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Heterogeneous Fenton catalytic degradation of nitrobenzene by controlled-release nano calcium peroxide

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ABSTRACT

Degradation of nitrobenzene (NB) *via* Fenton-like reaction is considered as an efficient approach for contaminated groundwater remediation. However, the poor stability of H_2O_2 limits the application of traditional Fenton reactions in soil and groundwater due to the transportation risks of H_2O_2. In this study, we synthesized a controlled release nano calcium peroxide (nCP) by coating it with polydopamine (PDA) as a solid H_2O_2 to construct a Fe(II)/PDA@nCP Fenton-like system for contaminants degradation. The phenol-quinone transformations of catechol groups on the PDA surface facilitated the Fe(II)/Fe(III) cycle, resulting in enhanced generation of hydroxyl radicals ($HO^•$) and effective long-term degradation of NB. Moreover, the PDA shell modulated the nCP decomposition rate and inhibited sharp pH fluctuations, and the NB removal efficiency was achieved up to 96.8% at pH ranging from 3.0 to 9.0. This study demonstrated the promising application potential of PDA@nCP as a solid-controlled release H_2O_2 source in Fenton-like system for groundwater contamination remediation.

Nitrobenzene (NB) is an aromatic nitro compound, frequently used in chemical and pharmaceutical industries [1]. But recognized as a widespread contaminant in soil and groundwater due to its carcinogenic, teratogenic, and mutagenic effects [2]. The electrophilic groups result in persistent features of NB and complicate its degradation from the environment [3]. Thus, developing green, effective, and environmentally friendly processes to clean up NB raises urgent environmental concerns. Advanced oxidation processes (AOPs) are considered as an effective approach for degrading NB, and in particular, the Fenton system was one of the most frequently used approaches due to its low cost and high reactivity [4]. Catalysts enable Fenton and Fenton-like reagents to produce reactive species, transforming NB into substances that are less toxic and more degradable with lower molecular weights, and then fully mineralized to water (H_2O) and carbon dioxide (CO_2) [5,6]. However, considering the large volume of soil and groundwater in contaminated sites, the effectiveness of the traditional system is limited by the sharp reactivity of H_2O_2, causing fast consumption before H_2O_2 reaches the contaminants. Additionally, the transportation and use of H_2O_2 are subject to strict requirements [7]. Therefore, finding a safe, stable and environmentally friendly alternative for H_2O_2 is crucial for further application. Nano-calcium peroxide (nCP) reacts with water to generate H_2O_2 with O_2 as a side product (Eqs. 1 and 2) [8]. Which is usually referred to as solid hydrogen peroxide. Although the ability of nCP to release H_2O_2 has gradually received more attention from researchers, the high reactivity of nCP causes a pH increase in this system, hindering the generation of $HO^•$ (Eq. 3) [9]. The escalation in pH accelerates the conversion from Fe(II) to Fe(III), hindering the operation of the Fe(II)/nCP Fenton-like process. Concurrently, the accumulation of OH^- inhibits the decomposition of H_2O_2, leading to limited utilization efficiency of H_2O_2. Thus, optimizing the use of oxidizing agents is crucial for advancing the application of Fe(II)/CP Fenton-like systems in remediating actual contaminated sites.

The surface functionalization of PDA showed great potential to overcome the drawbacks of nCP above. At present, researchers have advanced in the area of H_2O_2 release from nCP enhanced by a coating layer and the construction of a Fenton-like system for the degradation of organic pollutants. PEG200 was coated at nCP and constructed a Fenton-like system using FeS_2 as a catalyst for naphthalene degradation. The findings indicated that the system's pH remained stable while efficiently degrading naphthalene [10]. An nCP-based oxidant (Cool O_x^{TM}) system was designed to control-release H_2O_2 into the soil and exhibited a remarkable removal of petroleum hydrocarbons compared to traditional methods [11]. A reasonable choice of coating materials for nCP modification not only aids in building the Fenton-like reaction system but also en-

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hances its performance. The majority of research is centered on exploring the mechanism behind the enhanced H_2O_2 release from the coating layer. However, the theory of maintaining catalyst activity by the oxidant coating layer is usually overlooked.

