# Potential and Prospects in Molecular Orbital Level Micro-Electric Field for Low Energy Consumption Water Purification

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REVIEW

Earth and Environmental Sciences

Potential and Prospects in Molecular Orbital Level Micro-Electric Field for Low Energy Consumption Water Purification

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Abstract

Conventional water purification technologies struggle to simultaneously address purification efficiency and energy consumption. Molecular orbital level surface Micro-Electric Field (MEF)-driven water purification is an original and innovative concept conceived and developed by our group in recent years. The core idea involves creating electron-rich and electron-poor micro-areas on the nanomaterial surface, which drive pollutants or H$_2$O molecules to provide electrons in the electron-poor micro-areas while other environmental factors (such as H$_2$O$_2$ and O$_2$) obtain electrons in the electron-rich micro-areas. This process effectively utilizes the internal energy contained within wastewater and emerging contaminants (ECs). Centered on this core, this review systematically examines the discovery, construction, and characteristics of MEF and MEF-like systems and summarizes their application directions. The challenges, bottlenecks, and future development directions of MEF technology are also analyzed and discussed. Reviews of MEFs can facilitate the development of low-consumption, high-efficiency water purification technologies.

Keywords: Molecular Orbital, Micro-Electric Field, Low Energy Consumption, Water Purification, Pollutant Utilization
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1. Introduction

Providing safe water is an increasingly severe challenge as new pollutants continuously emerge in the era of rapid global industrialization[1]. Water pollution is exacerbated by emerging contaminants (ECs), making it more complex, difficult, and expensive to treat[2]. Currently, over 650 million people worldwide lack access to safe drinking water[3]. Alarmingly, every two minutes, a child under the age of five succumbs to preventable diarrheal diseases caused by poor water quality[4]. ECs, the primary culprits that threaten the ecological environment and cause these serious health events, have been frequently detected at levels in natural water environments, effluent from sewage treatment plants, and even drinking water sources [2]. This fact underscores the importance and urgency of disruptive innovation in water purification technology[5], particularly for the removal of refractory ECs from water.

Advanced oxidation technologies (AOTs) that employ highly oxidizing species, such as hydroxyl radicals (*OH) and superoxide radicals (O$_2^{-}$), as attacking factors have been found to possess the ability to eliminate organic pollutants that are difficult to biodegrade[6-8]. In particular, the rapid development of nanotechnology has brought in a new era for heterogeneous AOTs[9]. By regulating the size, morphology, and surface structure of nanomaterials, AOTs are endowed with water purification properties integrating adsorption, coagulation, catalysis, oxidation, and confined reactions[3], enabling rapid elimination of various pollutants in developed AOT systems[7]. These systems include Fenton/Fenton-like systems[10-13], persulfate activation systems[14-16], catalytic ozonation systems[17-19], photocatalytic
systems[20-22], and electrocatalytic systems[23,24]. These processes primarily rely on
the generation of free radicals to attack and degrade organic pollutants. However, high
energy consumption is a significant drawback of AOTs due to the inherent limitations
of these technologies, including the demand for large amounts of oxidants and
reductants as well as the necessity for driving forces such as light, electricity, and
ultrasonic energy[25]. Given the increasingly prominent constraints of global resources
and the environment, the development of next-generation water treatment technology
for EC elimination, focusing on low energy consumption and high efficiency, is
essential.

Numerous studies have shown that current AOTs are primarily surface reactions,
highlighting the key role of material surface characteristics. A series of recent studies
have emphasized that the construction of different defects on the material surface based
on molecular orbital polarization is conducive to the formation of confined electron-
rich/poor micro-areas, which results in the formation of surface Micro-Electric Field
(MEF) and manifests as surface electrostatic forces [6,8,26-29]. As depicted in Figure
1, the polarization distribution of electrons is achieved by constructing electron-
rich/poor micro-areas on the catalyst surface. This drives electron-rich substances, such
as pollutants and H₂O, to provide electrons and energy in the electron-poor micro-areas
via electrostatic adsorption and complexation, thereby decomposing the pollutants.
Simultaneously, other environmental factors, such as H₂O₂ and O₂, are activated by
obtaining electrons and energy in the electron-rich micro-areas. Different
environmental factor-mediated activation processes have led to the evolution of various
water purification technologies, including dual-reaction-center (DRC) Fenton-like processes, persulfate activation processes, photocatalysis, and water self-purification processes. The MEF-based process is found to be beneficial for utilizing internal energy, including pollutants, dissolved oxygen, salt ions in water, and even water molecules, through electron flow, energy flow, and mass flow. This provides a new direction for the development of low-energy-consumption water purification technologies.

Centered on this core, this review systematically examines the discovery, construction, types, and main characteristics of surface MEFs and similar configurations associated with MEFs (MEF-like configurations). It thoroughly explains and summarizes their application research directions in the field of water purification, particularly for EC elimination. These applications include DRC-based Fenton-like processes for water purification, persulfate activation processes for water purification, photocatalysis for water purification, and water self-purification through internal energy utilization. The challenges, bottlenecks, and future development directions of MEF and MEF-like technologies are also analyzed and discussed.

2. Construction and Properties of Surface MEF on Catalyst

2.1. Origin of Surface MEF

In most developed materials, inevitable defects are always generated on the surface. However, these microstructures do not reflect the characteristics and performance of MEFs and cannot drive the migration and transformation of pollutant electrons. The key to forming directional MEFs with the function of pollutant energy utilization is
regulating oriented electron flows at the molecular orbital level, which does not require additional energy. Generally, molecular orbital theory holds that electrons in a molecule no longer belong to a specific atom but move throughout the entire range of the molecule. Molecular orbitals are linear combinations of atomic orbitals of atoms in a molecule, which can form bonding molecular orbitals (such as $\sigma$ and $\pi$ orbitals) and antibonding molecular orbitals (such as $\sigma^*$ and $\pi^*$ orbitals) (Figure 2). Similarly, in solid materials, the outer electrons of internal atoms are also strongly influenced by neighboring atoms. Based on the different electronegativity and electrochemical characteristics of the atoms, the overlap of various atomic orbitals lead to the formation of strong interactions at the molecular orbital level, providing the possibility of non-equilibrium and the polarization distribution of electrons in a confined area on the material surface.

The most common methods to generate electron-oriented migration at the molecular orbital level include lattice substitution by elements with varying electronegativity, surface complexation based on cation-$\pi$ interactions, and interfacial coupling based on metal-organic polymerization. Specifically, cation-$\pi$ interactions are among the most important intermolecular binding forces occurring between cations and electron-rich $\pi$ orbitals[30]. The interaction between cations and delocalized $\pi$ orbitals perpendicular to the plane of the aromatic ring often results in particularly strong cation-$\pi$ binding, which surpasses the strength of hydrogen bonds and even charge-charge interactions in aqueous solutions[31]. The orbital interactions of cation–$\pi$ typically involve electron transfer of the type $\pi \rightarrow$ cation ($\sigma$ donation) and cation $\rightarrow \pi^*$ ($\pi$ back-donation)[30]. This electron transfer form can be easily regulated by reasonable structural modifications. It has been demonstrated that interfacial confinement can fundamentally alter the energetics of cation-$\pi$-mediated assembly[31]. Regulating the
polarity enhancement of electrons and energy on the material surface through cation-π interactions is promising.

Based on the aforementioned theoretical foundation, we summarize the concept of surface MEF for the first time. Surface MEF is induced by the non-equilibrium distribution of electrons on the catalyst surface through the interaction of multiple molecular orbitals and is manifested as a surface electrostatic force. In recent years, various types of surface MEFs have been successfully constructed using lattice substitution[6,27,32], surface coordination complexation[8,26,33,34], interfacial coupling and polymerization[35], and molecular doping[36] to trigger the uneven distribution of molecular orbital electrons on material surfaces. Compared with conventional Fe-C materials that use their potential difference (~1.2 V) to promote Fe corrosion to degrade pollutants[37,38], the generated surface MEF on the catalyst consistently maintains a steady state both at room temperature without additional energy input and during pollutant degradation. This demonstrates a very promising application prospect for environmental remediation, as well as the energy and chemical industries.

2.2. Design and Characterizations of Surface MEF

2.2.1. Surface MEF Construction through Lattice Substitution

The design concept of MEF involves modulating the catalyst structure so that electrons are nonuniformly distributed, forming electron density polarization centers. For metal oxide matrices, the solubility differences among various doping elements induce distinct deposition behaviors on the metal oxide matrix, resulting in their successful substitution into the matrix lattice during preparation[39]. The different electronegativities of doped elements create a synergistic effect, which alters the
electronic orbit and lowers the Fermi energy level of the matrix, leading to charge redistribution primarily occurring around the doped elements[40,41]. Based on the electronegativity differences of various elements, the initial configuration of surface MEF, composed of electron-rich Cu areas and electron-poor Ti/Al areas (Figure 3), was constructed on $d$-TiCuAl-SiO$_2$ Ns through lattice substitution[27].

On this basis, MEFs were successfully constructed by doping Mo, Fe, Co and Cu into the ZnS and Al$_2$O$_3$ lattice, respectively[6,25,42-45], and theoretically verified using density functional theory (DFT) calculations. For instance, lattice-doping Co into ZnO (OV-CoZnO MPs) induced a significant number of oxygen vacancies (OVs) at the site adjacent to Co atoms, as confirmed by X-ray photoelectron spectroscopy (XPS), Raman, and photoluminescence spectrum (PLS) analyses[38]. According to electron paramagnetic resonance (EPR) results, OV-CoZnO MPs exhibited a stronger EPR signal of unpaired electrons at $g = 2.097$ than ZnO, confirming that lattice doping with Co enabled more electrons to gather at oxygen vacancies through the formed -Zn-OV-Co-O- or -Co-OV-Zn-O- structural units, creating electron-rich OV centers and electron-deficient Co$^{3+}$ sites. It was also found that OVs with more electrons formed in [Bi$_2$O$_2$S]$_{2+}$ layers after S doping in BiOBr[46]. The same phenomenon regarding OVs was observed in the Fenton-like catalyst BiOCl[47]. These results indicated that OVs caused by lattice substitution functioned as electronic carriers and could serve as electronegative centers of the catalyst, deepening the understanding of constructing surface MEFs over catalysts. Furthermore, it was reported that substitutional doping with heteroatoms into the carbon skeleton could generate a unique electron distribution[48,49]. The doped heteroatom could introduce electronic states near the carbon Fermi energy level in the carbon framework, thus inducing local high spin density on the basal plane[50]. Based on this theory, numerous studies have been...
dedicated to the construction of surface MEFs for metal-free catalysts[51,52].

