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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.

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

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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 ($OH^{\cdot}$), 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

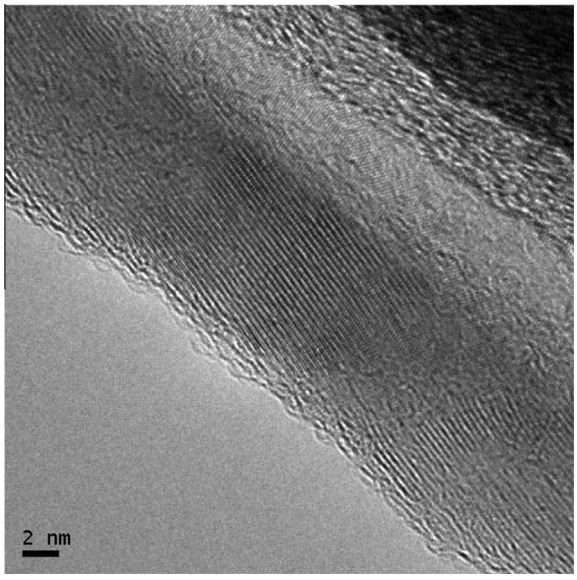

Fig. 1 – An electron microscopy picture of a CS-MWCNT. Graphene layers are stacked and are not parallel to the fiber axis. There are edges of graphene sheets on the surface.