detect and quantify the oxygen containing functional groups of the nanoparticles than the other methods [22].

Carbon nanofibers (CNFs) [1,2,5], which are large-sized ones composed of multi-walled carbon nanotubes, are easier to be technologically and economically produced than single- or double-walled CNTs [3,4]. The CNFs are also important materials similar to the small-sized carbon nanotubes. We previously showed 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 1-NP in various systems [24–29]. In situ fluorescence measurements using 1-NP as a physicochemical probe were performed in order to detect and quantify the adsorption sites on the surface of the CNFs dispersed in solvents and the sol−gel reaction systems of silicon alkoxide. This is a simple method not using a covalent-bonded probe molecule, but an adsorbed probe molecule. This measurements revealed that there are two adsorption forms; one is generated by the $\pi-\pi$ interaction between 1-NP and the graphene sheet and the other is the hydrogen-bonding interaction between 1-NP and the proton-acceptable groups such as –COOH (–COO$^-$) and –C=O [27–29] existing in a monolayer or a few layers on the surface. Our unique procedure to highly disperse the CNFs into solvents allowed these observations although the fluorescence of aromatic molecules adsorbed on carbon materials had never been observed due to its strong quenching. The fluorescence measurement allowed us to confirm the Langmuir-type adsorption of 1-NP on the graphene sheet and the proton-acceptable groups of the CNFs, and estimate the amounts of both sites and their adsorption equilibrium constants. The percentages of the oxidized carbon in the surface layer of the CNFs treated for 1 and 24 h were estimated to be 1.2% and 3.1%, respectively [28].

1-Aminopyrene (1-AP) is a Brönsted base and is expected to interact with acidic groups on a solid surface [30,31]. In our previous study [32], oxygen-containing functional groups produced on the surface of the acid-treated CNFs have been characterized by UV-visible spectroscopy and the

fluorescence measurements using 1-AP as a probe molecule in order to focus on such acidic groups such as –COOH [33,34].   1-AP has been found suitable as a fluorescence probe since its spectra drastically change with the acid–base equilibrium compared with those of aminonaphthalene or aminoanthracene.   However, it was difficult to disperse a high amount of the CNFs in water which adsorb 1-AP enough to examine the quantitative adsorption properties of 1-AP.   The acid-treated multi-walled carbon nanonubes (MWCNTs) with a smaller size are more easily dispersed in aqueous solvents.   In this study, acidic functional groups on the surface of the acid-treated MWCNTs were quantified by fluorescence measurements using 1-AP in order to verify the validity of the in-situ fluorescent probing.

2. Experimental

1-AP (Wako, S grade) was recrystallized three times from water.   Concentrated nitric acid, sulfuric acid, and sodium hydrogen carbonate (Wako, S grade) were used without further purification.   The water was ion-exchanged and distilled.   The MWCNTs (Iljin Nanotech, CM-95) have a diameter ca. 10–15 nm and a length of ca. 10–20 μm.   To produce the functional groups on the surface of the MWCNTs, they were treated with the liquid acid [16–18,27,28].   As a typical procedure, the MWCNTs were refluxed in concentrated nitric acid at 393 K for 24 h, rinsed with a large amount of water and dried at room temperature in vacuo.   The untreated MWCNT sample was labeled N-CNT and that of the HNO_3-treated was labeled A-CNT [27,28].   For a stronger treatment procedure, we applied a concentrated H_2SO_4/HNO_3 mixture (3/1 in volume).   First, the MWCNTs were irradiated with 28 kHz ultrasonic waves in this mixture at 313 K for 1, 12, and 24 h (AIWA AU-10C).   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.   Finally, they were refluxed in concentrated nitric acid at 393 K for 24 h.

After finishing the process, they were rinsed with a large amount of water and dried at room temperature in vacuo. These MWCNT samples treated by the H_2SO_4 and HNO_3 mixture for 1, 12, and 24 h were labeled AA-CNT-1h, -12h, and -24h, respectively. The surface structures of the untreated and three acid-treated MWCNT samples were hardly distinguished by their TEM images because only a surface layer was oxidized. These images agreed with previously reported results [35,36].

