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Radical scavenging reaction kinetics with multiwalled carbon nanotubes

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Abstract

Progress in the development of carbon nanotubes (CNTs) has stimulated great interest among industries providing new applications. Meanwhile, toxicological evaluations on nanomaterials are advancing leading to a predictive exposure limit for CNTs, which implies the possibility of designing safer CNTs. To pursue safety by design, the redox potential in reactions with CNTs has been contemplated recently. However, the chemical reactivity of CNTs has not been explored kinetically, so that there is no scheme to express a redox reaction with CNTs, though it has been investigated and reported. In addition, the reactivity of CNTs is discussed with regard to impurities that consist of transition metals in CNTs, which obfuscates the contribution of CNTs to the reaction. The present work aimed at modeling CNT scavenging in aqueous solution using a kinetic approach and a simple first-order reaction scheme. The results show that CNTs follow the redox reaction assumption in a simple chemical system. As a result, the reaction with multiwalled CNTs is semi-quantitatively denoted as redox potential, which suggests that their biological reactions may also be evaluated using a redox potential scheme.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2014.10.009.

1. Introduction

Carbon nanotubes (CNTs) may be useful for various medical, commercial, and industrial applications, and designing their structures has recently become an important issue in order to obtain tailor-made performances [1]. At present, their diameter and length are only rudimentarily controllable, while in the laboratory diameter-controlled double-walled .CNTs (DWCNTs) were synthesized [2,3]. The inner space of CNTs is utilized to deliver particular performances with various particles [4,5]. Industrially, atypical multiwalled CNTs (MWCNTs) are applied and commercialized [6–11]. Thus, modifications of CNT structures will become an important issue to synthesize and obtain appropriate functionalities and safety in use. Among the challenges with CNTs, particularly MWCNTs, a new and crucial goal will be to design safe CNT structures, while toxicological evaluations on CNTs are advancing leading to a predictive exposure limit for MWCNTs [12]. This groundbreaking challenge requires the identification of a key mechanism that controls toxicological phenomena [13]. The importance of physicochemical properties is often proposed, but the relative importance of specific properties has not been defined explicitly. Two critical points concerning CNT safety evaluations are summarized as the fiber paradigm and bioactivity, for example, the metal impurities of CNTs [14]. The former applies to not only CNTs but also other nanowires and microfibers and refers to the effects of physical contact with cells and tissues. The latter can be described as chemical reactions on the CNT surface and suggests an intrinsic phenomenon related to biological activities. The metal impurity issue has obscured the contribution of CNTs themselves to bioactivity. Thus, it is necessary to develop a model describing a reaction mechanism for CNTs.

Recent investigations suggest that an intrinsic CNT reaction mechanism may be described by a redox reaction system, because iron is not available on the CNT surface when Fe(III) oxides were formed [15,16]. These impurity effects and their removal are copiously discussed relating to their bioactivities [17–22]. A voltammetric method was used to compare the redox potential of SWCNTs to glassy carbons and associated with the redox potential of CNTs [20]. Nevertheless, Y. Liu et al. pointed out that these articles were inconclusive and could not be compared to each other [21]. They discussed that CNTs not only activate the specific molecular signaling associated with the oxidative stress activator protein but also exhibit reactive oxygen species (ROS) scavenging properties. Later, it was reported that, because these metals were capsulated into carbon shells, transition metals were not eluted by an acid wash and were not bioavailable [22].

To various degrees, transition metal impurities are usually oxidative to peroxides, while metal oxides are relatively stable. It is known that Fe(II) or Fe^{2+} ion generates hydroxyl radicals (OH’), a form of ROS, in the presence of hydrogen peroxide by the Fenton reaction, and that ROS induce inflammation of tissues. By contrast, Fe(III) oxide (Fe_2O_3) and carbide (FeC) do not generate ROS, because Fe(III) cannot be an electron donor except upon treatment with a strong reduction agent. As Fe(II) is supplied not only externally as metal impurities but also internally in a living body and essentially catalyzes peroxide-generating hydroxyl radicals, reduction reactions are required to eliminate the radicals. A question is whether the redox potential of CNTs is predictive of ROS generation [13], as CNTs inevitably have chemical reaction sites, for instance, dangling bonds. As of today, it has not been determined if CNT surfaces behave as electron donors or acceptors. If these reaction sites donate electrons to radicals, CNTs become ROS scavengers in an aqueous system.

The present work objectively investigated the chemical reactivity and redox potential of MWCNTs pseudo-quantitatively using its known scavenging ability for hydroxyl radicals. As the chemical reactivity has not been kinetically explored extensively, we hypothesized a simple first-order chemical reaction system for MWCNTs, hydrogen peroxide, and hydroxyl radicals, and designed an experimental method to verify the assumption. To embody it, chemical reactions with these components were investigated to eliminate unnecessary disturbances as much as possible. The present studies suggest that the experimental results agree with the assumption, which validates the study of redox potential to evaluate the chemical reactivity of CNTs.

2. Experimental

2.1. MWCNTs

Two kinds of MWCNTs were used in the present work: cup-stack MWCNTs (CS-MWCNTs) prepared by GSI Creos Corporation (Tokyo, Japan) and Nanocyl NC-7000 MWCNTs obtained from Nanocyl. The average diameter and length of CS-MWCNTs were 80 nm and 5 μm, respectively. In addition, the average diameter and length of Nanocyl NC-7000 were 9.5 nm and 1.5 μm, respectively. The former was provided in order to evaluate the influence on the scavenging performance of the chemical components. As CS-MWCNTs have many graphene edges on their surface as shown in Fig. 1, they might be relatively reactive chemically. CS-MWCNTs were characterized in a previous article [26]. The latter was used to measure the intrinsic radical scavenging rate of MWCNTs using a typical MWCNT produced by the catalytic chemical vapor deposition method. To reduce the surfactant amount to a minimal concentration against MWCNTs and obtain their good dispersion in water, a specially prepared CNTEC® produced by Kuraray Living Co., Ltd., (Tokyo, Japan) was used as described in Section 2.2.

