

# **Differentiation of Various Carbon Nanotubes Using Redox Potential: Classification on a “Nano-Basis” by Size and Surface Modification**

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## **Abstract**

Carbon nanotubes (CNTs) have been applied to various fields of industries, and designing their structures has recently become an important issue to utilize CNT characteristics in industrial applications and secure their safety to human beings and the environment. In the present work, the hypothesis that redox potential of CNTs can predict surface reactivity, which was advocated in the previous article, was reproducibly verified by the experiments. Kinetics of thinner CNTs agreed with the reported result. However, CNT diameter and surface modifications change the reaction kinetics substantially, while doped particles in the

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center hollow parts of CNTs (Peapods) show a tendency to shift redox potential in a different direction. These findings make it possible to predict redox potential of CNTs from the morphology.

## **1. Introduction**

Carbon nanotubes (CNTs) have been predicted 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, 2]. Our previous article clarifies that the surface chemical reactivity of MWCNTs agrees with the redox potential hypothesis in light of the scavenging reaction of hydroxyl radicals [3]. A recent report on surface reactivity of single-walled nanotubes (SWCNTs) with oxidant also discusses the chemical reactions based on the redox potential kinetically [4]. However, the reactivity on carbon basal planes or graphene has not been elucidated in detail. Since scavenging radicals is chemically a simple and fundamental reaction to seek reactivity of a material, such an investigation would stimulate industrial applications and accelerate toxicological screenings of CNTs.

A classic report concluded that active reaction sites of graphenes were at those edges [5], which apparently influenced subsequent studies on carbons. A measurement of chemical reactivity was conducted on various carbon surfaces using the conversion rate of carbon to methane [6]. On the other hand, the rate limiting process of carbon redox reaction was investigated and determined using a conversion from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  on carbon electrodes [7]. It is noteworthy that a popular method of voltammetry to determine chemical reactivity on a solid surface was shown to have limitations and not to be generally applicable to determination of reactivity on carbon surfaces; the redox potential could be measurable only if a specific combination of chemicals was appropriately designed [8, 9]. Nugent et al. reported that electron transfer rate on a carbon surface using a reaction of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  was a good indicator to determine the redox potential and that CNTs reduced  $\text{Fe}^{2+}$  [10]. However, affinity

between Fe and carbon was not elucidated by their study while Fe forms carbide with carbons at slightly higher than room temperature. Meanwhile, Meréndez et al. showed detailed chemical reaction kinetics of graphene by their theoretical and experimental work [11]. The authors pointed out the importance of unpaired electrons at carbons of a graphene basal plane. This supports Andrieux [7] and Nugent's discussions at room temperature [10], while it implies that many articles exploring functions of carboxyl moieties and oxygen atoms on CNT surfaces seem inappropriate for their assumptions and analyses. They concluded as quoted, "*main contribution to carbon surfaces is from oxygen-free Lewis basis sites with graphene layers*". Radovic, who is in the same group as Meréndez, disclosed the further numerical study on the reactions [12]. In addition, CNTs could stabilize reduction reactions in fuel cells [13]. Those investigations suggest that CNTs donate electrons to radicals in redox reactions relatively, and that CNTs also behave as electron acceptors as a Lewis acid if the surrounding condition is shifted significantly.

CNTs, particularly SWCNTs and DWCNTs are unique because they can be doped by adding a material into their hollow centers without changing surface morphology as "Peapods". Although there has been interestingly no report in which chemical reactivity or kinetics is measured experimentally, ab-initio calculations have been conducted and reported [14-17]. These articles specified particular structures and/or reaction conditions to solve those equations numerically, even though those conditions are not realistic in the real world. Chemical reactions of peapods were investigated using several dry methods with fullerene@SWCNTs [18,19]; however, those authors merely predicted the possibilities of electron behaviors on peapod surfaces rather than reporting experimental results. Thus, chemical reaction kinetics of peapods have not been explored yet. It is of interest that all of those reports determined or pre-determined CNTs as p-type materials instead of adopting general acid/ base understandings.

The present work objectively investigated two points on chemical reactivity of the CNT surface. Firstly, the hypothesis on CNT redox potential that was established in our previous report [3] can be applied to evaluations of different types of CNTs in order to prove its reproducibility. Secondly, a nano-basis of CNTs is examined with CNTs of different physical properties, where CNTs are grouped by diameter, morphology, and peapod to classify those reaction magnitudes and tendency. The definition of nano-basis of CNTs will be discussed in the results and discussion section. The usefulness of an experimental method, the so-called Tsuruoka-Matsumoto method established previously [3] is purposely presented, where a simple hydroxyl radical scavenging reaction occurs and the radical concentration is measured in ultra low concentration of surfactant and CNTs with Electron Spin Resonance. The present work will be utilized to understand and predict how physical properties of CNTs affect their redox potential.

