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### Ultrafine cobalt nanoparticle-embedded leaf-like hollow N-doped carbon as an enhanced catalyst for activating monopersulfate to degrade phenol



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#### ABSTRACT

While cobalt (Co) stands out as the most effective non-precious metal for activating monopersulfate (MPS) to degrade organic pollutants, Co nanoparticles (NPs) are easily aggregated, losing their activities. As many efforts have attempted to immobilize Co NPs on supports/substrates to minimize the aggregation issue, recently hollow-structured carbon-based materials (HSCMs) have been regarded as promising supports owing to their distinct physical and chemical properties. Herein, in this study, a special HSCM is developed by using a special type of ZIF (i.e., ZIF-L) as a precursor. Through one-step chemical etching

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Keywords: Monopersulfate Ultrafine ZIF Hollow Etching Phenol degradation with tannic acid (TA), the resultant product still remains leaf-like morphology of pristine ZIF-L but the inner part of this product becomes hollow, which is subsequently transformed to ultrafine Co-NP embedded hollow-structured *N*-doped carbon (CoHNC) via pyrolysis. Interestingly, CoHNC exhibits superior catalytic activities than CoNC (without hollow structure) and the commercial Co<sub>3</sub>O<sub>4</sub> NPs for activating MPS to degrade phenol. The  $E_a$  value of phenol degradation by CoHNC + MPS was determined as 44.3 kJ/mol. Besides, CoHNC is also capable of effectively activating MPS to degrade phenol over multiple-cycles without any significant changes of catalytic activities, indicating that CoHNC is a promising heterogeneous catalyst for activating MPS to degrade organic pollutants in water.

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#### 1. Introduction

While advanced oxidation processes (AOPs) are efficient approaches for wastewater treatments, and hydroxyl radical (HR)-based AOPs have been conventionally employed to oxidize organic contaminants, sulfate radical (SR)-based AOPs are increasingly adopted because SR possesses several merits including higher selectivity towards aromatic molecules, higher pH adaptability and redox potential, and longer lifespan than that of HR [1,2]. To produce SR, monopersulfate (MPS) has been frequently utilized as MPS is a commercially available, and environmental-friendly reagent [3]. Nevertheless, the self-decomposition of MPS to generate SR is slow; thus an "activation" is typically required to promote MPS decomposition to quickly produce SR [3–5].

Numerous methods have been employed for MPS activation including heat treatments [6], ultrasound [7], UV irradiation [6], alkaline [8], photocatalytic activation [9] and catalysts [4,10]. Amid these methods, usage of heterogeneous catalysts are proven as an efficient method for MPS activation [5,10–13]. Transition non-precious metal catalysts, in particular, cobalt (Co) is validated as one of the most effective non-precious metal catalysts, which also exhibit superior catalytic activities for MPS activation [7,14–18]. Nonetheless, Co nanoparticles (NPs) tend to aggregate in aqueous phase, thereby diminishing their catalytic activities; thus many efforts have attempted to immobilize Co NPs on supports/substrates to minimize the aggregation issue [17–19].

To date, carbonaceous materials are continuously adopted as supports for immobilizing Co because carbon is abundant, nontoxic and conductive [3,20,21]. Besides, the usage of carbon as supports could improve the dispersion of Co NPs and promote electron transfer, thus enhancing the catalytic activities [6,20–22]. Besides, the introduction of heteroatoms such as nitrogen (N) or sulfur (S) into carbon-based materials could significantly enhance the reactivity and electron transfer of these materials [20,21,23,24]. More recently, hollow-structured carbon-based materials (HSCMs) have been received tremendous attention due to their distinct physical and chemical properties including interior hollow structure, large contact surface area, abundant active sites, high stability and good conductivity [25-27], enabling them promising materials for various applications such as biomedicine, supercapacitors, lithium batteries, sensors and catalysis [27-32]. Therefore, such unique structure properties make HSCMs promising supports for immobilizing Co.

Recently, various approaches have been employed to fabricate HSCMs including hard-template method [33–35], soft-template method [36,37], chemical etching method [38–41] or *in situ* heat-treatment method [42,43]. Particularly, chemical etching method stands out as a promising approach to construct HSCMs using etching reagents, in which the precursor templates (e.g., metal organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs)) could retain their original appearances whereas inner voids or hollow structures inside the templates could be successfully fabricated, which eventually derived to HSCMs via heat treatment. Typically,

phenolic acids (i.e., gallic acid or tannic acid (TA)) have been widely employed to successfully construct hollow structured based materials [38,39].

Owing to their relatively large molecular weight, this feature enables them to attach on MOFs or ZIFs surface, protecting the outer layer and preventing full-destruction of precursors from further etching while the released proton (H<sup>+</sup>) ion can penetrate into precursors, subsequently creating voids or hollow structure inside [38,39]. Despite these aforementioned advantageous properties of HSCMs, there are limited studies implementing chemical etching methods for constructing HSCMs as supports to immobilize Co, which should be certainly promising for MPS activation to eliminate organic pollutants in water.

