Carbon 103 (2016) 404-411

Contents lists available at ScienceDirect

Carbon

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

Surface-tailored nanodiamonds as excellent metal-free catalysts for organic oxidation

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ARTICLE INFO

Article history: Received 16 December 2015 Received in revised form 14 March 2016 Accepted 15 March 2016 Available online 17 March 2016

ABSTRACT

Metal-free catalysis has demonstrated competitive performance in energy conversion and chemical synthesis, yet scenarios in environmental catalysis are scant. The application of carbocatalysis for preventing secondary contamination by heavy/noble metals is envisaged as benign remediation. In this paper, we report a facile alteration of the surface chemistry of nanodiamond, a biocompatible nano-carbon, for application to environmental catalysis. The modulation is able to improve the redox capability of potassium ferricyanide (III) and to enhance the performance of the nanodiamond for activating peroxymonosulfate (PMS) to produce sulfate and hydroxyl radicals for catalytic oxidation. Cyclic voltammetry analysis, electron paramagnetic resonance (EPR) spectra, classical quenching tests, and density functional theory (DFT) calculations are integrated for a mechanistic study. This paper discusses highly efficient green materials for environmental catalysis and offers new insights into the heterogeneous carbocatalysis.

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1. Introduction

Carbon as one of the most abundant elements on the earth offers several allotropes such as graphite, activated carbon, fullerene, nanodiamonds, carbon nanotubes, graphene, and carbon quantum dots. The versatile carbon/nanocarbon has triggered a myriad of emerging applications in biology, energy and environment [1–4]. Carbon- or nanocarbon-induced catalytic reactions (carbocatalysis) have significantly broadened the outlook of the scientific community and boosted the industrial revolution and the development of modern society. Carbocatalysts can function perfectly as transitional metal-based materials to facilitate the chemical reactions with ultrahigh reaction rates and low activation energy. Moreover,

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the metal-free nature of carbocatalysts is able to remarkably transform current industry to be less dependent on the metalbased catalytic systems that consume large quantities of noble, transition, and rare earth metals and their oxides. As a result, the barriers of high cost, severe passivation, various side reactions, and the eco-unfriendly nature of the metal catalysts can be overcome by the carbocatalysts [5–7].

Metal-based catalysts are controlled by variable polyvalent states, specific spin cultures, versatile crystal facets, and a tunable acid-base environment, but carbocatalysis relies strongly on the various defective sites and an active carbon lattice. The varying defective sites, surface chemical and electronic states, and covalent carbon framework would collaboratively deliver functions previously observed in metal enabling catalysis [8,9]. Among the carbocatalysts, graphene, carbon nanotubes, and other nanocarbons have been studied mostly for oxygen reduction reaction (ORR) [10–12], oxidative dehydrogenation (ODH) reactions [13,14], selective oxidation [6,15], and photocatalysis [16,17]. However, the poor stability of the nanocarbons, especially in oxidative reactions,





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has seriously hindered their practical applications [18–20]. The complexity of the carbon structure and the variable chemical properties also make carbocatalysts more difficult in mechanistic studies. Moreover, the toxic nature of some nanocarbons (such as carbon nanotubes and graphene) poses great threats to green chemistry and human health, limiting their application for environmental remediation.

Detonation nanodiamond has an sp³-hybridized carbon framework with nitrogen impurities embedded in the core and soot structures and has been employed for lubricants, nanosensors, drug delivery, and electrochemical coatings [21,22]. The excellent biocompatibility of detonation nanodiamond has suggested this compound as a promising candidate for environmental catalysis [23–25]. However, to the best of our knowledge, very few studies have been carried out to explore the catalytic activity of nanodiamonds (NDs) [9,26,27]. Efficient application of NDs for feasible liquid-phase reactions, i.e., water remediation, have never been reported.

In this paper, we have modulated commercial detonation nanodiamonds via rational design techniques to unveil the nondiamond substance and tailor the surface chemistry. The nanodiamonds were first refluxed with nitric acid to remove metal impurities and amorphous carbon. Meanwhile, the ND was functionalized with various oxygen groups, followed by one-step controlled pyrolysis with simultaneous nitrogen doping using a green and cheap N-rich precursor, melamine. We discovered that the surface-modified nanodiamonds can be a robust and efficient catalyst for enhanced electrochemical activity and peroxvmonosulfate (PMS) activation. For the first time, we probed the intricate interaction of the N-doped sp² graphitic shell and the sp³ core for the enhanced catalytic performance with density functional theory (DFT) calculations based on a graphene/diamond hybrid model. We dedicate this study to exploiting a robust and environmentally benign metal-free catalyst and revealing the intricate nature of nanodiamond-based carbocatalysis in heterogeneous reactions [27].

