



Research Paper

Nanodiamonds in sp^2/sp^3 configuration for radical to nonradical oxidation: Core-shell layer dependence



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ABSTRACT

Nanocarbons in molecular configurations of sp^2/sp^3 present versatile structural and electronic properties, exhibiting a complexity in the structure-activity chemistry. In this work, we employed detonation nanodiamonds constructed as a characteristic core/shell structure in the sp^2/sp^3 configuration to demonstrate the intrinsic correlation between the structure and catalysis. Annealed detonation nanodiamonds were found to show a superb activity for catalytic peroxymonosulfate activation and organic oxidation. A synergistic effect of charge transport was discovered at the interface to construct an electron-enriched carbon surface that further promoted the catalytic activity evidenced by the density functional theory (DFT) calculations. More importantly, both experimental results and theoretical predictions revealed that the catalytic oxidation via peroxymonosulfate (PMS) activation was intimately dependent on the proportion of graphitic carbon layer in the sp^2/sp^3 configurations. The increase of graphitic layers on nanodiamonds would alter the PMS activation from a radical-based reaction to a nonradical pathway for catalytic oxidation. The novel catalytic properties of tunable oxidative potentials from carbocatalysis may simulate fascinating prospects for environmental catalysis and organic synthesis.

1. Introduction

The state-of-the-art carbocatalysis has appealed great passions in the scientific community of electrochemistry and heterogeneous reactions owing to the fascinating physicochemical properties and metal-free nature of nanocarbon materials [1,2]. The intrinsic reactivity of graphitic carbon allotropes (graphene, carbon nanotubes etc.) has been illustrated to be intimately associated with the distorted carbon domains (activated by alien-atom doping) and the versatile defective sites as well as functional groups that exhibit unique electronic/spin cultures [3–6]. Manipulation of both the structure and functionality would offer a tool for tailoring the opening bandgap, enhancing the light-harvest capability, and promoting the charge transport/separation. To this end, nanocarbon hybridization using two or more compounds has been commonly proposed to achieve novel properties, attributing to the hetero-interacted interfaces and electron tunnelling effects [7–9]. However, for a mechanistic study, the active sites of the hybrids in

carbocatalysis are far more complicated and difficult to be elucidated.

Nanodiamonds (NDs) produced from a detonation method are comprised of a highly sp^3 -hybridized nanocrystal (5 ± 2 nm) in an irregular morphology with a high surface/volume ratio. NDs are normally terminated with hydrogen and oxygen atoms and partially covered by amorphous soot. Thermal annealing is able to eliminate the surface contaminants and partially decompose the outer sphere of the nanodiamonds to form a graphitic fullerene shell, hereby transforming the bulk nanocrystal into a uniform and self-assembled sp^2/sp^3 hybrid structure [10,11]. The graphitization of nanodiamonds involves multi-steps. At a low temperature range (300–800 °C), it would lead to de-attachment of moisture and oxygen functionalities (carboxyl, hydroxyl, and ketonic groups), and decomposition of surface soot and amorphous carbon [12,13]. When further annealing nanocrystals at above 900 °C, the carbon atoms at the terminal grain boundaries of sp^3 -hybridized diamond crystals would be rearranged into a π -conjugated framework, which will subsequently be constructed into a graphitic shell which

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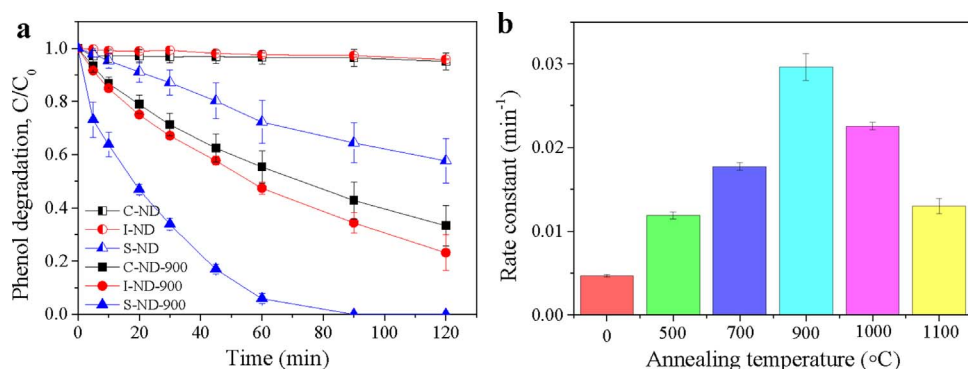


Fig. 1. (a) Carbocatalysis on pristine and graphitized nanodiamonds from different sources, and (b) effect of annealing temperature on the catalytic performance of S-ND.

covers the sp^3 diamond structure [14,15]. The removal of oxygen functionalities on outer sphere of diamond can also bring in structural defects and dangling bonds for further promoting the collapse and transition of sp^3 carbon to sp^2 network [16]. Therefore, the structure of nanodiamonds can be easily regulated by thermal annealing at high temperatures under inert/oxidative ambience to facilitate a mechanistic study that cannot be done on carbon hybrids.