Herein, in this study, we proposed preparing a hollowstructured carbon-based material using a special type of ZIF (i.e., ZIF-L) as precursor. The as-prepared ZIF-L exhibited 2-dimensions (2D) morphology with unique leaf-like appearance. Through one step chemical etching with TA, the resultant product still remained leaf-like morphology of pristine ZIF-L but the inner part of this product became hollow, revealing the successful transformation of coordination framework of ZIF-L to complex coordination network between Co ions and TA (Co/TA), which subsequently transform to ultrafine Co-NP embedded hollow-structured *N*-doped carbon (CoHNC) via pyrolysis in  $N_2$  atmosphere. This fabricated CoHNC was then used as a heterogeneous catalyst for activating monopersulfate (MPS) to degrade a typical organic pollutant, phenol, in water.

The catalytic activities of CoHNC for activating MPS to degrade phenol were evaluated using batch-type experiments. Several parameters affecting phenol degradation by CoHNC activated MPS were examined including MPS and CoHNC dosages, temperatures and pH variation. The effect of co-existing surfactant and salt was also examined. Radical scavengers and electron spin resonance (ESR) were employed to verify the contributions of potential radical species generated by CoHNC + MPS system.

#### 2. Experimental

#### 2.1. Materials

All chemical reagents involved in this study were purchased from commercial suppliers and used as obtained without any purification. Cobalt nitrate hexahydrate ( $Co(NO_3)_2$ · $6H_2O$ ) was purchased from Showa Chemicals (Japan). 2-methylimidazole (2-MIM), salicylic acid (SA), bisphenol A (BPA), acetaminophen (ACE) and carbofuran (CBF) were obtained from Acros Organics (Belgium). Tannic acid (TA) ( $C_{76}H_{52}O_{46}$ ), methyl alcohol (MeOH), *tert*-butyl alcohol (TBA) were purchased from Alfa Aesar (USA). Monopersulfate (MPS), sodium chloride (NaCl), sodium dodecyl sulfate (SDS), phenol ( $C_6H_5OH$ ) were obtained from Sigma-Aldrich (USA). Deionized (DI) water was prepared to less than 18 MOhm-cm.

#### 2.2. Preparation and characterization of CoHNC

The synthesis procedure of CoHNC is illustrated in Fig. 1. Firstly, ZIF-L was fabricated via the reported procedure with slight modifications [44]. A solution containing  $Co(NO_3)_2$  was added dropwise into another solution containing 2-MIM with a ratio of Co:2-MIM = 1:8. The resultant purple mixture was continuously stirred at room temperature for 2 h. Next, the precipitate was collected via centrifugation, washed with DI water and EtOH, and dried at 65 °C overnight to obtain ZIF-L. Then, a hollow-structured complex of Co/TA was afforded via a wet chemical-etching process [39]. The asprepared ZIF-L was dispersed into a beaker containing 300 mL mixture of DI water and EtOH (DI water/EtOH = 1:1 in volume) and 1 mg/mL of TA for 10 min under vigorous stirring. Subsequently, the resultant precipitate was then collected via centrifugation, washed thoroughly by EtOH/DI water and dried at 65 °C to afford complex hollow structure of Co/TA.

Next, this complex of Co/TA was pyrolyzed at 600 °C for 1 h under N<sub>2</sub> atmosphere to afford ultrafine Co NP-embedded hollow-nanostructured N-doped carbon (CoHNC). For comparison, Co NP-embedded N-doped carbon (CoNC) without the hollow structure was also prepared via the same procedure for preparing CoHNC without the wet chemical-etching process. Morphologies of those as-prepared materials were characterized by scanning electronic microscopy and transmission electronic microscopy (JEOL JSM-7800F and JEM-1400, Japan). The textural properties of CoHNC were analyzed by a volumetric analyzer (Anton Paar Autosorb IQ, Austria). Besides, the magnetic properties of CoHNC were analyzed by a magnetometer (Quantum Design, USA), while its crystalline structure was obtained by an x-ray diffractometer (Bruker, USA). The chemical composition of CoHNC was also determined using energy-dispersive X-ray spectroscopy (EDX) (Oxford Instruments, UK), X-ray photoelectron spectroscopy (XPS) (PHI 5000, ULVAC-PHI, Japan) and Raman spectroscopy (Tokyo Instruments. Nanofinder 30, Japan). Surface charges of CoHNC were also determined at different conditions using zeta potentials analysis (Malvern Instruments Ltd. Nano-ZS, UK). The concentration of Co concentration in water was measured using ICP-OES (Thermo Scientific Optima8300, USA).

#### 2.3. Catalytic degradation of phenol using CoHNC-activated MPS

The catalytic degradation of phenol using CoHNC activated MPS was performed using batch experiments. Typically, a certain amount of MPS (i.e., 15 mg) was added into 50 mL of aqueous

phenol solution (an initial concentration ( $C_0$ ) = 5 mg/L), followed by the addition of CoHNC (10 mg) into the phenol solution. At a certain reaction time (t), sample aliquots (0.3 mL) were taken out from the phenol solution, which were subsequently filtered using syringe filters to separate CoHNC. The residual phenol concentration of the filtrate  $(C_t)$  was then measured using highperformance liquid chromatography (HPLC) equipped with UVvis detector at 270 nm. To determine radical species generated from CoHNC activated MPS, electron spin resonance (ESR) was employed using 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) as a radical-trapping agent. The stability and reusability of CoHNC for activating MPS to degrade phenol was performed by reused CoHNC for multiple consecutive cycles of phenol degradation. Intermediate products derived from phenol degradation were determined by a mass spectrometer (Thermo Finnigan Corporation, LCQ iontrap mass spectrometer, USA). Co concentration in water was analvzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (PerkinElem Elan DRC II, USA).