## **2. Experimental**

### **2.1. CNTs and Peapods**

DWCNTs (Toray DWCNTs) were purchased from Toray Industries, Inc., Tokyo Japan. The physical properties can be found elsewhere [20]. Peapods of AuCl<sub>3</sub>@DWCNT were synthesized as described in a previous article, while the high temperature holding period was extended for 48 hours instead of 24 hours as reported [20]. This was because the batch size of the present work was about 10 times larger than that in the article. The synthesized peapods were washed in diluted HCl solution (1 mol/L) to remove excess AuCl<sub>3</sub> particles on the CNT surfaces, and then washed by excess distilled water and dried. The peapods were stored in a desiccator until used for the present evaluations. Transmission electron microscopy (TEM, JOEL JEM-2100 equipped with Cs-corrected unit EM-Z07167T) and X-ray fluorescence (XRF, Rigaku XRF ZSX Primus II, Tokyo, Japan) analysis spectroscopy of those peapods are shown in Fig. 1. A simplified analysis that was installed in the XRF (Application Package,

EZS103MNV) was conducted to determine the amount of Au in the peapods; the atomic concentration of AuCl<sub>3</sub> was approximately 3 mass% of the peapods. Surface modified MWCNTs were prepared from Creos 24PS (GSI Creos Corporation, Tokyo, Japan) and characterized by GSI Creos Corporation (Tokyo, Japan). The average diameter and length of Creos 24PS were 80 nm and 5 μm, respectively, and the detail characteristics of Creos 24PS were reported in our previous article [3]. Creos AR50 was mechanically milled on the surface of 24PS. Creos AR50HT-Pt prepared from Creos 24PS was graphitized at 2800 °C in argon atmosphere and deposited platinum by 20 wt% on the surface. Creos Dew 60 was modified Creos 24PS surface that was exposed to nitric acid in order to dope oxygen atoms. O1s on the surface of Creos Dew 60 were about twice as much as that of Creos 24PS by X-ray photoelectron spectroscopy (XPS, AXIS Ultra) analysis. The average diameter and length of Nanocyl NC-7000 were 9.5 nm and 1.5 μm, respectively. The detail of characteristics can be found in our previous article [3]. Measurements of scavenging of hydroxyl radicals by CNTs were conducted using the ultra-low concentration surfactant method (Tsuruoka-Matsumoto method), where surfactant was controlled to a minimal concentration against MWCNT mass. Their good dispersion in water was obtained and surfactant influence was avoided in the analysis. Also the method characteristically uses substrate, such as polyester fibers, on which the pre-dispersed CNTs are held with surfactant and from which the CNTs are dispersed into pure water homogeneously in ultra-low surfactant concentration. Nanocyl N-7000 was dispersed from a specially prepared CNTEC<sup>®</sup> produced by Kuraray Living Co., Ltd., (Tokyo, Japan) and the details are found in our previous article [3]. Those scavenging data with Nanocyl N-7000 refer to that article [3]. The other CNTs were similarly dispersed into pure water from CNTEC-mimics and surfactant concentration was around 1/10 of the CNT level. The individual content of CNTs in those CNTEC-mimics was as follows; Toray DWCNTs at 12.0 wt%, AuCl<sub>3</sub>@DWCNT at 11.0 wt%, Creos 24PS at 12.1 wt%, Creos AR50 at 10.5wt%, Creos AR50HT-Pt at 9.2wt%, and Creos Dew 60 at 8.5wt%.

