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## PAPER



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## 1. Introduction

In recent decades, the discharge of large amounts of organic pollutants *via* industrial wastewater and municipal sewage leads to their severe contamination in natural water systems, thus causing unexpected adverse effects on the health of ecosystem and humans. Persulfate-based advanced oxidation processes (PS-AOPs) have attracted extensive attention for removal of phenolic compounds because of the merits of high oxidation capacity, rapid reaction kinetics, and facile operation.<sup>1–3</sup> Unlike most metal oxide-catalyzed persulfate activation that produces a variety of radicals,<sup>4</sup> carbocatalysts trigger nonradical activation of persulfate, which is less susceptible to

# Enhanced nonradical catalytic oxidation by encapsulating cobalt into nitrogen doped graphene: highlight on interfacial interactions†

Xiaoyong Yu,‡<sup>a</sup> Lijing Wang,‡<sup>b</sup> Xin Wang,<sup>®</sup> Hongzhi Liu,<sup>a</sup> Ziyuan Wang,<sup>a</sup> Yixuan Huang,<sup>a</sup> Guoqiang Shan,<sup>a</sup> Weichao Wang<sup>®</sup>\*<sup>b</sup> and Lingyan Zhu<sup>®</sup>\*<sup>a</sup>

Supported metal catalysts are widely used for heterogeneous catalytic processes (e.g., Fenton-like reaction), but the mechanisms of interfacial processes are still ambiguous. Herein, unique nanocarbon based catalysts with Co nanoparticles encapsulated in nitrogen (N)-doped graphene (Co@NG) were prepared by calcination of Co based metal-organic frameworks (MOFs), which showed excellent catalytic performance for peroxymonosulfate (PMS) activation. Comprehensive characterization revealed that there were strong interfacial interactions between Co and the NG layer due to the presence of special nitrogen species, especially graphitic-N. Density functional theory calculations suggested that the strong interfacial interactions provided optimal active sites with low adsorption energy (-1.99 eV) for PMS accumulation, which enabled the generation of highly oxidizing NG-PMS\* intermediates as evidenced by in situ Raman microscopy. Electrochemical analyses revealed that the interfacial interactions facilitated surface-to-surface electronic communication across atomic interface-bonding (N-Co). Consequently, phenol was quickly degraded by the NG-PMS\* via direct oxidation by an anodiclike nonradical process, and reasonable graphitic-N (G-N) content and pore size are important for this process. Phenol at 1 mM was completely removed within only 12 min by Co@NG-900 (which was prepared at 900 °C), with an apparent rate constant 20 times higher than that of pure NG-900. This work sheds new insights on the critical role of interfacial interactions in nonradical PMS activation.

radical scavenging by nontarget compounds in complex water matrices.<sup>5</sup> The mechanism for nonradical persulfate activation by carbocatalysts is frequently ascribed to singlet oxygenation or mediated electron-transfer.<sup>5–7</sup> However, the relative importance of these potential nonradical pathways is debatable.

Carbocatalysts including graphene,<sup>8</sup> nanodiamonds,<sup>9</sup> carbon nanotubes,<sup>2</sup> carbon nitride,<sup>3</sup> and biochar<sup>10</sup> have been investigated for nonradical persulfate activation, but their performances are not satisfactory. In order to improve the activation efficiency of persulfate, multiple methods were proposed by adjusting surface functional groups,<sup>3,11</sup> modulating defects,<sup>12</sup> and adjusting the electron state of C atoms.<sup>6</sup>

In the last decade, particular attention has been paid to supported carbon-based material mediated synthetic approaches to prepare highly effective catalysts.<sup>13,14</sup> Recent investigations revealed the advantages in preparing highly efficient heterogeneous catalytic materials from MOF precursors by means of thermal decomposition for energy storage and conversion,<sup>15</sup> and hydrogenation.<sup>16</sup> Construction of strong interaction interfaces by encapsulating metal nanoparticles with supporters has been proven to be a promising strategy to greatly enhance the catalytic performance attributed to the novel characteristics originating from the physical and chemical interactions between the metal species and carbon

<sup>&</sup>lt;sup>a</sup>MOE Key Laboratory of Pollution Processes and Environmental Criteria, Tianjin Key Laboratory of Environmental Remediation and Pollution Control, College of Environmental Science and Engineering, Nankai University, No. 38 Tongyan Road, Jinnan District, Tianjin, 300350, China. E-mail: Zhuly@nankai.edu.cn

<sup>&</sup>lt;sup>b</sup>Department of Electronics, National Institute for Advanced Materials, Renewable Energy Conversion and Storage Center, Tianjin Key Laboratory of Photo-Electronic Thin Film Device and Technology, Nankai University, Tianjin 300071, China. E-mail: weichaowang@nankai.edu.cn

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<sup>‡</sup> Yu and Wang contributed equally to this work.

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materials.<sup>17–20</sup> Ito and Ohto encapsulated NiMo alloys in graphene to realize both high catalytic activity and high chemical stability. The interface between NiMo and graphene significantly reduced the adsorption energy of intermediates, thereby remarkably enhancing the oxygen evolution reaction (OER) activity.<sup>20</sup> Zeolitic imidazolate frameworks (ZIFs), as a member of the MOF family, always serve as excellent precursors for nanocarbon catalysts allowing abundant mesopores<sup>21</sup> and active nitrogen species.<sup>17,22</sup> Calcination of ZIFs can generate a core–shell structure with transition metal nanomaterials which were tightly encapsulated by a carbon shell or network.<sup>22,23</sup> Such capsule-like morphology coupled with nitrogen doping displayed significant interfacial interactions between embedded metallic nanoparticles and the coated carbon shells.<sup>25</sup>