#### 3. Results and discussion

#### 3.1. Characterizations of CoHNC

Morphologies of those as-fabricated materials were first characterized by SEM and TEM images. Fig. 2(a-b) shows typical leaf-like morphology of as-prepared ZIF-L with an average length of ca. 4.8  $\mu m$  and width of ca. 2.1  $\mu m$ , and the thickness of ZIF-L was a few nanometers. After chemical-etching process with TA, the leaf-like morphology of the resultant product was still obtained without any significant changes as displayed in Fig. 2(c), indicating that the morphology of the as-prepared ZIF-L was well-preserved after modification. Nevertheless, the inner layer of ZIF-L had been removed (Fig. 2(d)), leaving a huge void and hollow structure with a very thin external shell. This result reveals that although the morphology of pristine ZIF-L was remained, the inner part of this product became hollow after chemical-etching process with TA. This demonstrates that the coordination framework of ZIF-L was taken over by the complex coordination network between Co ions and TA, creating the hollow structure inside. Once this complex was pyrolyzed in N<sub>2</sub> atmosphere, the resultant product still possessed leaf-like morphology as shown in Fig. 3(a). TEM image of this product in Fig. 3(b) and (c) confirms that thin external layer and hollow structure were still observed with the appearance of many spherical ultrafine NPs distributed evenly over the surface. A closer view in Fig. 3(d) reveals that those ultrafine NPs ranged



Fig. 1. A scheme showing the preparation of CoHNC derived from ZIF-L through an etching process by TA.



Fig. 2. ZIF-L: (a) SEM, and (b) TEM images; the etched ZIF-L (i.e., Co/TA): (c) SEM, and (d) TEM images.

from 2.5 to 5 nm with a dominant size of 3.7 nm as presented in the inset. This result suggests that the complex hollow structure of Co/TA was successfully transformed to a composite which was comprised of hollow *N*-doped carbon (HNC) embedded with the ultrafine NPs possibly derived from Co.

Moreover, the chemical composition of this composite was further analyzed as shown in Fig. 4(a); noticeable signals of Co, C, N and O could be detected. Besides, XRD patterns of those asprepared materials were further analyzed. As shown in Fig. S1(a), ZIF-L exhibited several diffraction peaks, which are consistent with the reported literature, confirming that ZIF-L was successfully fabricated [44]. Nevertheless, the resultant product after modifications with TA showed an amorphous phase without any diffraction peaks (Fig. S1(b)), which was also in line with the reported literature [39], revealing that the coordination framework between Co ions and HMIM ligand was taken place by the complex coordination network of Co ions and TA, simultaneously creating the hollow structure as observed in TEM image of Fig. 1(d).

Moreover, when this complex of Co/TA was pyrolyzed under  $N_2$  atmosphere to form the composite of HNC embedded with ultrafine NPs, the resultant composite showed distinct diffraction patterns in Fig. 4(b). Particularly, a broad peak at around 26.2° could be attributed to carbon derived from TA; and several noticeable peaks at 44.2°, 51.4° and 75.7° could be assigned to the (111), (200), and (220) planes of metallic Co (JCPDS#15–0806). Besides, a notable peak at 36.9° was also detected, which could be ascribed to the (311) plane of CoO (JCPDS#43–1004), indicating the partial oxidation of metallic Co to CoO. This result validated that those aforementioned NPs were Co/CoO NPs, which derived from Co/TA complex coordination network, forming Co-embedded hollow *N*-doped carbon (CoHNC). Furthermore, Raman spectroscopy of CoHNC was characterized in Fig. 4(c). Typically, two tall peaks were detected at 1334 and 1585 cm<sup>-1</sup> could be assigned to D band and G band of carbon, which corresponded to the disordered carbon and graphitic carbon of CoHNC, respectively. On the other hand, a few small peaks located 191, 575 and 646 cm<sup>-1</sup> could be attributed to metallic Co and CoO, further confirming the existence of Co and CoO NPs within CoHNC [45].