2.2. Preparation of mixtures and ESR-DMPO method

The measuring mixture consisted of MWCNTs, hydrogen peroxide, ferrous chloride, and 5,5-dimethyl-1-pyrroline-1-oxide (DMPO). Hydrogen peroxide (hydrogen peroxide 30.0–35.5 mass%, Wako Pure Chemical Industries, Ltd., Osaka, Japan) was diluted to 0.1 M with ultrapure water. The 0.1 M solution was diluted to 1 mM with ultrapure water before use. Ferrous chloride (iron (II) chloride tetrahydrate, Wako Pure Chemical Industries, Ltd., Osaka, Japan) was dissolved in ultrapure water to 15.7 mM. This solution was also diluted 100 times before use. Frozen DMPO (Dojindo Laboratories, Kumamoto, Japan) was thawed at room temperature and diluted to 100 mM with ultrapure water. The DMPO solution was prepared each time and disposed within 24 h after preparation. The surfactant for CS-MWCNTs was sodium dodecyl benzen-sulfonate (SDBS) (Kanto Chemical Co., Inc., Tokyo, Japan) and was diluted to 45.9 mM with ultrapure water.

CNTEC® was made of polyester fibers coated with 12 wt% Nanocyl NC-7000 in dry condition. The weight ratio of the concentration of the surfactant to MWCNTs of CNTEC®, which was specially prepared, was fixed at 26.2:100 in dry condition. In 50 g of ultrapure water, 0.1 g CNTEC fibers were dispersed, which was sonicated for 30 min in a ultrasonic bath. The mixture was filtered with a Whatman filter paper (Whatman 42 with pore size at 2.5 μm) to remove polyester fibers and large agglomerates of MWCNTs. This solution was named as Solution A, which included 0.13 wt% of MWCNTs after drying the solution. Solution A was filtered with a Whatman filter paper (GF/F with pore size 0.7 μm) and then a Milipore filter (MF-Milipore GSWP 09000 m with pore size at 0.22 μm). This solution, named Solution B, included 0.036 wt% of MWCNTs. The procedure gave an advantage to balancing the surfactant interference despite alterations in MWCNT concentration. These solutions were used instead of CS-MWCNTs that were dispersed in the surfactant solution.

In all measurements, the peroxide concentration was in excess.

2.3. Electron spin resonance measurement

All solutions were mixed and measured at room temperature with electron spin resonance (ESR) (JES-FA100, JEOL). The ESR settings were as follows: frequency 9415.404 MHz, power 0.998 mW, field center 335 mT, sweep time 2 min, width ± 5 mT, and modulation frequency 100 kHz. All measurements were conducted within 5 min after mixing all of the solutions. The details were reported in a previous article [26].

ESR spectra were normalized using Mixture B in Table 1 with 0.1 ml CNT solution for all of the CS-MWCNT measurements. With Nanocyl NC-7000, Mixture A in Table 1 without surfactant was used. The ESR measurement results were obtained as relative values to a reference. In the present work, the radical concentration in a reference solution or specified MWCNT mixture was described using the normalized form:

$$\text{Scavenging ratio}=[\text{ESR signal of a sample}/\text{ESR signal of a reference}]=[\text{radical concentration of a sample }/\text{radical c}$$

As the ratio is 1 at MWCNT = 0, radical concentration with a change of CNT concentration was expressed as radical concentration ratio to the reference. On the other hand, the radical scavenging rate is described as:

$$\text{Scavenging rate}=\{1-(\text{Scavenging ratio})\}$$

ESR spectra were normalized using Mixture B in Table 1 with 0.1 ml CNT solution for all of the CS-MWCNT measurements. With Nanocyl NC-7000, Mixture A in Table 1 without surfactant was used. Thus, the scavenging ratio and rate represent the normalized hydroxyl radical concentration relative to the reference and the normalized hydroxyl radical concentration amount scavenged in a solution, respectively. All of the samples were measured at least five times and arithmetically averaged except the lowest and highest values. In the present work, a buffer to control solution pH was not added because the buffer apparently affects the reaction and the reactive components were in the aqueous solution. pH measurement was not conducted during ESR-DMPO measurement because it cannot be physically measured during the ESR spectrum measurements.

3. Results and discussion

3.1. Reaction kinetics hypothesized

According to recent findings, MWCNTs scavenge ROS [23–26]. All of these reports hinted that the reaction occurs at dangling bonds on CNT surfaces and MWCNTs supposedly act as electron donors or, at least, charge is transferred from those dangling bonds to radicals. Petersen et al. reported that SWCNTs also scavenge hydroxyl radicals by electron transfer [27]. Peng et al. found that MWCNTs attached with cadmium sulfide (CdS) were electron acceptors and catalyzed the conversion of water to hydrogen (and inevitably oxygen) in a photoreaction as a simulated photosynthetic reaction, where radical formation and degeneration were implicitly included [28]. This indicates that MWCNTs can be both electron acceptors and donators in redox reactions depending on their relative chemical potentials. If the redox potential is hypothesized for MWCNTs, they may decrease oxidant-induced inflammation of tissues, though the actual condition surrounding MWCNTs is complicated. One would be able to stoichiometrically predict oxidant stress once the redox potential of MWCNTs is determined in a reaction system. To conduct and specify CNT behavior in aqueous solution, it is necessary to model it using a simple first-order reaction profile for CNTs as the first step.

