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REVIEW ARTICLE

Dual-reaction-center catalytic process continues Fenton's story

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HIGHLIGHTS

- Dual-reaction-center (DRC) system breaks through bottleneck of Fenton reaction.
- Utilization of intrinsic electrons of pollutants is realized in DRC system.
- DRC catalytic process well continues Fenton's story.

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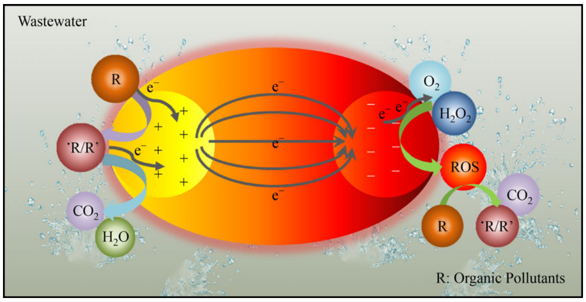
GRAPHIC ABSTRACT



ABSTRACT

Triggered by global water quality safety issues, the research on wastewater treatment and water purification technology has been greatly developed in recent years. The Fenton technology is particularly powerful due to the rapid attack on pollutants by the generated hydroxyl radicals (•OH). However, both heterogeneous and homogeneous Fenton/Fenton-like technologies follow the classical reaction mechanism, which depends on the oxidation and reduction of the transition metal ions at single sites. So even after a century of development, this reaction still suffers from its inherent bottlenecks in practical application. In recent years, our group has been focusing on studying a novel heterogeneous Fenton catalytic process, and we developed the dual-reaction-center (DRC) system for the first time. In the DRC system, H_2O_2 and O_2 can be efficiently reduced to reactive oxygen species (ROS) in electron-rich centers, while pollutants are captured and oxidized by the electron-deficient centers. The obtained electrons from pollutants are diverted to the electron-rich centers through bonding bridges. This process breaks through the classic Fenton mechanism, and improves the performance and efficiency of pollutant removal in a wide pH range. Here, we provide a brief overview of Fenton's story and focus on combing the discovery and development of the DRC technology and mechanism in recent years. The construction of the DRC and its performance in the pollutant degradation and interfacial reaction process are described in detail. We look forward to bringing a new perspective to continue Fenton's story through research and development of DRC technology.

1 Fenton's story and Fenton reaction

The story began in 1876 (Fenton, 1876), approximately 140 years ago. An interesting phenomenon was first reported by an undergraduate student named Henry J. Horstman Fenton: tartaric acid could be oxidized in the presence of ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2) or hypochlorous acid. Approximately 20 years later, while working at Cambridge University, Fenton reported the reaction again and claimed that the oxidation of tartaric acid was strongly promoted by ferrous ions with H_2O_2 (Fenton, 1894,1896; Fenton and Jones, 1900). However, perhaps because his research interests shifted, the story about this reaction did not continue in his later years. More unfortunately, this reaction was considered negative in the era of organic synthesis due to its inevitable

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destruction of the original substance structures. Therefore, this reaction lay dormant for more than half a century until it was rediscovered.

In 1932, the reduction of H_2O_2 by Fe^{2+} to produce hydroxyl radicals (•OH) was put forward by Haber and Weiss (Haber and Weiss, 1932). Another 30 years later, the reaction, already known as the "Fenton reaction", was used for organic pollutant degradation (Eisenhauer, 1964) in an era when public environmental awareness began to be awaken. It is now generally accepted that free radicals (•OH and superoxide radicals HO_2•/O_2•$^-$), especially •OH, which are produced through the process in Fig. 1, are the main active species to attack pollutants in the Fenton reaction.

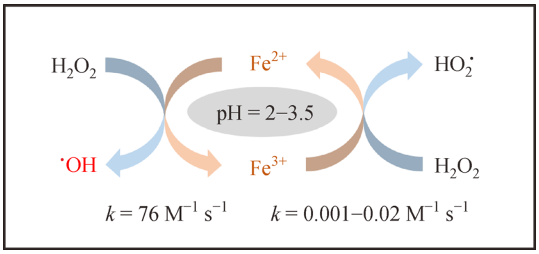


Fig. 1 Reaction mechanism of the classical homogeneous Fenton process.