In addition, surface properties of CoHNC were also characterized by XPS. Fig. 5(a) illustrates a full-survey spectrum of CoHNC, showing the presence of Co, N, C and O elements, which is consistent with EDX analysis. Next, the C1s spectrum of CoHNC was analyzed in Fig. 5(b); three underlying peaks located at 284.5, 286.1 and 288.4 eV could be detected and ascribed to C--C, C--N and C=O bonds, respectively [46]. Fig. 5(c) shows the O1s spectrum of CoHNC, which could be divided into multiple underlying peaks of C-O (529.3 eV), metal-oxygen (531.4 eV), C=O (533 eV) and adsorbed oxygen (534.2 eV) [47]. Moreover, the N1s spectrum of CoHNC was also analyzed and deconvoluted into several underlying peaks (Fig. 5(d)), corresponded to pyridinic N, pyrrolic N, quaternary N, and oxidized N–O species [48]. Besides, the Co2p spectrum of CoHNC was shown in Fig. 5(e). The peaks at 780.8 eV and 796 eV could be assigned to Co<sup>2+</sup> species whereas the peaks located at 779 eV and 794.7 eV could be ascribed to Co<sup>0</sup> species, further validating the presence of metallic and CoO NPs in CoHNC [49], which is consistent with XRD result. The intensities of Co<sup>2+</sup> species were slightly stronger than that of metallic Co species, possibly because the metallic cobalt present on the surface



Fig. 3. Carbonized TA-ZIF-L: (a) SEM, (b), (c), and (d) TEM images under different magnifications (The inset: a size distribution of Co NPs embedded in CoHNC).



Fig. 4. (a) EDX, (b) XRD patterns, and (c) Raman spectroscopy of CoHNC.

of CoHNC might be oxidized because of its ultrafine, leading to lower signal of metal Co in the XPS spectrum [50-52].

As CoHNC was comprised of metallic Co ( $Co^0$ ), making it a magnetic material, it was necessary to evaluate magnetization of CoHNC as displayed in Fig. 6(a). When the magnetic field was varied from 20 and -20 kOe, CoHNC exhibited a strong magnetization and the saturation magnetization was 55 emu/g, indicating that CoHNC possessed strong magnetic properties and metallic Co was certainly existed in CoHNC. This implies that CoHNC could be easily recovered from aqueous solution and conveniently utilized for consecutive degradation. The inset in Fig. 6(a) illustrates that CoHNC was highly dispersed in water but instantly assembled by a strong magnet. On the other hand, the textural properties of CoHNC were further measured using N<sub>2</sub> adsorption/desorption isotherms. As shown in Fig. 6(b), CoHNC exhibited a type IV isotherm with a small hysteresis loop, revealing that CoHNC might contain micropores and mesopores. The inset in Fig. 6(b) presents the pore size distribution, validating that CoHNC was certainly consisted of mesopores. Then, the specific surface area of CoHNC was measured as 317.2 m<sup>2</sup>/g with a pore volume of 0.36 cm<sup>3</sup>/g.

Since phenol degradation using CoHNC activated MPS was conducted under aqueous phase, it is crucial to determine the surface



Fig. 5. XPS of CoHNC: (a) a full-survey spectrum, (b) C1s core-level spectrum, (c) O1s core-level spectrum, (d) N1s core-level spectrum and (e) Co2p core-level spectrum.



Fig. 6. (a) Magnetism, (b) textural properties, and (c) zeta potential of CoHNC.

charges of CoHNC under various conditions using zeta potentials. Fig. 6(c) reveals that the surface charges of CoHNC were more positive under acidic conditions, which became more negatively-charges under basic conditions with a point of zero charge = 6.6.

#### 3.2. Phenol degradation by CoHNC-activated MPS

Prior to evaluating the catalytic activity of CoHNC-activated MPS for phenol degradation, it is crucial to verify whether CoHNC was able to remove phenol by adsorption in water. Fig. 7(a) shows that phenol was negligibly removed in the presence of CoHNC after 60 min, indicating that phenol could not be removed by CoHNC through adsorption. On the other hand, the concentration of phenol was also slightly decreased as  $C_d/C_0$  was only 0.9 when MPS was individually present, showing that the self-decomposition of MPS in water was extremely slow and catalysts are required to activate MPS to quickly produce SR radicals to degrade phenol. Since CoHNC

was derived from precursor ZIF-L, it was interesting to evaluate the catalytic activity of ZIF-L for MPS activation; phenol degradation using ZIF-L activated MPS system was found to be ineffective as almost no phenol concentration was eliminated (Fig. 7(a)). Nevertheless, once ZIF-L was etched and transformed to CoHNC via pyrolysis process, the combination of CoHNC and MPS could completely degrade phenol as  $C_t/C_0$  could reach to zero within 15 min (Fig. 7), revealing the outstanding catalytic activity of CoHNC to activate MPS for phenol degradation. The mineralization of phenol could be also achieved as *ca.* 80% as displayed in Fig. S2 (in Supporting Information (SI)), illustrating that phenol was certainly decomposed in the presence of CoHNC and MPS.