We hypothesize the following chemical reaction equations with MWCNTs and hydrogen peroxide (Fig. 2). First, in the light of the fact that a description of the Fenton reaction has not been agreed upon completely, a simple system consisting of hydrogen peroxide and Fe(II) can be written to characterize the present experimental system specifically as follows [29,30]:

$$\mathrm{Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+HO^{-}+HO^{\cdot}} \quad (1)$$

$$\mathrm{Fe^{3+}+H_2O_2 \rightarrow Fe^{2+}+H^{+}+HOO^{\cdot}} \quad (2)$$

$$\mathrm{Fe^{3+}+HOO^{\cdot} \rightarrow Fe^{2+}+H^{+}+O_2} \quad (3)$$

These equations can be summarized as follows:

$$\mathrm{3H_2O_2 \rightarrow 2H_2O+O_2+2HO^{\cdot}} \quad (4)$$

According to previous reports [12,20,22–25], it is agreed that CNTs scavenge hydroxyl radicals in an aqueous solution with hydrogen peroxide experimentally. The assumed reaction sites on the CNT surface including dangling bonds are denoted as Dn that acts as if they were single molecules. As long as Eq. (4) is true, a necessary condition to satisfy it with radical scavenging must become an equation as follows:

$$\mathrm{2Dn+2HO^{\cdot} \rightarrow 2Dn^{+}+H_2+O_2} \quad (5)$$

Accordingly, Eqs. (4) and (5) give the following equation:

$$3H_2O_2+2Dn \rightarrow 2Dn^{+}+2H_2O+H_2+2O_2 \quad (6)$$

Eq. (5) indicates that the reaction sites donate electrons to hydroxyl radicals finitely. This agrees with the assumption of H+ or OH radical generation by electron acceptance on CNTs by Peng et al. [28] In Eq. (6), the reaction rate constant should become “1” if the concentration of Dn is large enough and dominates compared to that of H_2O_2 from Eqs. (S5) to (S6) in the Supplemental. This suggests that this experimental condition must be avoided. Furthermore, the equations predict that the CNT amount, or mole equivalent of the number of reaction sites, is necessarily smaller than that of hydrogen peroxide. Thus, while the mole equivalent of CNTs or reaction sites has not been determined, a concentration ratio of hydrogen peroxide to CNTs should be sought in an experiment.

Eq. (5) requires one to measure the concentrations of hydrogen and oxygen in a scavenging reaction in order to verify the Fenton reactions. However, it is experimentally impossible to measure these concentrations in situ because of the measuring system of the ESR equipment and its measuring cell structure. Fortunately, Eq. (5) is a fictitious reaction to deduce Eq. (6) so that Eq. (5) is regarded as an intermediate reaction. Although the Fenton reaction gives many routes of reaction steps, it can be simplified in such a manner.

3.2. Influences of chemicals in a reaction system

Before conducting chemical tests to investigate whether Eq. (6) is appropriate to describe the present chemical reaction, it is necessary to investigate influences by chemicals in an ROS measurement. This has not been pursued previously, because the present approach with chemical kinetics had not been proposed nor systematically explored. In addition, it was reported that chemicals in similar systems significantly affect ESR-DMPO measurement [31]. We conducted a series of tests using CS-MWCNTs (Fig. 1), because they have many edges of graphene that are relatively reactive in comparison with highly crystallized CNTs [26]. Fig. 3a shows that the radical scavenging rate varies with a concentration change of the surfactant without CS-MWCNTs, where Mixture A in Table 1 was used. A reference solution was at 0 mM of the surfactant of Mixture A in Table 1. The results show that hydroxyl radicals are scavenged proportional to a surfactant concentration. Fig. 3a apparently indicates that the surfactant scavenges radicals. Fig. 3b shows the radical scavenging rate with a concentration change of MWCNTs in a fixed concentration of surfactant at 0.918 mM in a solution, where Mixture B was used in Table 1. Likewise, the reference solution was at 0 wt% of MWCNTs of Mixture B in Table 1. As the scavenging rate of hydroxyl radicals proportionally corresponds to the surfactant concentration according to Fig. 3a, Fig. 3b indicates that the scavenging rate is proportional to the concentration change of CS-MWCNTs at a fixed surfactant concentration, where the surfactant contribution is relatively low. This suggests that the ESR-DMPO method can measure radical concentration changes corresponding to a CS-MWCNT concentration change. However, an intrinsic CS-MWCNT scavenging performance cannot be measured using this method because the respective contributions of CS-MWCNTs and surfactant are not distinguished individually. Fig. 3c demonstrates the scavenging ratio with a change of hydrogen peroxide concentration at a fixed concentration of surfactant without CS-

MWCNTs. The scavenging ratio does not change with a change in hydrogen peroxide concentration, which indicates that hydroxyl radical generation depends on the duration of time after mixing these chemicals rather than the hydrogen peroxide concentration under the proposed experimental condition. It is in agreement with the previous literature [29,30]. Therefore, the surfactant is specifically a major influence factor in the present chemical reaction system. It is necessary to minimize the surfactant concentration to determine the intrinsic MWCNT radical scavenging performance.

In our radical scavenging tests with MWCNTs, pH measurements were omitted. On the one hand, there is physical obstruction in which the DMPO adduct has a very short lifetime and the measuring cell cannot be equipped with a pH cell inside due to physical constraints. It did not allow the measurement of pH in situ. On the other hand, the interaction among the buffer chemicals, MWCNTs, and DMPO is complicated and cannot be predicted. The reaction sites on MWCNTs might react with phosphate and DMPO could attach on the CNT surface [32]. It is noted that the pH of the solution mixture just before ESR measurement was approximately 6.5; this was almost equal to that of ultrapure water used. It is regarded that water stabilized pH due to the very low concentration. It would be optimal to estimate or measure the solution pH during ESR-DMPO spectra measurement.

3.3. Scavenging performance measurements with the minimal amount of surfactant and intrinsic redox potential of MWCNTs

As mentioned above, because of the influence of surfactant scavenging, performance measurements were conducted using a minimal amount of surfactant with MWCNTs to determine the intrinsic contribution of MWCNTs to radical scavenging. Fig. 4 shows a change in scavenging rate with a change of MWCNT solution volume, where Solution A or B was added into water. This figure clearly shows that the radical scavenging depends on MWCNT concentration. In this procedure, the surfactant concentration in Solutions A and B was identical. Because these solutions were diluted further with ultrapure water and hydrogen peroxide in the measurement, surfactant concentration was two to three digits lower than that of Mixture A or B, which were prepared using a conventional method with surfactant. As the surfactant amount was proportional to the MWCNT concentration which was low, the influence of the surfactant was believed to be negligible in Solutions A and B according to Fig. 3a. Fig. 4 demonstrates that the maximum of the hydroxyl radical scavenging rate depends on MWCNT concentration and shows their plateau points. This result suggests that the number of reaction sites was significantly different between these solutions.