In light of these results, special capsule-like catalysts (Co(a)NG) with strong interfacial interactions were prepared by adjusting the calcination process of ZIF-67 for nonradical peractivation. oxymonosulfate (PMS) Such capsule-like morphology coupled with nitrogen doping might equip the catalysts with significant interfacial interactions between embedded metallic nanoparticles and the coated carbon shells. The nonradical peroxymonosulfate (PMS) catalytic efficiencies of the as prepared catalysts were evaluated using phenol as a model molecule. The physico-chemical properties of the catalysts, including morphology, specific surface area, electrochemical properties, binding affinities and so on, were well characterized using a series of characterization techniques. Density functional theory (DFT) simulations were applied to calculate the interfacial interactions between the Co nanoparticles and capsulated graphene. Various electrochemical analysis methods were performed to study the nonradical oxidation process of phenol in the Co@NG/PMS system. To the best of our knowledge, this study is among the very first studies to in-depth explore the mechanism of metal-carbon interfacial interactions for peroxide activation in AOP reaction systems. The outcomes provide a new insight into heterogeneous catalyst design for improving peroxide activation.

## 2. Experimental section

### 2.1 Chemicals and materials

PMS (KHSO<sub>5</sub> $\cdot$ 0.5KHSO<sub>4</sub> $\cdot$ 0.5K<sub>2</sub>SO<sub>4</sub>), 2-methylimidazole (2-MeIM), *tert*-butanol (TBA), *p*-phthalic acid (PTA), 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), phenol, cobalt nitrate hexahydrate, zinc nitrate hexahydrate, boric acid, sodium tetraborate decahydrate, sodium thiosulfate, methanol and cobalt (Co NPs, 99.9%, 30 nm) were purchased from Aladdin Co., Ltd., Shanghai, China. 2,2,6,6-Tetramethyl-4-piperidinol (TMP) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. 2-Hydroxyterephthalic acid (2-OH PTA) was purchased from Tokyo Chemical Industry Co., Ltd., China. Methanol, acetonitrile, formic acid, acetic acid and phosphoric acid of HPLC grade were bought from Aladdin Co., Ltd., Shanghai, China. Other reagents used were of analytical-reagent grade and obtained from Tianjin Chemical Reagent Co., Ltd. All of the chemicals were used as received without further purification. All solutions were prepared in 18.2  $M\Omega$  cm ultra-pure water produced by a RephiLe Biocel water system (Shanghai, China).

### 2.2 Preparation of ZIF-based catalysts

The ZIF-67 precursor was synthesized according to a previous report with few modifications.<sup>24</sup> Solution A was prepared by dissolving 2 mmol of cobaltous nitrate hexahydrate in 50 mL of methanol under agitated stirring for nearly 5 min. Solution B was prepared by dissolving 8 mmol of 2-MeIM in 50 mL of methanol. Solution B was shaken for 5 min and poured in solution A with continuing stirring. The color of solution A changed from pink to dark purple immediately. After stirring for 10 min, the reaction solution was allowed to settle for 24 h. The resulting precipitates were collected by centrifugation, thoroughly washed with methanol several times and finally dried in a vacuum at 60  $^{\circ}$ C.

In a typical process for the synthesis of Co@NG composites (Co@NGs), 100 mg of ZIF-67 was put in a ceramic boat, heated to 500 °C at a ramp rate of 5 °C min<sup>-1</sup> and maintained for 1 h in a tube furnace. The furnace temperature was increased to a predetermined temperature (700, 800, 900, 1000 and 1100 °C respectively) at a ramp rate of 2 °C min<sup>-1</sup> and that temperature was maintained for 2 h to produce the desired Co@NG-T materials, where T is the pyrolysis temperature. The furnace was allowed to cool down to room temperature at a ramp rate of 5 °C min<sup>-1</sup>. During the whole process, the furnace was in an atmosphere of Ar. The as prepared Co@NGs were put in 0.1 M H<sub>2</sub>SO<sub>4</sub> for 2 h to remove the surface Co species. To understand the critical roles of Co nanoparticles encapsulated in Co@NGs, the obtained Co@NG-900 was treated in aqua regia at 80 °C for 4 h to remove Co from the composite, and the product was labeled NG-900. CoxO was prepared by calcining Co@NG-900 in a muffle furnace for 1 h at 350 °C.

### 2.3 Characterization techniques

The crystal structures and morphologies of the as-prepared catalysts were examined using a powder X-ray diffractometer (XRD, ESCALAB 250Xi) equipped with Cu K $\alpha$  radiation ( $\lambda$  = 0.15406 nm), field-emission scanning electron microscope (FESEM, G2F20 S-Twin), and high-resolution transmission electron microscope (HR-TEM, JEM-2100F). The elemental compositions were analyzed by continuum source atomic absorption spectrometry (CS-AAS, Analytikjena contrAA®700). The specific surface areas were measured using the Brunauer-Emmett-Teller (BET) method on a Micromeritics ASAP 2460 instrument at liquid-nitrogen temperature. The pore size distribution (PSD) curves were recorded by nonlocal density functional theory (DFT) measurements. The X-ray photoelectron spectroscopy (XPS) spectra fitted by the Thermo Advantage software using Shirley-type background were recorded on a Thermo Scientific ESCALAB 250Xi photoelectron spectrometer equipped with a monochromated Al Ka source. The thermogravimetric (TG) studies were conducted on a Mettler Toledo TGA/DSC1 thermo-analyzer with a heating rate of 2 K min<sup>-1</sup> in Ar flow. The ESR spectra were collected on a JES-FA200

spectrometer with a center field at 328.9 mT and a sweep width of 10.0 mT at room temperature.