$$CaO_2 + 2H_2O \rightarrow Ca(OH)_2 \downarrow + H_2O_2 \quad (1)$$

$$CaO_2 + H_2O \rightarrow Ca(OH)_2 \downarrow + 1/2O_2 \quad (2)$$

$$H_2O_2 + Fe(II) \rightarrow HO^{\bullet} + OH^- + Fe(III) \quad (3)$$

Dopamine hydrochloride was widely used in medical treatments and self-polymerized under alkaline conditions to form polydopamine (PDA) [12]. The abundant catechol groups on the PDA surface render the nanoparticles with a negative charge, leading to a strong electrostatic repulsion that enables PDA to effectively coat the nanoparticles, forming a shell structure with enhanced stability and dispersibility [13]. PDA has been used as a coating material, enhancing the capabilities of $NaBH_4$ to generate hydrogen. The PDA shell helps to moderate the sharp rise in pH, thereby protecting $NaBH_4$ from solution environment [14]. Simultaneously, the catechol groups on the pollutants enhanced the Fenton system's performance by regenerating Fe(II) and lowering pH to more acidic conditions [15]. These results indicate that the PDA shell effectively inhibits pH rise and facilitates Fe(II) regeneration in the Fenton-like system, owing to the surface catechol groups. Therefore in this study, we aim to: (1) Synthesize PDA@nCP as controlled released solid H_2O_2 and fully characterize its physicochemical properties; (2) evaluate the efficiency and kinetics of PDA@nCP for control releasing H_2O_2; (3) investigate NB degradation mechanism by Fe(II)/PDA@nCP Fenton-like system and the effects of groundwater condition such as pH, natural occurring anions. This study investigated the mechanisms of the PDA@nCP Fenton-like system for NB degradation, revealing its potential for groundwater contamination remediation.

All chemical reagents used in the experiment are shown in Text S1 (Supporting information). All experimental methods are shown in Texts S2-S6 (Supporting information).

Through the morphology and physicochemical properties of PDA@nCP, PDA shell was successfully coated in the surface of nCP and the coated process did not affect the crystalline structure of nCP (Figs. S1 and S2 in Supporting information). To ensure the high reactivity of Fe(II)/PDA@nCP Fenton-like system for NB degradation, the dosage of PDA@nCP and Fe(II) are optimized, and the highest degradation efficiency was achieved with the addition of 0.1 g/L of PDA@nCP and 0.65 mmol/L of Fe(II) (Fig. S3 in Supporting information). Neither PDA nor Fe(II) showed degradation or adsorption capacity for NB. After adding nCP, NB removal efficiency increased up to 62.4% due to the radical produced from the Fenton reaction (Fig. 1a). The pH of the solution dramatically increased to 9, which hindered further NB degradation [16]. In comparison, almost full degradation of NB (up to 96.8%) was achieved in the Fe(II)/PDA@nCP system. To investigate the enhanced degradation performance of Fe(II)/PDA@nCP Fenton-like system, the H_2O_2 release kinetics and the key reactive radicals are studied in the following work.

Previous studies indicate that suitable coating layers decrease the surface active sites of nCP, facilitating controlled H_2O_2 release and pH stability, thus improving H_2O_2 utilization efficiency [17–19]. Here we evaluated the H_2O_2 release capacity of PDA@nCP, and compared with bare nCP, the generation of H_2O_2 was dramatically improved after PDA coating. The PDA@nCP, containing 40% PDA is most efficient for H_2O_2 production compared with 20%-PDA@nCP and 60%-PDA@nCP after 60 min (Fig. 1b). Addition of PDA extended the release lifetime of H_2O_2, while PDA shell effectively moderated sharp pH increased (Fig. 1c). Notably, 60%-PDA@nCP released less H_2O_2 than 20%-PDA@nCP and 40%-PDA@nCP. Despite this, the 60%-PDA@nCP system achieved 78.4% NB degradation during the experiment (Fig. 1a). This is attributed to the phenomenon of the PDA shell. The controlled release of H_2O_2