The BET specific surface areas of the samples pretreated at 473 K for 12 h were measured by the volumetric gas adsorption method using nitrogen gas (BEL Japan BELSORP-mini). The samples were characterized by XPS using AlKα radiation (ULVAC PHI 5600). The AA-CNT-1h, -12h, and -24h, 1.0 mg, were individually dispersed in water by ultrasonic irradiation for 24 h. The suspension, 10 cm^3, was titrated with the $1.0{\times}10^{-4}$ mol dm^{-3} NaHCO$_3$ aqueous solution in order to estimate the number of the produced acidic functional groups on the MWCNT surface using a pH meter (TOA, HM-10P) [20].

The N- and AA-CNT-1h, -12h, and -24h were individually dispersed in the 1-AP solutions containing water and ethanol (8/2 in volume) at $1.0{\times}10^{-4}$ mol dm^{-3} by ultrasonic irradiation for 1−18 days. The resulting suspensions were centrifuged at 12,000 rpm, 8,060G to remove any precipitates (IWAKI CFM-1000). The UV-visible absorption, fluorescence, and fluorescence excitation spectra of the resulting supernatant suspensions were then measured. The UV-visible 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 concentrations of the AA-CNT-1h, -12h, and -24h in the supernatant suspensions were estimated by measuring the weight of the residual MWCNTs after solvent evaporation at 473 K for 12 h.

3. Results and discussion

3.1. Changes in UV-visible absorption spectra of MWCNT suspensions

The adsorption of 1-AP on the MWCNT samples and the dispersion of the MWCNTs into the liquid phase were examined by measuring the UV-visible absorption spectra of the MWCNT suspensions. The absorption spectra of the N-CNT and AA-CNT-1h, -12h, and -24h suspensions containing 1-AP were observed just after their preparation, and after the ultrasonic irradiation for 2–18 days. In the N-CNT suspension, the spectrum was only slightly changed with time. Apparently, 1-AP was not absorbed on the N-CNT surface. In a previous study, the 1-AP molecules were only slightly adsorbed on the N-CNF surface similar to 1-NP [27,28,32]. The N-CNF adsorbed pyrene better than 1-AP [37]. This result indicates that the polar amino group prevents the π–π interaction between the pyrene ring and graphene sheet although pyrene must be adsorbed on the carbon nanotubes by this interaction [38,39]. In the AA-CNT suspension, the absorbance gradually decreases with time. It was confirmed that 1-AP interacts with the acid-treated MWCNTs similar to the acid-treated CNFs. The change in the absorption spectrum of the AA-CNT-24h suspension is shown in Figure 1 as a typical example.
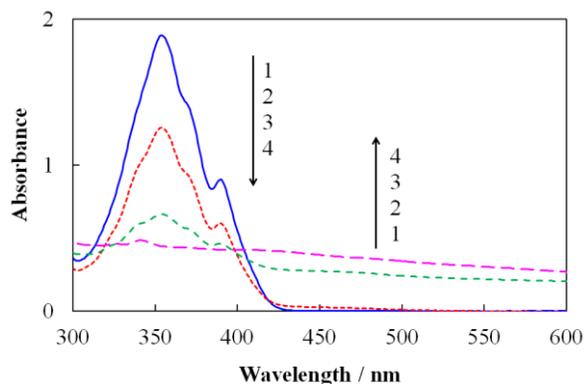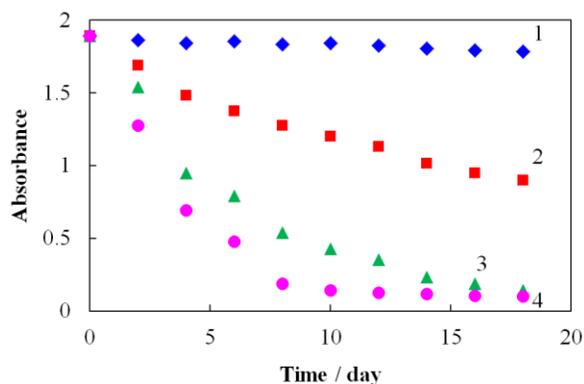

Figure 1 Absorption spectra of AA-CNT-24h suspension containing 1-AP observed (1) just after the preparation and after ultrasonic irradiation of (2) 2 days, (3) 6 days, and (4) 8 days.

