Carbon 95 (2015) 302–308

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Differentiation of chemical reaction activity of various carbon nanotubes using redox potential: Classification by physical and chemical structures

Shuji Tsuruoka [a, *], Hidetoshi Matsumoto [b, **], Vincent Castranova [c], Dale W. Porter [d], Takashi Yanagisawa [e], Naoto Saito [f], Shinsuke Kobayashi [f], Morinobu Endo [g]

[a] *Aquatic Innovation Center, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan*
[b] *Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan*
[c] *West Virginia University, Morgantown, WV, USA*
[d] *Pathology & Physiology Research Branch, National Institute for Occupational Safety and Health, 1095 Willowdale Rd. (M/S2015), Morgantown, WV, USA*
[e] *GSI Creos Corporation, 1-12, Minami-Watarida-cho, Kawasaki, Kanagawa 210-0855, Japan*
[f] *Department of Applied Physical Therapy, Shinshu University, School of Health Sciences, 3-1-1 Asahi, Matsumoto, Nagano, Japan*
[g] *Institute of Carbon Science and Technology, Shinshu University, Nagano 380-8553, Japan*

ARTICLE INFO

Article history:
Received 7 April 2015
Received in revised form
4 July 2015
Accepted 15 August 2015
Available online 17 August 2015

ABSTRACT

The present study systematically examined the kinetics of a hydroxyl radical scavenging reaction of various carbon nanotubes (CNTs) including double-walled and multi-walled carbon nanotubes (DWCNTs and MWCNTs), and carbon nano peapods ($AuCl_3$@DWCNT). The theoretical model that we recently proposed based on the redox potential of CNTs was used to analyze the experimental results. The reaction kinetics for DWCNTs and thin MWCNTs agreed well with the theoretical model and was consistent with each other. On the other hand, thin and thick MWCNTs behaved differently, which was consistent with the theory. Additionally, surface morphology of CNTs substantially influenced the reaction kinetics, while the doped particles in the center hollow parts of CNTs ($AuCl_3$@DWCNT) shifted the redox potential in a different direction. These findings make it possible to predict the chemical and biological reactivity of CNTs based on the structural and chemical nature and their influence on the redox potential.

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]. Industrially, modifications of CNT structures have become an important issue to obtain appropriate functionalities and safety in use, because multi-walled CNTs (MWCNTs) are applied and commercialized broadly. Under the circumstance a crucial goal will be to design safe CNT structures, since toxicological evaluations on CNTs are advancing leading to a predictive exposure limit for MWCNTs [3]. Our previous article [4] clarifies that the surface chemical reactivity of MWCNTs agrees with the redox potential hypothesis in light of the scavenging reaction of hydroxyl radicals, and discusses this groundbreaking challenge that requires identification of a key control mechanism of toxicological phenomena. The relative importance of specific physicochemical properties has not been defined explicitly, while critical points concerning CNT safety evaluations are summarized as the fiber paradigm and bioactivity, *e.g.*, metal impurities of CNTs [5]. The former refers to effects of physical contact with cells and tissues. The latter refers to chemical reactions on the CNT surface, relating to reaction kinetics of CNTs. In this regard, CNT chemical reactivity must be explored based on redox reactions. Although metallic impurities of CNTs have been discussed elsewhere [6–13], a reaction mechanism for CNTs is not beyond expectations [14–18]. Those researchers used hydroxyl radicals to explore the surface reactivity of CNTs because they were keen to determine whether reactive oxygen species were generated by CNTs. A recent report, concerning surface reactivity of single-walled nanotubes (SWCNTs) with oxidant species, discussed the redox potential kinetically [19].

---

[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: Tsuruoka.saitama@gmail.com (S. Tsuruoka), matsumoto.h.ac@m.titech.ac.jp (H. Matsumoto).

http://dx.doi.org/10.1016/j.carbon.2015.08.048
0008-6223/

Even though many researches strove to find out the reaction mechanism, the reactivity on carbon basal planes or graphene has been limited within solid-state functions.

A classic report concluded that active reaction sites of graphenes were at the edges [20]. After this report, chemical reactivity with various carbon surfaces was measured; the conversion rate of carbon to methane was a typical indicator [21]. On the other hand, the rate limiting process of carbon redox reaction was investigated using a conversion from Fe^{2+} to Fe^{3+} on carbon electrodes [22]. It is noteworthy that a popular method of voltammetry to determine chemical reactivity on a solid surface has limitations and is not generally applicable to measurement of true reactivity of particle material surfaces [23,24]. Nugent et al. reported that electron transfer rate can be specified on a carbon surface using a reaction of Fe^{2+} to Fe^{3+} in order to determine the redox potential [25]. However, they did not discuss affinity between Fe and carbon well, though it is known that Fe forms carbide with carbons at room temperature. Meanwhile, Menéndez et al. showed detailed reaction kinetics of graphene theoretically and experimentally [26]. The authors pointed out the importance of unpaired electrons at the carbons of a graphene basal plane. This supports Andrieux [22] and Nugent's [25] discussions, implying that functions of carboxyl moieties and oxygen atoms on CNT surfaces have not been understood appropriately. They concluded as quoted, "*main contribution to carbon surfaces is from oxygen-free Lewis* (acid and) *base sites with graphene layers*", where the reaction kinetics relates to redox potential. Radovic reported and strengthened the point by the mathematical study of the reactions [27]. In addition, the discussion was supported by CNTs' stabilization in reduction reactions of fuel cells [28]. Peng et al. found that MWCNTs doped with cadmium sulfide (CdS) were electron acceptors and catalyzed conversion of water to hydrogen (and inevitably oxygen) in a photoreaction, where radical formation and degeneration were implicitly included [29]. This shows that MWCNTs are both electron acceptors and donators in redox reactions depending on their relative chemical potentials. Those investigations suggest that CNTs behave as electron acceptors as a Lewis acid under a certain condition.