2.2.2. Surface MEF Construction through Surface Complexation

In the aforementioned works, the electronegativity difference of each element was utilized to modulate the non-uniform electron distribution, contributing to the formation of MEF on the catalyst surface. However, the intensity of the constructed MEF based on the electronegativity difference is quite limited, making the enhancement of the electronic structure and the construction of a stronger MEF challenging. Cation-π (M⁺-π) interactions, resulting from surface complexation, are electrostatic attractions between cations and electron-rich π orbitals. These interactions are stronger than hydrogen bonds and may even surpass charge-charge interactions[31,53-55]. The synergistic σ donation from the π system into an empty orbital of a metal and π back-donation of electron density from the occupied metal d orbitals into the π orbitals of the π system can significantly affect the structural and energetic parameters of the cation-π configuration[56]. In such a system, achieving directed and ordered migration of electrons in a specific manner may be key to overcoming the current bottleneck and building an efficient and stable surface MEF through cation-π interactions. Moreover, the electron density of the aromatic ring can be altered by replacing functional groups, resulting in an asymmetric potential of π binding to the ring and modifying the bond strength of the cation-π interactions[30]. Consequently, the intensity of the surface MEF can be progressively strengthened by constructing single, double, or even multiple cation-π electrostatic forces.

An electron distribution polarity-enhanced catalyst (OH-CCN/CuCo-Al₂O₃) was developed for the first time, consisting of Cu and Co co-substituted γ-Al₂O₃ combined with a carbon nitride (g-C₃N₄) substrate via a surface complexation method[8]. XPS,
Fourier transform infrared spectroscopy (FTIR), and extended X-ray absorption fine structure (EXAFS) analyses confirmed the complexation of Cu species and the phenolic hydroxyl group of g-C₃N₄. EPR results revealed that the strong signal observed in OH-CCN/CuCo-Al₂O₃ was attributable to the increased electron density around Cu due to σ donation (π → Cu) of the Cu(II)–π interactions, which implied the formation of electron-rich Cu areas in OH-CCN/CuCo-Al₂O₃. This conjecture was confirmed by DFT calculations. Cu species in the C-O-Cu cross-linker had the maximum valence-electron density of ~14.19 e Å⁻³, while the lowest valence-electron density was observed around the C atoms of g-C₃N₄. Inspired by this discovery, a more efficient MEF was constructed on a CuAlO₂ support with surface growth of g-C₃N₄ (CN-Cu(II)-CuAlO₂) by increasing the connection between Cu and g-C₃N₄. According to DFT calculations, the maximum valence-electron density (~4.0 e Å⁻³) was found around Cu, and the lowest valence-electron density (~0.2 e Å⁻³) was found around C atoms[26]. Similarly, stable MEFs on transition metals (e.g., Fe, Cu, Co, V, Mo and Zn) doped with g-C₃N₄, reduced graphene oxide (rGO), polyimide (PI), carbon, boron nitride (BN), and chicken manures were successfully constructed using a similar method[57-67].

2.2.3. Surface MEF Construction through Interfacial Coupling

Cation-π interactions can be enhanced by interfacial coupling, particularly the polar coupling process caused by nano zero-valent metal species, which often induces the utilization of multiple environmental factors. Interfacial coupling is considered another critical way to enhance the polarity of surface MEFs. Cao et al. developed the RSC-CNOP using a surface reduction modification method with a Cu-PI precursor[35]. The generated Cu(0) and Cu(I) on the catalyst surface triggered the anomalous bidirectional electron transfer to O atoms, forming electron-rich O centers with 8-fold
higher free electrons than conventional catalysts. Based on this, a nanoscale Cu(0) combined with Cu(II)-doped rGO (nZVCu-Cu(II)-rGO) was prepared using a modified annealing reduction method[68]. EPR analysis demonstrated that charge transfer from the π-electronic reservoir of the underlying graphene sheet to the introduced Cu (σ donation) was enhanced with increasing Cu species, resulting in a large number of electrons accumulating around Cu species. The increased electron polarization of the surface structure led to the formation of an electron-rich Cu center and an electron-deficient C center with valence-electron densities of approximately 4.0 e Å\(^{-3}\) and 0.81 e Å\(^{-3}\), respectively, as verified by DFT calculations. Moreover, based on interface coupling theory, the construction of surface MEFs in Cu\(^0\)@CuO\(_x\)-encapsulated nitrogen-doped graphitic carbon (Cu\(^0\)@CuO\(_x\)-NC), nZVI/FeOx/FeNy-anchored NC composites (nZVI/FeN\(_{5.5}\)O\(_{7.2}\)/C), and MOF-coated Cu(0) (ZVC@CMOF) catalysts has also been investigated[10,69,70]. Recently, a Fe-based composite catalyst (Fe\(^0\)-Fe\(_2\)C\(_z\)/Fe\(_x\)-GZIF-8-rGO) was developed through interfacial three-phase coupling[34]. DFT calculations demonstrated that the successful coupling among the three phases triggered more electrons transferred from GZIF-8/rGO to the generated Fe\(^0\), forming an extremely strong MEF on the Fe\(^0\)-Fe\(_2\)C\(_z\)/Fe\(_x\)-GZIF-8-rGO surface, with the surface potential energy as high as 663.96 kJ/mol. Therefore, the MEF on Fe\(^0\)-Fe\(_2\)C\(_z\)/Fe\(_x\)-GZIF-8-rGO could reduce the chemical bond energy of surface-adsorbed molecules without additional energy assistance, which might be very promising for low-energy water purification.

2.3. Interaction Forms of MEF and Different Substances

In addition to some metal oxide MEF-containing catalysts, most MEF-containing catalysts developed thus far are carbon-based materials. During the reaction, it was
found that water molecules could complex with the electron-deficient area of MEF to form an H-bonding molecular orbital interaction and delocalize electrons to the electron-rich area, resulting in oxidation into •OH[57]. In such a situation, the hydrogen peroxide (H$_2$O$_2$) added during the Fenton-like process could not directly interact with the electron-deficient area but instead bonded to the OH of the complexed H$_2$O through a hydrogen bond (H–O⋯O•••H–O), thus hindering the oxidation of H$_2$O$_2$[36]. However, in the presence of pollutants, the adsorbed pollutants could further replace the adsorbed water molecules and complex with the electron-deficient areas through π-π and H-bonding to form a surface-confined non-equilibrium electron orbital [36]. Thus, the adsorbed pollutants and their intermediates tended to delocalize electrons to the electron-rich areas through these strong electrostatic forces, enhancing catalyst stability[71,72]. Due to the occupation of the adsorbed pollutants at electron-deficient areas, H$_2$O$_2$ tended to adsorb on electron-rich areas through electrostatic force and was then directly and efficiently reduced to •OH, significantly improving H$_2$O$_2$ utilization. Han et al. and Lu et al. also found that dissolved oxygen (DO) confined in electron-rich areas could trap the delocalized electrons from H$_2$O/pollutants and then undergo a surface reduction process to form O$_2$•••/H$_2$O$_2$•••/OH for pollutant degradation[25,57]. Moreover, Wang et al. reported that an extremely strong surface MEF could significantly reduce the chemical bonding energy of pollutants with strong molecular orbital interactions with electron-deficient areas[34]. Specifically, through the electron delocalization effect of the surface MEF, the pollutants were first cleaved and then underwent hydrolytic hydroxylation and mineralization processes at room temperature, with O$_2$ acting as an electron-acceptor in electron-deficient areas. Based on the unique surface characteristics of MEF, MEF-containing catalysts exhibit high degradation efficiency for various pollutants[26,51,52]. According to the aforementioned
discoveries, the conversion pattern of surface-adsorbed substances depends on the intensity and structural characteristics of the MEF. Therefore, the directional regulation of the MEF structure allows it to play different roles in different systems. In the following sections, we will detail the role and application of surface MEF in various systems.

3. MEF Driving DRC Fenton-like Process for Water Purification

The Fenton reaction, one of the most powerful AOTs, has been widely used to eliminate ECs from water by generating *OH through the reaction of H$_2$O$_2$ and Fe$^{2+}$ or other reducing transition metals[6]. The development of heterogeneous Fenton/Fenton-like catalysts has significantly overcome the weaknesses of homogeneous reactions, such as a narrow working pH range, iron sludge accumulation, and difficulty in recycling[10]. However, the basic Fenton reaction principle remains unchanged, relying on the redox of H$_2$O$_2$ at single sites. The existence of a rate-limiting step is inevitable, often leading to low utilization efficiency of H$_2$O$_2$ and poor activity, especially under neutral conditions. The DRC Fenton-like process based on surface MEFs offers hope for solving these problems through different types, which can drive various environmental factors to participate in electron acquisition and supply in electron-rich/poor micro-areas, thereby reducing H$_2$O$_2$ consumption[64].

3.1. Lattice Substitution-Type MEF Driving DRC Process

Based on the lattice substitution method, in 2016, one kind of Fenton-like catalyst consisting of dandelion-like copper-aluminum co-doped silica nanospheres (DCAS Ns) with a polarization distribution of surface electrons was first developed through an enhanced hydrothermal method (Figure 4a)[9]. The substitution of Cu and Al for Si
resulted in a non-uniform distribution of electrons and the formation of different electrical regions, significantly increasing the number of reaction sites (Figure 4b). The successful formation of Al-O-Cu bonding bridges was confirmed by the variations in Cu and Al bonding energy before and after doping in XPS spectra (Figure 4c), as well as the variations in bond distance and coordination number of the Cu K-edge in EXAFS (Figure 4d). This catalyst exhibited exceptionally high activity and stability for the degradation and mineralization of various refractory pollutants under neutral conditions. The reaction rate was 5.2 to 13.4 times higher than that of the conventional Fenton catalysts (Figure 4e), accompanied by a high H₂O₂ utilization efficiency of 86.7% (Figure 4f). The efficient utilization of pollutant electrons by DCAS Ns was demonstrated by the 5-tert-butoxycarbonyl-5-methyl-1-pyrroline-N-oxide (BMPO) spin-trapping EPR technique, which greatly promoted the generation of •OH and prevented the formation of HO₂*/O₂• (Figure 4g).

In this approach, Ti, the third metal, was introduced to co-doped SiO₂ nanospheres with Cu and Al (d-TiCuAl-SiO₂ Ns), which further enhanced the polarization distribution of surface electrons. The Fenton-like reaction mechanism and H₂O₂ utilization efficiency were proposed and elucidated [27]. The successful formation of the electron-rich Cu region and the electron-poor Al/Ti region (M-O-M type MEF, where M represents metal species) was clearly demonstrated by EXAFS (Figure 5a), EPR (Figure 5b), XPS (Figure 5c), FTIR and cyclic voltammetry (Figure 5d) measurements. By utilizing the properties of different micro-regions of DRCs, H₂O₂ predominantly gained electrons in the electron-rich Cu region to generate •OH, and pollutants were oxidized in the electron-poor Ti/Al center for donating electrons. This resulted in nearly all the energy of H₂O₂ being applied to the degradation of pollutants. Separation of oxidation and reduction reactions led to reaction rates ~ 10-fold higher.
than traditional Fenton catalysts (Figure 5e) and 60% to 90% H$_2$O$_2$ utilization efficiency for the entire process (Figure 5f). This work suggested that the construction of an M-O-M type of MEF by lattice substitution could avoid the inefficient decomposition of H$_2$O$_2$ and significantly improve the Fenton-like catalytic activity.