2. Experimental section

2.1. Materials synthesis

The nanodiamonds (>97%, <10 nm, Sigma-Aldrich) were first oxidized with nitric acid (70%), refluxing at 373 K for 4 h to remove trace metal residues and non-diamond substances. The mixture was then filtered through a 0.45 µm filter membrane, washed with water and ethanol (absolute) several times and dried in an oven at 333 K. The oxidized nanodiamond (denoted as oND, 1.0 g) was mixed with melamine (1.0 g, > 99%, Sigma-Aldrich) in 100 mL ethanol, sonicated for 1 h and heated on a hot plate at 325 K to evaporate the ethanol while stirring. The dried mixture was ground and transferred to a tube furnace under N₂ at 973 K for an annealing period of 1 h. The heating rate was set at 5 K/min, and the sample was collected after the mixture was naturally cooled to room temperature. Thus, the nitrogen-modified nanodiamond (N-AND) was obtained. In addition, the oxidized nanodiamonds (oND) were directly annealed at 973 K without melamine to obtain pristine annealed nanodiamonds (AND).

2.2. Sample characterizations

The morphological information for the materials was obtained by scanning electronic microscopy (SEM) using a Zeiss Neon 40EsV FIBSEM with a field emission electron gun. The high-resolution transmission electron microscopy (HRTEM) was applied using a Titan G2 80-200 TEM/STEM with ChemiSTEM Technology

operating at 200 kV. X-ray diffraction (XRD) patterns were obtained on a Bruker D8-Advanced X-ray instrument using Cu-K_a radiation with λ at 1.5418 Å under the accelerating voltage of 40 kV and current of 40 mA. Fourier transform infrared spectra (FTIR, Bruker) were acquired in an ATR correction mode operating under a controlled atmosphere. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo ESCALAB 250 XPS microscope with monochromatic Al-K_{α} X-rays at a photon energy of 1486.7 eV. The measurement was carried out using a Kratos AXIS Ultra DLD system under UHV conditions with a base pressure less than 1 \times 10^{-9} mBar. Spectra were acquired with the pass energy of 20 eV and fitted using CasaXPS software. All spectra are calibrated to yield a primary C 1s component at 284.5 eV with the Shirley background, and the component fitting applied Voigt functions with a 30% Lorentzian component. The in-situ characterization method of electron paramagnetic resonance (EPR) was applied to probe the active radicals using 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 99%, Sigma–Aldrich) as the spin trapping agent. The EPR spectra were analyzed and exported by the spin-fitting package of Bruker Xeon software for DMPO-SO₄ ($\alpha_H = 0.78$, $\alpha_H = 1.48$, $\alpha_H = 9.6$, and α_N = 13.2) and DMPO-OH (α_H = 14.8, α_N = 14.8) under reaction conditions ([phenol] $_0 = 20$ ppm, catalyst = 0.2 g/L, PMS = 6.5 mM, DMPO = 0.08 M, temperature = 298 K).

2.3. Catalytic oxidation of phenol solution

Phenol degradation was performed in a 250 mL batch reactor with phenol solution (20 ppm), catalyst (0.2 g/L) and PMS (6.5 mM, 2KHSO₅·3KHSO₄·K₂SO₄, Sigma–Aldrich) in a water bath with a temperature controller for the kinetic studies. At a certain time interval, 1 mL of the reaction solution was withdrawn via a syringe and filtered using a 0.45 µm Millipore film, and then injected into a vial with 0.5 mL methanol as a radical scavenger. The mixed solution was analyzed using a Thermal-Fisher ultrahigh performance liquid chromatograph (UHPLC) with a C-18 column (Acclaim PA 5 μ m, 4.6 \times 150 mm), tested and recorded with a UV detector working at 270 nm to evaluate the phenol concentration. After each run, the used catalysts were washed with deionized water and ethanol three times each, filtered, and dried in an oven at 333 K overnight for reuse. The reaction parameters were set at following conditions: $[phenol]_0 = 20 ppm$, catalyst = 0.2 g/L, PMS = 6.5 mM, temperature = 298 K, unless specified elsewhere. Parallel tests of the key experiments and specific surface areas (SSAs) were carried out for presenting mean values and standard deviations.

