



Catalytic oxidation of organic pollutants on pristine and surface nitrogen-modified carbon nanotubes with sulfate radicals



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ABSTRACT

Employing metal-free nanocarbons or carbonaceous materials as a catalyst for environmental water remediation is a promising clean approach because the green carbon materials can completely prevent the potential toxic metal leaching and secondary contamination to water body. This study reports that pristine multi-walled carbon nanotubes (MWCNTs) can effectively activate peroxymonosulfate (PMS) and peroxydisulfate (or persulfate, perdisulfate, PDS) to produce sulfate radicals for oxidation of phenol solutions. Surface nitrogen modification was conducted by a facile synthesis via annealing MWCNTs with ammonium nitrate at a low temperature and the nitrogen modified MWCNTs (N-CNT) was characterized by a variety of techniques. It was found that surface nitrogen modification of MWCNTs produced different effects on PMS and PDS activation. N-CNT can significantly improve the phenol degradation with PMS, but decrease the degradation efficiency with PDS. Reaction kinetics and the mechanism in catalytic oxidation of phenol solutions with sulfate radicals over CNT-based materials were discussed.

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1. Introduction

Sulfate radicals ($\text{SO}_4^{\bullet-}$), either produced from peroxymonosulfate (PMS, HSO_5^-) or peroxydisulfate (or persulfate, perdisulfate, PDS, $\text{S}_2\text{O}_8^{2-}$), can be a promising alternative to hydroxyl radicals (OH^{\bullet}) for advanced oxidation in aqueous solution. They not only present a higher redox potential (2.5–3.1 V vs. hydroxyl radicals of 2.7 V), but show a better flexibility to a broad pH range than hydroxyl radicals [1–3]. At first, the sulfate radicals were mainly generated by activation of PMS or PDS using metal ions, such as Co(II), Mn(II), Fe(II), Ru(III), and Ag(I), etc [4,5]. The challenges in such homogeneous processes are the reuse and the toxicity of the metal catalysts, as well as the associated secondary contamination to the environment. Metals, metal oxides and supported metal oxides as heterogeneous catalysts were then employed [6–11], however, metal leaching still cannot be completely avoided [12].

Nanostructured carbons (nanocarbons), such as carbon nanotubes (CNTs), graphene oxide (GO) and graphene, possessing high thermal conductivity, high theoretical specific surface area (SSA),

unique carrier mobility, low-dimensional structure, sp^2 -hybridized carbon configuration, have demonstrated to be effective in a variety of catalytic processes [13–15]. It would be fascinating to introduce carbon/nanocarbon into environmental catalysis as a metal-free catalyst for heterogeneous remediation of organic pollutants in water. In a previous study, we noticed that activated carbon was able to activate PMS at a moderate level [16]. Recently, for the first time, we observed that reduced graphene oxide (rGO) showed a higher activity in degradation of phenol, 2,4-chlorophenol and methylene blue, compared to Co_3O_4 prepared by thermal decomposition of cobalt nitrate [3]. On the other hand, GO did not show any activity. Proper modification of rGO materials can significantly improve the adsorptive and/or catalytic oxidation performance in removal of organic pollutants. It was found that highly porous rGO can be prepared by an activation process using CO_2 at high temperature. The activation can significantly increase the SSA of rGO from 200 to higher than $1200 \text{ m}^2/\text{g}$, and largely improve the catalytic performance. For rGO, 100% MB removal was achieved in 4.0 h, and the time was reduced to 1.0 h on the activated rGO by CO_2 activation [17]. More recently, we reported that chemically compositional modification of rGO by nitrogen doping (N-rGO) can dramatically improve the catalytic activity in oxidation of phenol solutions. Unmodified rGO was able to degrade 52.5% phenol in 3.0 h with sulfate radicals, while N-rGO managed to remove all phenol in 45 min

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[18]. With the comparative analysis, sp^2 carbon, nitrogen dopants, and the oxygen-containing functional groups were suggested to be the origins of the catalytic activity.

Carbon nanotubes are built from sp^2 carbon units in hexagonal networks as in a graphene sheet, and the pristine CNTs have very limited functional groups, such as $-OH$, $-C=O$, and $-COOH$, which can be enriched by an oxidation process using various acids, ozone, plasma or heat treatment [19]. In the oxidative dehydrogenation of *n*-butane, 88.9% of the converted butane was burnt, yielding 1.6% alkenes over pristine CNTs. When the CNTs were functionalized with oxygen containing groups by refluxing and oxidizing in concentrated HNO_3 , the yield of alkenes was increased to 6.7% [20]. Yu et al. [21] reported that, in the selective aerobic oxidation of cyclohexane in liquid phase, CNTs displayed a reaction rate at 2–10 times higher than those of Au/ZSM-5 and FeAlPO catalysts. Luo et al. [13] reported that CNTs as metal-free catalysts exhibited an excellent activity in the selective oxidation of ethylbenzene to acetophenone in liquid phase with oxygen. It was found that CNTs played an important role in production of acetophenone through π - π interactions between the radical species, peroxide, and the graphene sheets of the CNTs. Moreover, surface carboxylic groups on the CNTs are unfavorable to ethylbenzene oxidation.

Nitrogen doping has been discovered to be very effective in enhancing the catalytic activities of CNTs. N-doped CNTs can be prepared by either in-situ doping during the synthesis or post-treatment of CNTs with nitrogen precursors. In-situ process can incorporate nitrogen into sp^2 carbon network (graphitic N), while post-treatment generally leads to the surface functionalization (pyridinic and pyrrolic N) [22]. In-situ synthesis of N-CNTs has been well developed, and a variety of nitrogen precursors, such as NH_3 [23], aniline [24], ethylene diamine [25], and acetonitrile [26] were employed to produce N dopants at a high temperature. Post-treatment at a low temperature would be cost-effective by employment of the commercially available CNTs, yet fails to incorporate nitrogen into sp^2 carbon networks.