The construction of surface DRCs by utilizing metal electronegativity differences to modulate electron distribution has been demonstrated to be viable. Additionally, substituted M-O-M type MEFs (Zn, Cu, Co, Bi, etc.) with different metal elements were developed to further investigate the optimal synergistic patterns between MEF and H$_2$O$_2$. Notably, in the study of a Co-doped ZnO (OV-CoZnO MPs) Fenton-like system[6], it was found that lattice-doping Co into ZnO wurtzite can lead to the generation of OVs with unpaired electrons (electron-rich OV regions), while an electron-poor region forms around Co$^{3+}$ (Figure 6a-c). In this particular surface MEF, the efficient transformation and degradation of pollutants through multiple pathways over a wide pH range (4.5 ~ 9.5) were achieved through the synergistic interaction between the poor/rich microregions on this MEF, with reaction rates up to ~17 times that of the non-MEF catalyst (Figure 6d). Moreover, under molecular orbital action, pollutants were adsorbed on the electron-poor Co$^{3+}$ region as electron donors to the system and were oxidized, thus achieving rapid electron cycling within this DRC system through the Co-OV bonding bridge (Figure 6e).

The aforementioned work indicated that OVs formed by metal doping indeed diversified the types of surface MEFs and greatly enhanced the molecular orbital polarization between the catalyst surface and the H$_2$O$_2$/pollutants. Additionally, the formation of OVs was also observed in surface MEFs developed with non-metal-doped metal oxides. In the case of I-doped BiO (f-BiOI MSs)[32], electron-rich oxygen regions and electron-poor OV regions were successfully constructed. The (101) and
(110) crystal planes in this catalyst were greatly exposed, providing numerous sites for the reaction. The rapid removal of refractory bisphenol A (BPA) by the Fenton-like reaction could be achieved within 3 min, with a reaction rate ~ 190-fold higher than that of the traditional Fenton catalyst, Fe$_2$O$_3$. The electron-rich oxygen region could effectively reduce H$_2$O$_2$ to *OH, while the electron-poor OVs captured electrons from the adsorbed pollutants and transferred them to the electron-rich region. With the synergistic effect of H$_2$O$_2$, this surface DRC was able to achieve rapid degradation and mineralization of pollutants in a wide pH range.

We expanded the construction of MEF beyond oxide substrates to include sulfides (M-S-M type MEF) and obtained promising results. In a study of Fe-doped ZnS quantum dots (Fe-ZnS QDs)[42], non-equilibrium surface DRCs with electron polarization distribution were successfully constructed by replacing a portion of Zn with Fe using an enhanced in situ synthesis method (Figure S1a). Due to the construction of the DRCs on the Fe-ZnS QD surface, trace H$_2$O$_2$ (less than 1mM) activation overcame the energy barrier for pollutant electron transfer (Figure S1b,c). Rapid pollutant removal was then achieved by reactive oxygen species (ROS) activated from DO utilizing pollutant electrons and energy, reaching 97.2% in just 15 s. The effect of pollutant structure on MEF performance was also explored (Figure S1d). Generally, pollutants with phenolic hydroxyl groups and carboxyl groups were more likely to interact with MEF, with electrons being utilized by cation-π interactions and other mechanisms. As a result, the removal efficiency for BPA by this MEF was significantly higher than that of SMZ. Experimental and theoretical studies demonstrated that constructing DRCs on the surface of Fe-ZnS quantum dots greatly strengthened the orbital interactions between each molecule and the catalyst surface, allowing pollutant electrons to be efficiently utilized for H$_2$O$_2$ reduction while DO was activated by
obtaining energy and electrons (Figure S1e). The construction of this specific MEF enabled the rapid removal of pollutants with the assistance of only trace amounts of H₂O₂, significantly reducing energy consumption in the Fenton reaction.

### 3.2. Cation-π-Type MEF Driving Pollutant Utilization

The lattice substitution of metal elements to construct MEFs has proven to be an effective method in Fenton/Fenton-like reactions. However, due to the extreme values of elemental electronegativity, there is a limit to the construction. Cation-π (M⁺-π) interactions were introduced to improve this limitation through surface complexation. In 2017, the Cation-π-type Fenton-like catalyst OH-CCN/CuCo-Al₂O₃ was successfully developed by complexing CuCo-Al₂O₃ with g-C₃N₄ through the C-O-Cu bonding bridge (Figure 7a,b)[8]. EPR spectroscopy (Figure 7c) and DFT calculations (Figure 7d) verified the generation of an enhanced electron-rich region around Cu due to Cu-π interactions and electronegativity differences among Cu, Co, and Al through the construction of C-O-Cu bonding bridges. Driven by the cation-π electrostatic force, the amount of *OH generated under near-neutral conditions was twice the amount of H₂O₂ involved in the reaction. Additionally, H₂O served as an electron donor and was oxidized into *OH at the N atom of OH-CCN, resulting in rapid pollutant removal with ~90% H₂O₂ utilization and a high turnover frequency (TOF) of the *OH yield (1.30 s⁻¹), which was more than ~85 times that of the traditional homogeneous Fenton reaction (Figure 7e,f). This work suggested that utilizing cationic-π interactions is an effective way to enhance surface electron polarization distribution, enabling MEFs to utilize pollutant energy as well as environmental factors (H₂O, O₂, and more) under molecular orbital interactions.

Subsequently, a more efficient surface complexation cation-π-type MEF (CN-
Cu(II)-CuAlO$_2$) was developed by growing g-C$_3$N$_4$ on a CuAlO$_2$ substrate via a C-O-Cu bonding bridge (Figure 8a-c)[26]. Due to the surface growth of this linker on the MEF surface, a Cu-rich electron region was formed with greatly reduced surface OVs, resulting in high activity and efficiency for the degradation of refractory pollutants (Figure 8d) while maintaining high H$_2$O$_2$ utilization (Figure 8e). During the Fenton-like reactions, the electron-rich Cu region was responsible for the efficient reduction of H$_2$O$_2$ to $^\bullet$OH, and the electron-poor C region captured electrons from H$_2$O$_2$ or pollutants, diverting them to the electron-rich area via the C-O-Cu bonding bridge (Figure 8f). This study significantly deepened the understanding of the enhancement of cation-$\pi$-type DRCs through surface complexation by functionalizing with organic solid-phase ligands.

In 2019, a C-O-Cu bonding bridge was successfully constructed in the study of Cu-doped mesoporous PI nanocomposites (Cu-MP NCs)[58]. Both experimental and theoretical results showed that Cu$^{+}$ and Cu$^{2+}$ combined with the aromatic ring of the PI substrate through the C-O-Cu bonding bridge, creating electron-rich Cu regions and electron-poor aromatic ring regions under the influence of cation-$\pi$ interactions. This specific surface MEF resulted in the adsorption and electron donation of pollutants on the electron-poor region ($\pi$-$\pi$ interactions), contributing to the inhibition of H$_2$O$_2$ oxidation and further accelerating the electron transfer cycle from the electron-poor to the electron-rich region. Additionally, O$_2$ was innovatively activated into O$_2$$^\bullet$ in the electron-rich Cu region, further improving the energy utilization of the system. With the assistance of H$_2$O$_2$, Cu-MP NCs was able to rapidly degrade refractory pollutants over a wide pH range (2.6–10.4).

The aforementioned work strongly demonstrated the feasibility of constructing efficient DRCs through surface complexation using Cu species to form C-O-M bonding
bridges. Based on this, other metal elements (Co, V, etc.) were introduced to construct C-O-M bonding bridges, significantly enriching the types of surface-complexed MEFs. A three-dimensional (3D) hybrid of vanadium tetrasulfide cross-linking graphene-like carbon (VSO C(π)) with π electrons was constructed to achieve a sustainable electron cycle of H₂O₂, DO, and pollutants at the solid-liquid micro-interface, exhibiting excellent performance in the removal of refractory pollutants[59]. The construction of C-S-V(π) and C-O-V(π) bonding bridges in VSO-C(π) triggered the directional electron transfer from C(π) to the V region, forming the surface electron polarization distribution MEF and enabling electron reduction of O₂ and H₂O₂ in the electron-rich V region. This sustainable electron cycling process resulted in exceptional activity (~ 90% rhodamine (RhB) removal without H₂O₂ (Figure S2a) and ~ 98% RhB removal with H₂O₂ (Figure S2b) in 15 min) and adaptability to complex environments (pH and salt changes), as well as a significant reduction in resource energy consumption. Moreover, C–O–Co bonding bridges were successfully developed through surface complexation via in situ modification of Co species to graphitic carbon-CN substrates (in-situ-Co-g-C₃N₄)[73] (Figure S2c,d). Notably, the electrons within these surface DRCs were rapidly transferred through the C-O-Co bonding bridge, achieving a reaction rate ~ 150 times higher than g-C₃N₄. Additionally, using this constructed MEF, the effect of pollutant concentration on MEF performance was investigated (Figure S2e). Both high and low concentrations could affect the contact probability between the pollutant and the MEF, thereby influencing electron transport. Under suitable reaction conditions, efficient H₂O₂ reduction and pollutant electron donation through π-π interactions were achieved in the electron-rich Co region and the electron-poor C region on the g-C₃N₄ aromatic ring, respectively (Figure S2f). The above construction of non-Cu-based MEFs through surface complexation provided a promising strategy for exploring more efficient
synergy with cation-π-type MEFs.