2.4. Theoretical calculation methods

Density functional theory (DFT) calculations were performed on the adsorption of PMS on different carbon systems: pristine diamond, diamond coated with graphene, and diamond coated with N-doped graphene. The spin-unrestricted DFT calculations were carried out by using the Dmol³ package [28]. Exchange–correlation functions were taken as generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) [29]. Double numerical plus polarization (DNP) was employed as a basis set. The convergence tolerance of energy was 10^{-5} Hartree (1 Hartree = 27.21 eV), and the maximal allowed force and displacement were 0.002 Hartree/Å and 0.005 Å, respectively. The DFT-D method within the Grimme scheme [30] was used in all calculations to consider the van der Waals forces. In the simulation, three-dimensional periodic boundary conditions were taken. A graphene cluster was adopted and coated on a diamond substrate to avoid lattice mismatch between the graphene and diamond. In all the calculations, all atoms were allowed to relax on the bottom layer of C atoms in the diamond to represent the bulk diamond.

3. Results and discussion

3.1. Characterization of nanodiamond samples

The morphological information of N-AND is shown in images from high-resolution transmission electron microscopy (HRTEM) (Fig. 1a). The diamond nanoparticles are randomly stacked together and aggregated to larger particles. Nanodiamonds usually have a large exposed surface and various functional groups, making them aggregate into larger primary and secondary structures in a more stable state [31]. The aggregation is closely related to the physicochemical properties of the facets and the thermal treatment conditions [31]. In Fig. 1a, the characteristic core—shell structure of the nanodiamond can be observed. The fingerprint of the diamond sp³bonded crystal structure was presented with a *d* spacing of 2.06 Å, corresponding to (111) diamond planes, further reflected by the bright rings of SAED (selected area electron diffraction, inset picture) patterns and verified by X-ray diffraction (XRD) patterns in Fig. S1. Besides, a graphitic shell (3.38 Å) was formed during the thermal annealing process owing to the transmission and reconstruction of the outer surface of nanodiamond crystal.

Electron energy loss spectroscopy (EELS) was used to reveal the C 1s core electrons at different sites of NDs [32]. Fig. 1b presents the carbon K-edge spectra at different positions (A and B in Fig. 1a) in N-AND. The peak at 285.5 eV can be assigned to the π^* transitions of sp² carbons from the graphitic shell, and the strong peak at



Fig. 1. a) HRTEM image and SAED pattern (inset) (Spot A: core and B: shell) of N-AND; b) Carbon and nitrogen K-edge spectra of N-AND; c) Nitrogen sorption isotherm and pore size distribution of N-AND; d) FTIR spectra; e) XPS survey; and f) N1s high resolution spectra of various nanodiamonds. (A color version of this figure can be viewed online.)

293.3 eV corresponds to the typical σ^* transition of 1s electrons from the sp³ hybridized core [9,21,32]. The different carbon states of the inner and outer parts of the nanodiamond demonstrated the core/shell structure. The weak π^* peak of the diamond core is attributed to the graphitic shell coating at the top and bottom of the nanodiamond. The nitrogen K-edge was found at approximately 400 eV in the diamond nanocrystals. Commercial nanodiamonds are known to contain a small fraction of nitrogen in the core and non-diamond parts [33]. The EELS spectra indicated that nitrogen was doped into the graphitic shell, as supported by X-ray photoelectron microscopy (XPS) in later discussion. The oxygen K-edge was also found at 544.5 eV of the coating shells and can be assigned to the surface oxygen functional groups.

