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Probing the interphase “HO• zone” originated by carbon nanotube during catalytic ozonation

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ABSTRACT

Carbon nanotube (CNT) is an attractive metal-free catalyst that can be explored in combination with ozone treatment. Using fluorescence microscopy image analysis, we investigated the production of hydroxyl radicals (HO•) within the solid-liquid interphase for CNT-mediated catalytic ozonation. The visualized results suggest that HO• was vastly generated via catalysis and accumulated within a surface region of the CNT (we defined this region as the interphase “HO• zone”). In this region, using 7-hydroxycoumarin as a HO• marker, the radical abundance was at least 1000 times higher than that in the aqueous bulk phase. Owing to the observed inhomogeneity of HO•, the CNT/ozone system effectively decomposed perfluorooctane sulfonate that was fairly resistant to non-catalytic ozonation, and the decomposition kinetics was not much inhibited by tert-butanol as bulk-phase HO• scavenger due to the remaining “HO• zone” at surface region available for reaction. A longevity trial revealed the sustained formation of the interphase “HO• zone” and strongly indicated that the graphitic structure may optimize the density of surface active sites responsible for the proliferation and local concentration of HO•. CNT, with good catalytic efficiency, longevity and stability, is anticipated as the basis of future nanomaterials able to promote HO• exposure in ozone treatment for advanced oxidation process.

1. Introduction

Carbon-mediated catalytic ozonation (CCO) is an attractive water treatment method that takes advantage of advanced oxidation processes (AOPs) (Beltrán et al., 2006; Moussavi et al., 2009). Although metal oxides have been extensively utilized (Yang et al., 2009; Trapido et al., 2005), carbon materials with metal-free framework have exhibited good performance in accelerating the transformation of ozone (O_3) into hydroxyl radicals (HO•) that serve as a powerful oxidant ($E^0(HO\bullet/H_2O) = +2.80$ V) (Nishiyama et al., 2015). The frequent study of CCO dealing with some persistent and/or bio-recalcitrant organics is motivated by the fact that HO•-induced oxidation owing to catalysis usually present to be much more efficient and complete than the combined effects of adsorptive removal and plain ozonation without a carbon catalyst. While activated carbon has been widely used for water and wastewater remediation (Faria et al., 2007; Sánchez-Polo et al., 2005), carbon nanotube (CNT), which is one of the smallest carbon-organized structures, has attracted increasing attention owing to its prominent physical and chemical properties. The structural integrity of CNT allows it to serve as redox mediator (van der Zee et al., 2003), its mesoporous properties allow higher surface availability for mass transfer, and the chemical stability gives it a higher lifetime in corrosive environments. Moreover, nanoscale carbon has been identified to be interface active (Kordač and Linek, 2006; Zhang et al., 2015) with potential to enhance mass transfer and allow an easier access of ozone to the active surface sites in a heterogeneous system. In recent years, CNT has been studied as ozone catalyst (Yan et al., 2015; Gonçalves et al., 2012; Tizaoui et al., 2015; Fan et al., 2014). Great efforts have been made in the surface modification of CNT (e.g., carboxylation (Qu et al., 2015), N-doping (Soares et al., 2016), and ball-milling (Soares et al., 2015)) to expedite the conversion of O_3 to HO•, as the production of an ample amount of HO• will increase the overall kinetics for water

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treatment.

Previous reports have focused on tracking the reaction pathway of CCO as a function of HO•, i.e., by following a global signal of HO• with a probe (e.g., EPR spin-trapping (Xiao et al., 2016)) or by studying the decomposition kinetics of O_3-persistant organics (Liu et al., 2011) or the HO•-attributable chemicals (e.g., *para*-chlorobenzoic acid (Sanchez-Polo et al., 2006)). To date, the production of HO• within the surface region has seldom been characterized, and this characterization is believed to be important for the evaluation of catalytic performance and for a better process control. The production of HO• via catalysis closely correlates with the surface chemistry (e.g. the presence of oxygen groups (Gonçalves et al., 2010), acid-base properties (Xing et al., 2014), etc.) or maybe a consequence of their interrelated function. Actually, it is difficult to directly link this production to one or more particular characteristics of carbon surface because any change in the catalytic ability may be confounded by differences in the available reactive surface area, since the size, morphology and distribution of the carbon particles will inevitably change in different systems or after long periods of surface exposure to oxidants such as O_3 and HO•. In addition, conflicting results have suggested that the oxidized surface is beneficial to (Oulton et al., 2015), is detrimental to (Liu et al., 2010), or has little effect on (Gonçalves et al., 2010) the HO·-assigned CCO.

