



The photochemistry of carbon nanotubes and its impact on the photo-degradation of dye pollutants in aqueous solutions



Bingdang Wu^a, Dunxue Zhu^a, Shujuan Zhang^{a,*}, Weizhen Lin^b, Guozhong Wu^b, Bingcai Pan^a

^aState Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210023, China

^bShanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201203, China

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ABSTRACT

It is reported that carbon nanotubes (CNTs) could either generate reactive oxygen species (ROS) under light irradiation or serve as high-efficient scavenger for ROS. However, it is unclear which role predominates as CNTs enter into aquatic environment. To answer this question, a systematic study of the photochemistry of a pristine and a surface-functionalized CNTs in aqueous suspensions was investigated with both time-resolved and steady state analytical approaches. The transient absorption spectra demonstrate that CNTs could be photo-ionized and trap hydrated electrons upon high energy irradiation. In steady state UV irradiation, CNTs could promote the generation of ROS, such as $^1\text{O}_2$ and $\cdot\text{OH}$. However, in the presence of H_2O_2 , the $\cdot\text{OH}$ scavenging effect predominated in the aqueous suspensions of CNTs. The presence of CNTs suppressed the photo-degradation of dye pollutants, as an integrated result of inner filter effect, adsorption effect, and ROS generation and scavenging effect. The results provide useful information for the understanding of the environmental implications of CNTs.

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1. Introduction

Carbon nanotubes (CNTs), as a class of carbon allotropes, can be visualized as tubes rolled up by graphene and capped with fullerene. According to the wall number, CNTs can be divided into two categories: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [1]. Besides the large specific surface area and length to diameter ratio, CNTs have many other unique properties, such as the single dimensional structure [2], high mechanical strength [3], controllable electronic property [4], and high temperature resistance [5]. These special characteristics make CNTs a type of promising materials. With the ever-increasing demand from industry and commerce, abundant productions containing CNTs are producing and will be produced, consumed and finally released to the environment [6]. As a result, their impact on the aquatic environment cannot be ignored [7]. On the other hand, more and more researchers are eager to utilizing CNTs to synthesize new materials for the purpose of pollution control [8]. For example, some researchers have combined CNTs with titanium dioxide to fabricate efficient and feasible photocatalysts for elimination of organic pollutants by using the energy of light [9–12]. The photochemistry of CNTs becomes an important topic, because it is

related with the fate, transport and transformations of both CNTs and other contaminants in aquatic and terrestrial environments.

Although CNTs have been studied for more than 20 years since their discovery in 1991 [13], the photochemistry of CNTs is still not fully comprehended. Great research efforts have been made on the photochemistry of CNTs in recent years. For example, Chen and Jafvert found that reactive oxygen species (ROS), such as singlet oxygen ($^1\text{O}_2$), superoxide radical (O_2^-), and hydroxyl radical ($\cdot\text{OH}$), could be generated by a carboxylated SWCNT (SWCNT-COOH) under a long time irradiation of natural sunlight [14,15]. Li and coworkers also detected the production of $^1\text{O}_2$ in the study of the photochemical transformations of MWCNT-COOH [16] and even explored how this transformation affects the mobility of CNT in water [17]. On the other hand, Fenoglio and coworkers supported the viewpoint that MWCNT may serve as a high-efficient scavenger of $\cdot\text{OH}$ and O_2^- [18]. The free radical scavenging abilities of CNTs was related to the structures of CNTs, including diameter, length, chirality and point defect [19–22]. Thus, there is an open question: what is the main role of CNTs in terms of photochemistry, generating or scavenging ROS? This seems like a paradox. To answer this question, we need to know exactly how ROS are generated or scavenged by CNTs. Considering the environmental significance, detection of ROS generated by CNTs was conducted under solar or UV irradiation on a long time scale up to several days to record the concentration evolution of target probing mole-

* Corresponding author.

E-mail address: sjzhang@nju.edu.cn (S. Zhang).

cules [12,14,15]. In this way, the generation of ROS was confirmed. However, it is difficult to know the balance of ROS generation and scavenging by CNTs. The lifetimes of the transient species generated by CNTs are key parameters in determining their environmental implications.

Time-resolved laser flash photolysis (LFP) and pulse radiolysis (PR) are powerful techniques for investigation of transient species. LFP and PR study of C_{60} and its derivatives has been performed in the latest decades [23,24]. In recent years, there were also some similar investigations on CNTs [25,26]. However, most of the LFP and PR studies on CNTs were aimed at either the compound of CNTs with other organic matter [27], semiconductors [28], and metallic compounds [29], or modified CNTs with functional groups [30,31]. Based on these studies, CNTs play a significant role in the intermolecular photochemical conversion by acting as an electron donor or electron acceptor. However, the photochemical transformation of neat CNTs in pure water is still unknown.

In the present work, the photochemistry of both pristine and surface functionalized CNTs in aqueous suspensions was investigated with both time-resolved and steady state analytical approaches, including LFP, PR, electron paramagnetic resonance (EPR) spectroscopy, and high performance liquid chromatography (HPLC). The effects of CNTs on the photo-degradation of dye pollutants were examined to evaluate their ROS generating and scavenging abilities.