SWCNTs and DWCNTs are particularly unique because they form carbon nano "Peapods" without changing surface structure. Peapods can be utilized for the semiconductor materials of electronic devices (*e.g.*, field-effect transistors and sensors) [30] and the templates leading to the formation of supra-molecular and 1-D nanostructures [30,31]. Although there has been interestingly no report in which chemical reactivity is measured experimentally, the first principle calculations of reactivity have been conducted and reported [32–35]. These articles specified particular structures and/or reaction conditions to solve those first principle equations numerically, even though the boundary conditions are not realistic. Chemical reactions of peapods were physically investigated using fullerene@SWCNTs [36,37]; however, these authors merely predicted the possibilities of electron behaviors on peapod surfaces rather than reporting experimental results. 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 chemical reactivity of the CNT surface. Firstly, the hypothesis on CNT redox potential established in our previous report [4] was applied to evaluations of different types of CNTs in order to prove its generalizability. CNTs with different diameter and surface morphology were chosen to pursue it. Secondly, a grouping of CNTs was attempted in terms of the physical properties and scavenging reaction behaviors. The established experimental method [4] was adopted, where hydroxyl radical scavenging was measured by the electron spin resonance (ESR) method. The present work presents a method to predict CNT redox potential using their physicochemical properties.

2. Experimental

2.1. CNTs and peapods

Fig. 1 shows TEM images of CNTs used in the present work, except Nanocyl N-7000, using JEM-2100 equipped with Cs-corrected unit EM-Z07167T, JOEL, Tokyo, Japan. The physical properties are summarized in Table 1 and can be found elsewhere [38,39]. DWCNTs were purchased from Toray Industries, Inc., Tokyo Japan. 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 elsewhere [4]. Creos AR50 was mechanically milled on the surface of Creos 24PS. Creos AR50HT-Pt prepared 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, Shimadzu AXIS Ultra, Kyoto, Japan) analysis. The average diameter and length of Nanocyl NC-7000 were 9.5 nm and 1.5 μm, respectively.

Peapods of $AuCl_3$@DWCNT were synthesized in our lab. The obtained Toray DWCNTs were washed in deionized pure water and ethanol to remove dispersant and residues, and then heated at 383 K to remove moisture. The peapods were synthesized using a glassware apparatus depicted in Fig. S1 in Supplemental. One hundred mg of DWCNTs were weighed on an electronic balance and placed in the main tube of a two-way Pyrex® glass tube. One hundred mg of $AuCl_3$ (Wako Pure Chemical Industries, Osaka, Japan) was placed in the side tube. The main tube was heated in a heating mantle at 423 K and de-gassed using a vacuum pump. This de-gassing was conducted in two steps; the DWCNTs were first dried and then a target pressure was achieved. After reaching 10^{-5} Pa inside the tube, the tube neck was melted and sealed. The main and side tubes were placed in a heating mantle at 773 K for 24 h, cooled down to room temperature, and peapods were taken out from the main tube. The synthesized peapods were washed in diluted HCl solution (1 mol/L) to remove excess $AuCl_3$ particles on the CNT surfaces, and then washed by excess distilled water and dried. The peapods were stored in a desiccator. Transmission electron microscopy and X-ray fluorescence (XRF, Rigaku XRF ZSX Primus II, Tokyo, Japan) analysis spectroscopy of those peapods are shown in Fig. 2. 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 $AuCl_3$ was approximately 3 mass% of the peapods.

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. By the method, the good dispersion of CNTs in water was obtained, and the influence of surfactant was minimized in the analysis. The method characteristically uses substrate, such as polyester fibers, on which the pre-dispersed CNTs are held and from which the CNTs with residual surfactant are dispersed homogeneously into pure water. CNTEC® was made of polyester fibers coated with 12 wt% Nanocyl NC-7000 in a dry condition. Weight ratio of concentration of the surfactant to MWCNTs of CNTEC® was specially fixed at 26.2–100 in a dry condition. CNTEC® fibers (0.1 g) were dispersed into 50 g of ultrapure water, which was sonicated for 30 min in an ultrasonic bath. The mixture was filtered through a Whatman filter paper (Whatman 42) to remove polyester fibers and large agglomerates of MWCNTs. The solution was filtered with a Whatman filter paper