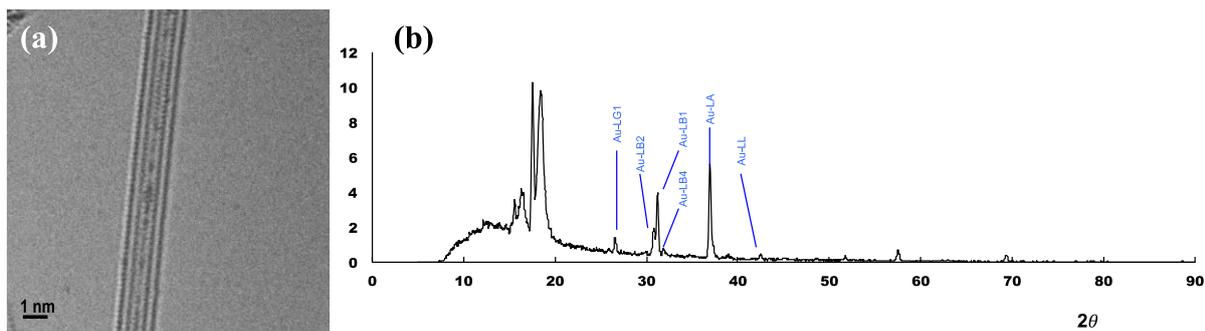


Fig.1 AuCl<sub>3</sub>@DWCNT characterization. (a) TEM image, (b) XRF spectrum. The vertical axis unit is A.U.

## 2.2. Preparation of Mixtures Measured and ESR-DMPO Method

The measurement method is similar to that of our previous article [3] as follows. A measuring mixture consisted of MWCNTs, hydrogen peroxide, ferrous chloride, and 5,5-dimethyl-1-N-oxide (DMPO). Hydrogen peroxide (hydrogen peroxide 30.0-35.5 mass%, Wako Pure Chemical Industries, Ltd., Japan) was diluted to 0.1 M with ultrapure water. The solution was stored in a refrigerator until the measurement. 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. 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 hours after preparation. Note that surfactant used in the present work was a zwitterionic type. Sample preparation for electron spin resonance was previously described [3]. 0.1 g CNTEC fibers were dispersed into 50 g of ultrapure water, which was sonicated for 30 minutes in an ultrasonic bath. The mixture was filtered with a Whatman filter paper (Whatman 42 with pore size at 2.5 μm) to remove polyethylene fibers and large agglomerates of MWCNTs. To obtain the lower concentration of CNTs, this solution was filtered with a Whatman filter paper (GF/F with pore size 0.7 μm) and then a Milipore filter (MF-Milipore GSWP 09000m with pore size at 0.22 μm). This

procedure did not change the surfactant concentration while the size distribution shifted, but the intrinsic chemical reactivity of CNTs did not change [3]. CNT concentration in the solution was measured by weighing CNTs after evaporation.

### **2.3. Electron Spin Resonance Measurement**

All solutions were mixed and measured at room temperature with Electron Spin Resonance (ESR) (JES-FA100, JEOL). ESR settings were the same as the previous work [3]: 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 minutes after mixing all of those solutions. The details were described in our previous article [21].

ESR spectra were normalized using Mixture in Table 1 with 0.1 ml CNT solution for individual CNT measurements. Thus, the scavenge ratio represents the normalized hydroxyl radical concentration in a solution. All of the samples were assessed at least five times and results were arithmetically averaged except the lowest and highest values. In the present work, pH buffer was not added because the buffer apparently affects the scavenging and adduct reactions. pH was not measured during ESR-DMPO measurement because a pH cell cannot be physically placed into the ESR cell.

## **3. Results and Discussion**

### **3.1. Reaction Kinetics of DWCNTs and Their Peapods**

Our hypothesis was adopted to analyze and evaluate results in the present work. According to the article [3], the Tsuruoka-Matsumoto method allows one to elucidate the redox reaction system as

$$S_{rad} = -q \ln|C_{Dn}| + qC_{Dn} + r \quad (1)$$

Or,

$$S_{rad} = -q \ln|C_{Dn} + s| + q(C_{Dn} + s) + r \quad (2)$$

where  $S_{rad}$  and  $C_{Dn}$  are scavenging ratio and MWCNT concentration in a mixture, and  $q$ ,  $r$ , and  $s$  are arbitrary constants.  $s$  is added to avoid taking  $C_{Dn}$  at zero in logarithmic axis numerically. We introduce a notion of “a nano-basis of CNTs” that means a size dependent and distinctive property in nano size that can be evaluated by a mathematical equation of kinetics. If a set of those coefficients for CNTs agrees with that for another, those kinetics of CNTs are regarded as having the same nano-basis of CNTs. Therefore, the hypothesis would be verified by reproducibility determining a nano-basis of CNTs. Note that experimental results and curve fitting using Eq. (2) are derived from Fig. S1 through S4 which present plots and/or standard deviations.