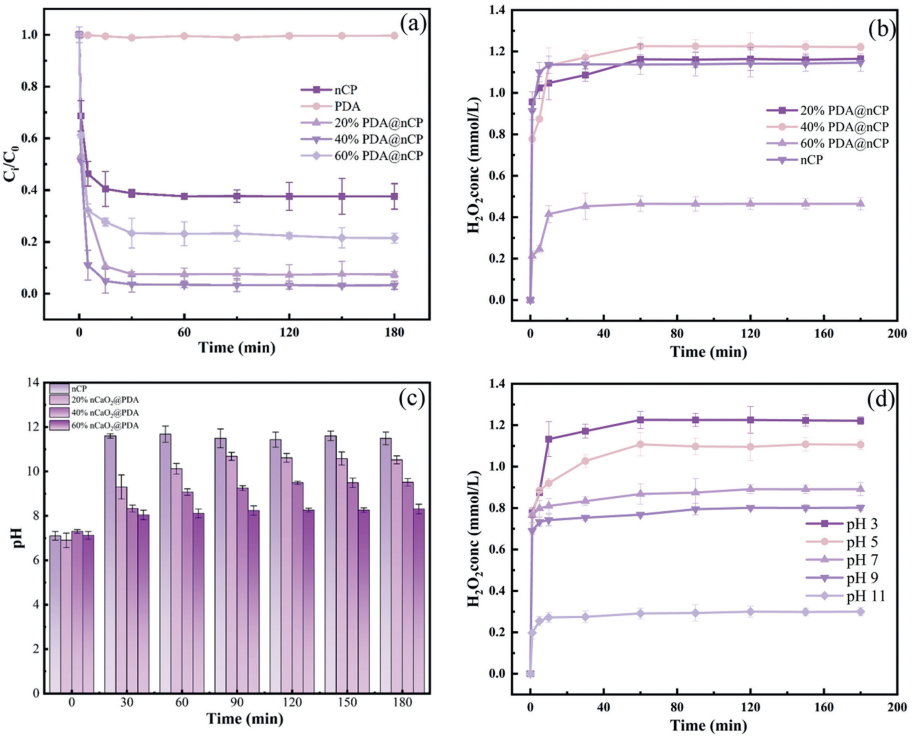

Fig. 1. (a) Degradation rate of NB by different systems. (b) H_2O_2 release from PDA@nCP with different PDA additions. (c) pH change for 20%, 40% and 60% PDA@nCP. (d) H_2O_2 release in solution under different initial pH. Except for the studied parameters, the remaining parameters were fixed at Fe(II) = 0.65 mmol/L, PDA@nCP = 0.1 g/L and NB = 10 mg/L.

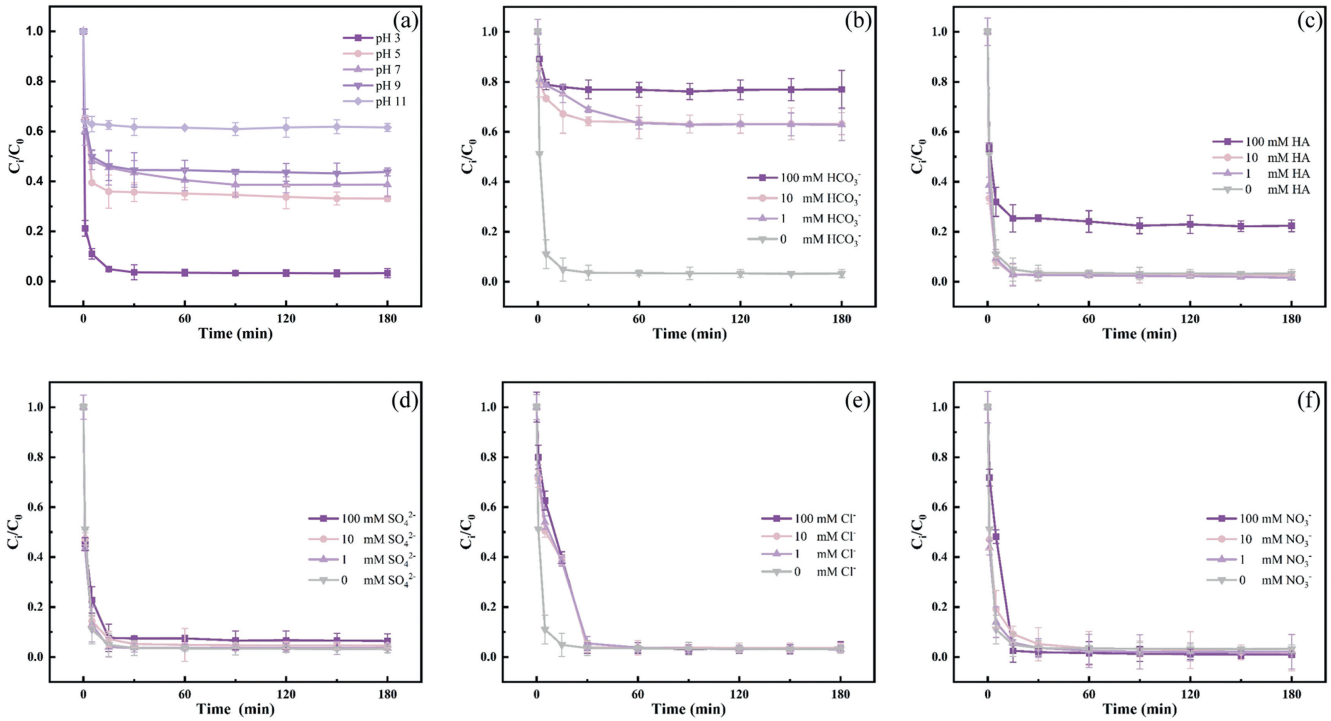

Fig. 2. (a) NB degradation with 40% PDA@nCP under different initial pH. The effect of different concentrations of HCO_3^- (b), HA (c), SO_4^{2-} (d), Cl^- (e) and NO_3^- (f) on NB degradation. Except for the studied parameters, the remaining parameters were fixed at pH 3, NB = 10 mg/L, Fe(II) = 0.65 mmol/L, PDA@nCP = 0.1 g/L and NB = 10 mg/L. mM: mmol/L.