Similarly, C-N-Fe bonding bridges were systematically investigated to verify the generality of surface-complexed MEFs for efficient synergy. C-Fe-N-C bonding bridges were directly constructed in lotus-like Fe-doped PI hybrid nanosheets (lf-Fe/PI HNs)[33], generating electron-rich Fe and electron-poor C regions (Figure S3a), respectively. This novel Fe-based MEF structure could rapidly remove refractory pollutants under neutral conditions, achieving reaction rates 7 to 10-fold higher than conventional Fe-based Fenton catalysts (Figure S3b). The Fe-N-C bonding bridge served as an electron transfer and electron storage carrier between pollutants and H$_2$O$_2$, enabling efficient reduction of H$_2$O$_2$ in the electron-rich Fe region and electron donation by pollutants in the electron-poor C region, which greatly reduced the energy consumption of water treatment (Figure S3c). Furthermore, in 2022, C-N-Fe bonding bridges and numerous OVs were constructed on C$_3$N$_4$ substrates through self-assembly and calcination processes in Fe$_x$O$_y$-d-g-C$_3$N$_4$ composites[60]. This specific surface MEF enabled OVs to exhibit two types of effects on different pollutants under air-saturated conditions (Figure S3d,e). Hydrophilic hydroxyl pollutants primarily donated electrons to OVs through surface complexation of Fe-N bonding bridges, while H$_2$O$_2$ was mainly effectively reduced to *OH by obtaining electrons in OVs. In contrast, when interacting with hydrophobic pollutants, H$_2$O$_2$ was decomposed to O$_2$ primarily in the Fe and OVs regions for electron donation. Therefore, this specific surface MEF exhibited higher Fenton-like efficiency for the degradation of hydroxyl-containing pollutants and hydrophobic pollutants mixed with the former than conventional Fenton catalysts (Figure S3f).
3.3. Enhanced Interfacial Coupling Driving H$_2$O$_2$-Assisted Purification Process

The cation-π electrostatic interaction plays a critical role in constructing MEF with electron polarization distributions of DRCs. This interaction can be enhanced by interfacial coupling, particularly the polar coupling process caused by nano zero valence metal species, which induces the utilization of dissolved O$_2$, H$_2$O, and pollutants in water assisted by H$_2$O$_2$. In 2019, reduction state Cu (RSC) species-doped carbon-nitrogen-oxygen polymers (RSC-CNOPs) and Cu(RSC)-O-C(π) bonding bridges were successfully fabricated by high-temperature polymerization[35]. Bidirectional electron transfer from RSC and C(π) to O (RSC→O←π) formed an electron-rich O region and an electron-poor C(π) region, resulting in ~8-fold higher free electrons in RSC-CNOPs compared to CNOPs (Figure 9a-c). In this way, excellent pollutant degradation performance, as well as efficient utilization of pollutant energy and electrons, was achieved when the specific DRCs synergized with H$_2$O$_2$ (Figure 9d). Under interfacial coupling cation-π interaction, this MEF captured and utilized electrons from H$_2$O and pollutants in the electron-poor C region and selectively reduced H$_2$O$_2$ in the electron-rich O region (Figure 9e).

Modulating the electron distribution in the electron-rich region to construct a reduced-state-enhanced surface MEF could improve the activity of Fenton-like reactions as well as H$_2$O$_2$ utilization. Nanoscale zero-valent Cu doped with Cu(II) reduced graphene oxide (rGO) hybrids (nZVC-Cu(II)-rGO) was successfully fabricated via an annealing reduction process[68]. Nanoscale Cu(0) and Cu(II) generated on the rGO surface were bonded to the substrate via a C-O-Cu bonding bridge, forming an electron-rich Cu(II) region and an electron-poor C region due to cation-π interactions.
The generation of Cu(0) strengthened the polarization of the electron-rich region on the surface MEF and greatly accelerated the electron transfer in the system, promoting the reduction of H$_2$O$_2$ to *OH in the electron-rich region. This surface MEF achieved ~ 77-fold and 13-fold higher conversion of organic pollutants than the graphene oxide (GO) system and the rGO system, respectively (Figure 10d). Pollutants in this system could significantly replace H$_2$O$_2$ as the electron donor and be efficiently oxidized and degraded in the electron-poor C region, with their electron energy fully utilized. Additionally, the encapsulated RSC with carbonized metal-organic framework (ZVC@CMOF)[10] and nitrogen-doped graphitic carbon substrate (Cu$_0$@CuO$_x$-NC)[69] were successfully developed, respectively, both achieving rapid pollutant removal and effective reduction of H$_2$O$_2$ (Figure 10e) and O$_2$ (Figure 10f) in the electron-rich Cu region, greatly reducing energy consumption in water treatment. Furthermore, reduced state Co, including nano zero-valent cobalt (nZVCo) and Co$^{2+}$ in co-doped silica nanospheres (mp-RSCo-SiO$_2$ NSs), was successfully developed and connected to the SiO$_2$ framework via the Co-O-Si bonding bridge. In Fenton-like reactions, the electron donation effect of organic pollutants was achieved through the "pollutant-Co$^{2+}$/SiO$_2$" pathway, which was subsequently utilized for efficient reduction of H$_2$O$_2$ to generate *OH. This constructed surface MEF rapidly removed a series of refractory pollutants in a wide pH range (3.1 to 10.9) through synergy with H$_2$O$_2$, achieving ~ 290-fold higher reaction rates than Co$_3$O$_4$. The construction of reduced-state MEF with the coexistence of zero-valent and low-valent metals provides a new strategy to improve pollutant electron utilization efficiency as well as the Fenton reaction rate.

Moreover, based on the primary cation-π DRCs catalytic system, the multi-state MEF constructed by multi-metal doping was found to strengthen interfacial coupled
cation-π interactions. Han et al. successfully prepared CMS-rGO NSs catalysts with Co and Mo dual electron-rich centers and C electron-poor centers by embedding Co-doped MoS$_2$ nanomicrospheres into rGO nanosheets (Figure 11a)[57]. The EXAFS results confirmed that the formed Mo-S-C bonding bridge between CoMoS$_2$ nanospheres and rGO nanosheets activates π electron transfer from rGO to metal centers (π → Mo and Co) (Figure 11b). Meanwhile, Co replaced Mo in the MoS$_2$ lattice to form Mo-O-Co bonds, further increasing the electron density around Mo species due to the greater electronegativity of Mo than Co. Consequently, the novel MEF of CMS-rGO NSs consists of dual-stage electron-rich centers at Mo and Co sites with electron-deficient centers around the graphene aromatic structure. This multistage DRCs nanocatalyst demonstrated impressive reactivity for in situ generation and synchronized activation of H$_2$O$_2$ at different active centers, resulting in rapid and efficient pollutant degradation (Figure 11c). The reaction rate was ~ 21-fold higher than that of conventional Fenton catalysts. Pollutants served as electron donors throughout the reaction, and were degraded directly in the electron-poor centers of CMS-rGO NSs. Simultaneously, pollutant electrons efficiently transferred to reduce H$_2$O$_2$ in the electron-rich centers (Mo or Co), producing •OH for pollutant removal (Figure 11d,e). The discovery of multi-stage MEF provides a new strategy for enhancing interfacial coupled cation-π interactions.

3.4. Metal-free MEF Driving H$_2$O$_2$ Activation Process

The aforementioned work demonstrated that the synergy of H$_2$O$_2$ with MEF surfaces did not directly depend on the valence change of the metal element but on the strength of the polarization of electronic microregions. The introduction of metal species only served to regulate electron distribution, and therefore, metal species were
not essential for MEF construction. By regulating the electron distribution on metal-free catalyst surfaces, H$_2$O$_2$-assisted metal-free MEFs can be developed. In 2018, non-metallic MEFs were successfully developed on the surface of 4-phenoxyphenol-functionalized rGO nanosheets (POP-rGO NSs) by surface complexation and copolymerization[36]. Experimental and theoretical studies verified the formation of electron-poor/rich microregions on the C-O-C bridge of POP-rGO NSs (Figure 12a,b). The efficient capture of pollutant electrons in the electron-poor C region and the effective reduction of H$_2$O$_2$ in the electron-rich O region were ultimately achieved on this specific metal-free MEF surface. When this metal-free MEF was synergized with H$_2$O$_2$, pollutants were degraded and mineralized quickly in a wide pH range, accompanied by high H$_2$O$_2$ utilization efficiency (Figure 12c). This work greatly expanded the types of H$_2$O$_2$-assisted MEFs and provided new perspectives for the construction of surface MEFs. Subsequently, in the study of 4-phenoxyphenol molecule-doped rGO nanocomposites (rGO-4-PP Nc) [74], we confirmed the formation of C-O-C bonding bridges, electron-rich O regions, and electron-poor C regions through a combination of experiments and DFT calculations. This study provided a theoretical computational basis for guiding practical synthesis and catalytic activity prediction of Fenton-like catalysts and offered an innovative perspective for the development of a new generation of metal-free MEFs by modulating electron distribution using organic polymers.

In summary, both metal substitution and surface complexation can be used to construct effective H$_2$O$_2$-assisted MEFs. Metal substitution is relatively simple for catalyst synthesis and surface modification, while surface complexation is more likely to form strongly enhanced MEFs. Additionally, H$_2$O$_2$-assisted MEFs can significantly increase the Fenton reaction rate while reducing H$_2$O$_2$ consumption. Given these
surface MEF construction strategies, research on H$_2$O$_2$-assisted MEFs for water purification is thriving.

3.5. Other DRC Fenton-like Processes

Based on the application of MEFs in the direction of DRC Fenton-like processes, many groups have continued to develop this theory. Since 2018, Shi’s group has developed a series of efficient DRC catalysts through surface complexation [75,76]. Zhuang et al. utilized GO hydrogels to develop DRC catalysts (α-FeOOH/RGO hydrogels) with a larger specific surface area and more pores for efficient electron transfer through Fe-O-C bonding bridges by modulating α-FeOOH/rGO hydrogels with ethylene glycol (EG) (Figure S4a) [75]. Benefiting from Fe-O-C bonding bridges and defects in specific DRCs, ROS were generated even without H$_2$O$_2$. Moreover, electron transfer from the pollutant to the Fe region on the DRC surface was demonstrated through DFT calculations. N elements were then further introduced into the FeOOH/RGO hydrogel to enhance the formation of dual reaction centers and simultaneously reduce the reduction potential of Fe(II)/Fe(III), which increased the Fenton-like reaction rate (Figure S4b) [76]. In addition, multiple metal species were introduced to the RGO hydrogel system based on single Fe modulation to promote Fe(II)/Fe(III) redox cycling and construct stronger DRCs[77]. Similarly, in research on PVA with α-Fe$_2$O$_3$[78], with Fe$_3$O$_4$@Fe/graphene aerogel (MGA) (Figure S4c) [79], and with Fe/S-doped aerogel (PGFe) [80], Fe-O-C bonding bridges, as well as stable DRCs, were constructed on their surface, resulting in excellent Fenton-like properties. Moreover, in research related to metal-doped substituted DRC (porous Cu-doped alumina (P-Cu-Al$_2$O$_3$) [81]) and metal-free DRC (biomass waste-based graphene (OG) [82]), surface DRCs with significant electron-poor/rich regions were successfully
constructed, which significantly promoted the effective utilization of H$_2$O$_2$ and the pollutant removal reaction rate. In 2018, based on research demonstrating that $\sigma$-Cu ligands formed by phenolic hydroxyl groups and surface Cu could promote the selective degradation of phenolic compounds, Wang’s group successfully constructed DRCs with a stronger electron polarization distribution by introducing the high electronegativity of Bi. The rapid degradation of pollutants and the effective utilization of H$_2$O$_2$ were achieved through the specific DRCs, $\sigma$-Cu-ligand, and OVs (Figure S5a) [83]. In addition, they complexed Cu-Al$_2$O$_3$ with g-C$_3$N$_4$ and C-dots to form the C-O-Cu bonding bridge to construct an enhanced MEF based on the idea of surface complexation (Figure S5b) [84]. Thus, $^*$OH can be generated from the electron-rich region by H$_2$O$_2$ reduction and from the electron-poor region by H$_2$O oxidation, respectively, realizing high H$_2$O$_2$ utilization. In terms of metal doping substitution, Yang’s group successfully constructed Fe-O-Zr bonding bridges[85], Fe-O-Ce bonding bridges[86], and Fe-O-Mn bonding bridges[87] by doping Fe into ZrO$_2$ substrates, CeO$_2$ substrates, and Mn/SiO$_2$ substrates, respectively. All the constructed surface DRCs effectively decomposed H$_2$O$_2$ to remove pollutants, and OVs even promoted O$_2$ reduction in the Fe$_2$O$_3$-CeO$_2$ system. In terms of surface complexation, Chen’s group complexed various metals on different carbon-based substrates to construct a series of different surface DRCs, enabling efficient activation of O$_2$ to produce H$_2$O$_2$ under electrocatalysis, and then efficient utilization of H$_2$O$_2$ in different DRC regions to produce ROS for pollutant degradation[88-91]. Yao’s group constructed Fe-Cu alloy DRCs to achieve rapid pollutant removal[92]. The introduction of Cu strengthened the adsorption of the Fe region on H$_2$O$_2$ and promoted the production of $^*$OH. Yao developed a shorter C-M bonding bridge (Figure S5c)[93] based on the C-O-M bonding bridge (Figure S5d)[94], enhancing the electron transfer between the two
regions of the DRC and achieving rapid pollutant removal. In addition, the direct utilization of electronegativity differences to construct reinforced DRCs has been demonstrated in many works, including reinforced bimetallic-organic framework DRCs[95], in situ enhanced Fe-Cu DRCs[96], and defect-rich CuVOx DRCs[97].