2. Materials and methods

2.1. Materials

A short-length SWCNT (S-SWCNT, purity: >90%, outer diameter: 1–2 nm, inner diameter: 0.8–1.6 nm, length: 1–3 μm , specific surface area: 486 m^2/g) and a hydroxylated MWCNT (MWCNT-OH, purity: >95%, -OH content: 5.58%, outer diameter: <8 nm, inner diameter: 2–5 nm, length: 10–30 μm , specific surface area: 192 m^2/g) from Shenzhen Nanotechnology Co., Ltd. (China) were used as received without further purification. The spin trap, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), was obtained from Sigma-Aldrich. Nitro blue tetrazolium chloride (NBT), 4-oxo-2,2,6,6-tetramethyl-4-piperidinol (TEMP), and tert-butanol (*t*-BuOH) were purchased from Aladdin Co., China. Acid orange 7 (AO7, $C_{16}H_{11}N_2NaO_4S$), also known as Orange II, was obtained from Shanghai Chemical Reagent Company. Rhodamine B (RhB, $C_{28}H_{31}ClN_2O_3$) was purchased from Tianjin Chemical Corp., China. They are all of chemical reagent grade and used without further purification. Hydrogen peroxide (H_2O_2) was purchased from Shanghai Chemical Reagent Company, China. Methanol of HPLC grade and all other chemicals of the highest purity available were used as received. Ultrapure water with a resistivity of 18.25 $\text{M}\Omega\text{ cm}$ was made with an Aquapro AFZ-0501-u system and was used for the preparation of solutions.

2.2. Sample preparation

Aqueous CNT stock suspensions were prepared by direct sonication. An aliquot of 10 mg S-SWCNT was added to 100 mL ultrapure water and sonicated with an ultrasonic cell crusher (JY88-II) for 4 h (the power is under 50 W). The same procedure was used for the preparation of the MWCNT-OH stock suspensions. The prepared suspensions were stored in dark at 4 °C until use. Unless otherwise stated, the concentration of CNTs used in the experiments was 40 mg/L. DMPO solutions were prepared with a pH 7.4 phosphate buffer solution. The pH of all other solutions were prepared as-is without any adjustment.

Stock solutions of 2 mM AO7 and 0.2 mM RhB were prepared by dissolving the dyes in ultrapure water. The initial concentrations used for irradiation experiments were 0.2 and 0.02 mM for AO7 and RhB, respectively. Prior to irradiation, the dye solutions in the presence of CNTs were kept in dark for 12 h to make sure the adsorption of dyes on the CNTs was equilibrated. The concentration of dyes after adsorption was calculated according to the absorbance at the characteristic wavelength (484 nm for AO7 and 554 nm for RhB) and was used to calibrate the adsorption effect on the degradation rate constant. The dye solutions in the presence of CNTs were labeled with “w/” whereas the solutions calibrated with CNT adsorption but in the absence of CNTs were labeled with “w/o”. The H_2O_2 dosage in the dye solutions was 0.5 mM.

2.3. Irradiation experiments

Irradiation experiments for dyes were carried out in a thermostatic rotating disk photoreactor (Nanjing StoneTech Electric Equipment Co., China) with a 300 W mercury which emits light in the UVA range (centered at 365 nm). More details about this photo-reactor and the output spectrum of the medium pressure mercury lamp used in this work has been reported in our previous work [32].

2.4. LFP and PR experiments

LFP experiments were carried out with a KrF excimer laser, which provides 355 nm pulses with duration of 10 ns and energy of 10–50 Gy per pulse. The laser and analyzing light beam passed perpendicularly through a quartz cell. The transmitted light entered a monochromator equipped with a R955 photomultiplier. The signals were collected using an HP54510B digital oscillograph and then recorded by the computer system.

PR experiments were conducted by using a linear accelerator providing 10 MeV pulse with duration of 8 ns. The dosimetry of electron pulse was determined with a thiocyanate dosimeter containing 10 mM KSCN solution saturated with nitrous. The average dose per electron pulse was 10 Gy. The apparatus for measurement and accounting is the same as that for LFP [33].

2.5. EPR and HPLC analysis

All the EPR spectra were recorded using a Bruker EMX-10/12 EPR spectrometer. The settings for the EPR spectrometer were as follow: center field: 3480 G; sweep width: 200.0 G; microwave frequency: 9.785 GHz; temperature 296 K, microwave power: 20 mW, field modulation: 0.1 mT at 100 kHz, scan time: 83.8 s. The light source for EPR determination was a 180 W mercury lamp. Quartz and glass capillary tubes with an inner diameter of 1 mm were used in the UV and visible light irradiation experiments.

HPLC experiments were carried out with a Dionex Ultimate 3000 HPLC system equipped with an UV detector. An Agilent 4.6 \times 150 mm, 5 μm ZORBAX Eclipse Plus C18 column was used for separation. Mixture of ultrapure water and methanol was served as the mobile phase. The mobile phase were eluted from 90:10 (methanol/ H_2O) to 10:90 (methanol/ H_2O) in 30 min for RhB. For AO7 detection, methanol and 0.1% formic acid solution were eluted from 90:10 to 10:90 in 30 min. All the samples containing CNTs had been filtered through a 0.22 μm membrane prior to HPLC analysis.

2.6. UV-Vis spectrum

The color fading of dye solutions after irradiation and the UV-Vis absorption spectra of CNTs in aqueous solutions were recorded

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