from 40%-PDA@nCP under different initial pH conditions (Fig. 1d). When the initial pH was acidic (pH 3), the H_2O_2 release from PDA@nCP amounted to 1.22 mmol/L. As the initial pH increased, the H_2O_2 release gradually decreased. Previous research indicates that introducing nCP into the system caused a sharp pH increase, which restricted H_2O_2 release [20]. Nevertheless, H_2O_2 released from PDA@nCP was detected even in alkaline conditions. The presence of a PDA shell substantially decreased the surface active sites of nCP, hence controlling the reaction rate and stabilizing the pH of the system. The PDA shell effectively controlled the sharp pH raised in the PDA@nCP system, thereby enhancing its efficiency in H_2O_2 release compared to the nCP system. Moreover, this characteristic can enhance Fenton-like systems by generating reactive species and facilitating H_2O_2 release. Thus, the PDA shell may not only enhance NB degradation *via* controlled H_2O_2 release in the Fe(II)/PDA@nCP system but also influence the catalyst conversion process.

Fig. 2a shows the effects of different initial pH levels on NB degradation by the Fe(II)/PDA@nCP Fenton-like system. As the initial pH of the system increased, the rate of NB degradation rate decreased correspondingly. The high concentration of H^+ in the system at pH 3 promoted the generation of $HO^•$ (Eq. 4), and the subsequent NB degradation. Under alkaline conditions, OH^- accelerated the conversion of Fe(II) to Fe(III), leading to catalyst passivation, which hindered the Fenton-like process. The presence of OH^- lowered the generation of reactive species, and Fe(II) activity, resulting in decreased NB degradation [21]. Meanwhile, it has been demonstrated that the release of H_2O_2 from nCP was significantly hindered in alkaline conditions [22]. However, a small amount of NB was still degraded in an alkaline solution in our study (Fig. S4 in Supporting information), which attributed to the PDA shell on PDA@nCP modulating the pH increase, enhancing H_2O_2 released in an alkaline solution, and then subsequently the surface catechol groups of the PDA shell potentially decreased Fe(II) passivation. In conclusion, the degradation of NB in the system was highly dependent on Fe(II) activity and H_2O_2 release in the Fe(II)/PDA@nCP Fenton-like system.

Four typical common groundwater anions (HCO_3^-, SO_4^{2-}, Cl^- and NO_3^-) and humic acid (HA) were selected to evaluate the effectiveness of the Fe(II)/PDA@nCP Fenton-like system and NB degradation in contaminated water. As shown in Fig. 2b, the degradation rate of NB reached 36.9% with the addition of 1 mmol/L and 10 mmol/L HCO_3^-. When the addition of HCO_3^- was increased to 100 mmol/L, the NB degradation rate dropped to 23.9%. It was speculated that HCO_3^- decreased the NB degradation rate through the following pathways: 1) Excess HCO_3^- addition caused a sharp pH increase, hindering Fe(II) activity and H_2O_2 released from PDA@nCP. Primarily, catalyst passivation and insufficient H_2O_2 released to limit the Fenton-like process, resulting in weakened NB degradation [23]. 2) HCO_3^- has a scavenging effect on $HO^•$, thus excess HCO_3^- and $HO^•$ initiate side reactions, producing less oxidation $HCO_3^•$ and $CO_3^{•-}$ (Eqs. 5 and 6) [24]. Additionally, HCO_3^- competes with NB for $HO^•$, diminishing the degradation efficacy of $HO^•$ on NB [25]. The cumulative effects of these pathways resulted in enhanced inhibition of NB degradation by HCO_3^-. Humic acids are organic compounds containing aryl and alicyclic rings along with diverse functional groups, which are ubiquitous in groundwater [26]. At a 100 mmol/L HA concentration, the degradation of NB by Fe(II)/PDA@nCP Fenton-like system was only 77.8% (Fig. 2c). HA competes with NB for $HO^•$, resulting in diminished NB degradation within the Fe(II)/PDA@nCP Fenton-like system [27]. In comparison to other anions, adding 100 mmol/L SO_4^{2-} resulted in 93.5% NB degradation (Fig. 2d). This could be attributed to the formation of $CaSO_4$ precipitates due to the dissociation of Ca^{2+} and SO_4^{2-} in the system (Eq. 7). The $CaSO_4$ precipitates adhered to the PDA@nCP surface, decreasing the reactive sites and influencing the NB degradation [9].