In comparison with the experimental results discussed in the previous section, the curvature in Fig. 4 is apparently different from that in Fig. 3b. Although it was true that the size distributions of MWCNTs in Solutions A and B were not identical after passing through those filters, the tendency of these curves was alike. The results are consistent with a previous report in which the size difference of particular MWCNTs did not significantly affect the scavenging characteristics though the surface morphological difference did [26]. Another report used MWCNT weight concentration in the horizontal axis instead of volumetric concentration used in Fig. 4. A single smooth line resulted when these results were plotted against each other [31]. From these facts, it is suggested that the scavenging reaction is proportional to the surface area of MWCNTs or the number of reaction sites. Besides, Fig. 4 indicates that the scavenging rate does not increase in a straight line as in Fig. 3a, or the first-order reaction to CNT concentration. Even though peroxide was excessive in quantity, radicals were generated but not so rapidly. Therefore, the scavenging rate exhibits a plateau. It indicates that there is an equilibrium point by an unknown mechanism. However, this is not the target of the present study. Thus, Eq. (5) is an intermediate reaction simply given to derive Eq. (6) with the Fenton reactions.

In Fig. 5, all plots measured with Solutions A and B are summarized together. The solid line is calculated by Eq. (7) as:

$$\mathrm{S_{rad}} = -\,\mathrm{q}\ \ln|\mathrm{C_{Dn}} + \mathrm{s}| + \mathrm{q}(\mathrm{C_{Dn}} + \mathrm{s}) + r \quad (7)$$

where S_{rad} and C_{Dn} are the scavenging ratio and the MWCNT concentration in a mixture. Detailed definitions are given in the Supplemental. Note that Eq. (7) is equivalent to Eq. (S8') in the Supplemental. In Eq. (7), q, r, and s are arbitrary constants and were calculated using the "Solver" function of Microsoft Excel (Microsoft® Excel® for Mac 2011, Version 14.3.9) to be 0.14936, 0.00000, and 0.00105, respectively. Fig. 5 clearly shows that the scavenging reaction ratio or the hydroxyl radical concentration ratio measured agrees with the solid line practically, which indicates that the hypothesis in Eq. (6) is appropriate to denote the reaction system.

Fig. 5 evidently shows that the experimental result agrees with Eq. (7). In Fig. 4, on the one hand, the results are individually plotted based on these prepared MWCNT solutions in order to show CNT concentration dependency. In Fig. 5, on the other hand, all plots are processed together with a change of CNT weight concentration. The former sets forth the radical scavenging reaction depending on the MWCNT surface amount. It is regarded as a technique to detect the reaction rates at very low concentrations of MWCNTs without a change of the other ingredients in the solution. The latter is used to analyze the reaction kinetics. These measurement standard deviations tend to be small at the lower MWCNT concentrations. It is probable that radical scavenging by the surfactant may become significant at higher MWCNT concentrations as the surfactant concentration is proportional to the MWCNT concentration. It is necessary to look for a method to determine the reaction rates of hydroxyl radicals– DMPO and hydroxyl radicals– surfactant to verify the point.

The plateau point is supposed as a pseudo-equilibrium point in this particular reaction system, and may be related to the number of reaction sites of MWCNTs. However, when Eq. (7) is expanded using the Taylor expansion, it is rewritten, if CDn is large enough, as:

$$\mathrm{S_{rad}} = -\mathrm{q}\left\{2\left(\mathrm{C_{Dn}} + \frac{\mathrm{C_{Dn}^{3}}}{3} + \cdots + \frac{\mathrm{C_{Dn}^{2n+1}}}{2n+1} + \cdots\right)\right\} + \mathrm{qC_{Dn}} + r = -\mathrm{q}(\mathrm{C}_D n) + \cdots + \frac{\mathrm{C_{Dn}^{2n+1}}}{2n+1} \quad (7')$$

Thus, S_{rad} is to be the infinite number and does not have an equilibrium point at large C_{Dn}, while it has an inflection point. It is considered that Eq. (7) may hold true for a condition at low MWCNT or reaction site concentration having a pseudo-plateau point. It means that the scavenging ratio becomes large at a high MWCNT concentration. At present, as mentioned above, this cannot be practically verified as the higher MWCNT concentration brings a greater influence of surfactant, and consequently the surfactant conceals the intrinsic scavenging activity by MWCNTs. It is necessary to develop a technique to disperse a large amount of MWCNTs at a very low concentration of surfactant. However, the intrinsic behavior of MWCNTs can be sought at very low concentrations of components. Differentiating Eq. (7) and setting to zero, it gives a pseudo-equilibrium point at which a slope of Eq. (7) is horizontal. To solve the equation, $C_{Dn} = s = 0.9985$, and $S_{rad} = q = 0.14936$. This result gives an answer to Eq. (S2); however, it does not specify the pseudo-equilibrium constants of K_1 or K_2, because the actual peroxide concentration in the chemical reaction system is not dynamically determined in the present procedure. It is necessary to seek and develop a measuring method for hydrogen peroxide in the solution in situ and obtain these constants. Even in view of them, Eq. (7) should be applied to the radical scavenging ability of MWCNTs and their bioavailability evaluations. Here, it has to be determined whether the given nano-carbons are to be electron acceptors or donators. Krusic et al. specified that fullerenes were endohedral and electron acceptors [33]. On the other hand, the physical properties of CNTs are significantly different from that of fullerenes, and particularly energy bands and density of state DOS) of CNTs are unique because of the cylindrical structure and chirality [34]. In addition, Ullah et al. proposed a concept of “charge carrier transport mechanism” and discussed that the electron transfer of semiconductive materials is relative [35]. Furthermore, Shi et al. pointed out that CNTs can either donate or accept electrons based on an electron transfer mechanism [36]. As the results of the present work correspond to the previous reports [23–27] and are not inconsistent with those discussions, the assumption of electron donation is reasonable. Thus, Eq. (7) is deemed to be appreciable to those evaluations. Fig. 4 and Fig. 5 show that the reaction kinetics between MWCNTs and hydroxyl radicals agree with Eq. (6); that is, MWCNTs donate electrons to those radicals.

