Single atom catalysts for heterogeneous catalytic ozonation

Yizhen Cheng[1,2], Zhonglin Chen[1], Shaobin Wang[2] and Xiaoguang Duan[2]

Single atom catalysts (SACs) have received soaring interest in environmental applications due to their ultrahigh atomic efficiency and drastically reduced metal loading. In this review, we summarized the preliminary efforts in applying SACs for heterogeneous catalytic ozonation (HCO). Mechanistic analyses revealed a creditable consensus that highly dispersed active single atoms can accelerate the decomposition of ozone (O_3) into surface-adsorbed *O and free O_2. However, the activity of SAC toward O_3 decomposition varies, depending on the central metal species and coordination environment. In this review, we discussed the synthesis and characterization of SACs, emphasizing their application and catalytic regimes in HCO. Also, limitations and prospects of SAC-based HCO were proposed to shed light on future studies.

Addresses
[1] State Key Laboratory of Urban Water Resources and Environment, School of Environment, Harbin Institute of Technology, Harbin 150090, China
[2] School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

Corresponding author:
Duan, Xiaoguang (xiaoguang.duan@adelaide.edu.au)

Introduction

To address the deteriorating environmental issues, it is highly imperative to advance modern decontamination technologies to realize high efficiency in a sustainable manner. Advanced oxidation processes (AOPs) are advantageous to rapidly oxidizing refractory pollutants by producing diverse reactive oxygen species (ROS), such as hydroxyl radical ($^{\bullet}OH$, 1.8–2.7 V) [1], sulfate radical ($SO_4^{\bullet-}$, 2.5–3.1 V) [2], superoxide radical ($O_2^{\bullet-}$, 1.7 V) [3], and singlet oxygen ($^1O_2$, 0.81 V) [4]. Notably, strengthening the interfacial interaction between catalysts and oxidants is the key to activating peroxide for ROS production [5]. Although homogeneous catalysts exhibit an excellent activity and are easy to define the active centres, their poor stability and non-recyclability hinder further application in environmental remediation [6,7]. In this regard, heterogeneous catalysts that can be assembled into bulky structures with well-designed catalytic sites are endowed with more applicability.

Single atom catalysts (SACs) are emerging heterogeneous catalysts, rendering the high dispersion of atomic metal sites on the supporting materials. Different from the conventional metal oxides, SACs with atomic-level dispersion and strong metal-substrate electronic interactions overcome the dilemma of metal agglomeration and leaching [8,9]. Likewise, anchoring metal atoms onto carbonaceous support can minimize the usage of metal and effectively remedy the friability of carbon materials in the oxidative environment [10••]. Due to the maximum exposure of metal sites and unique electronic properties, SACs displayed an outstanding catalytic activity in AOP systems, for example, ozonation, photocatalysis, and Fenton-like processes [11,12].

Unequivocally, O_3 oxidation is a typical and extensively implemented AOP technology for pollutant abatement [13]. Compared to the single ozonation process, heterogeneous catalytic ozonation (HCO) can fundamentally mineralize recalcitrant organics via not only direct ozonation but also indirect catalytic oxidation harnessing ROS [14]. However, low O_3 utilization efficiency and susceptibility to bicarbonate interference ($k_{\cdot OH/HCO_3^-} = 8.5 \times 10^6 M^{-1}s^{-1}$) are bottlenecks of the HCO technology, preventing it from industry-scale applications [15]. Inspiringly, Wang et al. reported that single-atom Co anchored on graphite carbon nitride (g-C_3N_4) were conducive to O_3 decomposition and generation of both solution hydroxyl radical ($^{\bullet}OH_{free}$) and surface-adsorbed hydroxyl radical ($^{\bullet}OH_{ad}$) [16••]. Shokuhi Rad et al. also suggested that single-atom Pt had a great potential to adsorb O_3 for catalytic activation [17]. To date, SACs have exhibited appealing advantages in catalytic ozonation in light of strengthening the binding of O_3 with the active metal sites and subsequent evolving diverse ROS for accelerated oxidation kinetics with deeper mineralization efficiency.