The pore structure and specific surface area (SSA) of the nanodiamonds were evaluated via nitrogen sorption as illustrated in Fig. 1c and Table 1. The SSA of N-AND decreased from 392.5 ± 5.4 (AND) to 371.4 ± 9.6 m²/g (N-AND) after nitrogen modification. Such a decline after N-doping was also found in graphene and carbon nanotubes in our previous studies [19,34]. The porous structures of nanodiamonds are consisting mainly of micropores (0–2 nm) and mesopores (2–50 nm). The thermal stability of NDs was found to decrease slightly after the annealing process (Fig. S4), possibly owing to the microstructural change, i.e., the conversion of the diamond surface of the core into a graphitic shell.

Fourier transform infrared (FTIR) spectroscopy was utilized to identify the adsorbed molecules and functional groups on the surface of different nanodiamonds as displayed in Fig. 1d. The broad peak between 3000 and 3700 cm⁻¹ is corresponding to the O–H stretching from the adsorbed water and hydroxyl groups. The peaks at 2800–3000 cm⁻¹ can be assigned to the C–H stretching and the other two strong peaks at 1635 and 1750 cm⁻¹ are related to C=C and C=O, respectively [35]. The peaks with a lower wavenumber from 900 to 1500 cm⁻¹ are related to the bending and stretching modes of the surface oxygen groups such as carboxylic acid, anhydride, epoxy, and nitrogen containing sites [31,36]. The peak intensities at 2800-3000 and 900-1500 cm⁻¹ declined after the thermal treatment, and the peaks for C-H almost disappeared due to the removal of adsorbed molecules and surface groups. The two peaks at 1635 and 1750 cm⁻¹ that still remained sharp for AND and N-AND suggest the thermal stability of the sp² hybridized carbon shells and the carbonyl groups (C=O) of surface tuned nanodiamonds.

Fig. 1e displays XPS spectra of different nanodiamonds before and after the controlled pyrolysis and nitrogen modification. This figure suggests that 9.18 and 0.92 at% of oxygen and nitrogen were incorporated into the oND, respectively. The N1s (Fig. 1f) of oD can be fitted into four species with binding energies at 397.6, 398.8, 401.4, and 403.7 eV, which were assigned to the amino groups, pyridinic N, graphitic N, and nitric oxides, respectively [12,34,37]. Most of the oxynitrides were removed from AND and N-AND due to the pyrolysis. In the denotation process, an artificial nanodiamond usually contains a certain amount of nitrogen in the core and amorphous carbon shell. The higher nitrogen level and tuned species of N-AND were derived from the nitrogen precursor of melamine by the controlled pyrolysis.

3.2. Catalytic performances of nanodiamonds

A cheap and stable oxidant, peroxymonosulfate (PMS, commercially known as Oxone), is non-toxic and easy to handle in water. PMS has been widely used in synthetic chemistry and environmental remediation under flexible pH conditions [38]. However, the popular metal-based heterogeneous systems (Fe, Co, Mn) for PMS activation suffer from harmful ion-leaching, and the stability of the reported metal-free catalysts is usually poor. We applied electron paramagnetic resonance (EPR) spectroscopy to observe the radical generation during the PMS activation of nanodiamond samples. As the free radicals commonly undergo self-quenching and consuming in a quite short lifetime, a typical spin trapping agent, DMPO, was utilized to capture the generated radicals to form a more stable adducts (DMPO-SO₄ and DMPO-OH) for EPR detection and radical identification. The EPR spectra in Fig. 2a indicate that PMS itself could hardly generate active radicals and that oND demonstrated poor catalytic performance for PMS activation. The strong EPR signals in the N-AND/PMS system confirmed that a large number of reactive radicals were produced. Both sulfate radicals (SO_4^-) and hydroxyl radicals (OH) were identified, and the latter were of a relatively higher intensity. The EPR spectra strongly suggest that N-AND is more efficient to activate PMS to generate sulfate and hydroxyl radicals, which is well consistent with the effectiveness of phenol degradation in different NDs/PMS systems as shown in Fig. 2b, suggesting the crucial roles of the reactive radicals for catalytic oxidation. The hydroxyl radical that was initially produced might work as an initiator to activate PMS for sulfate radical generation [39,40]. Besides, the electrochemical tests in Fig. S5 reveal that a higher catalytic redox activity can be expected in the ferri/ferrocyanide couple on the surface functionalized nanodiamonds (AND, N-AND) compared with pristine oND. The improved charge transfer from the surface modulation strongly enhanced the environmental catalysis, as demonstrated on reduced graphene oxide (rGO) in previous studies [18–20].