Eq. (7) implies that a high concentration of MWCNTs infinitely scavenge hydroxyl radicals, but the scavenging ability by MWCNTs is obviously not proportional to their concentration. Considering these points with the CNT surface structure, the results support our hypothesis semiquantitatively though a pseudo-equilibrium constant is not specified uniquely. One should consider calculating the constant if a CNT chirality gives a particular electron energy distribution and density of state specifically in the case of a thinner diameter [37]. As the electron energy distribution and DOS for thicker-diameter MWCNTs indicate no significant differences [38], a relationship between the redox potential of MWCNTs and chirality has to be clarified with thinner MWCNTs. Furthermore, it is necessary to investigate if Eq. (6) is reversible or kinetically represents an equilibrium condition. Eq. (6), for example, in a biological reaction, predicts that the induction of tissue inflammation after exposure to MWCNTs increases in a long-period test in which the electrons in MWCNTs are depleted, unless the living body can supply electrons to MWCNTs. It has been shown that pulmonary inflammation rapidly increases in the week after exposure to MWCNTs and gradually decreases to a normal condition within a month [39]. The present report suggests that the inflammation decrease may be related to the redox potential. Of interest is whether long-period exposures show a rebound of inflammation. With regard to the electron supply to

CNTs, Petersen et al. imply that particular biological reactions give electrons to CNTs [27]. To investigate the biological reaction kinetically, it is necessary to elucidate the Fenton reaction and reactions of biological molecules in the living body. Thus, MWCNTs may have redox potential, while their reactivity as electron acceptors must be proved using an alternative way [40]. Once the redox potential of MWCNTs is determined, MWCNT intrinsic toxicity via ROS can be estimated in tissues chemically using their physicochemical properties and surrounding conditions. Thus, it may be possible that the redox potential of MWCNTs can predict biological responses if the reaction conditions around MWCNTs are determined.

4. Conclusion

A chemical kinetics scheme to explain the hydroxyl radical scavenging mechanism with MWCNTs is proposed and proven by experiments in a simple chemical system with MWCNTs. Theoretical calculations agree with the experimental results. The surfactant was specified as an interfering factor in the present reaction system. Minimizing surfactant concentration allowed demonstration of the intrinsic behavior of MWCNTs in the system. MWCNTs behave as electron donors through their reaction sites, which is a reason why MWCNTs are ROS scavengers. While it is predicted that the surface morphology of MWCNTs can be characterized using chemical reactions on the surface, the present work clearly shows that experimental results agree with chemical kinetics assumed and previous reports. It suggests that this new approach may allow one to estimate toxic reactions based on chemical kinetics using the physicochemical properties of MWCNTs. Although it is necessary to determine the mole equivalent number of MWCNTs to calculate the absolute reaction and equilibrium constants, a model using redox potential and chemical kinetics may predict the intrinsic chemical reactivity of the MWCNT surface and, therefore, be applied to design safer CNT structures.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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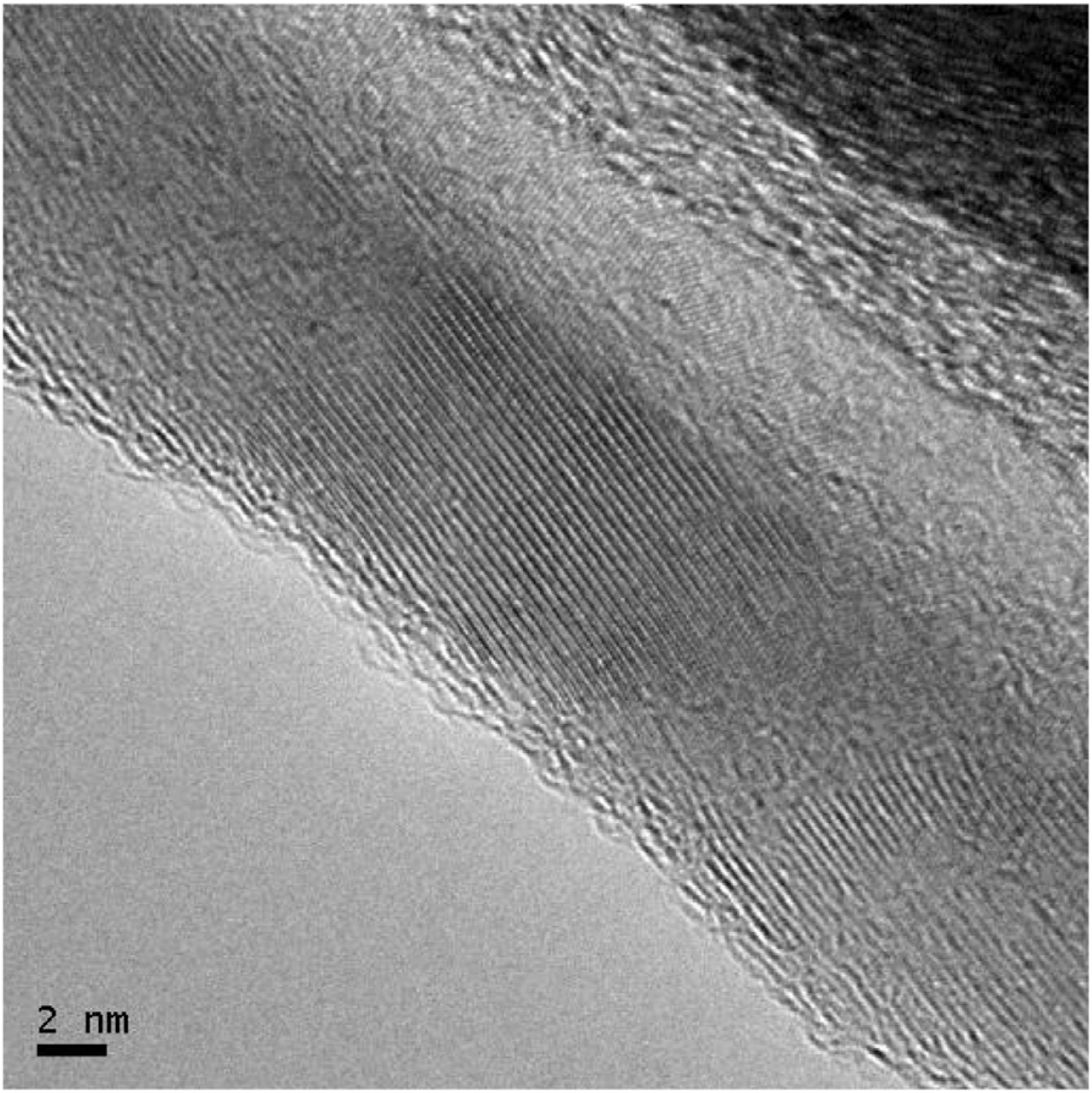