4. MEF-Like Configuration Driving Persulfate Activation for Water Purification

Persulfates, including peroxymonosulfate (PMS) and peroxydisulfate (PDS), are derivatives of H₂O₂ in which the hydrogen atom is replaced by the -SO₃ group. Similar to the DRC Fenton-like reaction involving H₂O₂, MEFs or MEF-like configurations on the catalyst surface also play a crucial role in the field of PMS/PDS activation. Especially for the effective utilization of the electrons from ECs, it is of great significance to reduce the energy consumption and improve efficiency of PMS activation technology for water purification. Representative types of MEFs mainly include: Lattice substitution-induced MEF-like configuration, cation-π-induced MEF-like configuration and metal-free MEF-like configuration.

4.1. Lattice Substitution-Induced MEF-Like Configuration Driving Persulfate Activation Process

Lattice doping is an important means to induce MEFs. In addition to directly causing the non-uniform distribution of electrons, it often promotes the directed transfer of electrons by the formation of vacancies. Acting as electron transfer stations in most redox reactions, oxygen vacancies (OVs) are capable of both accepting and donating
free electrons. For example, through lattice substitution of metal species, OVs-rich
ZnFe<sub>0.8</sub>Co<sub>0.4</sub>O<sub>2.4</sub> nanoparticles with non-uniform electron distribution surface were
obtained and proved by XPS analysis and H<sub>2</sub>-TPR measurements (Figures S6a,b) [16].
It is found that BPA can be quickly degraded within only 4 min in the
ZnFe<sub>0.8</sub>Co<sub>0.4</sub>O<sub>2.4</sub>/PMS suspension, with the reaction rate constant (k) approximately 12-
fold higher than that in the ZnFe<sub>2</sub>O<sub>4</sub>/PMS system (Figure S6c). Interestingly, due to the
DRC effect triggered by OVs, PMS ([O<sub>3</sub>S-O<sub>I</sub>-O<sub>II</sub>-H]) is adsorbed and trapped by
surface OVs in the form of O<sub>I</sub>-OV or O<sub>II</sub>-OV. The free electrons around the OVs can be
rapidly transferred to these O sites for the reduction of PMS, leading to the generation
of •OH, sulfate radical (SO<sub>4</sub>•–), and H<sub>2</sub> (Figure S6d). Meanwhile, pollutants are
adsorbed on metal Co sites, where their electrons are captured and transferred to the
surface OVs, achieving efficient electron recycling (Figure S6e).

Sulfur vacancies (SVs) caused by the inequivalent lattice substitution of Co for Zn
in ZnS QDs framework has also been found to have the function of regulating PMS
activation (Figures S7a-d) [98]. Compared to the ZnS QDs/PMS system, the Co-ZnS
QDs/PMS system exhibited significantly enhanced degradation of ECs, achieving
complete elimination of BPA within only 10 s (Figure S7e). For actual wastewater, the
fluorescence intensity of the fulvic-like compounds significantly decreased, indicating
effective removal of dissolved organic matter and a significant improvement in effluent
biodegradability (Figure S7f). Combining with DFT calculations, the stable adsorption
energies (E<sub>ads</sub>) of PMS on Co and SVs sites were -0.10 and -4.77 eV, respectively,
indicating a preference for PMS adsorption at SVs sites. The stable E<sub>ads</sub> of pollutants
on Co and SVs sites were -1.09 and -1.23 eV, respectively, suggesting that pollutants tended to adsorb at Co sites (Figure S7g). The interfacial reaction mechanism research revealed that driven by the constructed MEF-like configuration, the internal electrons of pollutants were captured by Co sites, which were then transferred to surface SVs for PMS activation. This process facilitated the efficient electron recovery, achieving water purification with high efficiency and low consumption (Figure S7h).

4.2. Cation-π-Induced MEF-Like Configuration Driving Persulfate Activation

Orbital interaction involving metal cation-π is an important form for electron transfer regulation. To accelerate the interfacial electron transfer of PMS for ECs degradation, cation-π-induced MEF-like configuration were constructed for PMS activation/excitation. Shi and Han et al. constructed cation-π-induced MEF-like configurations based on the formation of C-O-M bond bridge structures by the resourcelized conversion of chicken manure into DRC catalyst, which caused an unbalanced electron distribution on the catalyst surface, and allowed PMS to trigger the sustainable electron donation of ECs and electron gain of dissolved oxygen[66,99]. As a result, the systems exhibited excellent performance in removing various ECs with PMS. The degradation rate can even be maintained above 94.3 % after 10,000 cycles (Figures S8a,b). This MEF-like configuration can even efficiently purify actual wastewater, including the effluent from the dyeing and textile industry, pulp and paper industry and the kitchen oil wastewater, with a lower energy consumption.

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Zhang et al. reported a strategy through bonding atomically dispersed cobalt with nanospheric C-based graphene-like structures (SACo-NGs) to form metal cation-π structure, driving rapid and directional transfer of the electrons of pollutants to PMS on the catalyst surface [15]. It is found that Co-π structures (Co\(^{2+}\)-N-C\(_\pi\)) play a key role for the efficient activation of PMS, which results in ECs being greatly removed in a few minutes. During the reaction, pollutants can donate electrons for the system through π-π interaction accompanying by the direct oxidative degradation of pollutants. The obtained electrons are quickly transferred to the atomically dispersed cobalt sites through the formed cation-π structure, which promotes the activation of PMS (Figure S8c). This work demonstrates that single-atom catalysts (SACs) with adjustable coordination environments of metal sites are more conducive to regulating electronic structures and forming cation-π MEF-like configurations on the catalyst surface. Zhao et al. found that the inert element Zn can be turned into an active single-atom catalyst (SA-Zn-NC) by forming an atomic Zn-N\(_4\) coordination structure with cation-π structure on the catalyst surface [67]. During the reaction, electrons are spontaneously transferred from electron-rich contaminants and PMS to single Zn atoms, driving the reduction of DO to O\(_2^{•-}\) and \(^1\text{O}_2\) species over the electron-attracting single-atomic Zn-N\(_4\) site, thereby achieving the efficient elimination of ECs through multi-pathways including self-oxidation and attack by ROSs. In addition, Li et al. demonstrated that a single-atom Cu catalyst with a low N configuration (Cu-N\(_2\)) is more conductive to PDS activation than the saturated Cu-N\(_4\) configuration (Figure 13a) [100]. Benefiting from the generation of Cu (III) that derived from unsaturated Cu-N\(_2\) sites, Cu\(_\text{SA-NC}\) exhibited a
high metal utilization rate, selectivity for pollutant degradation, and resistance to matrix interference (Figure 13b). With the activation of PDS, 2,4-dichlorophenol (2,4-DCP) could be completely removed within 30 min in the CuSA-NC system, whereas only 15–20% of 2,4-DCP was removed in the Cu2O, CuO, and metal-free NC systems (Figure 13c). The results of continuous-flow experiments further demonstrate the good durability of CuSA-NC, making it promising for practical environmental remediation (Figure 13d).

4.3. PMS as Inducer Driving Electron Donation of Pollutants over Metal-free MEF-Like Configuration

The studies above indicate that MEF-like configurations on the catalyst surface play an important role in regulating the selective reduction of PMS without relying on the valence changes of metal species. These finding sheds light on the potential for regulating non-equilibrium electronic structures in metal-free catalysts.

Polyimide (PI) contains a significant number of delocalized π electrons, making it an ideal metal-free catalyst for PMS activation[101,102]. Cao et al. converted PI into L-ascorbic acid doped carbon-nitrogen-oxygen polymer nanoflowers (OvC-CNOP Nfs) with surface MEF structures through hydrothermal cascade pyrolysis processes (Figure S9a)[101]. The doped O atoms induced bidirectional transfer of electrons on aromatic rings through C-O-C bonding [C(π)→O←C(π)] to formed the reinforced O electron-rich centers and electron-poor C(π) centers (Figure S9b), triggering the sustainable electron donation of ECs and high-efficient PMS activation. As the results,
the reaction rate of the O$_{VC}$-CNOP Nfs system was approximately 10-fold higher than that of the unmodified CNOP system, even the refractory endocrine interferon BPA can be completely removed in just 1 min (Figure S9c,d). This work provides a primary reference for the construction of surface metal-free MEFs to drive PMS activation.

Based on the construction strategy of metal-free MEF-like configuration, Li et al. developed the multiporous oxygen-rich carbon-nitrogen nanosheets (OLAA-CN NSs) through a staged temperature-programmed calcination of L-ascorbic acid (LAA)-modified dicyandiamide precursor (Figure 14a)[14]. It is found that the oxygen species from L-ascorbic acid (OLAA) are introduced into the graphene-like basic matrix and replace partial N atoms to form the C-O-C-R structure, leading to the non-uniform distribution of electrons on the catalyst surface, and the formation of surface MEF-like structures according to a series of characterization techniques (Figure 14b). As a result, OLAA-CN NSs exhibits excellent performance for ECs removal in the presence of PMS and DO. Notably, BPA, CIP, and 2-CP can be completely degraded within only 1 min (Figure 14c). An innovative discovery was that PMS mainly played the role of an inducer to drive the donation of the electrons from ECs and these electrons are finally utilized by dissolved oxygen through the interface process (Figure 14d). This is a key progress for reducing resource and energy consumption through the construction of metal-free MEF-like configuration in advanced wastewater treatment.