Since CoHNC was comprised of  $Co^0$  and  $Co^{2+}$ , these Co species might react with MPS to produce SR as following equations (Eq. (1)-(4)) [19,53]:

$$Co^0 @CoHNC \rightarrow Co^{2+} @CoHNC + 2e^-$$
(1)



Fig. 7. Comparison of phenol degradation by MPS only, adsorption to CoHNC, ZIF-L activated MPS, CONC activated MPS, CoNPs activated MPS and CoHNC activated MPS. (Reaction conditions: catalyst = 200 mg/L, MPS = 300 mg/L, T = 30 °C).

$$HSO_5^- + e^- \rightarrow SO_4^{-} + OH^-$$
(2)

 $\label{eq:cohnc} Co^{2+} @ Cohnc \ + \ HSO_5^- \ \rightarrow \ Co^{3+} @ Cohnc \ + \ SO_4 \cdot - \ + \ OH^- \ \ (3)$ 

Besides,  $SO_5^-$  could be also transformed to SR, which subsequently reacts with phenol molecules and leads to phenol degradation as follows (Eq. (5)):

$$2 \text{ SO}_5 \cdot \overline{\phantom{a}} \rightarrow 2 \text{ SO}_4 \cdot \overline{\phantom{a}} \rightarrow 0_2 \tag{5}$$

Additionally, since CoHNC possessed hollow structure properties, which might contribute to its superior catalytic activities for phenol degradation, the pristine ZIF-L (non-etched one) had been also pyrolyzed to afford a composite of Co embedded *N*-doped carbon (CoNC), which exhibited a similar composition to CoHNC (Fig. S3(a)), and tested for activating MPS. As displayed in Fig. 7, phenol was certainly degraded as  $C_t/C_0$  could reach to 0.3 in the presence of CoNC + MPS after 60 min. This result illustrates that CoNC without hollow structure properties could also react with MPS to cause phenol degradation; however, its catalytic activity was lower than that of CoHNC, validating the advantageous hollow structure of CoHNC for MPS activation.

Furthermore, as Co<sub>3</sub>O<sub>4</sub> is regarded as a reference heterogeneous catalyst for activating MPS, commercial Co<sub>3</sub>O<sub>4</sub> NPs (Fig. S3(b)) was also tested and compared with CoHNC. While Co<sub>3</sub>O<sub>4</sub> NP was also capable of activating MPS as  $C_t/C_0$  of phenol degradation approached 0.67, CoHNC certainly outperformed the commercial Co<sub>3</sub>O<sub>4</sub> NPs. This further confirms that CoHNC with hollow structure properties is an advantageous and effective heterogeneous catalyst for MPS activation to degrade phenol in water. This also indicates that while  $Co_3O_4$  also consisted of  $Co^{2+}$ , its catalytic activity was noticeably less than CoHNC, suggesting that the embedment of Co NPs into HNC might create additional synergistic effects, such as swifter electron transfer, and protected catalytic active sites [54–57], to enhance its catalytic activities. Moreover, even though the commercial Co<sub>3</sub>O<sub>4</sub> NPs were also nano-sized, they were seriously agglomerated, thereby showing a very low surface area of  $\sim 2 \text{ m}^2/\text{g}$  and pore volume <0.01 cm<sup>3</sup>/g. Oppositely, ultrafine Co NPs could be almost mono-dispersed and evenly distributed over HNC matrix to increase active surfaces for enhancing its catalytic activities in the case of CoHNC. Additionally, since CoHNC was comprised of metallic Co and CoO NPs, it would be even more fascinating to investigate these cobaltic species individually for activating MPS to degrade phenol in water. First, metallic Co and CoO NPs were prepared via preparation methods from reported literature. The degradation of phenol using metallic Co and CoO NPs was investigated as shown in Fig. S4. Particularly, phenol was gradually degraded in the presence of metallic Co and MPS as  $C_t/C_0$  reached to 0.81 in 60 min, indicating that Co<sup>0</sup> was capable of activating MPS. Besides, when CoO NPs were used for MPS activation to degrade phenol, the degradation efficiency was slightly improved as  $C_t/C_0$  afforded to 0.59 within 60 min, revealing that CoO NPs could be also able to activate MPS. Nevertheless, the phenol degradation efficiencies of both metallic Co and CoO NPs were much lower than that of CoHNC-activated MPS, confirming the advantage of CoHNC for MPS activation to degrade phenol in water.

To elucidate the superior catalytic activities of CoHNC, CoHNC activated MPS was utilized to eliminate a series of refractory organic pollutants including salicylic acid (SA), bisphenol A (BPA), acetaminophen (ACE) and carbofuran (CBF). As illustrated in Fig. S5, CoHNC + MPS showed outstanding activities to degrade those contaminants. In particular, 100% of SA was removed within 30 min while ca. of 90% CBF, 85% of BPA and 50% of ACE were removed in 60 min. These results certainly validated the outstanding catalytic activity of CoHNC for activating MPS to degrade different organic pollutants in water.

#### 3.3. Effects of catalyst and MPS dosages on phenol degradation

As CoHNC activated MPS system effectively removed phenol, the effects of CoHNC and MPS concentrations were necessarily studied. Fig. 8(a) exhibits the degradation curves of different CoHNC dosages ranging from 100 to 250 mg/L. As discussed above, phenol was ineffectively degraded in the absence of CoHNC. Nevertheless, as a small amount of CoHNC (i.e., 100 mg/L) was added, the concentration of phenol was removed gradually as  $C_t/C_0$  was 0.16 in 60 min, which was further reduced to 0.07 at 150 mg/L of CoHNC. When the dosage of CoHNC was increased to 200 mg/L, 100% of phenol was afforded as  $C_t/C_0$  could approach zero within 15 min, which was even in a shorted time at 250 mg/L of CoHNC. In addition, the kinetics of phenol degradation using different CoHNC dosages were also measure using the pseudo first order equation (Eq. (6)) [58], which has been extensively employed for calculating the degradation kinetics by MPS:

$$C_t = C_0 \exp(-k_{obs}t) \tag{6}$$

where  $k_{obs}$  represents the observed pseudo first order rate constant. As displayed in the inset of Fig. 8(a), when the dosage of CoHNC increased from 100 to 250 mg/L,  $k_{obs}$  value was dramatically rose from 0.05 min<sup>-1</sup> to 0.419 min<sup>-1</sup>, confirming the advantageous of higher CoHNC dosage to phenol degradation by facilitating SR generation from MPS with abundant active sites.