Although the Fenton reaction has been redeveloped for decades, the classical Fenton process suffers from inherent intractable bottlenecks in the practical application of water treatment. First, the reaction must be performed in an acidic condition with a very narrow pH range (pH 2–3.5) (Tušar et al., 2012). As a result, in the actual wastewater treatment, a large amount of acid must be consumed to adjust the pH of the influent to ~3. After pollutant removal, it is necessary to readjust the treated water to neutral before discharge, which greatly increases the difficulty of the water treatment and operation cost. Second, a large amount of iron-sludge is produced and accumulated in the reaction (Yoo et al., 2017), which requires an additional treatment process in the practical water treatment procedure. The developed heterogeneous Fenton catalyst overcomes the problem of iron sludge and widens the pH response range of the reaction (Shi et al., 2014; Ou et al., 2018). However, their activities for contaminant degradation under neutral and mild conditions remain much unsatisfactory because of the inevitable rate limiting step (reduction of $M^{(n+m)+}$ to M^{n+} by H_2O_2) based on the classical Fenton reaction principle (Lyu et al., 2015b). Furthermore, excessive H_2O_2 consumption (above the stoichiometric amount by 100-fold) is required to maintain the whole redox process (Navalon et al., 2011). The assistance of external energies such as electricity, light irradiation, impulse and ultrasound (Lu et al., 2018; Bui et al., 2019; Huang et al., 2019; Saleh and Taufik, 2019) is often required to accelerate the electron cycles. It is extremely urgent to break through the classic Fenton reaction principle and solve the application bottleneck problem caused by the intrinsic mechanism.

2 Pollutant-associated promotion process of Fenton-like reactions

Since 2012, our group has been working on the development of heterogeneous Cu-based Fenton-like systems with no additional assistance (Zhang et al., 2012; Zhang et al., 2016; Zhang et al., 2017). It was found that Cu-based catalysts had more advantages than Fe-based catalysts in eliminating organic pollutants, such as a larger pH response range and a better catalytic activity under identical conditions. In 2015, we developed two kinds of copper-containing Fenton-like catalysts based on porous alumina (γ-Cu-Al_2O_3) (Lyu et al., 2015b) and porous silica (copper-doped mesoporous silica microspheres, Cu-MSMs (Lyu et al., 2015a), and dandelion-like copper–aluminum–silica nanospheres, DCAS Ns (Lyu et al., 2016b), respectively. According to the structural characterization analysis, both Cu^{2+} and Cu^+ were formed on the surface of the synthesized catalyst and chemically bonded to the catalyst support through Cu-O-Al or Cu-O-Si, which provided bridges to rapidly transfer electrons in the subsequent Fenton-like reaction. During the removal of aromatic/phenolic pollutants by the two Fenton-like systems, a surface σ-Cu^{2+}-ligand (pollutants)-associated promotion process of the heterogeneous Fenton-like reaction was found. As shown in Fig. 2, at the beginning of the reaction, phenolic pollutants and hydroxylation products (generated by the •OH attack) quickly complexed with the Cu^{2+} sites on the catalyst surface to form σ-Cu^{2+}-ligand complexes, which were reactive intermediates. In the Fenton-like reaction process, H_2O_2 could directly react with the activated σ-Cu^{2+}-complexes by attacking the aromatic ring with the phenolic OH group, which generated •OH and HO-adduct radicals that were oxidized to hydroxylation products by reducing Cu^{2+} in the σ-Cu^{2+}-complexes to Cu^+.

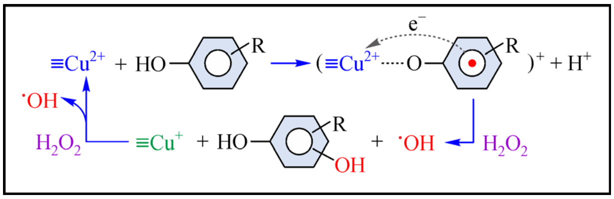


Fig. 2 σ-Cu^{2+}-ligand (pollutants)-associated promotion mechanism of heterogeneous Fenton-like reaction.