Fig. 1.

An electron microscopy picture of a CS-MWCNT. Graphene layers are stacked and are not parallel to the fiber axis. There are edges of graphene sheets on the surface.

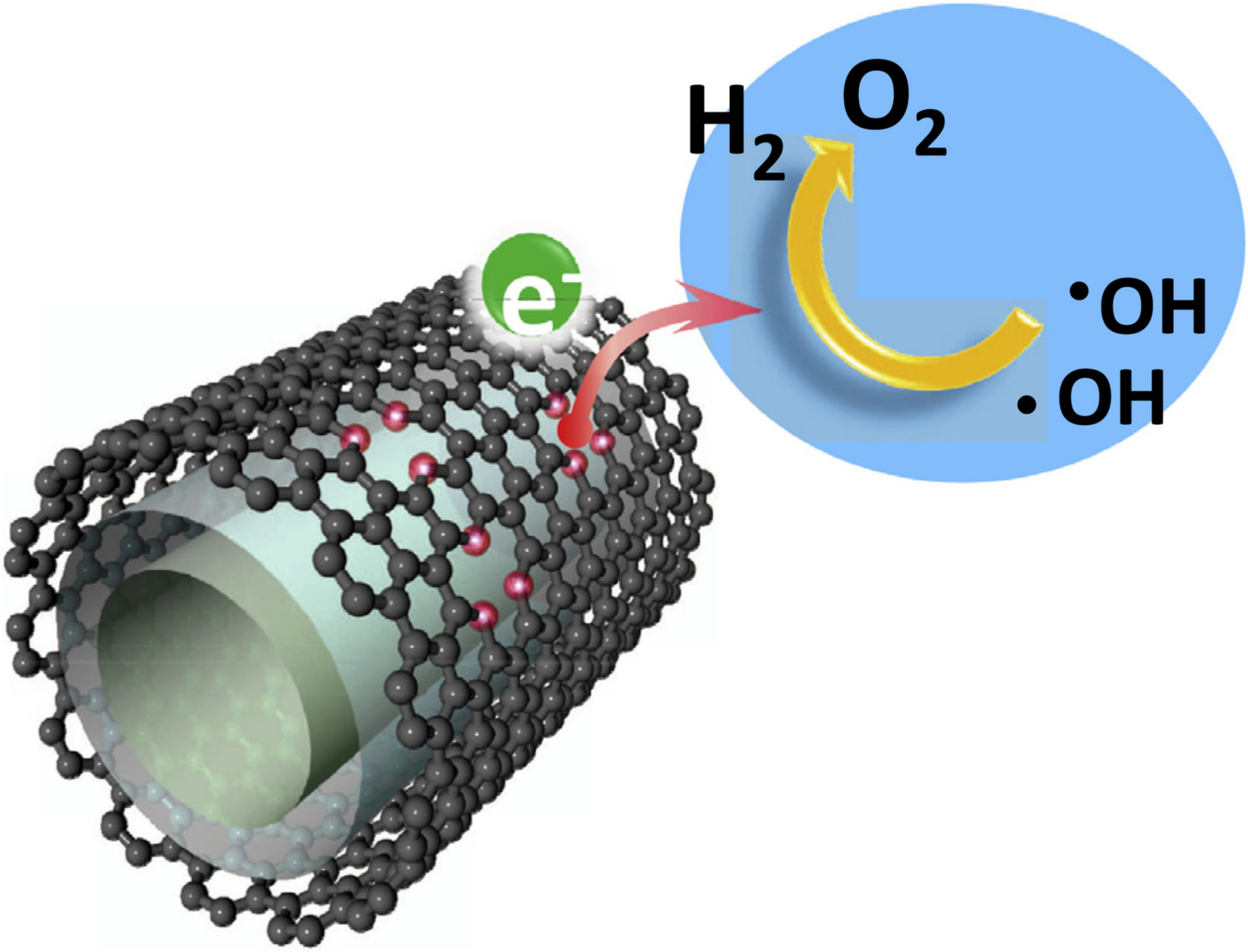

Fig. 2.
A schematic diagram to illustrate hypothesized reaction kinetics of hydroxyl radicals at a reaction site of MWCNTs. For easy visualization of the assumed concept, it is illustrated as if the reaction takes place at a dangling bond. Reaction sites donate electrons to hydroxyl radicals and result in hydrogen and oxygen as denoted in Eq. (6). (A color version of this figure can be viewed online.)