Figure 2 shows the changes in the absorbance of each MWCNT suspension at 350 and 500 nm plotted 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-CNT, but was adsorbed on the AA-CNTs. The AA-CNTs acid-treated for a longer time can adsorb 1-AP faster. The absorbance at 500 nm is regarded to correspond to the degree of the MWCNT dispersion according to a good correlation between the concentration and the absorbance of the carbon nanotubes in a solvent [40]. The absorbance increased with the ultrasonic irradiation time and reached saturation. These results indicated that the order of the degree of the MWCNT dispersion was that of the acid treatment duration and it is closely correlated to the amount of adsorbed 1-AP. Not only the surface modification by the acid treatment, but also the adsorption of aromatic molecules should play an important role in the MWCNT dispersion [28].
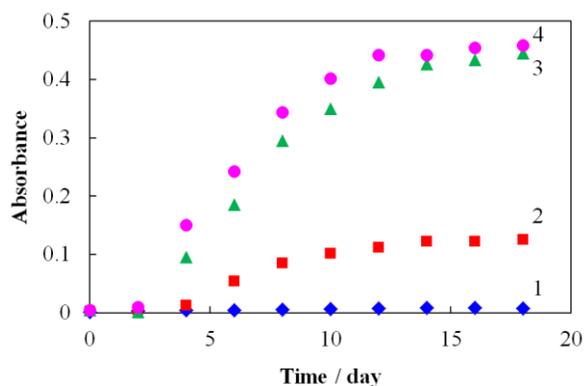
(a)

(b)

7

Figure 2 Changes in absorbance vs. ultrasonic irradiation time monitored at (a) 350 and (b) 500 nm in (1) N-CNT, (2) AA-CNT-1h, (3) AA-CNT-12h, and (4) AA-CNT-24h suspensions.

3.2. Changes in fluorescence spectra of MWCNT suspensions

1-AP exhibits a protonation equilibrium; the original species is called AP, and the protonated species is called APH^+. The protonation equilibrium constant of the ground state, pK_a, and the excited state, pK_a^*, are 2.8 and −1.2, respectively [41]. Therefore, in somewhat low-pH solutions, 1-AP existing as APH^+ in the ground state, is deprotonated to form AP in the excited states, and emits a fluorescence.

Figures 3 and 4 show the fluorescence spectra of 1-AP in the N-CNT and AA-CNT-1h suspensions, respectively, observed just after the preparation and after the ultrasonic irradiation. The fluorescence spectral band at around 440 nm is assigned to AP present in liquid phase of the suspension [30,31]. The spectrum of the N-CNT suspension only slightly changed even after the ultrasonic irradiation of 18 days. The fluorescence spectral bands at around 360–400 nm observed in the AA-CNT-1h suspension are similar to those of APH^+ in the acidic solution [30,31], and their relative intensities increased with the ultrasonic irradiation time. These results indicated that 1-AP is absorbed on the MWCNT surface to form APH^+-like species similar to that on CNF surface.
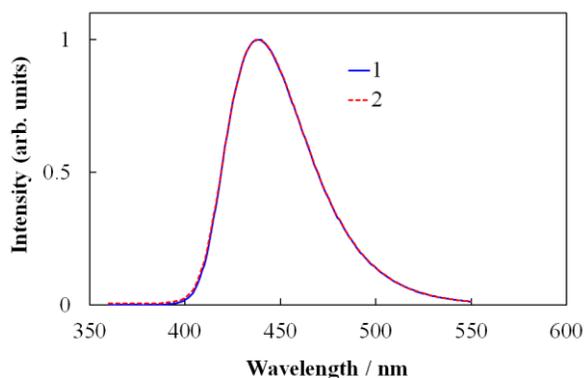
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Figure 3 Fluorescence spectra of 1-AP in N-CNT suspension observed (1) just after the preparation and after ultrasonic irradiation of (2) 18 days.
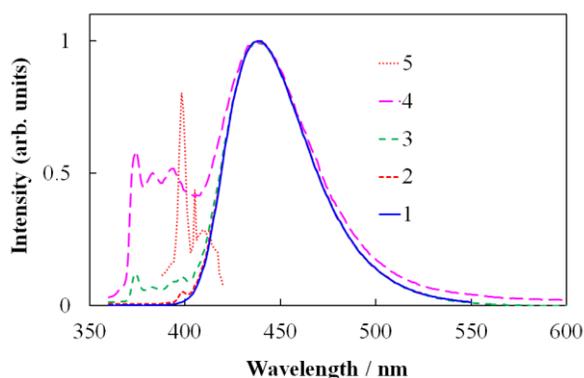