In addition to the weak oxidation of H_2O_2, this process made great use of pollutants as electron donors to reduce metal species. The rate-limiting step has been greatly surpassed, which was also clearly demonstrated by several technologies such as the electron paramagnetic resonance

(EPR) analysis, attenuated total reflection Flourier transformed infrared spectroscopy (ATR-FTIR) analysis and in situ Raman detection. Therefore, the catalysts is highly efficient in removing various kinds of aromatic/phenolic contaminants such as pesticide 2,4-dichlorophenoxyacetic acid, pharmaceuticals phenytoin, ibuprofen and diphenhydramine, and endocrine disruptor bisphenol A (BPA). The H_2O_2 utilization efficiency of the Fenton-like system remained at ~90% before the parenting compound completely disappeared. Afterward, the H_2O_2 utilization efficiency sharply dropped, and even returned to the value of the classical Fenton reaction. One implication of this work is that the stubborn rate-limiting step can be broken through by donating electrons through other species, such as electron-rich pollutants. However, the redox at a single reaction site limits the catalytic process, especially after the disappearance of aromatic pollutants. In addition, the reaction still relies on the redox of Cu^{2+}/Cu^{+}, leading to the release of Cu ions into the solution. Although the amount is small in this system, there is a risk of biotoxicity if they accumulate into the organism.

3 Early configuration of dual reaction center through lattice substitution

In 2016, we proposed an early configuration of the dual-reaction-center (DRC) Fenton-like catalyst. In the case of three different metals (Cu, Ti and Al) co-doped SiO_2 nanospheres (*d*-TiCuAl-SiO_2 Ns)(Lyu et al., 2016a), we found that not only Cu was successfully incorporated into the lattice of SiO_2 to form Si-O-Cu bonds, but also Ti and Al replaced the position of Si and entered into the catalyst lattice according to the extended X-ray absorption fine structure (EXAFS) analysis. As a result, different electronegativities of the lattice-doped metal species induced the uneven distribution of electrons on the catalyst surface. Through the connected lattice O^{2-}, a higher electron density was obtained near Cu to generate an electron-rich Cu center, and a lower electron density was found around the Ti/Al species to produce electron-deficient centers. As shown in Fig. 3, during the degradation of pollutants by the Fenton-like process, H_2O_2 was predominantly resolved to •OH in the electron-rich Cu centers, while the generated organic radical intermediates (˙R) were adsorbed and oxidized in the electron-deficient Ti/Al centers. The separation of oxidation and reduction reaction centers greatly increased the catalyst activity and H_2O_2 utilization efficiency, which was as high as 60%–90% in the whole reaction process.

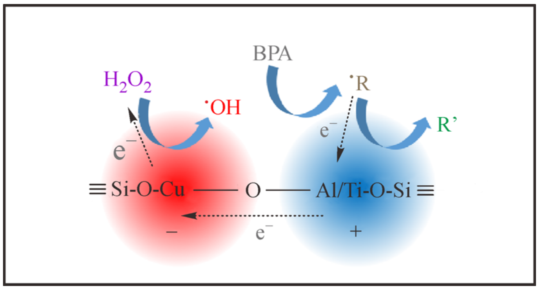


Fig. 3 The Fenton-like reaction mechanism on the surface galvanic-like cells of *d*-TiCuAl-SiO_2 Ns.

This work inspired us that it is possible to avoid the inefficient decomposition of H_2O_2 and greatly enhance the Fenton-like catalytic activity by constructing electron-rich/deficient micro-areas on the catalyst surface to generate DRC with a polarization distribution of electrons. However, how to achieve more efficient DRCs on catalyst surface became a difficult problem. It has been reported that the cation-π (M^+-π) interaction is one of the most significant intermolecular binding forces associated with aromatic recognition in chemical/biological processes (Lagutschenkov et al., 2010). The orbital interactions with the electron transfer of $\pi \rightarrow M^+$ (σ donation) and $M^+ \rightarrow \pi^*$ (π back-donation) can greatly affect the structural and energetic parameters of the cation-π configuration. The electron density of the aromatic ring can be changed by replacing functional groups, which results in an asymmetric potential of π binding to the ring and alters the bond strength of the cation-π interactions (Lagutschenkov et al., 2010).