### 2.4 Electrochemical characterization

The electrochemical studies were performed in 100 mM phosphate buffer solution (pH 7). A standard three-electrode configuration was applied using Ag/AgCl/KCl as the reference electrode, a platinum wire as the counter electrode (if needed), and an activator-coated glassy carbon electrode as the working electrode. Electrochemical impedance spectroscopy (EIS) was conducted using a potentiostat (PGSTAT 302N, Metrohm, Switzerland) to provide the redox information. The EIS was measured at open circuit potential over a frequency range from 100 kHz to 0.01 Hz with a sinusoidal excitation of 10 mV. Nyquist plots were fitted according to the equivalent circuit reported previously.25,26 The other electrochemical analysis tests, including linear sweep voltammetry (LSV), chronoamperometry, and chronopotentiometry, were carried out on an electrochemical workstation (CHI 760E, China). The details of the operation and the preparation of the activator-coated glassy carbon electrode are shown in Text S1.<sup>†</sup>

### 2.5 Detection of reactive oxygen species (ROS)

In order to verify the generation of  ${}^{1}O_{2}$  in the reaction system, TMP was chosen as a spin-trapping reagent, which is oxidized to 2,2,6,6-tetramethyl-4-piperidinol-*N*-oxyl radical (TMPN) by  ${}^{1}O_{2}$ .<sup>27</sup> DMPO was selected as the trapping agent for the detection of 'OH, SO<sub>4</sub>'<sup>-</sup>. PTA was used as a probe molecule to detect 'OH production to give 2-OH PTA with a rate constant of 3.3 ×  ${}^{10^{9}}$  M<sup>-1</sup> s<sup>-1</sup>.<sup>28</sup>

### 2.6 Catalytic activity tests

The catalytic performance was assessed in a 200 mL reactor containing 1 mM phenol with an initial pH of 7.2. Sodium borate (50 mM) rather than phosphate was used as a buffer reagent considering that the latter may activate PMS under neutral conditions.<sup>29</sup> The reaction temperature was maintained at 25 °C using an oscillator (180 rpm). In a typical experiment, 5 mg of the catalyst was added in 100 mL of 1 mM phenol solution, and the reaction was initiated by adding a certain amount of PMS aqueous solution. At predetermined time intervals, 1 mL of the reaction solution was withdrawn and immediately filtered into a high-performance liquid chromatography (HPLC) vial containing 0.1 mL of sodium thiosulfate solution (0.1 mM) to terminate the catalytic reaction. To identify the phenol degradation products, 50 mL of sample was collected and concentrated to 2 mL by solid-phase extraction (SPE) following the previously described procedure (Text S2<sup>†</sup>).

The concentration of phenol in the reaction solution was analyzed by HPLC (Agilent, 1260-Infinity) at a detection wavelength of 273 nm with a mixed solution of methanol and 0.1 vol% acetic acid (50:50, v/v) as the mobile phase. To disclose the catalysis mechanisms, several other organic compounds (PTA, 2-OH PTA) were also tested (listed in Table S1,† with detailed HPLC analytical conditions). The transformation products of phenol were identified using a Waters ultraperformance liquid chromatography system (UPLC) coupled with a Waters Xevo TQ-S tandem mass spectrometer (MS/MS) equipped with an electrospray interface (ESI). The details of the chromatographic and mass conditions of UPLC-MS in the negative ESI mode are described in Text S2. $\dagger$ 

The reaction rate was evaluated using a pseudo first order kinetic model (eqn (1))

$$\ln(C_0/C_t) = kt \tag{1}$$

where  $C_0$  is the initial phenol concentration,  $C_t$  is the concentration at a certain time *t* during the degradation process, and *k* is the reaction rate constant.

### 2.7 Computational methods

The spin-polarized density functional theory (DFT) calculations were performed by using the VASP code<sup>30</sup> within the local density approximation (LDA)<sup>31</sup> for all calculations. The cutoff energy for the plane wave basis was set to be 500 eV. Grids of  $5 \times$  $5 \times 1$  and  $15 \times 15 \times 1$  Monkhorst–Pack *k*-point grids were sampled for geometry optimization and electronic property calculations, respectively. The atoms were relaxed with convergence criteria for energy and force set to be  $10^{-4}$  eV and 0.02 eV Å<sup>-1</sup>, respectively. The charge transfer was analyzed with the Bader code.<sup>32</sup> To avoid the image interaction along the perpendicular direction, a vacuum layer of 15 Å was taken. The supercells of  $3 \times 3$  were taken to simulate the structures of Co (111), graphene and their composite. Four atom layers were used to simulate the surface of Co (111) and the bottom two layers were fixed.

The adsorption energy  $(E_{\rm ad})$  of PMS on different systems is defined as

$$E_{\rm ad} = E_{\rm catal+PMS} - E_{\rm catal} - E_{\rm PMS}$$

where  $E_{\text{catal+PMS}}$ ,  $E_{\text{catal}}$  and  $E_{\text{PMS}}$  represent the total energy of the relaxed catalyst with PMS, the energy of the catalyst and the energy of PMS, respectively.