On the other hand, an effective AOPs through the radical-organic interaction not only relies on the chemistry of target compound such as the stability to oxidation, but is kinetically subject to the availability of HO• radicals that would effectively work in an accumulated or concentrated state as the powerful oxidant. The latter point has not yet been clearly addressed for heterogeneous CCO system. Some reports have suggested that AOPs mainly occur in the aqueous bulk phase as a function of the amount of HO• generated and released from the surface during catalytic ozonation (Nawrocki, 2013; Gül et al., 2007; Beltrán et al., 2002). Contrary reports indicated that the aqueous bulk phase suffers from the severe stoichiometric limitations of HO• against notable AOPs (Faria et al., 2008; Liu et al., 2009). Generally, it is currently not a matter of consensus about whether HO• persist in the aqueous bulk phase or as concentrated species within the solid-liquid interphase during catalysis. The lifetime of HO· is extremely short in the aqueous phase since it is nearly non-selective in electrophilic reactions with organic/inorganic substances ($k_{HO\cdot}$~10^{8-10} M^{-1} s^{-1}) (Glaze and Kang, 1989). On this regard, the radical loss in the process of surface-to-bulk transfer should not be neglected when considering an effective use of HO• produced from a surface, since a fraction of HO• radicals would possibly deactivate in water or be consumed by competitive solutes. In lack of more clear evidence, it is the suspended question for catalytic ozonation about the inhomogeneity of HO• radicals and the way that HO• works for a kinetically favorable AOPs.

In this work, we addressed the aforementioned gaps related to the performance of the CNT surface for enhanced HO• generation and exposure during ozonation. Using fluorescence microscopy image analysis (FMI), we characterized the inhomogeneity and intensity of HO• production originating from CNT-mediated catalytic ozonation. To examine the impacts of the "HO• zone" formed within the solid-liquid interphase, a series of comparisons was made between the CNT/ozone system and non-catalytic ozonation using perfluorooctane sulfonate (PFOS) as a persistent contaminant, *para*-chlorobenzoic acid (p-CBA) as an indicator for HO•, oxalic acid (OA) as a frequently reported terminal product, and tert-butanol (TBA) as a model radical scavenger. To probe the origin of the interphase "HO• zone", different particle/ozone systems (CNT, fine graphite, and powdered activated carbon) were compared. To explore mechanistic details, the production of HO• radicals at the surface (indicated by FMI), the variation in surface chemistry for prolonged exposure to ozone (characterized by X-ray photoelectron spectroscopy [XPS]), and the formation of superoxide radicals ($\bullet O_2^-$) as an intermediate for the chain reactions (detected by electron paramagnetic resonance [EPR]) were studied.

2. Materials and methods

2.1. Materials and reagents

Commercial multiwalled CNT was acquired from DKNANO Co. Ltd. (Beijing, China). The materials and reagents are presented in the Supporting Information (SI). Relevant physical and chemical properties of the starting solid particles are listed in Table S1.

2.2. Procedures for catalytic ozonation

Reactions were performed in a semi-batch cylinder reactor with inner diameter of 10 cm. Solid powder at amount of 5 mg was ultrasonically dispersed to optimize the distribution and then transferred to the reactor with working volume of 1 L. Gaseous ozone was produced by a generator (5 g/h) using pure oxygen as the source gas, and bubbling introduced at the bottom of reactor at 1 L/min to initiate catalysis. As ozonation commenced, an aliquot of sample was withdrawn periodically from the reactor by a syringe, went through a 0.45 μm filter membrane to remove the solid phase, and was sent for analysis on the obtained liquid phase. While all the other reactions involved in this work took place in aqueous environment, the methanol in chromatographic purity was used as the liquid phase for detection of $\bullet O_2^-$ signal using EPR. The control of pHs, if specified, was completed by dropwise addition of 0.1 M hydrochloride or sodium hydroxide. All the experiments were performed under atmospheric pressure with solution temperatures controlled at 20 ± 1 °C by thermostat.

2.3. Conditions for the FMI

An inverted fluorescence microscope was utilized to obtain the images for FMI (OLYMPUS IX71). Fluorescence excitation was tuned to the form of WU (UV excitation, 330–380 nm; color separation, 400 nm; cut-off, 420 nm). The exposure time was set as 20 s for all the captured images in this work. The objectives used were 40 × OI3 and 100 × OI3 (UPlanApo, Oil-proof cap C2). The software for image acquisition was IX2-BSW Version 01.03. As a preliminary step, 30 mL of sample was withdrawn from the CNT/ozone system at a predetermined time and was immediately mixed with 1 mL coumarin solution (15 mM) at a volume ratio of 30:1. Afterwards, approximately 1 mL of the mixture was extracted by a glue-head dropper and transferred to a glass slide for image capturing/analysis. Additional information to support the use of coumarin as a HO· probe for the FMI is illustrated in Fig. S1.

2.4. Analytical methods

Analysis on PFOS solution was assisted by LC-MS/MS system consisting of Agilent1200 series liquid chromatograph and a triple quadrupole mass analyser (Agilent6410B). Detailed information are shown in the SI. Concentration of fluorine anion (F^-) along with decomposition of PFOS was detected by ion chromatograph (Dionex ICS-1500).

Concentrations of p-CBA and OA were respectively detected by HPLC (Waters 2695 Separations Module). The stationary phase was SunFire® C18 5 μm column (4.6 × 250 mm). The p-CBA was quantified at wavelength of 237 nm with an eluent solution mixed by A (30% ammonium biphosphate solution) and B (methanol)