4 Dual reaction center construction by metal-organic surface complexation

Inspired by the electron density modulation by replacing the functional groups and cation-π interaction, in 2017, we developed a kind of polar-enhanced DRC Fenton-like catalyst in the form of surface complexation for the first time (Lyu et al., 2017). In the work, hydroxyl-substituted carbon-doped g-C_3N_4 was combined with Cu and Co co-substituted γ-Al_2O_3 (OH-CCN/CuCo-Al_2O_3) through Cu-O-C bonding bridges (cation-π), which was confirmed by the appearance of a Cu–C coordination shell (coordination number 0.8 and bond distance 2.58 Å) with the in situ growth of g-C_3N_4 on the CuCo-Al_2O_3 surface according to the EXAFS analysis. This special structure induced the generation of clouds of electrons around the Cu species due to the π back-donation and formation of electron-rich Cu centers on the catalyst surface according to the EPR spectra analysis and density functional theory (DFT) computation (Fig. 4). An interesting phenomenon was first discovered in the OH-CCN/CuCo-Al_2O_3 aqueous system. After the catalyst was added to pure water, the dissolved oxygen in the water was adsorbed to the electron-rich Cu centers and quickly reduced to superoxide radicals (HO_2•/O_2•⁻) with no additional assistance (Fig. 5). Simultaneously, water was oxidized to •OH in the electron-deficient centers on the catalyst surface. This process did not involve any other substances, including H_2O_2 and

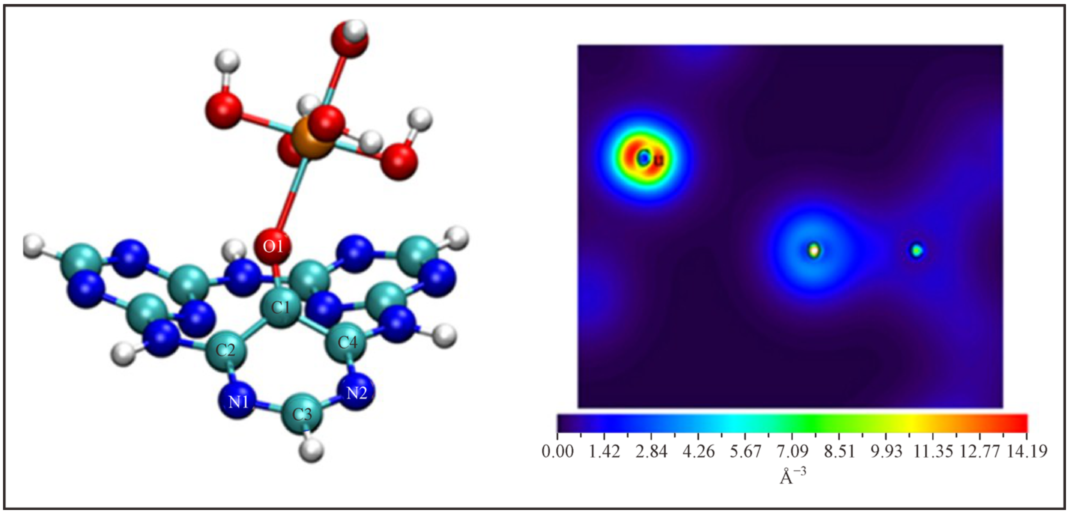
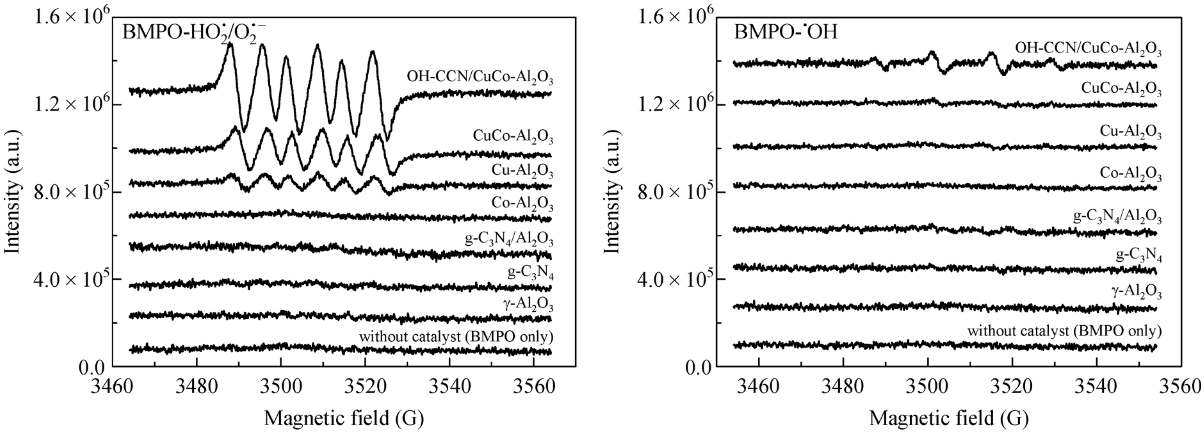


Fig. 4 Structure of OH-CCN/CuCo-Al_2O_3 and two-dimensional valence-electron density color-filled maps of Cu-O-C on OH-CCN/CuCo-Al_2O_3 (Lyu et al. (2017), with permission of Royal Society of Chemistry).