## 3. Results and discussion

# 3.1 Structure and characterization of the as-prepared catalysts

The powder X-ray diffraction (XRD) patterns of the assynthesized ZIF-67 material (Fig. S1†) matched well with the standard patterns of pure ZIF-67.<sup>24</sup> The MOF material was of typical rhombic dodecahedral shape with a particle size of 500– 700 nm, which was evidenced by the FE-SEM images (Fig. S2†). The obtained ZIF-67 was thermally transferred to Co@NGs in an atmosphere of argon (Scheme 1). The TG-DSC curves in Fig. S3† illustrate that decomposition of ZIF-67 mainly occurred at *ca*. 500–600 °C. Thus, ZIF-67 was calcined at four selected temperatures (*i.e.*, T = 700, 800, 900, 1000, and 1100 °C) to obtain the Co@NGs. The SEM images (Fig. S4†) indicate that the Co@NGs had a relatively smaller size and rougher surface than ZIF-67, which might be due to gradual decomposition and carbonization of the framework, and NC-900 maintained the Paper



Scheme 1 Preparation route and model of the N-doped graphene encapsulated Co nanoparticles (Co@NG) with well-controlled morphology, and the proposed overall Fenton-like reaction mechanism on Co@NG catalysts.

dodecahedron morphology very well (Fig. S5a†). In the Raman spectra (Fig. S6a†), the G band at ~1350 cm<sup>-1</sup> is a characteristic feature of graphitic layers, while the D (1590 cm<sup>-1</sup>) and D' (1840 cm<sup>-1</sup>) bands correspond to the disordered carbon or defective graphitic structures.<sup>33</sup> A high  $I_D/I_G$  band intensity ratio (0.63–1.01) (Fig. S6b†) indicates the generation of a large amount of defects,<sup>33,34</sup> implying that the N atoms were successfully doped in the graphitic layer given that the original concentration of nitrogen was relatively high (Fig. S7†).<sup>35</sup> The  $I_D/I_G$  (Fig. S6b†) of Co@NG-900 (0.75) was higher than that of Co@NG-1000 (0.68) and Co@NG-1100 (0.63), suggesting that more N atoms were present in Co@NG-900. In agreement with this, the elemental analysis (Fig. S7†) indicated that the N content declined distinctly as the calcination temperature was



Fig. 1 HR-TEM images of (a) Co@NG-700, (b) Co@NG-800, (c) Co@NG-900, (d) Co@NG-1000, and (e) Co@NG-1100; (f) an enlarged image of a Co nanoparticle capsulated in the graphene layers.

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higher than 900 °C. A broad and weak second-order (2D) band was observed at approximately 2700  $\text{cm}^{-1}$  in Co@NG-900, 1000 and 1100 (Fig. S6a<sup>†</sup>), and the shapes of the D and 2D bands (especially the lack of a typical graphite shoulder) are characteristic of few-layered graphene,<sup>33–35</sup> which was confirmed by the TEM images in Fig. 1. Other peaks, such as  $E_g$  (478 cm<sup>-1</sup>) and  $F_{2g}$  (517 and 618 cm<sup>-1</sup>), correspond to the Co element.<sup>36</sup> The HR-TEM image indicates that the Co nanoparticles were covered by graphene shells, and well dispersed without distinct aggregation in the Co@NGs pyrolyzed at a temperature as high as 900 °C (Table S2<sup>†</sup>), which could be attributed to the well separated carbon atoms in the 2-MeIM linker of ZIF-67. The two fringe spacings of 2.05 and 1.79 Å in Co@NG-900 (Fig. 1f) correspond to the (111) and (200) planes of Co nanoparticles, respectively.<sup>22</sup> Energy dispersive spectroscopy (EDS) elemental mapping images were taken to investigate the elemental distribution of the sample (Co@NG-900), as displayed in Fig. S8.<sup>†</sup> The elemental mapping images demonstrated the homogeneous distribution of N and C atoms within the entire nanoarchitecture, while the distribution of N atoms matches well with that of Co atoms.

The XRD patterns of the Co@NGs (Fig. 2a) exhibited five diffraction peaks at around 44.2, 51.6, 76.0, 92.4, and 97.8°, respectively, characteristic of metallic Co (JCPDS no. 15-0806). The peak at *ca.* 25.8° in the high temperature materials corresponded to the interlayer spacing of 3.42 Å, arising from the



Fig. 2 (a) Powder XRD patterns of NG-900 and Co@NG materials; (b)  $N_2$  adsorption and desorption isotherms of Co@NG materials.

turbostratic ordering of the carbon and nitrogen atoms in the graphite lavers.<sup>37</sup> Fig. 2b shows that all of the N<sub>2</sub> adsorptiondesorption isotherms were classified as type IV sorption isotherms. A typical type H4 hysteresis loop at the relative pressures  $(P/P_0)$  from 0.45 to 1.0 appeared when the pyrolysis temperature was higher than 900 °C, indicating the presence of a large amount of mesopores. The DFT pore-size distribution indicated there were a number of micropores smaller than 2 nm in the Co@NGs (Fig. S9<sup>†</sup>), which presumably originated from the intrinsic pore structure of ZIF-67. When the T was 1000 and 1100 °C, more mesopores in the range of 10-30 nm were produced. This suggested that Co@NGs with a hierarchically porous structure and large surface area were produced at high calcination temperatures, which are beneficial for efficient permeation of the reactants to access the abundant active catalytic sites.

The high-resolution XPS spectra of the Co@NGs indicated that the content of oxygen decreased with an increase in the pyrolysis temperature (Fig. S10a<sup>†</sup>), suggesting that the oxygencontaining functional groups on the carbon surface decomposed at high pyrolysis temperatures.<sup>38</sup> Doping nitrogen is considered as an efficient way to improve the electronic and catalytic properties of graphene.<sup>5</sup> Therefore, it is imperative to understand the types and contents of nitrogen in the Co@NG materials. Five peaks with binding energies at 398.4, 399.2, 400.5, 401.2 and 403.1–403.5 eV were deconvoluted, which can be assigned to pyridine-N (N1), N–Co, pyrrole-N (N2), graphitic-N (G-N) and oxidized-N (O-N), respectively (Fig. 3a).<sup>24,39</sup> The C–N bond is more vulnerable during the high-temperature calcination due to its lower binding energy (305 kJ mol<sup>-1</sup>) than that of



Fig. 3 High-resolution XPS N 1s (a), and Co 2p (b) spectra; and the contents of different N (c) and Co (d) species of Co@NG materials.