Relationships between hydroxyl radical concentration ratio and CNT concentration are plotted in Fig. 2 using Toray DWCNTs, their peapods, and Nanocyl N-7000. Those plots of experimental results are shown in Fig. S1 and those lines were calculated using Eq.(2). The plots for Toray DWCNTs obviously agree with Nanocyl N-7000, and hence both sets of those coefficients are similar, forming a single line. It is noteworthy that it is not an easy task to control a CNT concentration without agglomeration, balancing an ultra low surfactant concentration in a relatively higher CNT concentration, and that the measuring ranges do not overlap completely. Even with such considering the experimental limitations, the obtained result suggests that both of CNTs share the same kinetics in redox potential. On the other hand, in the same figure the peapods of  $\text{AuCl}_3\text{@DWCNT}$  does not agree with Toray DWCNTs at all, though they are postulated having the same surface morphology and characteristics. To confirm those plot tendencies, one can refer to Fig. S1 in which the DWCNTs and peapods are plotted in logarithmic and normal axes for  $C_{Dn}$ ; the latter also includes those standard deviations. The normal grid apparently shows smooth changes of  $S_{rad}$  with an increase of  $C_{Dn}$ . In Fig.2, as the peapod line lies around  $S_{rad} = 1$  horizontally, the

peapods intrinsically appear inert in the scavenging reaction. It means that electrons are not donated nor accepted on the peapod surface in the solution. The particles doped in the center hollow tubes significantly influence the surface electron behaviors and redox reactions through the rolled graphene layers. The phenomena were implied [25] but had not been reported experimentally.

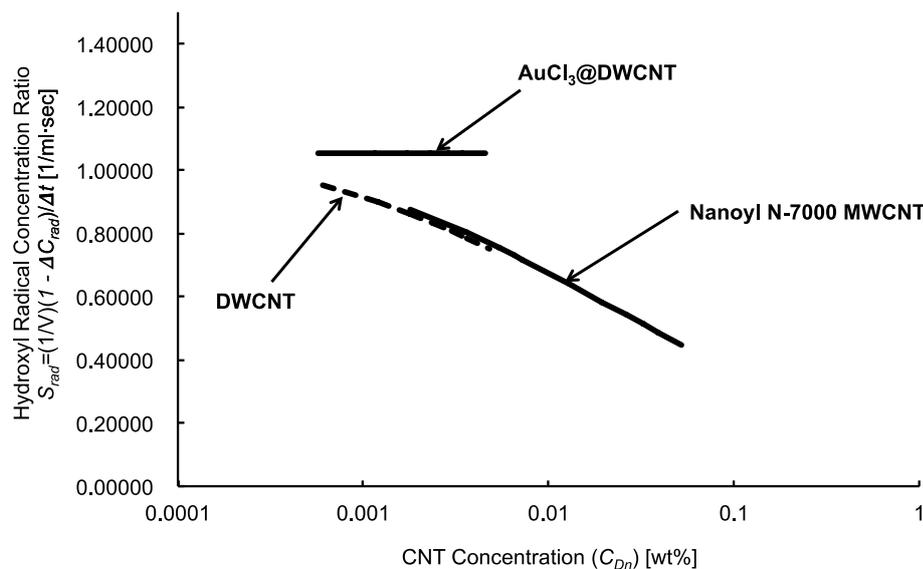


Fig. 2 Relationship between hydroxyl radical concentration ratio and CNT concentrations of Toray DWCNTs, AuCl<sub>3</sub>@DWCNT peapods, and Nanocyl N-7000.

Surface reactivity of peapods has been measured and discussed based on work function in light of solid state physics. Shirai and Ata measured work function values of HOPG, MWCNTs, and SWCNTs, and values were at 4.80, 4.95, and 5.05 eV, respectively [22]. The measurement was conducted using Ultraviolet Photoelectron Spectroscopy (UPS). Later, these values using the same measurement method reported ranged from 5.44 to 5.64 eV [23], and using thermionic emission method from 4.7 to 4.9 eV for SWCNTs, DWCNTs, and MWCMTs [24]. In those studies CNTs were interestingly regarded as p-type semiconductors and electron acceptors. However, Kotimäki [25] conducted an elaborated experiment on the phenomena and pointed out that the determination of p- and n- types relatively depended on electrode materials that were attached to CNTs. Furthermore, electron state of CNT surfaces

was significantly influenced by particles included in the center hollow tubes of SWCNTs. Note that Kotimäki used fullerenes and metallofullerenes as particles included. Because of the issue of attached electrodes the author questioned a previous study [26] in which peapods including azafullerenes were determined as n-type. These discussions indicate that electrons on CNT surfaces are definitely affected by particles included in the inner hollow tubes of CNTs, and that work function of those surfaces depends on measuring methods. Also, the values of work function for CNTs might be obtained in extreme and/or computable conditions only, which makes it difficult to estimate chemical reactivity for CNTs at room temperature.