Figure 4   Fluorescence spectra of 1-AP in AA-CNT-1h suspension observed (1) just after the preparation and after the ultrasonic irradiation of (2) 1, (3) 4, and (4) 11 days with (5) the differential spectrum between the spectra (1) and (2).

A peak was observed at 398 nm after 1 day (spectrum 2).   The differential spectrum (5) from that observed just after preparation (1) exhibited the peaks at 398, 405, and 415 nm.   This is similar to the spectrum of 1-AP in cyclohexane having peaks at 399, 405, and 420 nm [30].   In a previous study, the ^1L_b fluorescence of 1-NP, which is observed in nonpolar environments, was seen on the CNFs due to

the π–π interaction between 1-NP and the graphene sheet [27–29].   A large amount of 1-AP molecules must also be adsorbed on the graphene sheet of the acid-treated CNFs because they are better dispersed in the liquid phase than the N-CNF [35,36].   Such a fluorescence was temporally observed in the present system containing 1-AP, and then hidden by the strong APH^+-like band.

It was previously reported that the ion-pair fluorescence of 1-NP was generated by the relatively strong hydrogen-bonding interaction between 1-NP and the oxidized groups, such as –COOH, –C=O, and –OH [27,28].   A Brönsted base, 1-AP, is expected to interact with the acidic oxygen-containing groups.   Therefore, 1-AP selectively detected the acidic groups such as –COOH [32].

3.3. Quantitative characteristics of 1-AP adsorbed on acid-treated MWCNTs

The physicochemical properties for the MWCNT samples were determined by conventional methods. Table 1 shows the BET specific surface area, ratio of C/O atoms, and concentration of the adsorption sites for each sample estimated by the BET method, XPS analysis, and $NaHCO_3$ titration, respectively. The specific surface area of the MWCNTs was not significantly changed by the acid treatment.   The surface structures of the samples were hardly distinguished by their TEM images because only a surface layer was oxidized as previously reported [35,36].   Based on the results of the XPS analysis and $NaHCO_3$ titration, the relative amount of oxygen atom and concentration of the adsorption sites reasonably increased with an increase in the acid-treatment time.   However, in the XPS analysis, it was difficult to distinguish some oxygen-containing groups because the amount of oxygen atom was very low.   These results indicated that Brönsted-acidic functional groups were produced on the acid-treated MWCNT surface and their number increased with the treatment time.

Table 1 Physicochemical properties for the MWCNT samples determined by conventional methods

	Specific surface area / m^2 g^{-1}	Ratio of C/O atoms	Concentration of adsorption sites / mol g^{-1}
N-CNT	200	98.3 / 1.7	-
AA-CNT-1h	210	97.3 / 2.7	4.0×10^{-5}
AA-CNT-12h	220	96.1 / 3.9	6.0×10^{-5}
AA-CNT-24h	240	94.5 / 5.5	1.9×10^{-4}