(a) (b)

Fig. 5 BMPO spin-trapping EPR spectra for (a) HO_2•/O_2•$^-$ and (b) •OH in various methanol dispersions without H_2O_2 (Lyu et al. (2017), with permission of Royal Society of Chemistry).

pollutants, which was equivalent to water acting as the electron donors for the whole system. After adding H_2O_2 into the system, instead of O_2, H_2O_2 was adsorbed to the electron-rich centers and rapidly reduced to •OH (Fig. 6). Meanwhile, water was still oxidized by providing electrons to the electron-deficient centers to generate additional •OH. Therefore, twice as much •OH was generated in the catalyst suspension as the reaction amount of H_2O_2, which results in a high H_2O_2 utilization efficiency rate (~90%) and a high turnover frequency (TOF) of the •OH yield (1.30 s^{-1}), which was more than 85 times of the traditional homogeneous Fenton reaction. This DRC system shows excellent performance in eliminating and mineralizing various organic contaminants under natural conditions.

Based on this discovery, we developed a more efficient DRC catalyst CN-Cu(II)-$CuAlO_2$ through a surface growth of carbon nitride (CN) compounds on the $CuAlO_2$ support (Lyu et al., 2018a). The Fenton-like activity and efficiency of the new DRC catalyst showed great improvement in a broad pH range. The structure characterization suggested that the surface growth of CN compounds greatly increased the proportion of Cu(II) on the surface of CN-Cu(II)-$CuAlO_2$, which contributed to a strong connection between CN and surface Cu species via the C-O-Cu bridges to induce the cation–π interactions in the synthesis process. Both experimental results and theoretical calculations demonstrated that many DRCs were produced on the catalyst surface because of the cation–π interactions. A

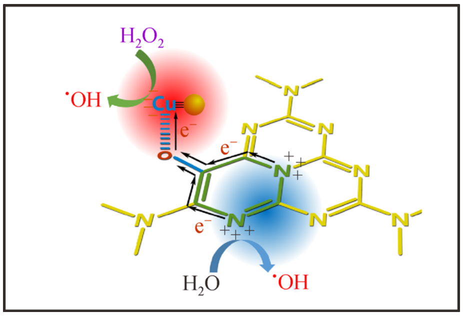


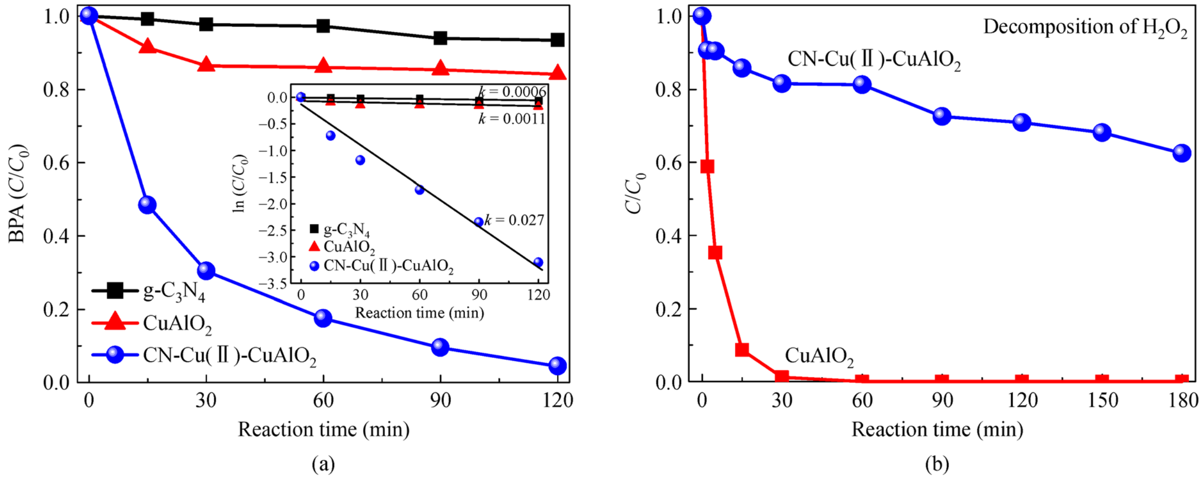
Fig. 6 DRC mechanism in the OH-CCN/CuCo-Al_2O_3 Fenton-like system.