The present work experimentally shows that electron behaviors on CNT surfaces are definitely influenced by particles included in the hollow tubes and, considering our previous article [3], CNTs donate electrons. The peapods of AuCl<sub>3</sub>@DWCNT do not donate nor accept electrons in the present case because the hydroxyl radical concentration does not change. This is simply explained as a kind of redox potential and a usual behavior of acid and base interactions. Although a surface reactivity measurement in the field of solid materials gives CNTs p-type characteristics, the present results indicate that CNT surfaces can be either condition of electron donors or acceptors, and those reactions can be characterized by chemical kinetics and Eq. (2), which suggests that chemical kinetics of CNT surface reactions are determined by the coefficients of  $q$ ,  $r$ , and  $s$ . They characterize redox potential of CNTs and allow one to predict chemical reactivity and bioactivity of CNTs.

### **3.2. CNTs Characterized by Redox Potential**

Since there is a variety of physical sizes and surface morphologies of CNTs, it is necessary to investigate compatibility among those CNTs regarding the kinetics by Eq. (2) characteristically. Like Fig. 2, Fig. 3 shows an experimental result of relationship between hydroxyl radical concentration ratio and CNT concentrations with Nanocyl N-7000 and Creos 24PS. The lines were calculated using Eq.(2). It is apparent that those sets of coefficients do

not agree with each other, and a rapid decrease of  $S_{rad}$  for Creos 24PS with an increase of CNT concentration is caused by significant contribution of the first term of the right-hand side of Eq. (2). It implies that  $C_{DN}$  in the first term has an index that is larger than one and the scavenging kinetics differ from that of Nanocyl N-7000. A comparison between Fig.2 and Fig.3 suggests there is a threshold on a nano-basis of CNTs characterized by chemical kinetics.

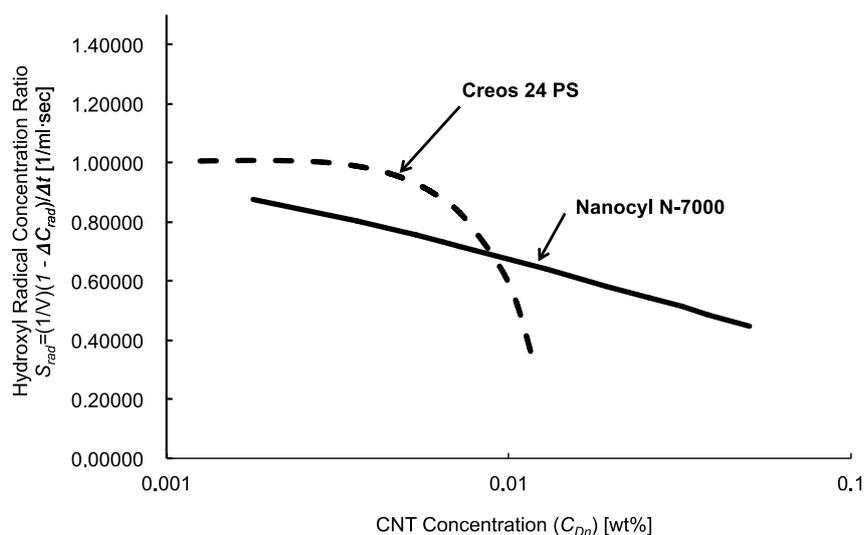


Fig. 3 Relationship between hydroxyl radical concentrations and CNT concentrations of Nanocyl N-7000 and Creos 24PS.

Fig. 4 shows the same drawings as Fig.3 but Creos 24PS derivatives were measured and summarized using Eq.(2). Surface morphologies of those derivatives were modified from Creos 24PS. One can find plots of experimental results with standard deviations in Fig. S3 through S5. What is interesting is that all of the surface modified products to enhance surface reactivity have the similar reaction kinetics, which differ from the original Creos 24PS. Furthermore, those surface modified ones indicate the more significant contribution of the first term of Eq. (2). The surface reactivity was substantially enhanced by an increase of electron donation. Since those products are modified by an increase of the number of dangling bonds or an addition of platinum particles on the surfaces, the results are straightforward. In addition, the product modified by oxygen doping similarly enhances the scavenging reaction

with hydroxyl radicals. Although radicals react with ketone or carboxyl on the CNT surfaces, the present work cannot verify a reaction model mentioned in a previous article [11]. The high reactivity also indicates that hydrogen peroxide is directly decomposed on those surfaces rather than being indirectly digested through the Fenton reactions and hydroxyl radical formation.