$$H^+ + H_2O_2 + Fe(II) \rightarrow HO^• + Fe(III) + H_2O \quad (4)$$

$$HCO_3^- + HO^• \rightarrow CO_3^{•-} + H_2O \quad (5)$$

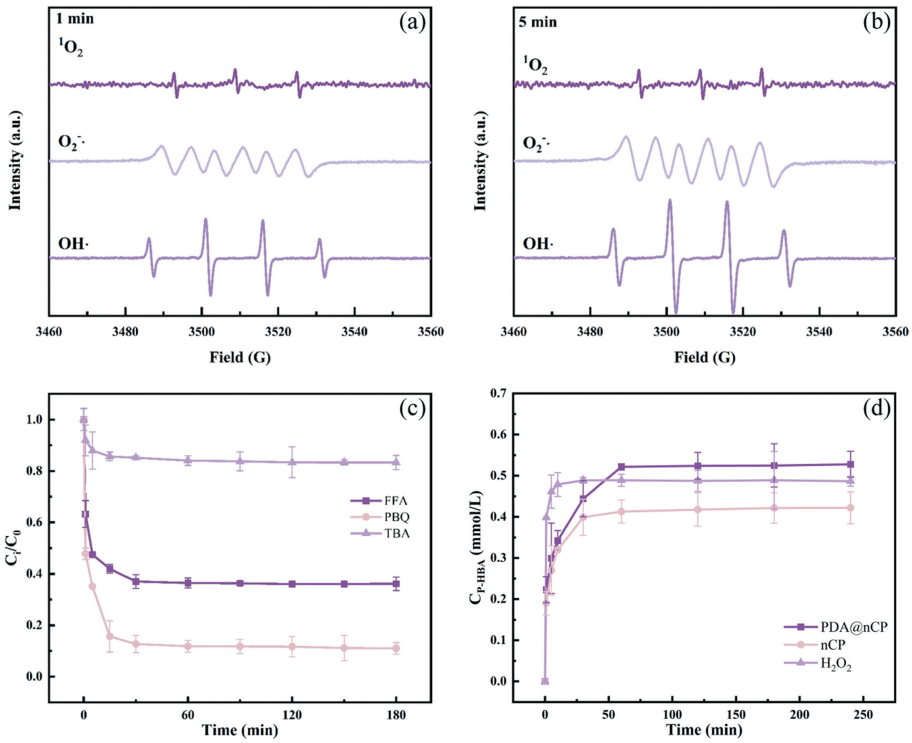

Fig. 3. EPR characterization of PDA@nCP Fenton-like system: (a) 1 min, (b) 5 min, (c) radical scavenging experiment, (d) capture experiment of HO•. Except for the studied parameters, the remaining parameters were fixed at pH 3, Fe(II) = 0.65 mmol/L, PDA@nCP = 0.1 g/L and NB = 10 mg/L.

$$HCO_3^- + HO^\bullet \rightarrow HCO_3^\bullet + OH^- \quad (6)$$

$$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4 \downarrow \quad (7)$$

Based on the discussion that followed the effects of Cl^- and NO_3^- additions on NB degradation were determined to be comparable to the degradation rate observed with optimum additions (Figs. 2e and f). The Fe(II)/PDA@nCP Fenton-like system exhibits strong tolerance to common groundwater ions, particularly Cl^- and NO_3^-. These findings offer theoretical support for constructing Fe(II)/PDA@nCP Fenton-like systems in remediating NB-contaminated groundwater. However, the mechanism by which the PDA shell enhances the Fe(II)/PDA@nCP Fenton-like system remains unclear. Therefore, the mechanism behind the generation of reactive species in the Fe(II)/PDA@nCP Fenton-like system was explored.

Previous studies have identified HO•, $O_2^{\bullet-}$ and $^1O_2$ as the primary reactive species in Fe(II)/nCP Fenton-like reactions [28,29]. Therefore, electron paramagnetic resonance (EPR) was used to characterize the reactive species in the Fe(II)/PDA@nCP Fenton-like system. Figs. 3a and b showed the characteristic 1:2:2:1 DMPO-HO• peak captured by DMPO at 1 min and 5 min [30]. With the progression of the Fe(II)/PDA@nCP Fenton-like reaction, the intensity of the DMPO-HO• peak increases after 5 min, indicating HO• stabilization in the system. Additionally, DMPO and TEMP were used to capture $O_2^{\bullet-}$ and $^1O_2$ [31,32]. The results confirmed the presence of $O_2^{\bullet-}$ and $^1O_2$, as evidenced by six characteristic peaks for DMPO-$O_2^{\bullet-}$ and three for TEMP-$^1O_2$. However, the specific contributions of each reactive species to NB degradation within the system remain unclear.

To identify the primary reactive species responsible for NB degradation, their contribution was investigated through reactive species scavenging experiments. *tert*-Butanol (TBA), 1,4-*p*-benzoquinone (PBQ), and furfuryl alcohol (FFA) were selected to scavenge HO•, $O_2^{\bullet-}$ and $^1O_2$ [33,34]. The NB degradation rate was found to be 16.7% after TBA scavenged HO•, 89% after PBQ scavenged $O_2^{\bullet-}$ and 63.99% after FFA scavenged $^1O_2$ (Fig. 3c). These results indicate that all three reactive species contribute to NB degradation, but HO• plays the primary role in this Fenton-like system.