the C-C bond (379 kJ mol<sup>-1</sup>),<sup>40</sup> and the cleavage of C-N bonds led to partial loss of nitrogen (Fig. S10<sup>†</sup>).<sup>38</sup> The N2 and G-N were proved to be effective in improving the adsorption capacity and catalytic activity in PMS activation.41 As shown in Fig. 3a, c and Table S3,† the nitrogen species experienced distinct changes during pyrolysis at high temperatures. The percentages of N1 and O-N decreased, leading to predominant N-Co and N2 in the high temperature materials. It is worth noting that Co@NG-900 and Co@NG-1000 had a relatively high content of G-N, which was more thermostable than N1. However, the N-Co content in the Co@NG-1000 declined obviously compared to Co@NG-900, which might be attributed to the serious aggregation of Co nanoparticles, loss of nitrogen and destruction of graphene shells. All these would lead to a weakened interaction between the graphene shells and the encapsulated Co nanoparticles. Co@NG-900 possessed an appropriate nitrogen content and a relatively high ratio of G-N and N-Co, equipping it with relatively higher electron mobility and more active sites, which are beneficial for interfacial interactions between Co and the NG shells.42

The high resolution spectrum of Co  $2p^{3/2}$  in Co@NGs was deconvoluted into three peaks at 778.4, 780.2 and 782.6 eV, corresponding to Co<sup>0</sup>, CoC<sub>x</sub>N<sub>y</sub> and CoN<sub>x</sub>, respectively (Fig. 3b, d and Table S4†).<sup>43</sup> The peak corresponding to the Co–Co bond shifted to a higher energy compared to the pristine Co nanoparticles (778.1 eV).<sup>44</sup> This implied there was a strong interaction between the confined Co nanoparticles and N doped graphene shells. Previous studies demonstrated that the strong interaction between encapsulated metal nanoparticles and carbon shells could greatly facilitate electron transfer *via* the atomic interface-bonding channels, which helped to reduce the local work function and the adsorption quantity.<sup>44,45</sup>

### 3.2 Catalytic activities of the Co@NGs

The catalytic performance of the Co@NGs was evaluated for phenol removal by activating PMS. As shown in Fig. S11,<sup>†</sup> less than 1.5% of phenol was degraded by PMS alone. A control test revealed that about 4.5% of phenol was adsorbed by Co@NG-900 within 12 min. The phenol removal efficiency was distinctly enhanced as Co@NGs (Co@NG-700, 800, 900, 1000 and 1100) were applied, which was 48.5, 57.5, 100, 93.2, and 87.5% in 12 min, respectively. The phenol removal kinetics fitted the first-order reaction model very well ( $R^2 > 0.96$ ), and the apparent rate constant (k) and the surface area normalized rate constants (k') were calculated (Table S2<sup>†</sup>). As shown in Fig. 4a, when the temperature rose from 700 to 900  $^{\circ}$ C, the *k* increased from 0.045 to 0.397 min<sup>-1</sup> with an increase in the content of G-N (Fig. 3). The k increased sharply from Co@NG-800 to Co@NG-900 due to the mass production of mesopores (Fig. S9 and Table S2<sup>†</sup>), which is beneficial for phenol and/or PMS to approach the catalytic sites. A slightly decline of k was observed when the temperature further increased from 900 to 1100 °C, which might be owing to the reduced specific surface area (Table S2<sup>†</sup>) and severe damage of the encapsulated structure. The k value of Co@NG-900 was 0.397 min<sup>-1</sup> ( $R^2 = 0.988$ ), which was approximately 20.9 times of NG-900 (k = 0.019), although the surface

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Fig. 4 (a) First-order kinetic model of phenol removal with Co@NG materials within 12 min; (b) rate constant of Co@NG materials compared with Co NPs and NG-900; (c) ESR spectra with DMPO (DMPO<sup>+</sup>−OH, green ◆; DMPO-X, black ▼); (d) bulk oxidation of 0.1 mM PTA and the production of 2-OH PTA with Co@NG-900 and Co<sub>x</sub>O. Reaction conditions: [phenol] = 1.0 mM, [PMS] = 3.0 mM, catalyst = 0.05 g L<sup>-1</sup>, T = 298 K, initial solution pH = 7.2.

area of NG-900 (344.3 m<sup>2</sup> g<sup>-1</sup>) was 2.5 times of Co@NG-900 (Table S2<sup>†</sup>). In addition, the turnover frequency (TOF) of Co@NG-900, which was calculated by dividing the k value by the catalyst concentration, was as high as 7.94 min<sup>-1</sup> for phenol degradation. This TOF was remarkably higher than that reported for other catalysts for non-radical and radical PMS activation, which was in the range of 0.12-2.27 (Table S5<sup>†</sup>) and 0.16-3.10 (Table S6<sup>†</sup>), respectively. The nanoparticles of pure Co<sub>r</sub>O and Co, which did not contain nitrogen doped graphene layers, only achieved a phenol removal efficiency of  $\sim$ 43 and 65% (k = 0.056 and 0.107 min<sup>-1</sup>) in 12 min, respectively (Fig. S12<sup>†</sup>). Attributed to the proper nitrogen species (especially G-N and  $CoC_x N_y$ ) distribution, Co@NG-900 displayed the strongest interaction between the encapsulated metal nanoparticles and carbon shells, which helped to reduce the local work function. In addition, the much abundant mesopores enabled it to have higher adsorption capacity, and to facilitate the diffusion of pollutants to the active sites. These collectively contributed to its best catalytic performance. These results suggested that the strong interaction between the confined Co species and N-doped graphene shells played a vital role in improving the PMS activation.