Figure 1
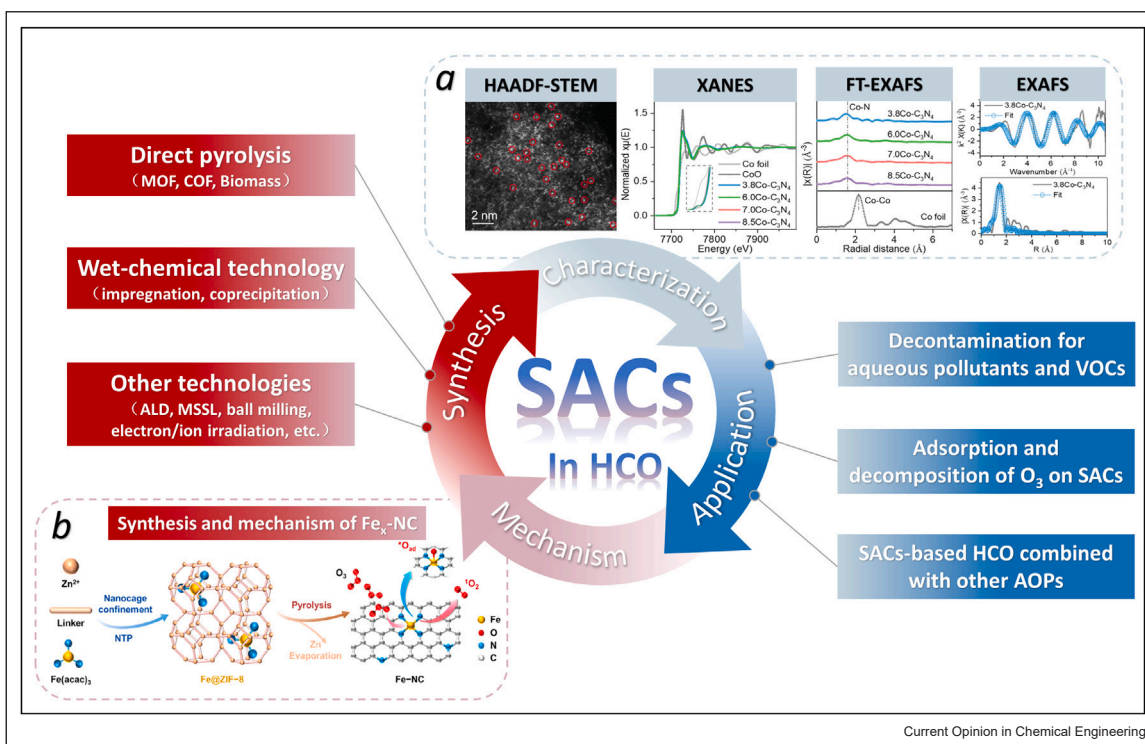
Synthesis, characterization, and application of SACs-based HCO.
Reprinted with permission from **(a)** Ref. [62] Copyright 2023 John Wiley and Sons and **(b)** Ref. [43] Copyright 2023 American Chemical Society.

However, the exploration of SAC-based HCO is still in the infant phase, lacking a comprehensive and critical review. In this mini-review, we summarized the recent advances and SACs applied in HCO and the associated regimes (Figure 1). Particularly, we proposed challenges and prospects for SAC-based HCO in water decontamination.

Synthesis and characteristics of single atom catalysts

A universal strategy for precise SACs design and mass production with low cost is the prerequisite for large-scale applications. Additionally, accurate recognition of the coordination environment of embedded single atoms is critical to reveal the structure-activity relationship in catalysis. Common active single metal atoms and substrate species are shown in Figure 2a and b.

Synthesis strategies

The direct pyrolysis of metal-containing and carbon-rich precursors can produce carbon-based SACs. For instance, metal–organic frameworks (MOFs) with well-defined metal coordination and carbon/nitrogen ligand are extensively used precursors for developing SACs under inert gas atmospheres (for example, N_2, Ar, He) and high temperatures (> 700°C) [18,19]. MOF-derived

SACs are promising catalysts for AOP due to their hierarchically porous structures, excellent electrical conductivity, and well-dispersed single metal sites [20,21]. In addition, the evaporation and etching of the sacrificing zinc (Zn) component in bimetallic Metal-Zn-MOF will create vacancies and defects as additional adsorption and binding sites to host the target active metal centers [22]. Covalent organic frameworks, polymers, and versatile biomass are also versatile carbon-rich precursors for anchoring metal atoms and synthesizing SACs [23–25]. However, direct pyrolysis spontaneously leads to the production of metal nanoparticles (NPs), requiring further acid purification to derive SACs.