On the other hand, phenol degradation by various MPS concentrations was also examined in Fig. 8(b). At 200 mg/L of MPS, phenol was gradually eliminated as  $C_d/C_0$  reached to 0.15, implying the



Fig. 8. Effects of (a) CoHNC dosage, (b) MPS dosage, (c) temperatures and (d) pH variation on phenol degradation using CoHNC activated MPS. (Reaction conditions: catalyst = 200 mg/L, MPS = 300 mg/L, T = 30 °C).

insufficient of SR produced from MPS to phenol degradation. When MPS dosage rose to 300 mg/L, phenol was completely degraded as  $C_t/C_0$  approached to zero in 15 min, which was even faster at higher MPS dosage (i.e., 400 mg/L), suggesting that lower dosage of MPS might cause incomplete phenol degradation because of insufficient SR species while higher MPS dosages with sufficient produced SR were more favorable to fully eliminate phenol in water. Moreover,  $k_{obs}$  value was also calculated (the inset in Fig. 8(b)) as 0.123 min<sup>-1</sup>, 0.2367 min<sup>-1</sup> and 0.4174 min<sup>-1</sup> at COHNC dosage of 200 mg/L, 300 mg/L and 400 mg/L, respectively, further affirming the advantageous of higher MPS concentration to phenol degradation. For further experiments, 300 mg/L of MPS was particularly chosen to examine other parameters.

## 3.4. Effects of temperatures, pH and surfactant and salt on phenol degradation

Since temperature is another crucial parameter for degradation of phenol using CoHNC-activated MPS, the effect of different temperatures on phenol degradation was performed and exhibited in Fig. 8(c). It can be seen that phenol was degraded faster along with the increase of temperature. In particular, while phenol was completely eliminated within 15 min at 30 °C, the complete degradation of phenol was remarkably obtained in a shorter time at higher temperatures, revealing the positive effect of higher temperature on phenol degradation as SR was quickly generated from MPS at elevated temperatures. Moreover, the corresponding  $k_{obs}$ was calculated as 0.2367 min<sup>-1</sup> at 30 °C, which was significantly increased to 0.309 min<sup>-1</sup> and 0.417 min<sup>-1</sup> at 40 °C and 50 °C (Fig. S6(a)), respectively, further ascertaining that the activation of MPS was much favorable at elevated temperatures for generating SR, thus leading to expeditious phenol degradation.

In addition, as  $k_{obs}$  was increased at higher temperatures, the relationship between  $k_{obs}$  and temperatures was further correlated via Arrhenius equation (Eq. (7)) as following:

$$\ln k_{\rm obs} = \ln A - E_{\rm a}/RT \tag{7}$$

where A is the temperature-independent factor, T represents the solution temperature in Kelvin (K), R is the universal gas constant, and  $E_a$  indicates the activation energy of phenol degradation. As displayed in the inset of Fig. 8(c), the correlation of ln  $k_{obs}$  versus 1/T exhibited a linear regression with  $R^2 = 0.991$ , and then the corresponding  $E_a$  was determined as 44.3 kJ/mol. For comparison,  $E_a$  values of some recent studies for phenol degradation using MPS as summarized in Table S1, and CoHNC exhibited a much lower  $E_a$  than most of the reported values, validating that CoHNC was an efficient and heterogeneous catalyst for activating MPS to degrade phenol in water.

As phenol degradation using CoHNC activated MPS is performed in aqueous media, pH values of solution are also critical parameter influencing to MPS activation. Therefore, the effect of different pH (i.e., 3–11) was necessarily studied as shown in Fig. 8(d). One can be noted that phenol degradation efficiency was certainly influenced under different pH conditions. Particularly, at pH = 7, a neutral condition, phenol degradation was still effectively achieved. When initial pH of phenol solution was adjusted to pH = 5 of weak acidic condition, phenol degradation efficiency was slightly influenced as  $C_t/C_0$  could reach to nearly 0.09 with the corresponding  $k_{obs}$  value decreased to 0.151 min<sup>-1</sup>, which was even significantly influenced at strong acidic condition of pH = 3 as  $k_{obs}$  dropped to 0.077 min<sup>-1</sup> (Fig. S6(b)). These results revealed that phenol degradation using CoHNC activated MPS was unfavorable under acidic conditions, especially the strong acidic condition, possibly due to the stability of MPS under acidic conditions [59], leading to slower MPS activation.