PDA shell enhanced the generation of reactive species in the Fe(II)/PDA@nCP Fenton-like system. Thus, further investigation of Fe(II)/PDA@nCP, Fe(II)/nCP and Fe(II)/H_2O_2 systems was conducted to find out the relationship between the PDA shell and the system's reactive species by determining HO•. H_2O_2 release from PDA@nCP was analyzed before the experiment to determine the H_2O_2 content needs to be added to the Fe(II)/H_2O_2 Fenton system. HO• production in the systems was quantified by sodium benzoate (Text S5 in Supporting information). It was found that the HO• production in the Fe(II)/nCP system significantly lowered than in the Fe(II)/H_2O_2 system (Fig. 3d). This may be primarily due to the nCP decomposition increasing the pH of the reaction solution. Previous studies have indicated that an excessively high pH is detrimental to HO• production [35]. Notably, 60 min after initiating the reaction, the Fe(II)/PDA@nCP system produced 0.041 mmol/L more HO• than the Fe(II)/H_2O_2 system. Additionally, the pH changes in both the Fe(II)/PDA@nCP system and the Fe(II)/H_2O_2 system were measured (Fig. S5 in Supporting information). The Fe(II)/PDA@nCP system exhibited a greater pH change upon H_2O_2 release compared to the Fe(II)/H_2O_2 system. This suggests that the generation of HO• in the Fe(II)/PDA@nCP system may be driven by the catalytic activity of Fe(II). In other words, the PDA shell structure may facilitate enhanced Fe(II)/Fe(III) cycling. In light of this, more research on HO• generation in the Fe(II)/PDA@nCP system with an emphasis on the PDA shell's surface functional groups was conducted.

XPS was used to characterize changes in surface functional groups and chemical composition on the PDA@nCP surface before and after the reaction. The O 1s peaks before and after the reaction in the Fe(II)/PDA@nCP system are shown in Fig. 4a. Two characteristic peaks were observed: quinone (C=O, 533.08 eV) and phenol (C-OH, 531.56 eV and 532.51 eV) are found in PDA@nCP

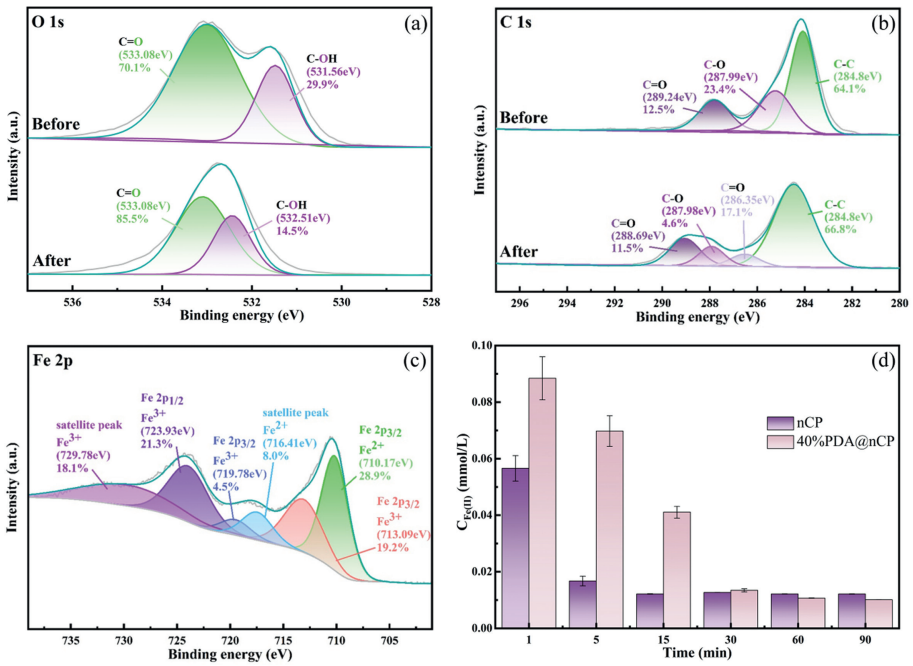

Fig. 4. XPS spectra of (a) O 1s orbitals before and after the reaction, (b) C 1s orbitals before and after the reaction, (c) Fe 2p orbitals after the reaction. (d) Fe(II) concentration in different systems. Except for the studied parameters, the remaining parameters were fixed at pH 3, Fe(II) = 0.65 mmol/L and PDA@nCP = 0.1 g/L.