**4.4. Other MEF-Like Configuration Driving Persulfate Activation**

The construction of MEF-like structures is conducive to generating surface
potential differences that trigger the electron gain and loss processes of persulfate and pollutants in the two polar centers, enabling the synchronous occurrence of oxidation and reduction reactions. However, implementing the construction of this potential difference on the surface of many inert materials is challenging.

It has been discovered that the photo-assisted process enhances the potential difference, facilitating rapid persulfate activation, efficient pollutant degradation, and resolving the issue of photogenerated electron-hole recombination in photocatalysis. Wang et al. developed a nanoscale iron molybdate (Fe$_2$(MoO$_4$)$_3$) catalyst by introducing metal atoms into molybdate nanoparticles to induce the unbalanced electron distribution on the catalyst surface, thereby constructing the MEF-like structures[103]. Based on the Fe$_2$(MoO$_4$)$_3$ system, BPA (10 ppm) can be rapidly degraded through the heterogeneous photo-combined PDS activation (HPPA) process, and the degradation rat increased 98-fold compared to that without light (Figures S10a,b). Combined with the electrochemical characterization, the instantaneous photocurrent of the Fe$_2$(MoO$_4$)$_3$/PDS/light system was increased 5 fold compared to that of the original Fe$_2$(MoO$_4$)$_3$ electrode system (Figure S10c), accompanied by the smallest arc radius in the EIS Nyquist plot (Figure S10d). During the HPPA reaction, PDS and DO molecules are rapidly activated and generated SO$_4$$^-$/OH and O$_2$$^-$ radicals by capturing photogenerated electrons at CB (electron-rich centers) and driving the electron-donor of ECs around electron-poor centers at VB (holes) through $\pi$-$\pi$ interaction. This synergistic process not only inhibited the electron-hole recombination but also enabled rapid dual-pathway degradation of pollutants through free radical attack and hole
oxidation (Figure S10)[103]. In actual systems, the formation of MEF-like structures on the catalyst promotes the utilization of abundant DO and pollutant energy in water, significantly reducing PDS consumption and achieving efficient water purification triggered by trace PDS. This approach is cost-effective and feasible. Other interesting studies[104,105] reported that the selective regulation of photo-assisted reaction process can be achieved by introducing metal atoms into the catalyst to cause the change of the surface electronic structure, leading to efficient PMS activation and ECs degradation.

5. MEF-like Configuration Driving Photocatalysis for Water Purification

Semiconductor photocatalysis is a promising advanced oxidation technology for water treatment that utilizes clean solar energy[106-108]. For photocatalysis, lattice substitution, vacancy introduction, and functional group grafting are effective methods to polarize surface charge distribution for MEF construction. MEF not only promotes the separation and transfer of e⁻/h⁺ but also strengthens the electron donation from adsorbed pollutants, which modifies the energy band structure of the catalyst. Some studies have proposed the concept of an internal electric field (IEF) formed by polarizing the charge distribution in local microregions. The construction mechanism is similar to that of MEF, so this type of IEF can be considered equivalent to MEF. It should be noted that the IEF formed by a heterogeneous structure on large-scale interfaces differs from the MEF, as discussed in this review.
A dual-oxygen group (C-O-C and C=O) doped CN (ACN*) was synthesized using N lattice insertion for the photocatalytic degradation of pollutants (Figure 15a)[109]. Due to the strong electronegativity of O elements, the O atoms in the C-O-C and C=O groups exhibited higher valence-electron densities than the C and N atoms in the g-C3N4 skeleton. This constructed the surface MEF in ACN* and provided a direct surface driving force to promote the separation and transfer of e⁻/h⁺ (Figure 15b). More importantly, the electron-poor area could strengthen the adsorption of aromatic pollutants and promote direct electron delocalization from the pollutant to the catalyst. The adsorbed pollutants have been integrated with ACN* and regulated the band structure of ACN*. The photocurrent intensity of ACN* with pollutant adsorption was 2-3 times higher than that of ACN*. Moreover, more O₂⁻ was generated with the assistance of pollutant adsorption for pollutant degradation (Figure 15c-e).

Additionally, defects of catalysts tend to intensify the uneven distribution of electrons and promote the construction of surface MEFs. We prepared a partially low-polymerized g-C3N4 (LCN) with more C-NH₄ exposure by attacking oxygen-doped g-C3N4 with high-temperature vapor[110]. Increased C-NH₄ exposure reinforced the charge polarization distribution to construct surface MEFs. In this case, the electron-rich area was centered at C-NH₄, while the electron-poor area was distributed at the C-N skeleton. The surface MEFs reinforced the interaction between pollutants and catalyst, further promoting electron delocalization from the pollutant to the catalyst (Figure 15f,g). The optical absorption intensity of LCN_BPA was further extended in the visible-light range compared to that of LCN (Figure 15h), and the separation and transfer
efficiency of e\(^{-}\)/h\(^{+}\) (Figure 15i) were also significantly improved. These results indicated that the adsorbed pollutant modified the energy band structure and could be directly excited by light irradiation, accompanied by the cleavage of pollutant molecules. Additionally, owing to surface MEFs, more O\(_2\cdot\cdot\cdot\) was generated in g-C\(_3\)N\(_4\) with C vacancy defects (HTCN) by the modification of pollutant adsorption (Figure 15j). This finding indicates that the energy of the pollutant molecule was utilized by the photocatalytic system[111].

Lattice doping can also be performed on inorganic photocatalysts. Interstitial carbon-doped Bi\(_3\)O\(_4\)Cl (C-doped Bi\(_3\)O\(_4\)Cl) nanosheets were synthesized with glucose as a carbon source, exhibiting a 126-fold increase in IEF between layers due to carbon introduction into Bi\(_3\)O\(_4\)Cl[112]. The interlayer IEF drove electrons and holes transfer from e\(^{-}\)/h\(^{+}\) separation sites to the [Bi\(_3\)O\(_4\)] and [Cl] slices for surface reactions (Figure 16a). Our group reported a layered structural BiOBr doped with sulfur (S-BiOBr)[46], consisting of covalent [Bi\(_2\)O\(_2\)S\(^{2+}\)] layers and exchangeable bromide ions [Br\(_2\)]\(^{2-}\). Due to the lower electronegativity of the S atom than that of the Br atom, a strong interlayer IEF was constructed between the covalent [Bi\(_2\)O\(_2\)S\(^{2+}\)] layers and exchangeable bromide ions [Br\(_2\)]\(^{2-}\), which acted as a driving force for charge carrier separation and transport (Figure 16b). Notably, after 30–60 s of illumination, CIP could be continuously degraded in the S-BiOBr suspension in the dark condition (Figure 16c), and the signal of BMPO-\(O_2\cdot\cdot\cdot\) in the S-BiOBr suspension with CIP adsorption was significantly enhanced (Figure 16d). With the assistance of the enhanced IEF, electrons arising from the R\(^{\ast}\) radical could be sequentially transferred to the S-BiOBr, where O\(_2\) was reduced.
to O$_2^{•−}$, acting as a major contributor to CIP oxidation in the dark condition.

Grafting electron-withdrawing/donating moieties onto organic photocatalysts via molecular copolymerization can promote the polarization of charges in organic photocatalysts due to the unique flexibility of organic semiconductors[113]. Molecular copolymerization differs from conventional semiconductor heterojunctions, which builds up an IEF at the two-phase interface[114]. Similar to surface MEFs, countless charge polarization regions can be formed on a smaller scale and evenly distributed in catalysts between the electron-donating and accepting moieties. Fan et al. incorporated aromatic rings into g-C$_3$N$_4$ by connecting them with 3s-triazine units, effectively facilitating charge transfer and separation[115]. Chen et al. also prepared an aromatic ring-terminated g-C$_3$N$_4$ (ARCNSs) via a one-step copolymerization approach with quinazoline-2,4-diamine as the precursor of the terminated aromatic rings, which extended the electron delocalization of g-C$_3$N$_4$[116]. Furthermore, Chu et al. incorporated an electron-deficient pyromellitic dianhydride (PMDA) monomer into the skeleton of g-C$_3$N$_4$ (Figure S11a)[117]. The two electron-withdrawing anhydride groups in PMDA not only separated the reduction and oxidation sites but also promoted a shift of the negative region from melem to the O atoms of PMDA, which enhanced the separation and transfer of h$^+$/e$^−$ for MO degradation (Figure S11b-d). Perylene plane series materials are also ideal photocatalysts for adjusting the delocalized $\pi$-electrons by introducing electron-withdrawing groups[118]. Perylenetetracarboxylic acid nanosheets (PTA) were synthesized via a simple hydrolysis reassembly of PTCDA.

The $\pi$ orbital of the PTCDA molecule was evenly distributed on the entire molecular...
plane, whereas a nodal plane appeared on the $\pi$ orbital of the PTA molecule between the perylene plane and the carboxyl group (Figure S11e). The electron cloud mainly centered at the carbonyl oxygen in PTA, and the excited charge density difference of PTA was $4.53 \times 10^{-3}$ eV Å$^{-3}$, which was significantly stronger than that of PTCDA $(0.97 \times 10^{-3}$ eV Å$^{-3}$) (Figure S11f). The intensity of the electric field between the perylene plane and the terminal carboxyl group in PTA was approximately 10.3 times that of PTCDA, efficiently producing anisotropic charge migration to promote surface reactions (Figure S11g,h). In fact, the IEF on two-dimensional layered materials can be classified as a surface MEF. However, most of the above studies focused on hydrogen or H$_2$O$_2$ production by utilizing the IEF/MEF for charge transfer, neglecting the role of electron-rich and the electron-poor areas. The interaction between the pollutant and electron-poor area and the utilization of the pollutant were not considered during the pollutant degradation process. Therefore, the further development and comprehensive utilization of surface MEFs have great prospects in the field of photocatalytic water treatment.

6. MEF Driving Water Self-Purification by Internal Energy Utilization

6.1. MEF driving surface pollutant conversion and oxygen reduction

Previous research has confirmed that constructing MEFs by modulating the surface structure of catalysts can drive the energy utilization of organic pollutants for water purification. However, efficient pollution degradation in such a process still
requires a small amount of oxidant or additional energy assistance. Additionally, we have found that the electrostatic force of surface MEFs on the catalyst is crucial for the energy utilization of organic pollutants. Inspired by this discovery, we have hypothesized that further directional modulation of the catalyst surface structure could enhance the MEF potential difference and strengthen the adsorption of surface molecules on MEFs. This, in turn, could weaken their chemical bonding energy through strong surface orbital interactions. Under such conditions, it might be possible to trigger interfacial chain reactions using weak electron acceptors such as O$_2$ to achieve a self-purification process of wastewater.