Figure 5 shows the fluorescence spectra of 1-AP observed in aqueous suspensions including the AA-CNTs prepared at different initial 1-AP concentrations. The fluorescence intensity of the APH$^+$-like species relative to that of the AP decreases with an increase in the 1-AP concentration, i.e., the ratio of 1-AP in the liquid phase becomes higher, indicating that the adsorption approaches an equilibrium state. The Langmuir-type adsorption of 1-AP on the functional groups of the MWCNTs was assumed in this study. The total concentration of 1-AP, C, is written as

$C = [\text{AP}] + [\text{APH}^+]$

where AP and APH$^+$ are 1-AP existing in the liquid phase and on the MWCNT surface, respectively. The ratio of the fluorescence intensity of AP, I_{AP}, to that of APH$^+$, $I_{\text{APH+}}$, is defined as R. The desorption in the excited states can be ignored because the diffusion rate of molecules is much lower than the fluorescence lifetime.

$$R = \frac{I_{\text{AP}}}{I_{\text{APH+}}} = A \frac{[\text{AP}]}{[\text{APH}^+]}$$

where A indicates the ratio of the spectroscopic constant of AP to that of APH$^+$ defined by the molar extinction coefficient, ε, and fluorescence quantum yield, Φ.

$$A = \frac{\varepsilon_{\text{AP}}}{\varepsilon_{\text{APH+}}} \times \frac{\Phi_{\text{AP}}}{\Phi_{\text{APH+}}}$$

These equations can be applied to the Langmuir isotherm as follows.

$$\theta = \frac{[APH^+]}{[F]} = \frac{K[AP]}{1 + K[AP]}$$

where θ is the fractional surface coverage and F is the adsorption site due to the π-π interaction on the AA-CNT surface, and K is the adsorption equilibrium constant on the F site.   The value [F] is the molar amount of the F sites existing on 1 g of the MWCNTs.   In order to determine the quantitative adsorption properties of the AA-CNTs, the MWCNT concentrations in the suspensions should be considered to depend on the 1-AP concentration.   Figure 6 shows the MWCNT concentrations observed as a function of the initial concentration of 1-AP in the AA-CNT suspensions.   The amount of the 1-AP adsorbed on the AA-CNTs was corrected to that per 1 g of the AA-CNTs.
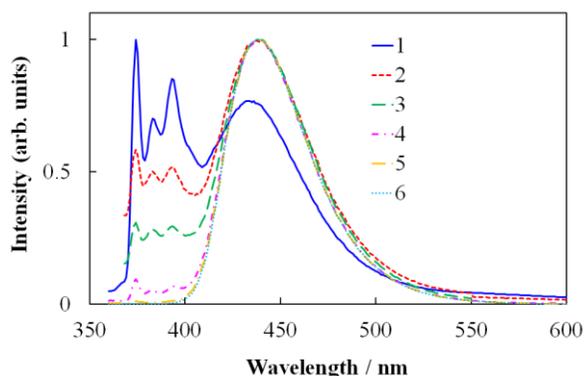

Figure 5   Fluorescence spectra of 1-AP in AA-CNT-24h suspensions, in which the initial concentrations of 1-AP are (1) 8.0×10^{-6}, (2) 5.0×10^{-5}, (3) 8.0×10^{-5}, (4) 1.0×10^{-4}, (5) 2.0×10^{-4}, and (6) 5.0×10^{-4} M, observed after ultrasonic irradiation of 18 days.   The excitation wavelength is 350 nm.
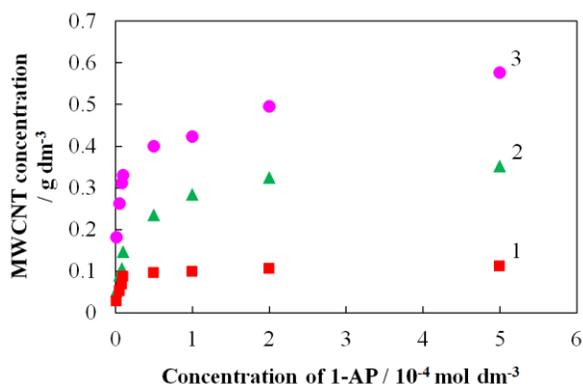
Figure 6 Dependence of the MWCNT concentrations in (1) AA-CNT-1h, (2) AA-CNT-12h, and (3) AA-CNT-24h suspensions on the initial concentration of 1-AP.

