



Occurrence of radical and nonradical pathways from carbocatalysts for aqueous and nonaqueous catalytic oxidation



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ABSTRACT

Metal-free activation of superoxides provides an efficient and environmentally benign strategy for heterogeneous catalytic oxidation. In this study, nanocarbons with varying carbon-conjugation structures and functional groups were investigated for peroxymonosulfate (PMS) activation. It was discovered that radical and nonradical oxidations could occur on different carbocatalysts depending on the carbon structure. Radical oxidation occurs exclusively on MWCNTs and CMK-3, similar to a metal oxide, MnO₂. Both radical and nonradical oxidations are very pronounced in nanodiamond (AND-900)/PMS whilst nonradical oxidation is dominated in reduced graphene oxide (rGO-900)/PMS. Density functional theory (DFT) calculations were employed to explore the PMS adsorption and O—O bond activation on the different carbon configurations for an in-depth probe of the activation mechanism. The intact sp²-conjugated π system in MWCNTs and electron-rich ketonic groups (as Lewis basic sites) in CMK-3 can stimulate PMS dissociation to generate SO₄^{•−} and •OH, similar to metal-based catalysts. However, the defective edges at the boundary of carbon network are able to facilitate the organic degradation without generation of the reactive radicals, which is well supported by both experiments and the DFT calculation. The emerging nonradical oxidation induced by the carbocatalysis is superior to the radical oxidation on most metal oxides for effective degradation of various organics. The influences of solution pH, various anions (H₂PO₄^{2−}, HCO₃[−] and Cl[−]) and background organic matters (humic acid) on the nonradical oxidation were further evaluated. The nonradical oxidation on carbocatalysts can be utilized as a green and effective oxidation strategy for aqueous environmental remediation and nonaqueous phase oxidation.

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1. Introduction

The environmental deterioration, coming along with the industrialization and civilization of our modern society, has triggered worldwide concerns on the detrimental aspects to a sustainable future. Considerable efforts have been made to utilize the state-of-the-art technologies such as physical adsorption, flocculation/coagulation, photocatalysis, bio-degradation, and chemical oxidation for remediation of the contaminated atmosphere, waterbody, and soil in the eco-system [1–4]. Advanced oxidative processes (AOPs) are most widely used for decomposition of toxic organic contaminants in wastewater into harmless mineral acids,

carbon dioxide and water, taking advantage of the reactive species from activated superoxides. For instance, Fenton reactions are based on a homogeneous Fe²⁺/H₂O₂ system to produce hydroxyl radicals (•OH) which attain the destruction of a wide range of organic contaminants in aqueous solutions [5,6]. However, Fenton reaction requires stoichiometric dosages of the oxidant (H₂O₂) and ferrous salts, both are chemically unstable resulting in intensive inputs for transportation, storage and handling [7]. The reaction is also restricted by metal catalysts, strict reaction environment (pH < 3), generation and coagulation of sludge [8,9].

Sulfate radicals (SO₄^{•−}), produced from peroxydisulfate salts, have demonstrated a great capability of attacking organics via electron and hydrogen abstraction/addition, similar to hydroxyl radicals [10,11]. Moreover, sulfate radicals possess a higher standard reduction potential and present more selective degradation of organics with unsaturated bond and aromatic structure especially at neutral conditions [12–15]. As a typical peroxydisulfate

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salt, peroxymonosulfate (PMS, also known as oxone) with an asymmetric structure (HO-SO_4^-) can be activated by various transition-metal ions and metal oxides to generate both $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ [16–18]. The variable chemical states and unoccupied orbitals of the metal-based catalysts are believed to enable the electron transfer in a redox cycle to activate PMS molecules to produce the reactive radicals.

More recently, as promising alternatives in terms of green remediation technologies, nanocarbons such as graphene and carbon nanotubes were discovered to be able to effectively activate PMS to produce free radicals [19,20]. The eco-friendly and metal-free nature of the nanocarbons with ultrahigh pore volumes and specific surface areas (SSAs) can serve as excellent candidates for adsorption and carbocatalysis in environmental remediation, completely preventing the toxic metal ion leaching even in a strong acid or alkaline environment. Distinct from the metal oxides with exposed facets and valence states, most of the carbocatalysts are constructed with various defects, heteroatoms doping, functional groups, and carbon configurations, making it more difficult to investigate and identify the intrinsic active sites accounting for carbocatalysis [21,22]. It is believed that different active sites may play unique roles in heterogeneous catalysis due to the characteristically chemical states, reactive potential, and binding structure with the reactants.

Previously, Fenton or Fenton-like reaction was believed to be exclusively radical-based oxidation. However, few recent investigations suggested that nonradical reactions may occur for some catalyst systems. The nonradical processes were first revealed in a homogeneously selective hydrocarbon activation in which transition metal ions (Fe^{III} or Ru^{III}) were able to interact with H_2O_2 to form metal-oxo ($\text{Fe}^{\text{V}}=\text{O}$ or $[\text{Ru}_3^{\text{IV,IV,III}}=\text{O}]^+$) species as active intermediates to facilitate the cleavage of C–H bond and promote the catalytic oxidation without radical generation [23,24]. Croué and co-workers discovered a copper oxide (CuO) can effectively activate ozone (O_3) and persulfate (PS) for contaminant degradation with an outer-sphere electron-transfer mechanism [25,26]. N-Doping on highly crystallized single-walled carbon nanotubes could also induce the nonradical oxidation with PMS [27]. However, little has been reported in nonradical reaction in pristine carbocatalysts.