On the other hand, phenol degradation efficiencies were also affected at higher pH values. Specifically, while phenol degradation efficiency was slightly decreased as  $C_t/C_0$  approached to nearly 0.15 at weak alkaline condition of pH = 9 and its corresponding  $k_{obs}$  was 0.123 min<sup>-1</sup>, phenol degradation was substantially affected at strong alkaline condition of pH = 11 as  $C_t/C_0$  merely reached to 0.6 and its corresponding  $k_{obs}$  was dramatically decreased to 0.032 min<sup>-1</sup>. These results indicated the negative effect of higher pH to phenol degradation, probably because MPS might decompose with less SR produced under alkaline conditions [59,60], thereby leading to insufficient SR to degrade phenol. In addition, the alkaline condition would also render the surface of CoHNC more negatively-charged because of accumulation of hydroxyl ions, which made the electrostatic repulsion grow stronger, restraining contact between SO<sub>5</sub><sup>-</sup> and CoHNC.

Additionally, as wastewater commonly contains salts and surfactants, which possibly influence MPS activation, it would be more practical to investigate effects of these supplement components on phenol degradation using CoHNC activated MPS. In order to perform this experiment, relatively high dosages of NaCl as salt and SDS as surfactant were added into phenol solution as shown in Fig. 9(a). When 500 mg/L of NaCl, a most common salt, was introduced, phenol degradation was notably influenced as  $k_{obs}$ decreased from 0.2367 to 0.086 min<sup>-1</sup> (Fig. S6(c)), implying that phenol degradation was interfered in the presence of NaCl. This is probably because chloride ions from NaCl could react with SR to generate reactive chloride species (e.g., Cl<sup>-</sup> and Cl<sub>2</sub><sup>-</sup>) as following equations (Eq. (8)–(9)) [61]:

$$Cl^{-} + SO_4 \cdot ^{-} \rightarrow Cl \cdot + SO_4{}^{2-}$$

$$\tag{8}$$

$$\mathrm{Cl} + \mathrm{Cl}^- \rightarrow \mathrm{Cl}_2 \cdot^-$$
 (9)

Since the as-generated chlorine radicals possess lower oxidation potential in comparison with SR, these chlorine radicals might restrain phenol degradation efficiency. Nonetheless, more than 80% of phenol was still capable degraded using CoHNC + MPS system in the presence of high-concentrated NaCl, showing the highly-stable catalytic activity of CoHNC for phenol degradation. In addition to salt, surfactants might also influence MPS activation for phenol degradation. As displayed in Fig. 9(a), phenol degradation efficiency was certainly influenced in the presence of SDS as an anionic surfactant, revealing the negative effect of SDS to phenol degradation using CoHNC + MPS system. This is possibly because anionic SDS might be deposited on the surface of CoHNC, then



Fig. 9. Effects of (a) surfactant and salt on phenol degradation using CoHNC activated MPS, (b) reusability of CoHNC for multiple-cycles of phenol degradation, (c) and (d) XRD pattern and Raman spectroscopy of used CoHNC (Reaction conditions: CoHNC = 200 mg/L, MPS = 300 mg/L, T = 30 °C).



**Fig. 10.** (a) Effect of scavengers on phenol degradation using CoHNC activated MPS (Reaction conditions: CoHNC = 200 mg/L, MPS = 300 mg/L, T = 30 °C), (b) ESR spectra of CoHNC for activating MPS ( $\Box$ : DMPO-OH; O: DMPO-SO<sub>4</sub><sup>-</sup>).

forming strong electrostatic repulsion between CoHNC and anionic phenol, thereby diminishing the exposure of CoHNC and phenol. Nevertheless, CoHNC + MPS system was still capable to degrade more than 60% of phenol in the presence of highly-concentrated SDS, further validating the superior catalytic activity of CoHNC for MPS activation.

#### 3.5. Reusability of CoHNC for activating MPS

Since CoHNC exhibited superior catalytic activities for activating MPS to degraded phenol, it was important to verify whether CoHNC could remain its superior catalytic activity for consecutive degradation of phenol. Fig. 9(b) displays that 100% phenol removal was still efficiently achieved over 5 continuous cycles by the used CoHNC, confirming that CoHNC could retain its stable and superior catalytic activity for activating MPS to degrade phenol. Besides, Co ion leaching is another crucial parameter for practical applications. Thus, Co leaching experiment was further investigated. Based on ICP-MS analysis, the Co concentration over 5 consecutive cycles was only 0.01 mg/L, which is significantly smaller than the initial concentration of CoHNC used in the experiment (i.e., 200 mg/L), further validating the highly stability of CoHNC. Moreover, XRD pattern of the used CoHNC was also analyzed as shown in Fig. 9 (c), which is similar to that of pristine CoHNC, whereas Raman spectrum of the used CoHNC was also characterized (Fig. 9(d)), showing that Co species and carbon structure of CoHNC were well-preserved. These results certainly confirm the superior stability of CoHNC, which contributed to its durable catalytic activity for continuously activating MPS to degrade phenol. In addition, the core-level spectrum of Co2p of the used CoHNC was also revealed as indicated in Fig. S7 (in Supporting Information (SI)). It can be noted that the Co species in CoHNC were still well-retained in comparison with the pristine CoHNC, further validating the stability of CoHNC. Nevertheless, the intensities of Co species were slightly changed, which could possibly contribute to the electron transfer during the oxidation process.