Based on this assumption, a novel and efficient surface MEF was created using the lattice substitution method on 3D pomegranate-grain-like nanoparticle-integrated molybdenum (Mo) lattice-doped zinc sulfide (ZnS) composites (MZS-1)[25]. The (002) crystalline plane of MoS$_2$ was observed, and the Raman peaks for Zn-S bond vibration showed a blue shift after introducing Mo in ZnS (Figure 17a,b), confirming the formation of Mo-S-Zn bonding bridges in MZS-1. Doping Mo in the lattice of ZnS induced electron transfer from Zn to Mo through the Mo-S-Zn bonding bridge, driven by their electronegativity difference. Thus, the non-equilibrium distribution of electrons on the MZS-1 surface was enhanced, resulting in a strong surface MEF (Figure 17c). Notably, the MZS-1 system achieved over 80% catalytic efficiency for RhB even after continuous operation for 168 h (Figure 17d). Pollutants were easily chemisorbed on surface MEF to form a strong interfacial interaction during the reaction. They then donated electrons to the catalyst surface to be oxidized by the delocalized $\pi$-$\pi$ conjugation effect. Additionally, the complexation between DO and MEF effectively reduced the activation energy barrier of O$_2$, making it easier to activate O$_2$ into ROS.
(·OH, O2\(^{•−}\) and \(^{1}\)O\(_2\)) by utilizing delocalized electrons and energy in the electron-rich Mo area (Figure 17e). Thus, the entire RhB elimination process involved two independent processes (Figure 17f): direct oxidation due to the electron delocalization effect and oxidative degradation by ROS. This study achieved sustainable DO activation for water purification by utilizing the energy of pollutants through surface MEF, which provides new insight into developing low-energy consumption and sustainable wastewater treatment technology.

On this basis, Cao et al. further enhanced the nonequilibrium electron distribution on an nZVI/FeO\(_x\)/FeN\(_y\)-anchored NC composite (nZVI/FeN\(_{5.5}\)O\(_{7.2}\)/C) surface by constructing cation-π bonds[70]. Based on EXAFS and EPR results (Figure S12a,b), iron species were produced in situ in the NC composites through Fe-O-C and Fe-N bonding bridges, which transferred electrons from C(π) and N to Fe simultaneously (N → Fe ← π) through these bonding bridges. This resulted in the formation of a strengthened surface MEF comprising electron-rich Fe microcenters (ERCs) and electron-poor C(π)/N microcenters (EPCs) on nZVI/FeN\(_{5.5}\)O\(_{7.2}\)/C. During the reaction, the surface-adsorbed organic pollutants formed an enhanced π-π molecular orbital interaction with EPCs, followed by electron delocalization, transferring delocalized electrons to ERCs through cation-π bonds (Figure S12c), and being oxidized, leading to rapid microreduction of O\(_2\) into O2\(^{•−}\) around ERCs of MEF (Figure S12d). Based on these enhanced MEF surface characteristics, nZVI/FeN\(_{5.5}\)O\(_{7.2}\)/C showed exceptionally high activity and efficiency (62–100%) for degrading both dyes (RhB and methylene blue (MB)) and refractory pollutants (BPA, CIP, and 2-CP) within 2–60 minutes at room temperature and atmospheric pressure (Figure S12e,f). Notably, this process was free from interference by NOM in sand filter water, indicating the potential application prospects of nZVI/FeN\(_{5.5}\)O\(_{7.2}\)/C (Figure S12g). This finding provides new insight for
addressing the key limitation of the classical wet air oxidation process through the MEF-type catalytic system.

The aforementioned studies confirm that the electrostatic force of surface MEFs on a catalyst is key to the energy utilization of organic pollutants. Han et al. creatively constructed a dual-stage MEF structure consisting of a dual-stage electron-poor and electron-rich microregion on the CMS-rGO NSs surface[57], generating particularly strong electrostatic forces. This unique structure enabled CMS-rGO NSs to possess a wide working pH range and approximately 75–100% degradation efficiency for RhB, MB, methyl orange (MO), and AO7 without adding any other substance or assistance to the CMS-rGO NSs suspension (Figure S13a,b). Moreover, 98% RhB removal was achieved within 60 min, even after 7 successive cycle runs (Figure S13c), indicating the excellent stability of CMS-rGO NSs. By utilizing strong surface MEFs, H2O was readily adsorbed at the electron-deficient center and delocalized electrons to the electron-rich Mo/Co centers, where it was oxidized into •OH. These delocalized electrons could also be trapped by O2 to form HO2*/O2*− and H2O2 at the electron-rich Mo/Co centers. Additionally, the organic pollutant could replace the adsorbed H2O and form a surface-confined non-equilibrium electron orbital with the electron-deficient graphene aromatic structure area of MEF through strong π-π molecular orbital interactions. Consequently, the adsorbed pollutants could directly delocalize electrons to the electron-rich Mo/Co centers by strong electrostatic force, continuously reducing O2 (O2 → O2*− → H2O2 → •OH) for pollutant degradation. In the process, efficient pollutant destruction was achieved through two pathways (Figure S13d): direct degradation by MEF and •OH attack. This discovery provides a new strategy for H2O2 generation-activation and pollutant degradation by constructing MEFs on the catalyst surface.
These studies demonstrated that a strong surface MEF enables the utilization of pollutant electrons with the assistance of O$_2$. Typically, these MEFs were constructed in one or two phases through single or double chemical bonding bridges. However, if the electrostatic force of the surface MEF could be further enhanced by constructing a heterogeneous structure with multistage cation-π interactions, the destruction and mineralization of pollutants could be achieved through a self-purification process on the catalyst surface. Using surface complexation and electron polarization theory, an iron-based composite catalyst (Fe$^0$-Fe$_x$C$_z$/Fe$_x$-GZIF-8-rGO) was successfully developed (Figure 18a)[34]. The series of characterization results confirmed that the Fe-O-C, Fe-N, and C-O-Zn-N chemical bond bridges were formed among the three phases (Fe$^0$-Fe$_x$C$_z$/Fe$_x$, GZIF-8, and rGO) of Fe$^0$-Fe$_x$C$_z$/Fe$_x$-GZIF-8-rGO, resulting in the formation of strong (Fe or Zn)-π electrostatic force. Therefore, a dual-stage MEF consisting of the electron-rich areas around Fe species and the electron-deficient areas around GZIF-8/rGO was formed on the catalyst surface with a surface potential energy of 310.97 ~ 663.96 kJ/mol (Figure 18b). As a result, in the Fe$^0$-Fe$_x$C$_z$/Fe$_x$-GZIF-8-rGO air-saturated suspension, 27.4 ~ 67.5% total organic carbon (TOC) removal of various pollutants was achieved within 180 min without additional energy assistance (Figure 18c). The same catalytic efficiency as that under the air-saturated condition was achieved under the N$_2$-Fe$^{3+}$ condition, but not in the N$_2$ and Cu$^{2+}$ conditions (Figure 18d). The results indicated that the surface MEF could complex the pollutants by forming strong π-π and H-bonding molecular orbital interactions, thereby reducing their chemical bonding energy to ~ 0.7 eV and delocalizing their electrons to the catalyst surface, leading to the surface cleavage of the adsorbed pollutants. Additionally, under the action of the strong surface MEF, O$_2$/Fe$^{3+}$ was confined to adsorb at the electron-rich Fe species area and trap delocalized electrons to form O$_2^•$/Fe$^{2+}$ (Figure 18e).
triggering the hydrolytic process of adsorbed pollutants with H$_2$O, continuously converting H$_2$O into •OH (Figure 18f) for water purification. This work has opened a new avenue for the development of sustainable wastewater self-purification treatment technologies that utilize pollutant energy driven by surface MEF.

### 6.2. MEF driving the selective preferential removal of micropollutants from wastewater

Natural organic matter (NOM), a significant source of dissolved organic carbon (DOC) in water, negatively impacts water purification. However, removing NOM using current water treatment technologies remains a scientific challenge. After confirming the stability and high catalytic efficiency of MEF on Fe$^0$-Fe$_y$C$_z$/Fe$_x$-GZIF-8-rGO, humic acid (HA) (10 mg/L) was also found to be highly degraded over Fe$^0$-Fe$_y$C$_z$/Fe$_x$-GZIF-8-rGO (Figure S14a) [119]. However, the mineralization of HA underwent three stages within 480 min (Figure S14b). It was found that HA complexed with the electron-poor rGO/GZIF-8 area through $\pi$-$\pi$ and H-bonding molecular orbital interactions, delocalizing their electrons to electron-rich Fe species areas through cation-$\pi$ bonding bridges. This process results in complete cleavage of HA into a few aromatic ring compounds and a large number of alcohols and alkanes within 120 min. After 120 min, the generated alkane adsorbs on alcohol to form a strongly polarized alkane-alcohol complex, including electron-rich hydroxyl group areas in alcohol and electron-poor areas in alkane (Figure S14c,d). Consequently, the electron-rich hydroxyl group area in alcohol tended to adsorb at the electron-poor rGO/GZIF-8 area to form a strong H-bonding interaction, promoting electrons from alkane to delocalize directly to the electron-rich Fe species area of MEF. This process accelerates interfacial electron cycle transfer (Figure S14e). The delocalized electrons trapped by O$_2$ at the electron-rich Fe
area of MEF trigger the alkane’s surface cleavage and hydrolytic process, leading to more \(^{•}\)OH generation for reactant degradation (Figure S14f). This finding enhances our understanding of the significance of the surface complex characteristic of surface MEF and provides new insights into complex mixture-containing water purification utilizing an O\(_2\)-assisted MEF catalytic system.