The effect of oxidants (PMS, PDS, and H<sub>2</sub>O<sub>2</sub>) on the catalytic activity of Co@900-NG was also investigated. Co@900-NG exhibited a higher catalytic performance with PMS (100% removal of phenol) than with PDS activation (34% removal) within 12 min (Fig. S13<sup>†</sup>). This was attributed to the difficulty in breaking O-O bonds in a symmetrical structure like PDS molecules.<sup>46</sup> H<sub>2</sub>O<sub>2</sub> cannot be activated by Co@900-NG, may be due to the stronger bond energy of O-O in H<sub>2</sub>O<sub>2</sub> than that in persulfate and a poor affinity toward the catalyst. The reusability is important for practical applications of a heterogeneous catalyst. The performance of the Co@NG-900 nanoparticles was tested for 5 consecutive cycles using the same reaction parameters. The results in Fig. S14<sup>†</sup> show that, even after 5 consecutive cycles, the catalyst exhibited a high catalytic activity as indicated by  $\sim$ 85% degradation of phenol within 12 min.

### 3.3 Mechanisms for the highly efficient catalytic effect

To confirm the primary ROS in the PMS/Co@NG-900 system, ESR with spin-trapping reagents of TMP and DMPO was applied to detect the generation of  ${}^{1}O_{2}$  and free radicals accordingly. As illustrated in Fig. S15,<sup>†</sup> a characteristic 1:1:1 triplet signal with a g-value of 2.0056 appeared in the presence of Co@NG-900, which was indexed to 2,2,6,6-tetramethylpiperidine-N-oxyl (TMPN).<sup>27</sup> The <sup>1</sup>O<sub>2</sub> evolution during phenol degradation is illustrated in Fig. S16.<sup>†</sup> In the presence of phenol, the <sup>1</sup>O<sub>2</sub> formation rate had no correlation with the removal rate of phenol, implying the minor role of  ${}^{1}O_{2}$  in the reaction. As shown in Fig. 4c, the characteristic 1:2:2:1 signals of DMPO-'OH adducts (with  $aN = aH = 14.9 \text{ G})^{47}$  were detectable in the presence of Co@NG-900, while the sulfate radical was not detected. To certify the presence of 'OH, PTA was used as a probe molecule to detect 'OH production (Fig. 4d). 2-OH PTA was not detected in the entire reaction period when Co@NG-900 was added. However, obvious signals of 2-OH PTA were detected when Co<sub>x</sub>O was used as the catalyst. These suggest that the detected signals of DMPO-'OH might be due to the false positive detection of 'OH in the Co@NG-900/PMS system.28

The false positive detection involves a direct electron transfer reaction of the spin trap (R) followed by a nucleophilic attack by water (reaction (2)).

$$DMPO \xrightarrow{-e^{-}} DMPO'^{+} \xrightarrow{+OH} DMPO - OH$$
(2)

Radical quenching experiments were conducted to identify the active species responsible for phenol removal. As shown in Fig. S17,† the addition of methanol (MeOH, radical scavenger for 'OH and  $SO_4$ <sup>-- 48,49</sup>) and *tert*-butyl alcohol (TBA, radical scavenger for 'OH<sup>48</sup>) displayed marginal impacts on phenol removal, confirming that the free radicals did not play vital roles in phenol oxidation in the Co@NG-900/PMS systems.

The electrochemical properties of the Co@NGs were evaluated to probe the charge transfer capacity and redox potential in PMS or/and phenol solution. Two semicircles of Bode plots were distinct for Co@NGs (Fig. S18a<sup>†</sup>), implying that two chemical processes might be involved.<sup>50,51</sup> The Nyquist plots contained two-time constants for Co@NGs (Fig. S18b<sup>†</sup>), which was consistent with the Bode plots. The equivalent circuit of the EIS data is shown in Fig. S19,<sup>†</sup> in which the resistance, *R* ( $R_{ct}$  and  $R_r$ ), and constant phase element (pseudo-capacitance), CPE, could be fitted to all the data.<sup>25,26</sup> The  $R_{ct}$  was much smaller than the reaction resistance  $R_r$ , suggesting that the PMS activation was dominated by  $R_r$  (Table S7<sup>†</sup>). The  $R_r$  of Co@NG-900 (0.91 k $\Omega$ ) was the smallest, while that of Co@NG-700 (16.4 k $\Omega$ ) was the largest among all the Co@NGs. However, the pure Co nanoparticles displayed a single semicircle (Fig. 5a), implying



**Fig. 5** (a) Nyquist plot of Co@NG-900 and Co NPs; (b) *in situ* Raman spectra partial and whole views in the Co@NG-900/PMS and NG-900/PMS systems; (c) LSV and *Tafel* slope (inset of c) on the Co@NG-900 and NG-900 electrodes in phenol solutions; the changes of opencircuit potential curves of NG-PMS complexes on Co@NG-900 and NG-900 electrodes (d) and in different phenol proportions (e); (f) amperometric *i*-*t* curve measurements upon the addition of PMS and phenol with Co@NG-900 and NG-900 electrodes.

that completely different mechanisms were involved in PMS activation compared to Co@NGs.

In situ Raman analyses (Fig. 5b) were conducted to detect the surface chemistry evolution during PMS activation for phenol degradation. Besides the characteristic peaks of  $HSO_5^-$  for PMS alone at 884 and 1063 cm<sup>-1</sup>, a new peak ( $HSO_5^{-*}$ ) emerged at around 796 cm<sup>-1</sup> upon the addition of Co@NG-900 or NG-900 into the PMS solution.<sup>2</sup> This new peak might be ascribed to the bending vibrations of the prolonged peroxo O–O bond in the metastable NG–PMS\* intermediate. Moreover, the peak intensity of  $HSO_5^-$  was weaker and that of  $HSO_5^{-*}$  disappeared in the presence of phenol, suggesting that  $HSO_5^{-*}$  was consumed by phenol during the oxidation process.