# 3.6. Effect of scavengers and plausible mechanism of phenol degradation using CoHNC activated MPS

As SR  $(SO_4^-)$  was generated from MPS activation, SR may further react with H<sub>2</sub>O to produce HR ( $\cdot$ OH) via the following equation (Eq. (10)):

$$SO_4$$
·- +  $H_2O \rightarrow SO_4^{2-}$  + ·OH + H<sup>+</sup> (10)

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Therefore, it is crucial to verify the contributions of these potential species (i.e., SR and HR) to phenol degradation by CoHNC activated MPS. In this regard, two particular radical scavengers, tertbutyl alcohol (TBA) and methanol (MeOH), were selected to probe the presence of these radical species. Since TBA does not contain  $\alpha$ hydrogen, TBA could react rapidly with HR; therefore, TBA was employed as a scavenger for probing the presence of HR. In Fig. 10(a), phenol degradation efficiency was certainly influenced when TBA was introduced as  $C_t/C_0$  only approached to 0.16 with the corresponding  $k_{obs}$  was decreased from 0.237 min<sup>-1</sup> to 0.086 min<sup>-1</sup> (Fig. S3(d)), indicating the existence of HR, which might contribute to phenol degradation by CoHNC + MPS. On the other hand, since MeOH possesses  $\alpha$ -hydrogen, which could readily react with both SR and HR species, MeOH was further adopted as a scavenger of those species. In the presence of MeOH, phenol degradation became much slower, in which only 40% of phenol was degraded in 60 min and its  $k_{obs}$  was dramatically reduced to 0.028 min<sup>-1</sup> (Fig. S3(d)). This result suggested that HR and SR were certainly existed and contributed to phenol degradation. For further confirming radical species generated from CoHNC-activated MPS, ESR analysis was employed as shown in Fig. 10(b). When DMPO was used as a spin-trapping agent, no significant signal was detected from MPS + DMPO. Nonetheless, when MPS and CoHNC were combined with DMPO, a distinct signal was obtained, and attributed to the hyperfine splitting of oxidation adduct products of DMPO-OH and DMPO-SO<sub>4</sub> [62-67]. These results verified that phenol degradation by CoHNC-activated MPS could be involved both with SR and HR.

#### 3.7. A potential phenol degradation pathway for by CoHNC/MPS

Since CoHNC was validated to exhibit promising catalytic activity for activating MPS to degrade phenol, it would be essential to study phenol degradation pathway by CoHNC-activated MPS. Thus, degradation intermediates of phenol were determined by mass spectrometry and summarized in Table S2. Based on these degradation intermediates, a potential degradation pathway of phenol by CoHNC-activated MPS could be proposed in Fig. 11.

Firstly, phenol was oxidized and inserted by a hydroxyl group to form P1 and P2 (*resorcinol*/hydroquinone), which were further oxidized to become P3 (*cyclohex-4-ene-1,3-dione*), and P4 (*benzo-quinone*), *respectively*. Subsequently, these intermediates might be attacked and undergone a ring-opening reaction, resulting in P5 (2-hydroxyacetic acid), which would be then oxidized to produce many smaller molecules, such as P6 (*carbonic acid*). These small



Fig. 11. A potential degradation pathway of phenol degradation by CoHNC + MPS.

molecules would be further oxidized and eventually decomposed into  $CO_2$  and  $H_2O$ .

#### 4. Conclusion

In this study, a special Co-based catalyst was successfully prepared using a 2D leaf-like ZIF-L as precursor. Through one-step chemical-etching modification with TA, the resultant product still remained leaf-like morphology of pristine ZIF-L but the inner part of this product became hollow, which was subsequently derived into ultrafine Co NP-embedded hollow N-doped carbon (CoHNC) via pyrolysis in N<sub>2</sub> atmosphere. This CoHNC exhibited more superior catalytic activities than CoNC (without hollow structure) and the commercial Co<sub>3</sub>O<sub>4</sub> NPs for activating MPS to degrade phenol.  $E_a$  of phenol degradation by CoHNC + MPS was determined as 44.3 kJ/mol, which was comparable or even lower than most reported values. Besides, CoHNC was also capable of effectively activating MPS to degrade phenol over multiple-cycles without any changes of catalytic activities, indicating that CoHNC could be a promising heterogeneous catalyst for activating MPS to degrade phenol in water.

#### **CRediT** authorship contribution statement

**Duong Dinh Tuan:** Data curation, Writing– original draft. **Wei-Jie Liu:** Data curation. **Eilhann Kwon:** Data curation, Visualization, Investigation. **Bui Xuan Thanh:** Writing – review & editing. **Venkata Subbaiah Munagapati:** Writing–original draft. **Jet-Chau Wen:** Data curation, Visualization, Investigation. **Grzegorz Lisak:** . **Chechia Hu:** Data curation, Writing– original draft. **Kun-Yi Andrew Lin:** Data curation, Writing– original draft.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### **Appendix A. Supplementary material**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2021.08.027.

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