Due to the competition of mg-level DOC, the complete removal of micropollutants in water remains a significant international challenge. It was reported that DOC can adsorb micropollutants through its rich functional groups to form a polymeride[120]. Inspired by the interfacial interaction mechanism between surface MEF and the polarized alkane-alcohol complex, the preferential destruction of micropollutants from DOC-containing water was achieved by investigating the interaction of micropollutants with HA/DOC in synthetic and real wastewater under the action of MEF[29]. As depicted in Figure 19a,b, compared with the Fe\(^0\)-Fe\(_y\)C\(_z\)/Fe\(_x\)-GZIF-8-rGO suspension, the degradation efficiencies of various pollutants increased in the Fe\(^0\)-Fe\(_y\)C\(_z\)/Fe\(_x\)-GZIF-8-rGO/HA suspension, and a higher degradation efficiency was observed in municipal wastewater and raw drinking water (Figure 19c,d). According to the three-dimensional excitation/emission matrix and EPR analysis, and DFT calculation results, we first reported that micropollutants tended to form a polar HA/DOC-micropollutant complex with HA in synthetic wastewater through \(\pi-\pi\) electrostatic force (Figure 19e), consisting of an electron-poor aromatic structure area of the micropollutant and an electron-rich phenolic group area of HA in the complex. During the reaction, a strong orbital interaction occurred between the electron-rich phenolic group area of HA in the HA/DOC-micropollutant complex and the electron-poor rGO/GZIF-8 area of Fe\(^0\)-Fe\(_y\)C\(_z\)/Fe\(_x\)-GZIF-8-rGO, forming a surface-confined nonequilibrium electron orbital with MEF. This surface-confined nonequilibrium electron orbital greatly enhanced the
electrostatic interaction between the complex and MEF. Consequently, due to the enhanced electrostatic force, the micropollutants in the complex preferentially transferred more electrons across the HA/DOC media to the electron-rich Fe area (Figure 19f) and were oxidatively cleaved, thereby enhancing the electron transfer between MEF and the HA/DOC-micropollutant complex. With the delocalized electrons were continuously trapped by O₂ (Figure 19g), the surface cleavage and hydrolysis processes of micropollutants in the HA/DOC-micropollutant complex were carried out at the electron-poor rGO/GZIF-8 area of MEF, converting more H₂O into *OH (Figure 19h). Therefore, the preferential destruction and mineralization of micropollutants in real water were achieved through the above chain reaction process. This work developed a novel catalytic system that achieved the preferential degradation of micropollutants through a self-purification process by utilizing MEF on the catalyst surface, which is very promising for future combined micropollution-water purification. In addition, many researchers have devoted significant effort to the self-purification of pollutants by modulating the surface structure of catalysts to drive O₂ activation. Gu et al. constructed a diatomic site on a dual-adjacent Fe atom-doped MnO₂ catalyst[121]. The surface structural properties enabled CO to be confined and adsorbed on the Mn site of MnO₂ (Figure S15a). Furthermore, the surface dual-adjacent Fe atoms were able to absorb O₂ to form a strong chemical bond of Fe(O = O)Fe. The feedback π electrons of the Fe d-orbital were then transferred to the vacant orbital of O₂, reducing the chemical bond energy of O₂. Therefore, the O atom in Fe(O = O)Fe tended to bond with the carbon atom in CO and then desorption to form CO₂, with an activation barrier of only 0.17 eV. Gong et al. developed a Zn-carbon nanotubes (CNTs) composite by directly sintering a mixture of zinc and CNTs [122]. During the reaction, Zn was found to donate electrons to the CNT area and was oxidized into ZnO. Meanwhile, the surface-
adsorbed O\textsubscript{2} was driven by the potential drive of the internal electrolysis of Zn to capture electrons and undergo a two-electron conversion process on CNTs, producing a large amount of H\textsubscript{2}O\textsubscript{2} for wastewater treatment without additional assistance. Lyu et al. reported a novel catalyst consisting of Pd subnanoparticles encapsulated by hierarchical TS-1 (HTS-1) for the selective oxidation of benzyl alcohol\cite{123}. In addition to the benzoic acid chemically adsorbed on Pd sites, some H\textsubscript{2} and O\textsubscript{2} tended to strongly interact with Pd sites and were dissociated to form reactive intermediates (MARI) containing a single H/O atom (H\textsuperscript{*} and O\textsuperscript{*}). More O\textsubscript{2} was chemically adsorbed on the Ti sites and formed MARI containing an intact O–O bond (OO\textsuperscript{**}), which was then converted into H\textsubscript{2}O\textsubscript{2} with the adsorbed intermediate H\textsuperscript{*}. The generated H\textsubscript{2}O\textsubscript{2} subsequently complexed with Ti\textsuperscript{4+} sites to form Ti-OOH active species for the efficient oxidation of benzyl alcohol. Li et al. reported that Co\textsubscript{3}O\textsubscript{4} complexed with carbon (C-Co\textsubscript{3}O\textsubscript{4}) caused a disorder on the surface lattice of Co\textsubscript{3}O\textsubscript{4}, constructing a large number of exposed active sites of electron-rich OVs and Co\textsuperscript{3+} on the catalyst surface\cite{124}. Formaldehyde (HCHO) was readily chemisorbed on the Co\textsuperscript{3+} sites through a strong interaction and was converted into dioxymethylene (Figure S15b). Meanwhile, O\textsubscript{2} and H\textsubscript{2}O were able to capture electrons from the electron-rich OVs area to effectively form activated O\textsubscript{2} and OH for the continuous mineralization of surface-adsorbed dioxymethylene. The above research achieved the self-purification of pollutants by modulating the surface structure of catalysts to drive O\textsubscript{2} activation, which was a little bit similar to the surface MEF effect. Although the researchers did not summarize the characteristics and role of the surface structures of these types of catalysts in the articles, these findings provided significant inspiration for the successful design and construction of MEF on the catalyst surfaces.
7. Conclusions and Outlooks

MEFs constructed on the surface of catalysts using various methods have been widely used to drive pollutant degradation in various technical fields, including Fenton processes, photocatalysis, PMS activation, catalytic ozone oxidation, and water self-purification through internal energy utilization. This has significantly enhanced efficiency and reduced consumption during the degradation of ECs. In particular, the advent of MEF-based self-purification technology has greatly reduced the energy consumption of water treatment in response to the global goal of carbon neutrality. Moreover, MEF-containing catalysts often exhibit high structural stability even after multiple consecutive cycles of pollutant degradation, as confirmed by results from inductively coupled plasma mass spectrometry (ICP-MS), X-ray diffraction (XRD), XPS, and $^{57}$Fe Mössbauer spectra [34, 59, 69]. Recently, electrochemical methods have been used to test the stability of MEF, with results showing that the corrosion current density of the MEF-containing catalyst decreased from 10.99 $\mu$A/cm$^2$ to 4.67 $\mu$A/cm$^2$ after reacting with pollutants, indicating corrosion inhibition. In contrast, the conventional Fe-C catalyst exhibited a significant increase in this value from 20.82 $\mu$A/cm$^2$ to 120 $\mu$A/cm$^2$ [119]. These results confirm that the surface MEF stability is significantly strengthened due to the cation-$\pi$ interaction and the electron-donating effect of pollutants during the reaction. This is the key to achieving continuous and efficient water purification using MEF-containing catalysts. This technology is revolutionary and forward-looking, with great development potential, providing a fast track for the development of low-energy water treatment technology. It is also of great scientific significance and practical value in treating compound micro-polluted water by achieving preferential and selective removal of ECs through precise modulation of
surface MEF.

In the future, the development of MEF faces significant challenges, particularly in terms of adaptability to complex environmental media and expansion into multidisciplinary fields. The primary development directions of MEF are: I) Development of an accurate construction technology for MEF based on the REDOX potential of reactants. At present, the characteristic construction of MEF has been realized for the degradation of some types of ECs, such as antibiotics, endocrine interferons, pesticides, and synthetic dyes. However, it remains challenging to construct the REDOX potential accurately based on the specific environmental factors involved in the reaction, which is the bottleneck that needs to be overcome in the future; II) Precise regulation and modification of multistage MEF at the atomic orbital level. Currently, research on regulating and constructing single-stage MEF is simple and productive. However, pollutants in actual water environments and wastewater are diverse and complex, requiring the construction of multistage MEF to meet the needs of actual complex pollution; III) Research on the impact of complex environmental media, such as salt, acid-alkali, temperature, and suspended nanoparticles, on MEF and the development of innovative avoidance strategies. This is necessary to address actual water treatment needs; IV) Application development outside the field of water purification, including energy, agriculture, medical technology, and intelligent manufacturing. The application of MEF is not limited to the environmental field, as it represents a fundamental theory of surface electron polarization distribution, which is the cornerstone of regulating ordered molecular reactions and can contribute to the development of multidisciplinary fields.
**Data availability**

The data are available from corresponding authors upon reasonable request.

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**Author contributions**

Lai Lyu designs the structure of this review, writes the sections of Abstract, Introduction, Construction and Properties of Surface MEF on Catalyst, and Conclusions and Outlooks, and revises and edits the full text. He is responsible for the coherence of the full text.

Yumeng Wang writes the sections of Construction and Properties of Surface MEF on Catalyst, and MEF Driving Water Self-Purification by Internal Energy Utilization.

Chao Lu writes the section of MEF Driving DRC Fenton-like Process for Water Purification.

Fan Li writes the section of MEF-like Configuration Driving Photocatalysis for Water Purification.

Wenrui Cao writes the section of MEF-Like Configuration Driving Persulfate Activation for Water Purification.
Yingtao Sun is responsible for the drawing and presentation of visualizations.

Chun Hu incubats the idea for the topic, designs the structure of this review, and directs the writing of the full parts. She is responsible for the review and revision of the full text.

**Conflict of interest**

The authors declare no conflict of interest.

**Supplementary information**

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Figure 1. Common interfacial reaction mechanism of the MEF-based technologies.
Figure 2. Molecular orbitals obtained from linear combination of atomic orbitals (LCAO) in molecules.
Figure 3. Schematic diagram of electron cloud density distribution on $d$-TiCuAl-SiO$_2$ Ns. Adapted with permission from Ref. [125], copyright 2017 Progress in Chemistry.
Figure 4. (a) TEM image and FESEM of DCAS Ns. (b) Schematic illustration of pollutants or H$_2$O$_2$ in contact with the catalyst with the active component in the bulk, the multiporous catalyst and DCAS Ns. (c) XPS spectra for Cu 2p$_{3/2}$ for DCS Ns and Cu 2p$_{3/2}$ for DCAS Ns. (d) EXAFS curve fitting of DCS Ns and DCAS Ns (solid line-experimental signals, dotted line-fitted curves). (e) BPA degradation and TOC removal in different suspensions with H$_2$O$_2$. (f) H$_2$O$_2$ decomposition and the utilization efficiency of H$_2$O$_2$ during the degradation of BPA in the DCAS Ns suspension. (g) BMPO spin trapping ESR spectra recorded at ambient temperature for various DCAS Ns samples with H$_2$O$_2$ in aqueous dispersion for BMPO–*OH and in methanol dispersion for BMPO–HO$_2$*/O$_2$•: (1) fresh DCAS Ns; (2) DCAS Ns adsorbed BPA; and (3) DCAS Ns used for 15 min in the Fenton reaction with BPA. Adapted with permission from Ref. [9], copyright 2016 The Royal Society of Chemistry.
Figure 5. (a) Fourier transforms of k$^3$-weighted EXAFS oscillations obtained at the Cu K-edge of the various samples. (b) Solid EPR spectra of various samples. (c) Cu 2p$_{3/2}$ XPS spectra for d-TiCuAl-SiO$_2$ Ns, d-Cu-SiO$_2$, Ns d-CuAl-SiO$_2$ Ns and Ti 2p XPS spectra for d-TiCuAl-SiO$_2$ Ns. The inset shows the LMM X-ray induced Auger parameter for the sample. (d) CV of various electrodes prepared from the corresponding samples. (e) Fenton catalytic degradation of BPA in various suspensions at initial pH 7. (f) The utilization efficiency of H$_2$O$_2$ in the d-Cu-SiO$_2$ Ns, d-CuAl-SiO$_2$ Ns and d-TiCuAl-SiO$_2$ Ns suspensions. The inset shows the corresponding decomposition of H$_2$O$_2$. Adapted with permission from Ref. [27], copyright 2016 The Royal Society of Chemistry.
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Supporting Information

for

Potential and Prospects in Molecular Orbital Level Micro-Electric Field for Low Energy Consumption Water Purification

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