Wet-chemical technology can achieve the large-scale production of SACs via impregnation and co-precipitation. The metal precursor is typically anchored to various supports (e.g. graphene, graphite-carbon nitride (g-C_3N_4), and titanium oxide (TiO_2)) via the two approaches [26–28]. For example, a single-cobalt (Co) catalyst was fabricated by dicyandiamide impregnation with a metal salt to prevent the formation of crystalline metal NPs, ensuring Co is firmly attached to C_3N_4 [16••]. Likewise, electrostatic adsorption and ion exchange can also pre-immobilize metal atoms by the wet-chemical approach. Huang et al. designed a SAC (single

Figure 2
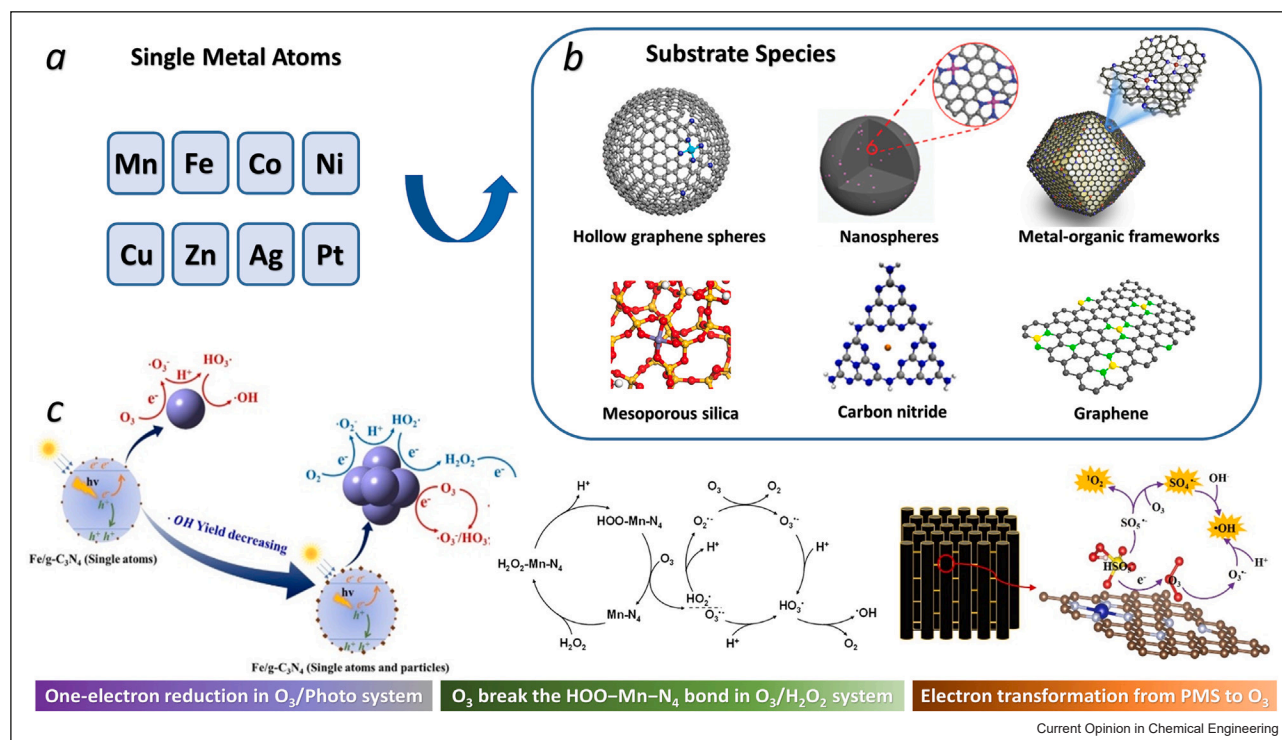
Characteristics of single atom catalyst and its reaction mechanism in combined AOP systems. **(a)** Active single metal atoms. **(b)** Common substrate species. **(c)** Reaction mechanisms of SACs in combined AOP systems.
Reprinted with permission from **(b)** Ref. [26,64,65] Copyright 2018 American Chemical Society, Ref. [35,42] Copyright 2023 Elsevier and Ref. [66] Copyright 2018 John Wiley and Sons. **(c)** Ref. [27,56] Copyright 2021 Elsevier and Ref. [40] Copyright 2023 American Chemical Society.

Pt-bonded silicon carbide (SiC) substrate) by attaching $PtCl_6^{2-}$ on aminated SiC through electrostatic interaction [29]. Such strong bonds between the active metal center and the scaffold (also known as strong metal-support interactions) are beneficial to isolating single atoms for better dispersion and improving structural stability.

Other physicochemical techniques are also developed to synthesize SACs, including atomic layer deposition (ALD), mass-selected soft-land (MSSL), ball milling, and electron/ion irradiation [30–33]. However, ALD and MSSL require delicate operations and high energy consumption, preventing mass-scale production. Thus, it is highly desirable to develop novel strategies for SACs manufacturing with well-defined structures and high loadings in the future.