very obvious phenomenon was observed: the degradation activity for organic pollutants in the DRC-rich Cu(II)-$CuAlO_2$/H_2O_2 system was greatly improved (Fig. 7(a)), while the consumption of H_2O_2 was much less than that of non-DRC systems (Fig. 7(b)). In the reaction involving H_2O_2, H_2O_2 was effectively reduced to •OH in the electron-rich Cu center, while the electron donors such as H_2O_2 and pollutants were captured by the electron-deficient center on the CN rings; then, the obtained electrons were diverted to the electron-rich center through C-O-Cu bonding bridges (Fig. 8).

Similarly, the C-O-Cu bonding bridges were also successfully constructed on the Cu-doped mesoporous polyimide nanocomposites (Cu-MP NCs) (Lyu et al., 2019), which was confirmed by the appearance of the Cu–C coordination shell that backscattered from adjacent C atoms to the Cu species via the EXAFS analysis. The C-O-Cu bonding bridges further stimulated the cation-π interactions between metal ions and benzene-like rings, leading to the generation of electron-rich Cu centers and electron-deficient C centers at the benzene-like rings. The new breakthrough is that the form of electron-donating effect of the pollutants was clarified. The strong π-π stacking between the aromatic rings of the pollutants and the benzene-like rings of Cu-MP NCs led to the mutual dispersion and diffusion of their electrons. Once the electrons in the electron-rich Cu centers were deprived by H_2O_2 or O_2, the electron diffusion equilibrium in the electron-deficient centers was broken, so the pollutants began to provide electrons for the system through the π-π interaction and π → cation interaction. This process greatly inhibited the H_2O_2 overoxidation by using the pollutants as electron donors.

To further enhance the polarity of the surface DRCs of Cu-MP NCs, we reductively modified the surface to form a new catalyst RSC-CNOP (Cao et al., 2019), resulting in the generation of a large amount of reduction state Cu species (RSC, including zero-valent copper and cuprous copper) on the catalyst surface. The XPS spectrum revealed that the atomic ratio of Cu(0) and Cu(I) on RSC-CNOP was ~1.1:1. The produced $Cu_{(RSC)}$-O-$C_{(p)}$ bonding bridges in RSC-CNOP triggered the anomalous bidirectional electron transfers from $C_{(p)}$ to the O center and from $Cu_{(RSC)}$ to the O center (RSC → O←π). The amount of free electrons in the formed electron-rich O centers of the new DRC catalyst was 8 times as that of the non-DRC sample.

After recognizing the importance of reducing metal species to enhance the polarity of the surface DRCs, we developed a novel nanoscale zero-valent Cu (nZVCu)-containing rGO hybrid (nZVCu-Cu(II)-rGO) based on a modified annealing reduction method (Lyu et al., 2020). The XPS analysis suggested that both Cu(0) and Cu(II) species were generated on the nZVC-Cu(II)-rGO surface



(a) (b)

Fig. 7 (a) BPA degradation curves in various suspensions with H_2O_2 (Insert shows the corresponding kinetic curves); (b) H_2O_2 decomposition curves during BPA degradation in $CuAlO_2$ and CN-Cu(II)-$CuAlO_2$ suspensions. Reaction conditions: Natural initial pH, pollutant 25 mg/L, catalyst 1.0 g/L, H_2O_2 0.01 mol/L (Reprinted with permission from Lyu et al. (2018a). Copyright 2018 American Chemical Society).