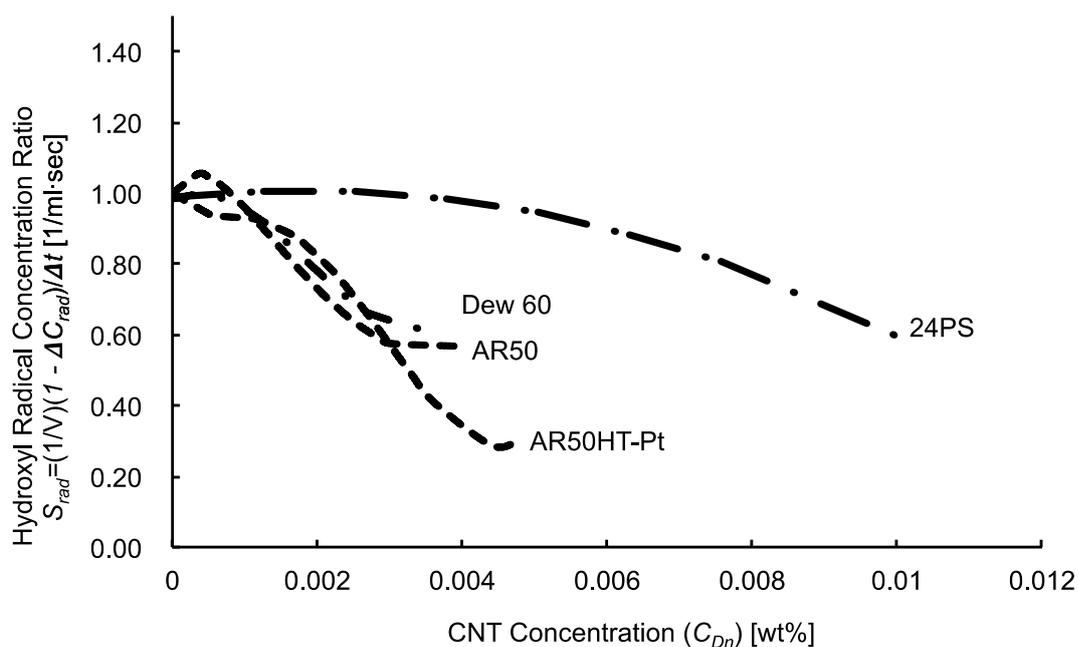


Fig. 4 Relationship between hydroxyl radical and CNT concentrations of Creos 24PS and its derivatives.

### 3.3. Nano-Basis of CNTs with Their Morphology

As mentioned above, Toray DWCNTs and Nanocyl N-7000 are identical in their kinetics elucidated by Eq.(2), while Creos 24 PS and the derivatives are very different from the former two CNTs. This indicates that the hypothesis expressed by Eq. (2) is reproducible among a Nano-Basis of CNTs, and CNTs can be characteristically classified into two types of nano-bases of CNTs. Furthermore, surface modification of CNTs gives the other nano-basis of CNTs. Thus, the nano-basis classification depends on CNT diameter and surface modification. For instance, a thinner type of CNTs kinetically shares a set of  $s$  values in Eq. (2) such as

Toray DWCNTs and Nanocyl N-7000, and the surface reaction is merely determined by CNT concentration. This simplifies CNT characteristics in chemical reactions, which allows ones to postulate bioactivities without experimental results individually. Therefore, CNTs without surface modification are classified into two groups of nano-bases of CNTs unless CNTs do not include other particles inside. Of course, it is necessary to investigate if another set of coefficients exists between Nanocyl N-7000 and Creos 24PS by size. On the other hand, Eq.(2) can be generally applied to redox reactions on CNT surface by adjusting the indices of the first and second terms of the equation though radical scavenging kinetics cannot be summarized into a unique one. To generalize the redox potential of CNTs theoretically, it is necessary to investigate the present experimental results with an assumption of electron pairs described by Mendéz's discussion [11], though it is beyond scope of the present work.