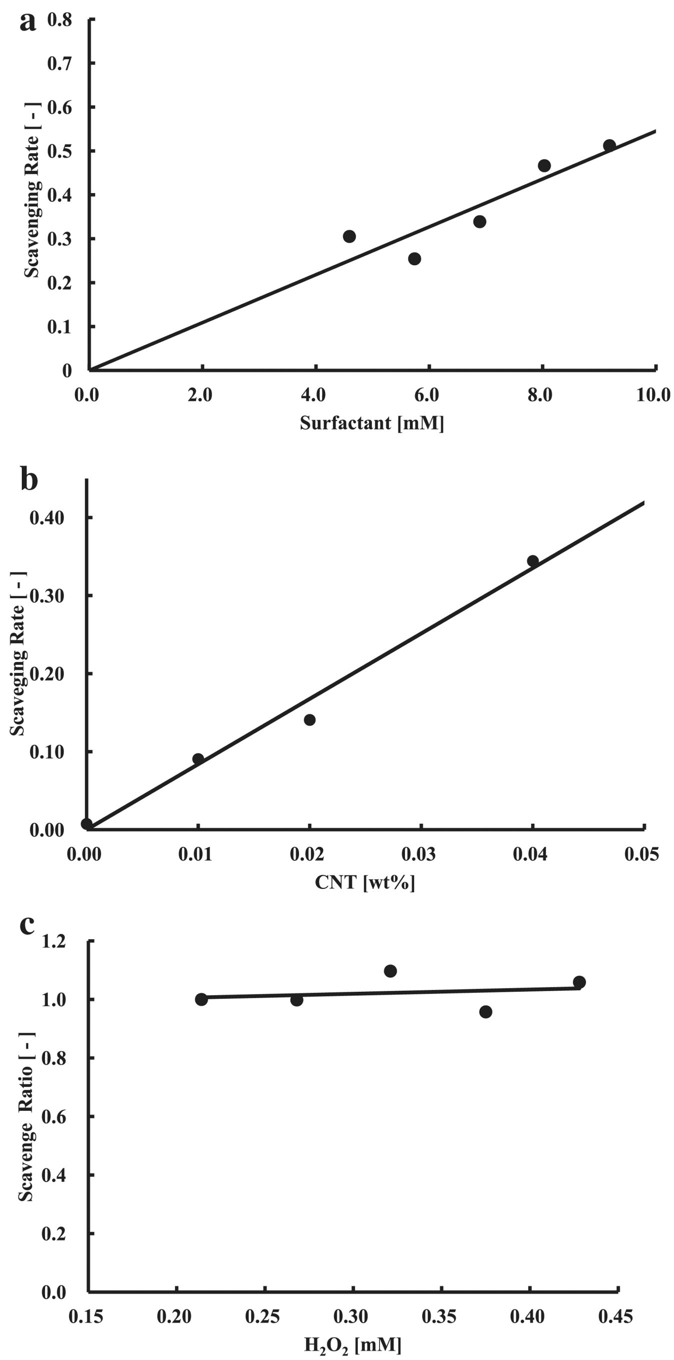

Fig. 3.

Influences of chemical components in the scavenging reaction system. Vertical axis shows the scavenging rate of hydroxyl radicals that were generated by the Fenton reaction with hydrogen peroxide. (a) Influence of surfactant without CS-MWCNTs. The scavenging rate is proportional to surfactant concentration. (b) A scavenging rate change with a change of CS-MWCNT concentration at a fixed surfactant concentration of 0.918 mM. Scavenging rate proportionally corresponds to the MWCNT concentration change. (c) The scavenging ratio with a change of hydrogen peroxide concentration in fixed concentrations of $FeCl_2$ and surfactant in Mixture B without CS-MWCNTs in Table 1. It is apparent that the radical concentration is constant at the measuring time in the solution.