Environmental catalysis of nanodiamonds was further evaluated by activation of PMS for decomposition of organic pollutants. Fig. 2b shows that a typical contaminant, phenol, can barely be oxidized by PMS without a catalyst. Only 4.8% of the phenol was removed by PMS. Nanodiamond (N-AND) with a smaller particle size (<10 nm) and a high surface/volume ratio (SSA, 371.4 \pm 9.6 m²/ g, Table 1) gave 12.1% phenol removal via adsorption. The oxidized nanodiamond (oND) showed a poor catalytic activity toward phenol oxidation. Only 25.9% of the phenol was decomposed in 180 min by the oND/PMS system. The catalytic activity of nanodiamond was dramatically enhanced, producing complete phenol degradation in 120 min. After nitrogen modification, 100% phenol removal could be achieved in 45 min. N-AND also showed a higher

Table 1

Pore structure, surface chemistry	y and activity of nanodiam	onds
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Catalyst	S _{BET} m ² /g	V _{pore} cm ³ /g	N Content at%	O Content at%	Reaction rate ppm min ⁻¹	Ea kJ/mol
oND	312.8 ± 7.9	1.12	0.92	9.18	0.05 ± 0.02	58.9
AND	392.5 ± 5.4	1.22	0.60	8.19	0.57 ± 0.02	45.5
N-AND	371.4 ± 9.6	0.79	1.93	7.75	1.55 ± 0.09	71.7
N-AND 3rd run	262.2 ± 3.7	0.66	1.19	12.75	0.07 ± 0.03	-



Fig. 2. a) EPR spectra of PMS activation (DMPO-OH: \bullet , DMPO-SO₄: \bullet), and b) Phenol catalytic oxidation on various nanodiamonds. (A color version of this figure can be viewed online.)

activity than the most popular metal-based catalyst, α -MnO₂, which achieved complete phenol removal in 120 min. In comparison to various other nanocarbons (Fig. S6). N-modified nanodiamond produced the best catalysis among all the carbocatalysts such as fullerene, carbon nanotubes, and graphene based materials (GO, rGO, and N-rGO). The modified NDs also exhibited high catalytic oxidation efficiencies of methylene blue (MB) and 2,4dichlorophenol (DCP, Fig. S7). For phenol oxidation, the effects of reaction parameters on degradation efficiencies were evaluated and are shown in Figs. S8 and S9. The reuse performances are illustrated in Figs. S10 and S11. The deactivation after catalytic oxidation was also possibly due to alteration of surface chemistry and the coverage of adsorbed intermediates via strong interaction with the sp²-conjugated carbon network of nanodiamond surface, and the activity can be partially recovered via facile thermal treatment to attain a more reductive and cleaner surface of nanodiamond.

Fig. 3 shows that the apparent reaction rate constants decreased from 0.072 \pm 0.005 to 0.043 \pm 0.003 and 0.035 \pm 0.004 min $^{-1}$ when 0.22 M tert-butanol or ethanol was added to the reaction systems. It is known that both ethanol and tert-butanol are able to quench hydroxyl radicals with high reaction rates at (1.2–2.8) \times 10⁹ M $^{-1}$ s $^{-1}$ and (3.8–7.6) \times 10⁸ M $^{-1}$ s $^{-1}$, respectively



Fig. 3. Identification of reactive species with radical quenching tests in N-AND/PMS. (A color version of this figure can be viewed online.)

[41]. However, sulfate radicals tend to react with alcohols with α -H on the carbon atom connected to the hydroxyl group, and the tertbutanol without α -H shows a slower reaction rate $(4.0-9.1) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ with SO₄ than ethanol with a reaction rate of $(1.6-7.7) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [41,42]. The remarkable decrease in the rate constants in this study suggests that the reactive radicals played dominant roles in phenol degradation. Moreover, the quenching effects from tert-butanol and ethanol indicate that both hydroxyl and sulfate radicals are responsible for the oxidation process, consistent with EPR spectra.