To understand the mechanisms, linear sweep voltammetry (LSV) was performed, and the results are shown in Fig. 5c. The LSV curve could be divided into three parts. As the electrode potential ( $\varphi$ ) was in the range of 0.40–0.57 V, phenol could not be oxidized, and the *j* fluctuated around 1.5 mA cm<sup>-2</sup>, suggesting that the electrode potential was lower than the oxidation potential of phenol. As the  $\varphi$  increased and was in the range of 0.57–0.82 V, phenol started to be oxidized on the anode to generate a sharp and increasing current, and the surged current density of Co@NG-900 was greater than that of NG-900. It was

deduced that the oxidation potential of phenol on NGs materials was around 0.57 V.2,12 However, the current density gradually declined as the potential surpassed 0.82 V, which might be due to the fact that the mass transfer velocity of phenol molecules in the solution was much slower than the oxidation rate on the anode because of the fast consumption of phenol. The corresponding Tafel plots were constructed according to the LSV curves, and the Tafel slope was determined by fitting LSV data to the Tafel (Text S1<sup>†</sup>). The Tafel slope, which is determined by the rate-limiting step in electrocatalysis, is an inherent property of catalysts.52 The Tafel slopes of Co@NG-900 and NG-900 were calculated to be 266 and 188 mV dec $^{-1}$ , respectively (inset in Fig. 5c), suggesting that Co@NG-900 manifested a faster reaction rate than NG-900 with the elevated applied potentials, which might benefit from the strong interfacial interaction between Co and the NG shell in Co@NG-900.

In situ measurements of open circuit potential of surface HSO<sub>5</sub><sup>-\*</sup> on Co@NG-900 and NG-900 were conducted to reveal the formation of NG-PMS\*. Upon addition of PMS in the solutions, the open circuit potential in both Co@NG-900 and NG-900 systems increased immediately (Fig. 5d), corroborating the formation of NG-PMS\* complexes. A larger change was observed for the potential of Co@NG-900/PMS (0.64 V) than for NG-900/PMS (0.37 V), fortifying that the intrinsic redox potential of NG-PMS\* on Co@NG-900 was higher than that on NG-900, which might be because that encapsulation of Co in the catalysts enhanced the interaction between PMS and NG. However, as phenol was added, the potential of the Co@NG-900 and NG-900 dropped immediately to around +0.60 V, and then declined slowly. To further explore the relationship between the potential of NG-PMS\* and phenol oxidation, different amounts of phenol were added. As can be seen in Fig. 5e, when the phenol concentration was lower than PMS, the potential dropped distinctly with the increase of phenol, but it remained relatively constant ( $\sim$ 0.60 V) if the amount of phenol further increased. This might be due to the continuous consumption of the surface-active complexes until the potential dropped below the phenol's oxidation potential (0.57 V).

To understand the charge transfer in the oxidation process of phenol, amperometric *i-t* curves were recorded to monitor charge migration in the reaction systems (Fig. 5f), and the working electrode was biased to the applied potential +0.6 V. When PMS was injected, a negative current emerged promptly, whereas the addition of phenol generated a positive current. These observations indicated that the electrons transferred from phenol to PMS in the presence of Co@NG-900 or NG-900.12 The higher  $\Delta I$  observed for Co@NG-900 (79.7  $\mu$ A) than NG-900 (16.2  $\mu$ A) might be attributed to the excellent catalytic activity of Co@NG-900. The degradation products of phenol identified in the Co@NG-900/PMS and CoxO/PMS systems are listed in Table S8.<sup> $\dagger$ </sup> In the Co<sub>x</sub>O/PMS system, the identified products included benzoquinone, hydroquinone and some small ring opening products (such as lactic acid and maleic acid), while the oligometric intermediates like di- or terphenyls (m/z = 185and 277) were observed in the Co@NG-900/PMS system. According to the anodic-like oxidation mechanism, phenoxyl radicals in various resonance forms were produced via oneelectron oxidation of phenol in the Co@NG-900/PMS system, and they were further oxidized through C–O and C–C coupling between phenol radicals to generate oligomeric intermediates.<sup>53</sup>

According to the above analyses, the mechanism of nonradical oxidation was elucidated *via* an anodic-like oxidation process by Co@NGs. Due to the strong interfacial interaction between Co and the NG shells, the intrinsic redox potential of NG-PMS\* was greatly improved. When the equilibrium potential of the complexes exceeded the oxidation potential of phenol, phenol was decomposed *via* an anodic-like oxidation over Co@NG-900, and the higher oxidation potential greatly promoted the phenol oxidation.

### 3.4 DFT calculations

To clarify the mechanisms of the significant increase in the activity of the Co@NG system, DFT calculations were also performed. Co (111) with single-layer graphene was used to simulate the structure of Co@NG according to the HR-TEM images (Fig. 1). The structures of NG and the Co@NG are shown in Fig. S20 and S21.<sup>†</sup> The lattice parameters of graphene and Co (111) are 2.447 Å and 3.425 Å, respectively. The interlayer spacing of Co (111) is 1.98 Å, which is similar to the measured result 2.05 Å. The 1  $\times$  1 unit cell was used to test the adsorption of graphene on the surface of Co (111). The hcp configuration where the center of the carbon ring is above the surface Co atoms was found to be the most stable adsorption conformation with the distance of 2.07 Å between them.<sup>54</sup> To obtain the PMS adsorption configuration, the lateral and vertical adsorption structures of PMS (Fig. S22<sup>†</sup>) were considered. The higher lateral adsorption energy of PMS than the vertical one suggested that PMS is apt to be laterally adsorbed on the surface of Co@NG (Table S9, Fig. S23 and S24<sup>†</sup>). However, PMS was adsorbed on Co nanoparticles vertically, and was directly decomposed into O and HSO<sub>4</sub> (Fig. 6a), certifying that PMS was activated in different ways by pure Co nanoparticles and the