**Table 1.** Solution mixture components for CS-MWCNTs

Solutions	Amount of solutions taken [ml]						
	FeCl <sub>2</sub>	CNTs in surfactant	DMPO	Surfactant	H <sub>2</sub> O <sub>2</sub>	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

#### 4. Conclusion

A hypothesis advocated in our previous article [3] was reproducibly verified by the present experimental results. The Tsuruoka –Matsumoto method is useful to conduct the measurement. Thinner CNTs share the same characteristics in redox potential, which is determined by a nano-basis of CNTs. Particles doped in the center hollow tubes significantly affect CNT surface reactivity, which suggests that electrons on the surfaces are influenced by

interior particles through graphene layers. This particular work with AuCl<sub>3</sub> shows that those particles control electron donation to radicals. In conclusion, CNT diameter and surface modifications change the reaction kinetics by size effects. Doped particles in the center hollow parts of CNTs also change the redox potential of CNTs by electron distribution change in CNT layers. Such findings allow one to predict chemical and biological reactivities of CNTs using a nano-basis of CNTs.

### **Disclaimer**

The findings and conclusions in this report are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

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## Supplemental

Experimental results are plotted with their standard deviations and those fitting lines are calculated using Eq.(2).

$$S_{rad} = -q \ln|C_{Dn} + s| + q(C_{Dn} + s) + r \quad (2)$$

where  $q$ ,  $r$ , and  $s$  are arbitrary constant coefficients. Eq. (2) is numerically solved using “Solver” function in Microsoft Excel (For Mac2011 Ver.14) to determine  $q$ ,  $r$ , and  $s$ . The detail derivation of Eq. (2) refers to our previous article [3].

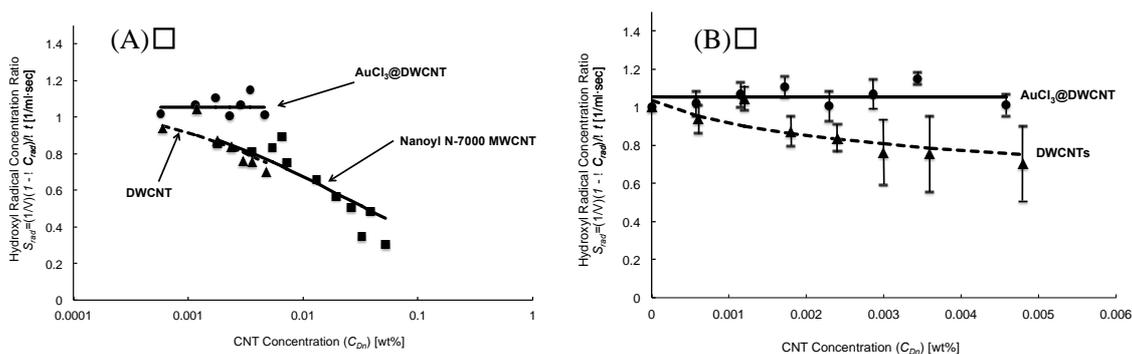


Fig. S1. Relationship between hydroxyl radical concentration ratio and CNT concentrations. (A) Toray DWCNTs, AuCl<sub>3</sub>@DWCNT peapods, and Nanocyl N-7000. (B) Toray DWCNTs and AuCl<sub>3</sub>@DWCNT peapods. Vertical bars show those standard deviations of experimental results.

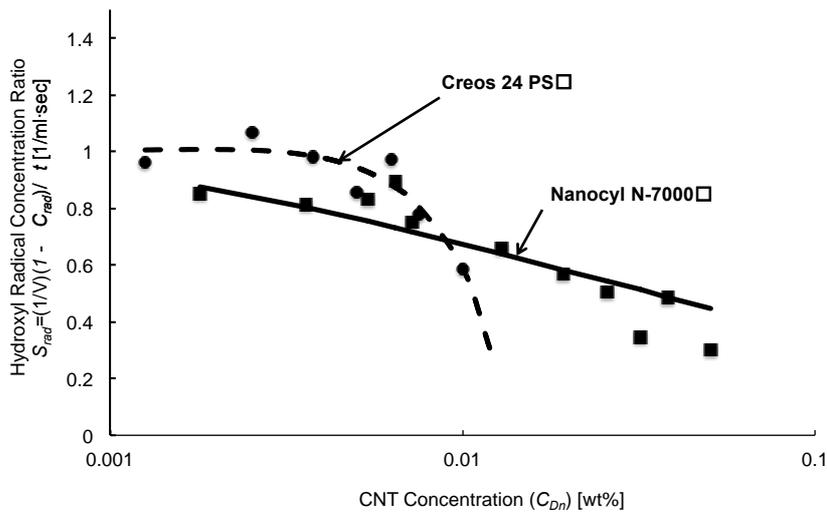


Fig. S2. Relationship between hydroxyl radical concentration ratio and CNT concentrations of Creos 24PS MWCNTs and Nanocyl N-7000.