The Langmuir isotherm of 1-AP on the surface of the AA-CNTs was obtained by the curve fitting calculation using the known variables, C and R, and the parameters, A, K, and [F]. The experimental and simulated relationships between θ and [AP] are plotted in Figure 7. The experimental values are well-fitted to the Langmuir isotherm. The resulting constants of A, K, and [F] are summarized in Table 2. It was confirmed that a longer acid treatment caused the chemical modification to generate higher amounts of the Brönsted-acidic functional groups and improve the adsorption ability on the MWCNT surface. The constants should be the average values for the adsorption sites of various Brönsted-acidic functional groups. The concentrations of the adsorption sites for the samples were similar to those determined by the NaHCO$_3$ titration. About 2% of carbon in the MWCNTs was oxidized by the 24-h acid treatment based on the molar amount of 1 g carbon, 8.3×10^{-2} mol. The XPS analysis indicated that the oxygen percentage for AA-CNT-24h was 5.5%. The oxidized carbon percentage for AA-CNT-24h can be estimated to be about 2% if all the oxidized carbons were assumed to form carboxyl groups. The present fluorescence measurement quantified the functional groups existing in the surface layer. The percentage of the surface carbons to all the carbons in the present MWCNT is 9−13%.

13

Parts of the AA-CNT-24h surface layer, 15−22%, were presumed to be oxidized on which the functional groups were produced.
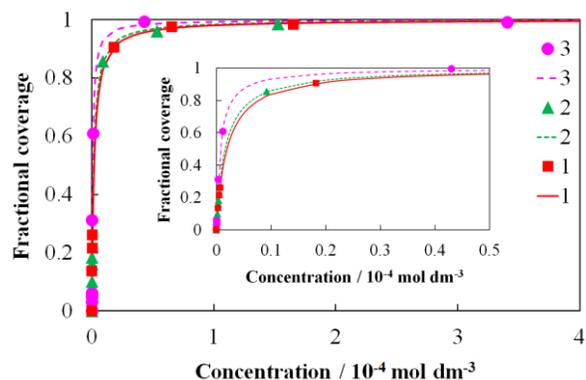

Figure 7 Langmuir isotherm for 1-AP adsorption on (1) AA-CNT-1h, (2) AA-CNT-12h, and (3) AA-CNT-24h suspensions.

Table 2 Constants for the acid-treated MWCNT samples estimated by fluorescence measurements using 1-AP

	Spectroscopic constant	Adsorption equilibrium constant / mol^{-1} dm^3	Concentration of adsorption sites / mol g^{-1}
AA-CNT-1h	48	5.1×10^5	3.5×10^{-4}
AA-CNT-12h	66	6.2×10^5	4.8×10^{-4}
AA-CNT-24h	86	1.4×10^6	1.6×10^{-3}

4. Conclusions

Brönsted-acidic functional groups produced on the acid-treated MWCNT surface were quantified using 1-AP as a fluorescent probe.   1-AP was adsorbed on the MWCNT surface by the hydrogen-

bonding interaction between the amino group of 1-AP and the acidic functional group, such as −COOH on the MWCNT surface, to form APH$^+$-like species. The Langmuir-type adsorption of 1-AP on the functional groups of the MWCNTs was confirmed and their amounts and adsorption equilibrium constants were determined. A longer acid treatment caused the chemical modification to generate higher amounts of the acidic functional groups and improve the adsorption ability on the MWCNT surface. The MWCNT sample having a higher amount of functional groups was better dispersed in the 1-AP solution, and adsorbed a higher amount of 1-AP. About 2% of carbon in the MWCNTs was oxidized by the 24-h acid treatment. This value corresponded to 15−22% of carbon in the surface layer. The present fluorescence measurement quantified the functional groups existing in the surface layer. The number of the oxidized carbons was consistent with that determined by XPS analysis and NaHCO$_3$ titration.

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