Benefited from a characteristic core/shell architecture, the partially graphitized nanodiamonds may present a novel catalytic behavior of the graphene-based materials meanwhile embracing new properties from the diamond part via a delicate sp^2/sp^3 control. The graphite/diamond structure has demonstrated a better activity than other carbon materials in oxidative dehydrogenation (ODH) reactions [14,17]. However, such a synergistic effect was barely investigated in the aqueous-phase reactions, and the impacts of the shell thickness on the electronic/geometric variations, i.e. diamond-based catalysis mechanism, have not been elucidated yet. Here we reported a case study of catalytic oxidation from peroxymonosulfate (PMS) activation on controlled graphitized nanodiamonds. This study helps reveal the relevance between the structural transformation and catalytic activity in carbocatalysis. We discovered that the new creation of graphitic carbon layer on nanodiamonds would greatly promote the PMS activation, meanwhile the rational rearrangement of sp^2/sp^3 configurations induces different reaction pathways towards catalytic oxidation.

2. Experimental

2.1. Chemicals and catalyst synthesis

Three nanodiamonds, such as I-ND (Ray Techniques Ltd., Israel), C-ND (XFnano Materials Tech Co. Ltd., China), and S-ND (< 10 nm, Sigma-Aldrich, Australia), were received and purified by thoroughly acid washing to remove the potential metal residues. Then, the pristine nanodiamonds were placed in a tubular quartz reactor and treated by thermal annealing under nitrogen at 5 °C/min and held at 500–1100 °C (donated as ND-X, X = 500–1100) for 1 h. The derived samples were cooled down naturally, washed with ethanol (70 wt%) and ultrapure water, and dried at 60 °C in an oven.

2.2. Characterizations of carbon materials

The structure of nanodiamonds was revealed by high-resolution transmission electron microscopy (HRTEM) images acquired on a Titan G2 80–200 TEM at 80 kV. The electron energy loss spectra (EELS) at high and low energy regions were analyzed on the same TEM at 120 kV. X-ray photoelectron spectroscopy (XPS) was employed to estimate the elemental composition of nanodiamond surface under ultrahigh vacuum conditions ($< 1 \times 10^{-9}$ mBar) on a Kratos AXIS Ultra DLD system. The surface property and porous structure of nanodiamonds were measured at liquid nitrogen temperature (–196 °C) on a TriStar instrument and calculated by the Brunauer-Emmett-Teller (BET) and

Barret-Joyner-Halenda (BJH) equations. The crystalline information of nanodiamonds were analyzed by X-ray diffraction (XRD) with a Cu K α X-ray gun ($\lambda = 1.5418 \text{ \AA}$). Electron paramagnetic resonance (EPR) was performed to analyze the spin numbers of structural defects in nanodiamonds. In a typical analysis, the nanodiamond power was placed in the center of the EPR instrument. The EPR parameters were recorded as [Sweep width] = 200 G, [Sweep time] = 30 min, [g-factor] = 2.003, [Attenuation] = 12.7 dB, [Center field] = 3517.75 G, and [Power] = 9.98 mW.

2.3. Catalytic performance evaluation

The experiments were conducted with the dosages of the chemicals and catalysts as carbocatalysts (0.1 g/L), target organics (20 mg/L phenol), and the oxidant (PMS, 2 g/L). The reactor system was kept stirring at 400 rpm at 25 °C to form a homogeneous suspension. At set time intervals, the solution mixture was filtered via a 0.45 μm membrane to remove the solids and mixed with methanol to react with the remaining free radicals in the filtrate. Phenol concentrations were detected on a Thermal-Fisher high-performance liquid chromatography (HPLC) with an OA column at 270 nm.

3. Results and discussion

3.1. Catalyst characterization and performance

Firstly, the catalytic activity of pristine and annealed nanodiamonds (NDs) from different sources were screened. As indicated in Fig. 1a, the pristine nanodiamonds e.g. C-ND (XFnano Materials Tech Co. Ltd, China) and I-ND (Ray Techniques Ltd., Israel) can hardly decompose PMS to generate reactive species for phenol decomposition. Only around 42.3% phenol removal was achieved on S-ND (Sigma-Aldrich, Australia). However, it was proved that the catalytic performance of the pristine nanodiamonds can be significantly improved by thermal annealing (900 °C, Fig. S1). For example, C-ND-900 and I-ND-900 attained 66.7% and 76.9% organic removals in 120 min, respectively, and S-ND-900 yielded complete phenol degradation in 90 min with PMS. Fig. S2 and Table S1 show that the specific surface areas (SSAs) of the nanodiamonds were slightly increased after the high-temperature treatment because of the thermal expansion of highly stacked nanoparticles. The high surface energy of nanoscaled crystals gives rise to the agglomeration of nanodiamonds. Interestingly, S-ND-900 possesses the lowest surface area (365 m^2/g vs 394 m^2/g of C-ND-900 and 375 m^2/g of I-ND-900) yet demonstrates the highest activity, suggesting that the surface area is not the key factor dominating the catalytic behavior. Moreover, XRD patterns (Fig. S3) illustrate that the S-ND-900 exhibited the lowest crystalline intensity among the three annealed nanodiamonds, which might facilitate the decomposition of the outer shell of the diamond (111) terminating planes and transformation into a graphitic (001) shell [18,19]. Meanwhile, the texture of the denotation nanodiamonds from different sources may also influence the annealing processes as well as

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