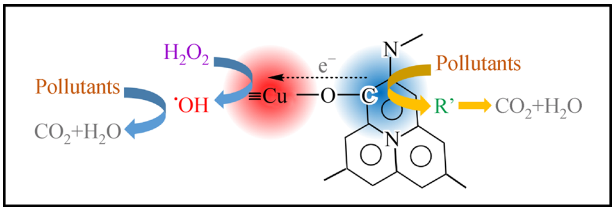


Fig. 8 DRC mechanism in the CN-Cu(II)-$CuAlO_2$ Fenton-like system.

with the atomic ratio of 1.2:1. The intensified electron-rich/deficient centers were produced on the catalyst surface around the nZVCu-enhanced Cu(II) and rGO-aromatic rings based on the EPR analysis and DFT calculations. The generated nZVCu consolidated the polarization of DRC and remarkably accelerated electron transfers of the solid-liquid interfaces. Therefore, in addition to the destruction by free radicals, the pollutants were effectively degraded at the electron-deficient sites through the electron-donation effect. In addition, the DRC systems did not depend on the redox of metal ions to activate H_2O_2. H_2O_2 did not directly contact and react with metal species during the DRC process. Therefore, the release of metal ions such as Cu ions was greatly inhibited.

5 Development of metal-free dual reaction center Fenton-like system

All of the above works suggested that the activation of H_2O_2 and the oxidative removal of organic contaminants did not depend on the direct redox reaction with metal ions in the DRC system. The introduction of metal species was only to trigger the electron-rich/deficient area formation on the catalyst surface. Therefore, it is possible to establish a metal-free DRC system for water purification by the Fenton-like reaction, as long as the uneven distribution of surface electrons on the metal-free structure can be achieved. This idea was realized in 2018. We used the method of doping reduced graphene oxide (rGO) nanosheets with 4-phenoxyphenol (POP) molecules to affect the delocalized π-electrons of graphene, which resulted in the uneven distribution of surface electrons (Lyu et al., 2018b). The novel DRCs consisting of C and O centers were generated in the structure of the obtained metal-free catalyst POP-rGO NSs caused by the C-O-C bridges. According to the XPS and FTIR analyses, in the C-O-C bridges of POP-rGO NSs, the O atoms originated from the deprotonated phenolic OH groups of the POP molecules, while the C atoms were partly from the POP molecules and partly from the rGO structure. Because of the special C-O-C connecting mode, the free electrons were quickly attracted to the electron-rich O centers from the electron poor C centers based on the EPR analysis and DFT calculations. Therefore, a new upgrade of metal-free Fenton-like process was discovered in the POP-rGO NSs system. In the electron-rich O center, H_2O_2 was effectively reduced to •OH and destructed the pollutants. In the electron-deficient C centers, H_2O_2 and the pollutants could serve as electron donors for the metal-free system to maintain the balance of electron gains and losses, which is accompanied by the oxidative degradation of the pollutants (Fig. 9). Therefore, this metal-free catalyst exhibited good activity and high efficiency for the removal of organic pollutants through the dual degradation pathways. This finding addresses the bottleneck problems of the conventional metal-based Fenton/Fenton-like reactions and can be used to develop more advantageous metal-free Fenton-like catalysts by DRC theory.

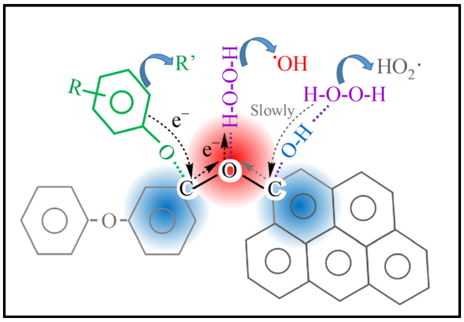


Fig. 9 DRC mechanism in the metal-free POP-rGO NSs Fenton-like system.

6 Environmental implication and innovation of DRC Fenton-like system

In summary, to successfully construct DRCs in the catalyst structure, two methods can be applied: 1) Lattice substitution using metal species with different electronegativities to induce the uneven distribution of surface electrons and 2) metal-organic surface complexation or metal-free molecular doping to construct electron transfer bridges. The former is simple for catalyst synthesis and surface modification, while the latter more likely forms a strong polarity of the electron-rich/deficient centers.