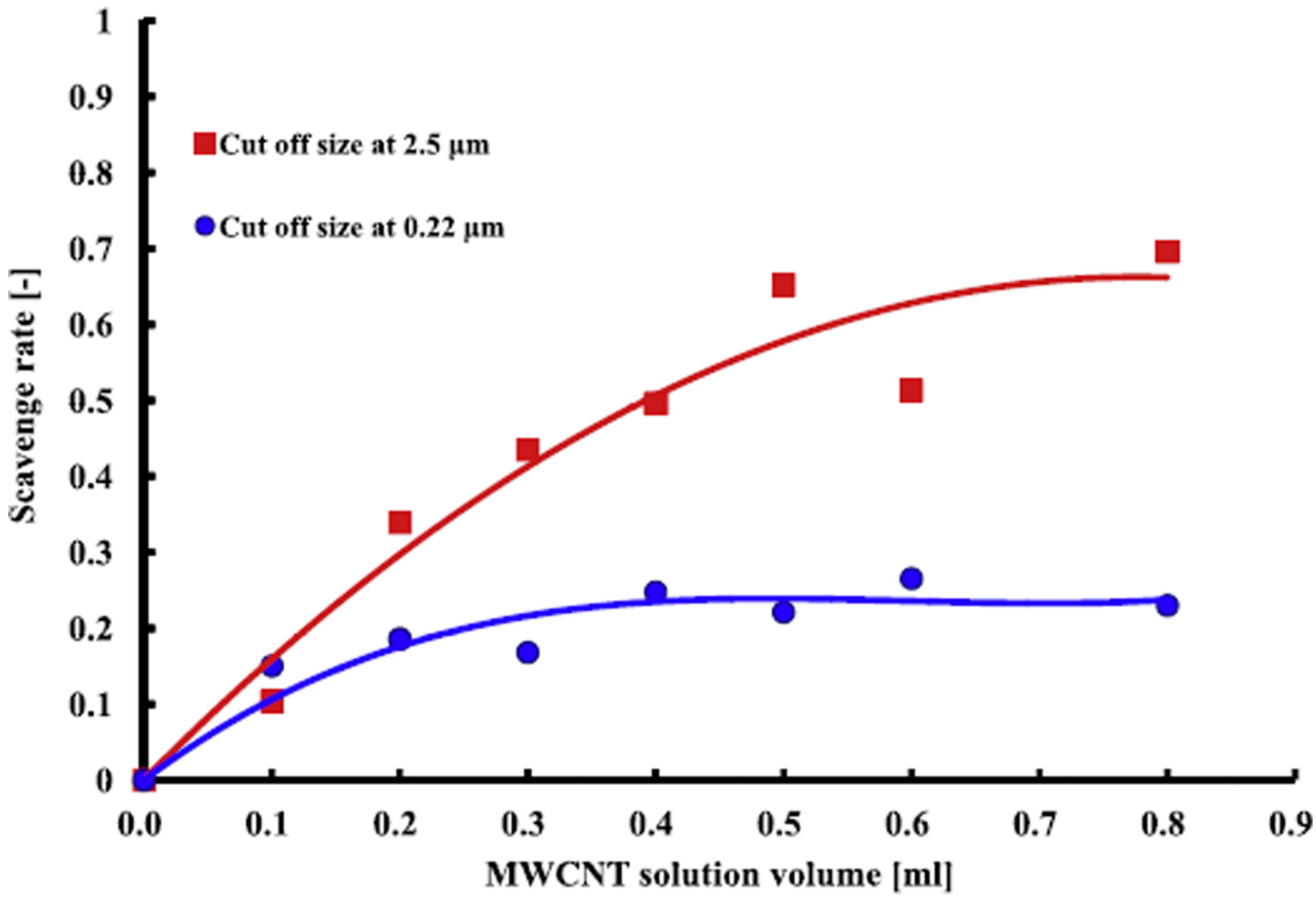

Fig. 4.

Radical scavenging rate with a volume change of MWCNT solutions A and B. Solutions A and B are filtered at 2.5 and 0.22 μm, respectively, to control MWCNT weight concentration. These fitting curves are binominal for Solution A and section three approximations for Solution B, respectively. From these fitting curves, the equilibrium points of Solutions A and B are found to be at 0.78 and 0.38, respectively. (A color version of this figure can be viewed online.)

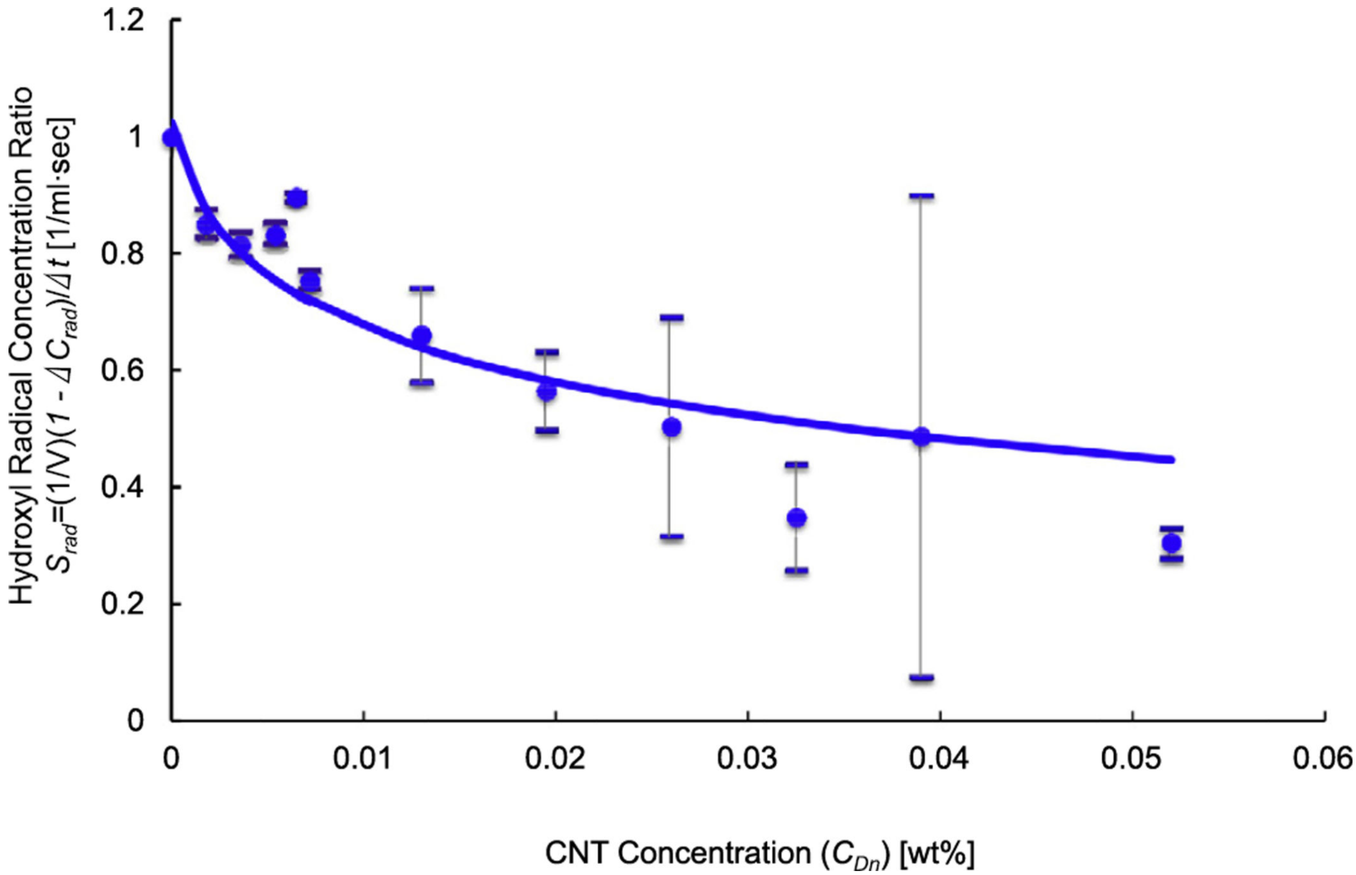

Fig. 5.

A change of hydroxyl radical concentration Srad in the solution with a change of MWCNT weight concentrations C_{Dn}. The solid line is calculated using Eq. (7). Standard deviations of these plots by measurement are indicated with vertical bars. (A color version of this figure can be viewed online.)

Table 1

Solution mixture components for CS-MWCNTs.

Amount of solutions taken (ml)							
Solutions	**$FeCl_2$**	**CNTs in surfactant**	**DMPO**	**Surfactant**	**H_2O_2**	**Ultrapure water**	**Total volume**
Mixture A	0.4	None	0.4	0.4–0.8	0.4	Balance	2.0
Mixture B	0.4	0–0.4	0.4	Balance	0.4	0.4	2.0