In this study, we investigated diverse nanocarbons in different dimensions, carbon types, and functional groups to reveal the pristine carbocatalysis in an aqueous-phase catalytic oxidation of various organic compounds such as dyes, phenolics, and antibiotics. The nonradical oxidation was for the first time discovered on reduced graphene oxide and annealed nanodiamond. The defective edges are believed to be the active sites to mediate the novel oxidation pathway. We also employed DFT calculations for theoretical understandings of the occurrence of the nonradical mechanism. Moreover, versatile environmental implications of inorganic anions, halogen, and background organic matters in water were estimated in the emerging nonradical reaction induced by carbocatalysis. We dedicate this work to proposing a novel and effective technology of oxidative catalysis for organic degradation and green remediation, which can be used in both aqueous and nonaqueous oxidations.

2. Experimental

2.1. Materials and preparation

The simulated pollutants and chemicals such as phenol (≥ 99.5 wt.%), methylene blue (dye content ≥ 82 wt.%), 1,2-dihydroxyphenol (≥ 99.0 wt.%), sulfachloropyridazine (analytical standard), and humic acid (inorganic residue ~ 20 wt.%) were obtained from Sigma-Aldrich, Australia. Multi-walled carbon

nanotubes (MWCNTs, OD 10–20 nm, length 30 μm , purity >95 wt.%) were purchased from Timesnano, China. A cubic-ordered mesoporous carbon (CMK-3, specific surface area (SSA) >900 m^2/g , pore volume 1.2–1.5 cm^3/g , pore diameter 3.4–4 nm) was obtained from XF NANO, China. Diamond nanopowders (particle size <10 nm (TEM), bulk density 0.2–0.7 g/mL) were obtained from Sigma-Aldrich, Australia. Annealed nanodiamonds were obtained by treating the pristine samples in a tubular furnace under nitrogen atmosphere at 900 °C for 1 h (denoted as AND-900) at a heating rate of 5 °C/min. Graphene oxide (GO) was prepared via a modified Hummers' approach [28]. Reduced graphene oxide (rGO) was prepared via the same thermal treatment as AND-900 and labelled as rGO-900. The detailed procedure for preparation of several metal oxides can be found in previous studies [26,29,30].

2.2. Characterization of carbocatalysts

Transmission electron microscopy (TEM) was conducted on a JEOL JEM-2100F instrument operating at 200 kV and the images are shown in Fig. S1. The rGO-900 presents as folded sheets with a silky-smooth morphology, whereas the AND-900 is randomly stacked together with a characteristic core/shell structure. CMK-3 has a structure of well-ordered porous layers. The crystalline structures (Fig. S2) of the carbocatalysts were recorded on an X-ray diffraction (XRD) instrument (Bruker D8 Advance) under a filtered $\text{Cu-K}\alpha$ radiation at $\lambda = 1.5418$ Å. The great peak at $2\theta = 26.3^\circ$ of rGO-900 and MWCNT is corresponding to the (002) facet of the sp^2 -hybridized graphitic carbon network, while the peak at $2\theta = 42.0^\circ$ of AND-900 can be ascribed to the sp^3 -bonded diamond core with a d-spacing of 2.1 Å. The disorder degree of carbon materials was reflected in Raman spectra (Fig. S3), acquired from an argon ion laser equipped ISA laser Raman instrument at 514 nm. The intensity ratios ($I_{\text{D}}/I_{\text{G}}$) of rGO-900, MWCNTs, and CMK-3 were estimated to be 1.70, 1.35, and 1.17, respectively, suggesting the different degrees of heteroatoms doping and defective sites (edges and vacancies). The surface graphitic curvatures of annealed nanodiamonds are well reported to possess various surface defects with ill-defined structures [31,32]. The thermal behavior of the nanocarbons was recorded on a Mettler–Toledo–Star instrument under air atmosphere at a heating rate of 5 °C/min from 35 to 900 °C (Fig. S4). Annealed nanodiamonds presented a better thermal stability owing to the robust core structure. Surface functional groups of the carbocatalysts were analyzed by a Fourier-transform infrared (FTIR) spectroscopy (Fig. S5) on a PerkinElmer instrument. Most of the functional groups on rGO-900 and AND-900 were removed after the thermal annealing. The specific surface areas (SSAs) and pore structure of the nanocarbons were obtained on a TriStar II equipment and estimated by the Brunauer–Emmett–Teller (BET) equation and Barrett–Joyner–Halenda (BJH) method, respectively (Fig. S6). CMK-3 presents the largest SSA and pore volume due to the well-ordered mesoporous structure. X-ray photoelectron spectroscopy (XPS) was utilized to probe the surface compositional information under an $\text{Al-K}\alpha$ X-ray radiation. All XPS spectra (Fig. S7 and Fig. S8) were calibrated with $\text{C}1s$ at 284.5 eV and analyzed with CasaXPS software. The oxygen contents decreased from 32.0 at% (GO) to 6.0 at% (rGO-900) owing to the removal of oxygen functional groups during the heat treatment. The oxygen level of nanodiamond slightly dropped from 5.7 at% (ND) to 3.7 at% (AND-900). The structure and chemical properties of the carbocatalysts are summarized in Table S1.

2.3. Experimental procedure

The as-made metal-free catalysts were evaluated for catalytic oxidation of organics with PMS. A 20 ppm phenol solution was prepared from a 1000 ppm phenol stock solution with a pH of

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