3.3. Mechanistic and theoretical studies

The proposed mechanism of PMS activation of nanodiamonds is illustrated in Fig. 4a. We suppose that the nucleophilic ketonic groups on the nanodiamond shell possess high electron densities and offer great catalytic potential to conduct a redox process for PMS activation to generate active radicals. This supposition was verified by employing two models of molecular catalysts, benzoquinone (C=O) and hydroquinone (C-OH), to mimic ketonic and hydroxyl groups (seen in Fig. 4b), respectively [26]. The EPR spectra in Fig. 4b indicate that benzoquinone presents a higher intensity than hydroquinone, especially for hydroxyl radical, suggesting that ketonic groups are more active in PMS activation. The ketonic groups are able to undergo a self-redox cycle to activate PMS for radical generation, as reported for activation of persulfate and hydrogen peroxide [26,43,44]. Only a small number of ketonic groups at the defective edges would facilitate the PMS activation. while superabundant oxygen groups will not be effective [20,45]. The excess dangling oxygen groups occupy the defective edges, partially preventing the interaction between PMS and the carbon lattice and minimizing the reductive degrees of the carbon network, which determines the charge-transport from the carbon to PMS.

The enhanced performance in the generation of reactive radicals in modified nanodiamonds was investigated by theoretical computations. Fig. 4c–e present the relaxed atomic structures of a PMS molecule adsorbed on three carbon models, pristine diamond, graphene/diamond and N-doped graphene/diamond. The diamond surface is very active and induces a close interaction between PMS and graphene/N-doped graphene (NG), reflected by the strong covalent bonds between the nanodiamond surface and the added models. The adsorption energy (E_{ads}) and bond length (l_{0-0}) of

b) a) SO_4 HO-SO Relative intensity a.u ЭH 3460 3480 3560 3500 3540 3520 Field [G] d) c) e)

Fig. 4. a) Mechanism of PMS activation on nitrogen-modified nanodiamond; b) EPR spectra of small-molecular catalysts for activation of PMS (DMPO-OH: •, DMPO-SO4: •); Mechanism and DFT calculation for the adsorption of PMS on c) diamond; d) graphene/diamond; and e) N-doped graphene/diamond. The red, gray, white, and yellow atoms are O, C, H, and S atoms, respectively. Note that the atoms in diamond are presented as lines to show the configurations more clearly. (A color version of this figure can be viewed online.)

Table 2	Та	ble	2
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The adsorption energy $(\rm E_{ads})$ and the bond length $(\it l_{\rm O-O})$ of SO₃O-OH in PMS activation.

Configuration	$E_{\rm ads} ({\rm eV})$	l _{O-O} (Å)
Free PMS	_	1.326
diamond	-3.67	1.461
Graphene/diamond	-2.46	1.421
N-Graphene/diamond	-5.44	1.482

SO₃O-OH are listed in Table 2. The adsorption of PMS on N-doped graphene/diamond exhibits the lowest adsorption energy and demonstrates the best performance for PMS activation among all the models. Moreover, the l_{O-O} of PMS was weakened and lengthened to 1.461 and 1.421 Å on the diamond and graphene/ diamond surfaces, respectively, compared with the free PMS molecules (1.326 Å). Moreover, the O–O bond was further prolonged to

1.482 Å on N-graphene/diamond surface, suggesting a remarkable enhancement in the catalytic activity.

For better understanding of the N-doping effect, the atomic charge of the systems was also calculated using the Mulliken method (Figs. S12 and S13). The doped N-atom altered the charge redistribution of the graphene lattice significantly, especially for the adjacent carbon atoms because of the higher electronegativity (N $\chi = 3.04$ vs. $C\chi = 2.55$). The electron density on the N-atom performs as Lewis basic sites to conduct electron transfer, and the positively charged carbon atoms improve the activation of the O–O bond. The emerging physicochemical features synergistically facilitate the splitting of PMS in the N-doped graphene/diamond system. In addition, with the presence of the diamond substrate, graphene and N-doped graphene demonstrate better performance to activate PMS. The C atoms in the graphene lattice can obtain electrons from the C atoms in the diamond facets through the strong covalent bonds (Fig. 4e). This process increases the catalytic

performance of graphene with super-abundant electrons that better facilitate electron transport to PMS molecules, consistent with the observation on double- or triple-walled carbon nanotubes where an intact inter-graphitic tube can contribute charge-transfer to the electron- or hole-abundant outer shells via a fantastic electron-tunneling effect. As a result, the carbocatalysis is improved for adsorption and dissociation of reactants and intermediates for oxygen evolution reactions (OER) [46,47]. Interestingly, the calculations also indicate that the diamond surface without a graphitic shell is very active for PMS activation. The poor activity of oND in this study is attributed to the coverage of the amorphous carbon and various functional groups, which hinder the interaction of PMS and the sp³-hybridized diamond crystal defects.