before and after the reaction [36,37]. The relative abundance of C-OH decreased from 29.9% (531.56 eV) to 14.5% (532.51 eV) after 4 h of reaction, while C=O relative abundance increased by 15.5%. This indicated phenol-quinone transformations on the PDA@nCP surface. The XPS spectra of C 1s orbitals before and after the Fe(II)/PDA@nCP reaction are presented in Fig. 4b. Before the reaction, the C-O peak at 287.99 eV indicated C-O presence, while after the reaction, a new C=O peak at 286.35 eV emerged, and the relative abundance of C-C at 284.8 eV increased. The C 1s XPS spectra reveal an increase in quinone content on the PDA@nCP surface and a continuous disruption of the PDA shell, leading to more exposed C-C bonds. Fig. 4c shows the XPS spectra of the Fe 2p orbital after the reaction. The Fe 2p spectra confirm the presence of Fe(II) on the reacted PDA@nCP surface[38]. Notably, the phenol-quinone transformations in both the C 1s and O 1s orbitals on the PDA@nCP surface were observed. Previous reports suggest that phenol-quinone transformations trigger the conversion transformation of Fe(III) to Fe(II) in the system, thereby facilitating the Fe(II)/Fe(III) cycle[15,39]. The phenol-quinone transformations in the abundant catechol groups on the PDA shell surface aid in Fe(II) regeneration and enhance the Fe(II)/Fe(III) cycle. Thus, this confirmed our earlier hypothesis about the enhancing effect of the PDA shell in the Fe(II)/PDA@nCP Fenton-like system.

Dissolved Fe(II) concentrations in nCP and PDA@nCP Fenton-like systems were compared to evaluate the effects of the PDA shell on Fe(III) transformation during degradation of NB (Fig. 4d). The concentration of Fe(II) in Fe(II)/nCP system dropped dramatically after 5 min and then remain at a stable level of 0.017 mmol/L. This is possible because the fast nCP decomposition is accompanied by a sharp pH increase leading to the precipitation of dissolved iron ions. In comparison, the Fe(II) content in the Fe(II)/PDA@nCP system is generally higher than in Fe(II)/nCP system, and the Fe(II) decreasing period is prolonged over 5 times. This may be attributed to the catechol groups in the PDA coating, which provide a pathway for the transformation of Fe(III) to Fe(II), facilitating the Fe(II)/Fe(III) cycle. On other hand, we compared the ratios of Fe(II) to Fe(III) for the two systems (Fig. S6 in Supporting information) to demonstrate more visually the strengthening of Fe(II)/Fe(III) cycles by the PDA shell. Additionally, the PDA shell structure effectively moderated the sharp pH increase in the solution and maintained Fe(II) stability. XPS analyses suggest that the transformation from Fe(III) to Fe(II) was directly associated with phenol-quinone transformations on the PDA surface.

In the Fe(II)/PDA@nCP Fenton-like system, the PDA shell is coated on the nCP surface, hence preserving Fe(II) activity preventing abrupt pH rises, and promoting NB degradation. PDA@nCP allows the controlled release of H_2O_2 (Fig. 5a). Compared to nCP, PDA@nCP exhibited a longer controlled release lifetime for H_2O_2. Additionally, the PDA shell inhibited sharp pH increase in the solution and facilitated H_2O_2 release, which is favorable for a Fenton-like reaction [17]. Reactive species such as $HO^{\bullet}$, $O_2^{\bullet-}$ and $^1O_2$ are produced by H_2O_2 catalyzed by Fe(II) for degrading NB in solution and converting Fe(II) to Fe(III). Simultaneously, the catechol groups in the PDA shell undergo phenol-quinone transformations, induced by Fe(III), converting Fe(III) back to Fe(II). This transformation facilitated the Fe(II)/Fe(III) cycle. The Fe(II)/PDA@nCP system continuously produced reactive species with Fe(II) regeneration, ultimately achieving the remediation and degradation of NB through the diffusion of these species.

LC-MS was used to analyze the intermediates produced by NB degradation (Table S1 in Supporting information). The NB was detected before the reaction (retention time: 9.97 min, $m/z = 124.6$), as shown in Fig. S7a (Supporting information). The peaks of nitrophenol appeared at $m/z = 140.3$ and 140.8 (retention time: 11.41 min) depicted in Fig. S7b (Supporting information) [40]. At a retention time of 11.49 min, the mass spectrogram showed three diphenol isomers along with traces of NB ($m/z = 111.2$ and 124.6, Fig. S7c in Supporting information) [41]. Two isomers of dibenzoquinone were found at $m/z = 109.1$ and 109.6 (retention time: 7.45 min, Fig. S7d in Supporting information). Meanwhile, the various dicarboxylic acids formed after NB underwent ring-opening during the reaction (Figs. S7e and f in Supporting information) [42].