For the environmental significance of DRC technology, its successful achievement in the Fenton/Fenton-like reaction has shown significant advantages in four aspects compared to the classic heterogeneous Fenton reaction. 1) Remarkable promotion of activity. In the DRC Fenton-like systems, pollutants are degraded by free radicals and through electron-donation effect in the electron-deficient centers. The dual degradation pathway results in a rapid removal of pollutants. In addition, the redox of metal ions is no longer involved in the system, so the rate-limiting process of Fenton reaction is resolved, and the overall electron transfer rate of the system is accelerated, which greatly increases the activity. 2) Great increase in H_2O_2 utilization efficiency. In the DRC Fenton-like system, instead of H_2O_2, pollutants serve as electron-donors in the electron-deficient centers, so H_2O_2 is no longer oxidized to O_2 but mainly reduced to •OH. This is equivalent to one molecule of H_2O_2 driving the degradation of two molecules of pollutants, which is completely different from the classic Fenton reaction process, which consumes two H_2O_2 molecules to produce one •OH for pollutant degradation. Therefore, the utilization efficiency of H_2O_2 is greatly increased in the DRC Fenton-like system. 3) Enhancement of catalyst stability. In the DRC Fenton-like system, the repeated oxidation and reduction reactions of the metal ions are not involved. The existence of metal in the catalyst is mainly to induce the formation of DRCs on the catalyst surface instead of directly participating in the Fenton/Fenton-like reaction. Hence, the release of metal ions in the DRC Fenton-like system is often small and negligible, which ensures the long-term stability of the catalyst. 4) Lack of sensitivity to pH change. Many results have shown that DRC Fenton-like systems have a wide working pH range, and their activities are not obviously affected by the acid-base environment. In general, the catalytic activity of metal materials is very sensitive to changes in pH because surface hydroxyl groups form at the metal sites in aqueous environments. Nevertheless, DRC Fenton-like systems can successfully avoid the pH effect on the activity, largely because surface electron-rich/deficient sites (instead of metal species) form and dominate the Fenton-like reaction process.

With the above analysis, the most environmental significance of DRC technology is the utilization of the intrinsic energy and electrons of pollutants to eliminate the hazards and toxicity of the pollutants by creating surface electron–rich/deficient areas. This technology revolutionizes the traditional concept for pollutant degradation and changes the electron cycle processes of the classical Fenton reaction for pollutant degradation by constructing a special surface of the electron polarization distribution. In terms of the application scope of DRC technology, in addition to being used in the field of municipal and industrial wastewater treatment like the classical Fenton reaction, the DRC process can be used for the advanced purification of drinking water and polluted groundwater by removing organic micro-pollutants such as trace amounts of antibiotics and pesticides that are released into water environments. Of course, some limitations remain in DRC technology, including the complexity of DRC construction, steric hindrance in the reaction process, and effect of salt on the reaction, which must be further solved. In the future, researchers can also conduct comprehensive and in-depth research on DRC technology from many aspects, including development of more efficient DRC construction forms, precise control of the electron transfer orientation, adaptive regulation of various reaction conditions and multi-field development and applications of the DRC technology.

With the development of DRC technology, we have constructed a multistage DRC catalyst to achieve the in situ production and reduction of H_2O_2 in different electron-rich centers through the utilization of the electrons of pollutants (in the electron-deficient centers) without light, electricity or other assistance (Han et al., 2019). In addition, we have successfully applied DRC ideas to other advanced oxidation technologies, including PMS activation (Gao et al., 2018; Gao et al., 2019; Cao et al., 2020) and photocatalysis (Wang et al., 2019). Till now, many research groups have devoted effort to study the DRC mechanism and systems, and different types of DRC catalysts have been developed (Wang et al., 2018; Xu et al., 2018; Xie et al., 2019; Zhuang et al., 2019a; Zhuang et al., 2019b). Obviously, the DRC catalytic process is of great environmental implication for solving the application bottleneck of the Fenton reaction for water treatment and high-efficiency utilization and conversion of pollutants, which has opened another door for the Fenton reaction and well continues Fenton's story.

7 Conclusions

We briefly reviewed the development of the Fenton/Fenton-like reaction and its bottleneck problems in the process of degrading pollutants. Then, we analyzed that the key to the bottleneck problems lay in the inherent property of the basic Fenton reaction mechanism. Based on this analysis, we reviewed in detail the DRC theory that broke through the classical Fenton reaction mechanism. The construction and development of DRC and its performance in the pollutant degradation and interfacial reaction mechanism are described in detail. Two methods can be applied to successfully construct the DRC in the catalyst structure: 1) Lattice substitution by using metal species with different electronegativities to induce the uneven distribution of surface electrons and 2) metal-organic surface complexation or metal-free molecular doping to construct electron transfer bridges. The largest environmental significance of DRC technology was the utilization of the intrinsic energy and electrons of pollutants to eliminate the hazards and toxicity of the pollutants by creating surface electron–rich/deficient areas, which revolutionized the traditional concept for pollutant degradation.

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