Nanodiamonds feature a sp³-bonded core and sp²-hybridized graphitic shell with various defects and surface functional groups (Fig. 1a and b). Acid reflux and controlled pyrolysis are able to remove the non-diamond impurities, adjust the oxygen functional groups and induce nitrogen doping. As a result, an enhanced catalytic performance was demonstrated in environmental catalysis for water remediation. Based on a pseudo first-order kinetic model, the apparent reaction rates of oND, AND and N-AND were estimated to be 0.05 \pm 0.02, 0.57 \pm 0.02, and 1.55 \pm 0.09 min⁻¹, respectively. The AND and N-AND demonstrated stunning 11.4- and 31.0-fold enhancements compared with oND, respectively. The catalytic activity of a nanodiamond can be improved by the removal of amorphous carbon and the functional groups on the nanodiamond surface via thermal annealing [27,31]. Nitrogen modification to the nanodiamond shells can further enhance the performance in PMS activation for phenol degradation. The electrochemical activities of the nanodiamonds followed the same trend with PMS activation (N-AND > AND > oND). The intrinsic driving force of PMS activation apparently lies in the difference of electrostatic potential between carbocatalysts and PMS, evidenced by CV results that the tailored nanodiamond shell possesses stronger interactions and faster electron-transfer tendencies with PMS to break up the O–O bond, thereby generating active radicals for oxidation reactions. Moreover, N-doping may be able to promote the adsorption capability of organic molecules onto the activated graphitic shell via strong $\pi - \pi$ interaction, which synergistically enhances the oxidation processes.

In a previous study, we implemented the experimental tests and density functional theory (DFT) calculations to reveal that nitrogen dopants (especially substitutional doping) can induce high positive charge densities to the neighboring carbon atoms [19,34,48]. In this study, for the first time, we utilized theoretical calculations to unravel the enhanced catalysis of the characteristic sp²-/sp³-hybrid structure of nanodiamonds. The essence of PMS activation lies in the breakup of the O–O bond in $HO-SO_4^-$ (PMS) to generate ions and reactive radicals. PMS would first adsorb and bond with the carbon network, then the O-O bond was weakened, and the intricate electron transfer was facilitated from the carbocatalysts to PMS to be dissociated into reactive radicals. Different from metalbased catalysis with variable chemical states, the active sites on nanocarbons are believed to play pivotal roles in this process. Thus, the surface-tailored N-AND with versatile defective sites, oxygen groups, nitrogen-doped graphitic shell, and sp³-hybridized diamond core structure, demonstrated much greater catalytic performance. Theoretical calculations also revealed that curvaturestructured graphene with partially delocalized π -electrons and defective sites presents a superb chemical activity [9,49,50].

4. Conclusions

In summary, we found that nanodiamonds demonstrated superior catalytic performance toward electrochemistry and PMS activation for oxidative degradation of water contaminants. Compared with other nanocarbons and classical metal-based catalysts, the surface-modified nanodiamonds presented a much better stability in oxidation reactions. The active sites on nitrogendoped carbon hybrids for PMS activation were revealed by employing small molecular catalysts and DFT calculations, enabling the first insights into the intricate N-doped sp²-/sp³-carbon hybrid structure and mechanism toward enhanced catalytic performance. This study contributes to developing state-of-the-art technologies for green catalysis and environmentally benign remediation.

Acknowledgment

This work was partially supported by the Australian Research Council (ARC) under project of DP130101319. X. D. acknowledges the scientific assistance and fruitful discussions with Dr. Kane O'Donnell from the WA X-ray Surface Analysis Facility (LE120100026). H. S. would like to gratefully acknowledge the financial support from the Curtin Research Fellowship. Z. A. acknowledges the financial support from the Chancellor's Research Fellowship Program of the University of Technology, Sydney, and technical support from the National Computational Infrastructure (NCI) through the merit allocation scheme and using NCI resources and facilities in Canberra, Australia.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2016.03.034.

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