Fig. 5b shows the two pathways for NB degradation in the Fe(II)/PDA@nCP Fenton-like system. In the first pathway, $HO^{\bullet}$ attacked NB, completing the denitrification reaction to form phenol. Subsequently, under the continuous action of $HO^{\bullet}$, phenol trans-

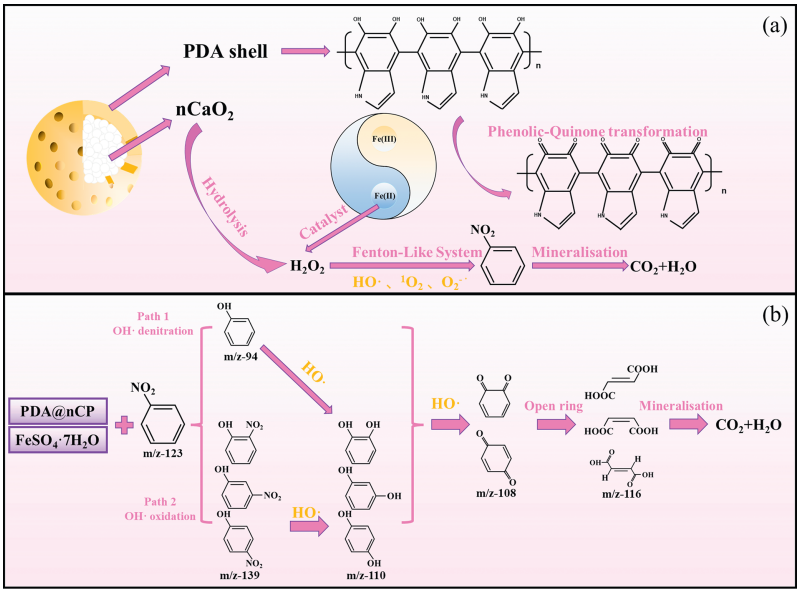

Fig. 5. (a) Mechanism of NB degradation by the Fe(II)/PDA@nCP Fenton-like system. (b) NB degradation pathway.

formed into three isomers including catechol, resorcinol, and hydroquinone. Simultaneously, phenolic intermediates undergo dehydrogenation to form 4-benzoquinone and 2-benzoquinone. In subsequent steps, quinones undergo ring-opening and ring-cleavaged to form three dicarboxylic acids: maleic acid, fumaric acid, and oxalic acid. Eventually, these three dicarboxylic acids are mineralized to CO_2 and H_2O [23]. During the second pathway, NB was directly oxidized by HO• to form three isomers including 2-nitrophenol, 3-nitrophenol, and 4-nitrophenol. In the presence of HO•, the three nitrophenol isomers transformed into the same diphenols as in pathway 1. The subsequent quinone formation and ring-opening processes were identical to pathway 1, ultimately mineralizing NB to CO_2 and H_2O [6]. At the same time, we analyzed the toxicity of the individual intermediates (Fig. S8 in Supporting information).

In conclusion, we synthesized a PDA@nCP as controlled released H_2O_2 by coating nCP with a PDA shell. These findings demonstrated that the PDA shell structure effectively prevented the pH increase in the Fe(II)/PDA@nCP Fenton-like system, thereby favoring the controlled release of H_2O_2. The Fe(II)/PDA@nCP Fenton-like system was able to degrade 96.8% of NB by extending the controlled released lifetime of H_2O_2 for 60 min compared to the bare nCP and allowing for a maximum release level of approximately 1.22 mmol/L. The HO• productions of Fe(II)/PDA@nCP were higher than that of Fe(II)/nCP system by 0.108 mmol/L, and the presence time and concentration of Fe(II) in Fe(II)/PDA@nCP system were also higher than that of Fe(II)/nCP system. From this, the catechol groups of the PDA shell boosted Fe(II)/Fe(III) cycling, accelerated the transformation of Fe(III) to Fe(II), and enhanced NB degradation in the Fe(II)/PDA@nCP Fenton-like system. The biological toxicity assessment demonstrated that the by-products of NB degradation by Fe(II)/PDA@nCP Fenton-like system were safe and clean, suggesting the great potential for using PDA@nCP in the remediation of NB-contaminated groundwater. Except for HCO_3^- and high concentration of HA, Fe(II)/PDA@nCP Fenton-like system has good tolerance properties to naturally occurring anions in groundwater.

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.

CRediT authorship contribution statement

Haoyu Luo: Writing – original draft, Visualization, Validation, Software, Methodology, Data curation. **Jinsong Chen:** Writing – original draft, Visualization, Validation, Software, Methodology, Data curation. **Mengfei Luo:** Visualization, Validation, Data curation. **Hui Ma:** Validation, Software, Methodology, Conceptualization. **Shengyan Pu:** Writing – review & editing, Supervision, Project administration, Conceptualization.

Acknowledgments

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2024.110367.

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