**Fig. 6** Side views of PMS adsorbed on (a) Co (111), (b) graphitic NG, and (c) Co@graphitic NG respectively. The blue, gray, violet, red, yellow and light pink represent Co, C, N, O, S and H atoms, respectively. (d) Charge density difference ( $\rho_{total} - \rho_{substrate} - \rho_{PMS}$ ) between Co@graphitic NG and PMS (isosurface contour is 0.01 e Å<sup>-3</sup>). The khaki and green denote the electron accumulation and electron depletion, respectively. (e) Work function of Co@NG-g. (f) Work function of composite systems. NG-g, NG-pd and NG-pl represent graphitic, pyridinic and pyrrolic nitrogen doped graphene.

Table 1 PMS adsorption onto different catalysis models. Q is the charge transfer from catalysis to PMS.  $Q_{Co}$  is the charge transfer from Co to graphene pristine or doped

	$d_{\mathrm{O-O}}\left(\mathrm{\AA}\right)$	$E_{\rm ad}~({\rm eV})$	<i>Q</i> (e)	$Q_{\rm Co}\left({\rm e}\right)$
Free DMS	1 21			
FIEE PMS	1.51			
G	1.39	-0.92	0.52	_
Graphitic NG	1.44	-1.99	0.86	_
Pyridinic NG	1.39	-1.11	0.57	_
Pyrrolic NG	1.39	-1.14	0.55	_
Co	1.44	-3.16	0.73	_
Co@G	1.44	-1.69	0.8	1.78
Co@graphitic NG	1.45	-2.05	0.87	1.71
Co@pyridinic NG	1.43	-1.55	0.78	1.95
Co@pyrrolic NG	1.43	-1.59	0.78	2.15

Co@NG composites (Fig. 6b and c). The O–O bond in PMS tends to be adsorbed above the C atoms, and the vertical distance between PMS and the surface is less than 2.5 Å (Fig. S25†).

To investigate the activating ability of the different catalysts, the length of the O–O bond  $(d_{O-O})$  of PMS, adsorption energy  $(E_{ad})$  and charge transfer (Q) from the catalysts to PMS are calculated and listed in Table 1. For the single-layer graphene, doping with nitrogen introduced extra electrons which serve as Lewis basic sites to facilitate PMS adsorption on the NG surface, which facilitated electron transfer during the process of phenol oxidation. The graphitic NG impressively enhances the PMS adsorption with more prolonged O-O bonds than the pristine G. Analogously, the construction of Co encapsulated in graphitic NG (Co@graphitic NG) leads to the longest  $d_{O-O}$  and strongest adsorption, implying that Co@graphitic NG predominates PMS activation in the composite systems, which was consistent with the degradation kinetics (Fig. 4a), XPS analysis (Fig. 3c) and electrochemical analysis (Fig. 5c, d and f). To further unravel the mechanisms of the enhanced activity, the charge density differences and work function (WF) of the composite catalysts were calculated, which are important for the activities of catalysts44,55 (Fig. 6d-f). The increased C pz charge on the surface of graphene owing to the electronegativity difference between C and Co atoms improved the interfacial interactions between the encapsulated Co and NG shells. Due to the significant decrease in the Fermi level by graphene encapsulation and N-doping, the work function of the Co@NG composites all decreased to <4 eV (Fig. 6f), which is significantly lower than that of Co (111) (5.41 eV) or single-layer graphene (4.49 eV) (Fig. S26<sup>†</sup>). Considering that Co might be coated by several layers of graphene, the Co (111) surface covered with double-layer graphene was also mimicked. Fig. S27<sup>†</sup> shows that there is also charge distributed on the surface layer of graphene and the WF is 4.10 eV. Therefore, it is the extra charges distributed on the surface of the catalyst and the decreased work function that may improve the PMS activating ability and the redox ability of formed  $HSO_5^{-*}$ .

### 4. Conclusions

In this work, unique composite catalysts of grapheneencapsulated Co nanoparticles with extremely high catalytic

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activity for remediation of organic pollutants were prepared via facile thermal decomposition of MOFs in an Ar atmosphere. A Co/N-doped graphene interface was generated, and the strong interactions between the N-doped graphene shells and confined Co nanoparticles improved the interfacial electron shuttling via  $CoC_x N_y$  atomic interface-bonding channels. DFT calculations indicated that the confined metal nanoparticles in graphene shells not only reduced the local work function for PMS adsorption, but greatly improved the potential of surface-active complexes on the graphene shells, which greatly improved the redox ability of HSO<sub>5</sub><sup>-\*</sup>, and the appropriate N species doping facilitates this process. Thus the interfacial interaction was greatly boosted and the surface nonradical oxidation performance was remarkably enhanced. As a result, 1 mM phenol could be completely decomposed in only 12 min with the reaction rate constant  $k = 0.397 \text{ min}^{-1}$ . Our study provides novel insights into the active interfacial interactions for peroxide activation and enhancing the non-radical oxidation process, which provides a facile strategy for development of other "interface engineering catalysts" in future.

## Author contributions

L. Y. Zhu supervised the project. X. Y. Yu and L. Y. Zhu conceived the project and designed the experiments. X. Y. Yu synthesized the catalysts and performed most of the reactions and characterization. With the help of X. Wang carried out electrochemical characterization. With the help of G. Q. Shan carried out ROS analysis. L. J. Wang who is supervised by W. C. Wang performed the DFT calculation. X. Y. Yu, L. J. Wang and L. Y. Zhu prepared the manuscript.

## Conflicts of interest

The authors declare no conflict of interest.

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