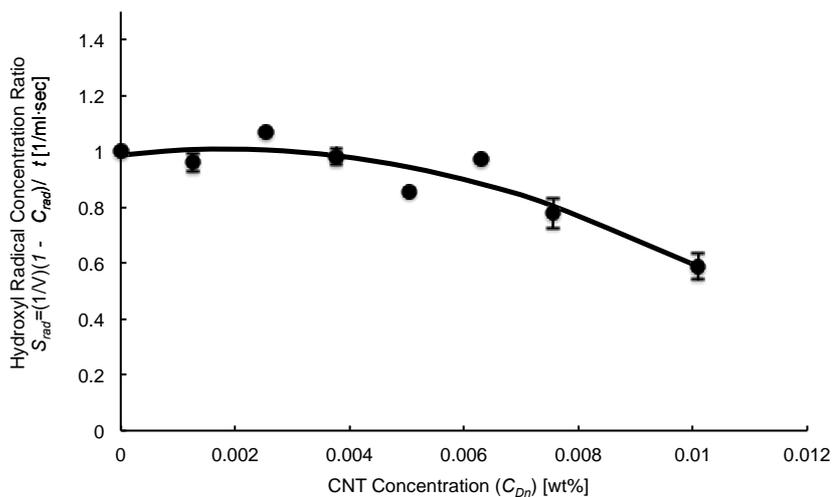


Fig. S3. Relationship between hydroxyl radical concentration ratio and CNT concentrations of Creos 24PS MWCNTs. Vertical bars show those standard deviations of experimental results.

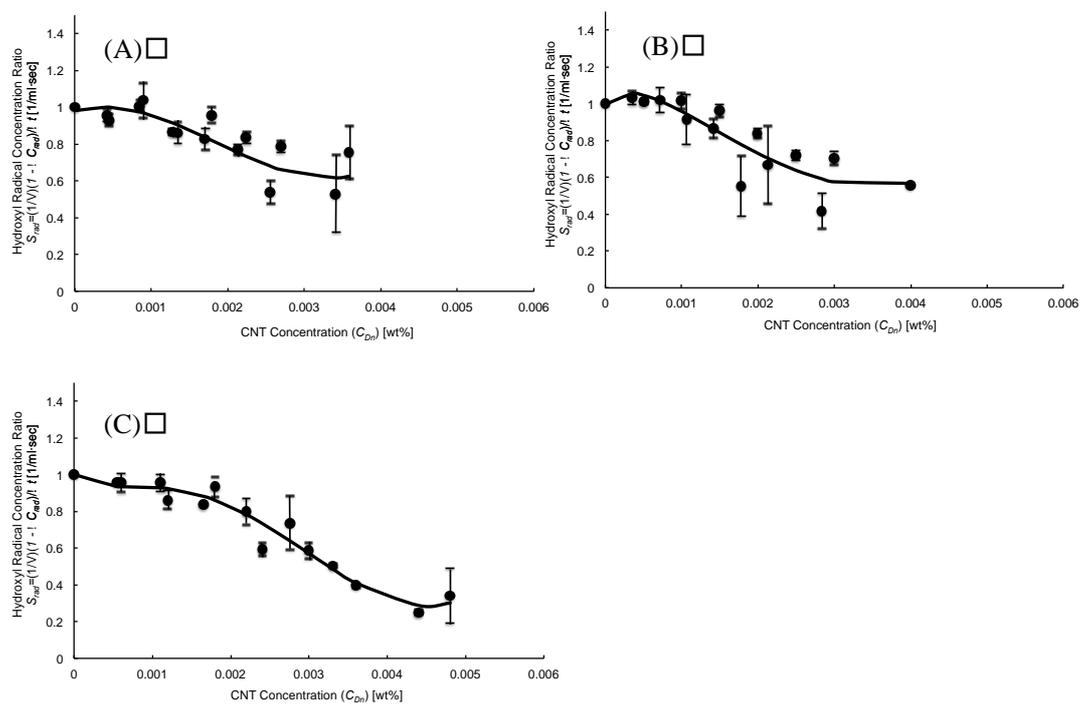


Fig. S4. Relationship between hydroxyl radical concentration ratio and CNT concentrations of derivatives from Creos 24PS MWCNTs. Vertical bars show those standard deviations of experimental results. (A) Dew 60, (B) AR50, and (C) AR50HT-Pt