Herein, we reported a facile nitrogen modification method of CNTs by thermal treatment of commercial CNTs with ammonium nitrate at a low temperature of 350 °C. Surface functionalization of CNTs was achieved by introduction of pyridinic and pyrrolic N, with bulk properties remaining unchanged. This material facilitated the mechanistic study in identification of the catalytically active sites of nanocarbons in producing sulfate radicals from PDS and PMS. For the first time, pristine CNTs and nitrogen modified CNTs (N-CNTs) were demonstrated effectively for catalytic degradation of phenol solutions with sulfate radicals. The activity of N-CNTs was comparable to N-doped rGO in activation of PMS for phenol oxidation.

2. Experimental

2.1. Materials and preparation of N-CNTs

Commercial MWCNTs were purchased from Chengdu Organic Chemicals, China. The products were prepared by chemical vapor deposition (CVD) using C_2H_4 as a carbon precursor and nickel based catalyst, and purified by refluxing in 6 mol/L hydrochloric acid for several hours. The CNTs have a diameter of 10–20 nm, a length of 30–100 μm , and a purity of >95% by weight. For preparation of N-CNTs, 1.0 g of CNTs and 1.0 g of ammonium nitrate were dissolved in 50 mL of ethanol, and the mixed solution was stirred for 30 min. Then solution temperature was raised to 50 °C to evaporate ethanol whilst stirring. The dried mixture was then put into a furnace for calcination at 300, 350 or 400 °C for 1 h at a heating rate of 5 °C/min, further washed by ethanol once and ultrapure water for three times, and N-CNT-30, N-CNT-35 and N-CNT-40 were then obtained, respectively. N-CNT-35 showed the highest activity so

it was chosen for detailed characterization and further oxidation reactions.

2.2. Characterization of carbon materials

Raman spectra were recorded on an ISA (Dilor) dispersive Raman spectrometer with argon ion 514 nm lasers. X-ray diffraction (XRD) patterns were obtained on a Bruker D8-Advanced X-ray diffractometer with $Cu K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), at accelerating voltage and current of 40 kV and 40 mA, respectively. Scanning electron microscopy (SEM) was performed on a Zeiss Neon 40EsB FIBSEM. Transmission electron microscopy (TEM) has been carried out using a JEOL 3000F field emission TEM. Quantification of chemical composition was carried out using electron energy loss spectroscopy (EELS) on the TEM. Chemical states of elements were also analyzed by X-ray photoelectron spectroscopy (XPS) using Thermo Escalab 250 with a monochromatic $Al K\alpha$ X-ray source. All binding energies were calibrated by the C 1s peak at 284.6 eV arising from adventitious carbon. The Brunauer-Emmett-Teller (BET) surface area and pore size distribution were evaluated by nitrogen sorption at $-196^\circ C$ using a Quantachrome Autosorb AS-1.

2.3. Catalytic oxidation of phenol solutions

The catalytic oxidation of phenol was employed to probe the efficiency of activation of potassium peroxymonosulfate (Oxone[®], $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ from Aldrich) and potassium peroxydisulfate ($K_2S_2O_8$ from Sigma-Aldrich). The reactions were carried out in a 500 mL reactor containing 20 ppm of phenol solution. The reactor was attached to a stand and dipped into a water bath with a temperature controller. A catalyst sample at 0.2 g/L was firstly added to the solution and stirred for 10 min. Then PMS or PDS was added to the mixture to start the reaction. The pH of reaction solution was not adjusted, and was about 6.5 at first, then gradually decreased to 2–3 due to the influence from oxidation processes. At each time interval, 1 mL of solution was withdrawn by a syringe and filtered by 0.45 μm Millipore film. The filtered solution was injected into a high performance liquid chromatography (HPLC) vial which was filled with 0.5 mL of methanol as a quenching reagent. Phenol solutions were measured by a HPLC (Varian) with a C-18 column. The adsorption tests were performed without addition of any oxidant.

3. Results and discussion

3.1. Characterization of pristine and N-modified CNTs

Fig. 1(A) shows Raman spectra of pristine and N-CNT-35. For the two samples, D-band at around 1313 cm^{-1} and G-band at around 1579 cm^{-1} were observed. The former band (D-band) originates from the disorder-induced features due to the finite particle size effect, lattice distortion, or amorphous carbon background [27,28]. The G-band arises from the Raman active in-plane atomic displacement E_{2g} mode [29]. The overtone of D band, 2D band, was found at 2633 cm^{-1} . The broad peaks after 2870 cm^{-1} were suggested to be symmetric and asymmetrical C–H stretch vibrations of the CH_3 group and asymmetrical C–H stretch vibrations of the CH_2 group [30]. It was noticed that, after nitrogen modification at temperature of 350 °C, the peak positions were not changed. The ratio (I_D/I_G) of the D-band intensity to the G-band intensity is known to be proportional to the degree of order of carbons [27]. In this study, the I_D/I_G values of pristine CNT and N-CNT-35 were calculated to be 2.06 and 2.01, indicating that nitrogen modification did not significantly change the sp^2 carbon network of the CNT materials. I_D was much higher than I_G , suggesting the faulty long-range ordered crystalline and the existence of disordered carbon structures, as

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