Characteristics techniques

Morphological and textural characteristics, coordination configuration, and electronic properties of SACs determine their catalytic capacities, which can be identified by various advanced characteristics approaches. In respect of structure and morphology, aberration-corrected high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) can directly visualize the spatial distribution (approximately 0.1 nm) of metal atoms under the dark field [34]. Compared with conventional transmission electron microscopy (TEM) and scanning electron microscopy (SEM), HAADF-STEM is the most convincing technique for observing the atomic metal dispersion in SACs [35]. Extended X-ray absorption fine spectroscopy (EXAFS) and X-ray absorption near-edge structure (XANES) are two typical approaches to revealing the coordination environment and chemical states of SACs, respectively [36,37]. Besides, attenuated total reflection-Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, and Mössbauer spectroscopy are also used to elucidate the chemical states and functionality of SACs [38•]. Therefore, the physiochemical properties of SACs should be analyzed comprehensively using various techniques.

Applications of single atom catalysts for heterogeneous catalytic ozonation

HCO has excellent potential in pollutant abatement owing to its easy operability and strong practicability. The highly dispersed SACs with a low metal loading (< 10 wt%) can trigger ROS production by accelerating O_3 decomposition with excellent reusability because of minimized metal usage and controlled metal leaching.

Particularly, the versatile SAC platform provides diverse metal coordination structures, leading to fine-tuned reactivity and selectivity to evolve different ROS via HCO. To this end, this section will comprehensively showcase the recent advances in applying SACs for HCO (Table 1).

Decontamination capacities

Pharmaceutical and personal care products, pesticides, and oxalic acid (OA) are typical organic pollutants that are persistent, migratory, and biotoxic [39]. Their long-term exposure and accumulation will contaminate the water environment. Transition metal(e.g. Fe, Co, Mn, Cu)-based SACs showed exceptional performance in HCO for treating organic wastewater [16,40–42]. Specifically, the efficiency of single-atom iron (Fe) with a high valence ($O_3/Fe^{III}-N_2O_2-C$) was 190% higher than O_3 alone when treating the secondary effluent [41•]. The Fe center with the highest positive electrostatic potential can combine with the terminal O atom of O_3 to produce $^\bullet OH$ rapidly ($R_{ct} = 6.72 \times 10^{-8}$). Likewise, single-atom Fe anchored on a carbon framework ($Fe-N_4$) showed outstanding performance in catalytic ozonation of secondary effluent from landfill leachate. $Fe-N_4/O_3$ achieved 91% OA degradation and ~100% pHBA removal and the efficiencies are 57 and 2.2 times of pure ozonation, respectively. [43]. Wang et al. reported that single-atom Co on g-C_3N_4 ($O_3/Co-N_4$) achieved 100% oxidative destruction of OA ($k_{O_3/OA} < 0.04 M^{-1}s^{-1}$) by producing highly reactive $^\bullet OH$ [16••]. However, single-atom Fe on g-C_3N_4 ($Fe-N_x$) exhibited negligible activity in catalytic ozonation, suggesting that the central metal species and associated coordination chemistry collectively regulated the HCO activity [27]. To date, the cases of employing SACs for HCO and aqueous pollutant removal are still limited. The structure-activity/selectivity of SACs on different support needs to be further revealed.

Different from aqueous micropollutants, volatile organic compounds are gaseous organic compounds, such as methanol (CH_3OH), isopropanol (IPA), and methyl mercaptan (CH_3SH). Na^+ doping in SAC-Pt (Na-Pt/TiO_2) promoted the formation of $^\bullet OH$ at single-atom Pt sites during ozonation, realizing a high CH_3OH conversion efficiency (100%) and CO_2 selectivity (91.34%) [44]. Additionally, atomically dispersed Pt/FeO_x could catalyze the ozonation of toluene at room temperature, benefiting from the synergistic effect between single-atom Pt and the surface hydroxyl group on Pt-FeO_x [45•]. The amorphous FeO_x support provided extra acid sites for the $^\bullet OH$ production and surface oxidation of toluene. Therefore, metal oxide supports also play an important role in regulating the performance of dispersed single-atoms for HCO. Ma et al. proposed that the electronic metal-support interaction induced significant electron perturbation between anchored Mn and scaffold SiO_2 [46]. Then O_3 will adsorb onto the Si-O-

Mn configuration for activation, which subsequently attacks CH_3SH at the interface. Therefore, the adsorption and transformation of O_3 on SACs determine the efficiency in pollutant removal, which will be fully discussed below.

Migration and transformation of O_3 on single atom catalysts

The adsorption of O_3 onto the catalyst is the prerequisite for O_3 activation and initiating interfacial redox reactions. For instance, SAC-Pt on graphene exhibits high reactivity to adsorb O_3 and enable elongated peroxide O-O bond, resulting in ROS for pollutant degradation [17]. Notably, different single metal atoms show discrepant O_3 adsorption configurations, depending on the oxygen binding energy of the central metal and the coordination environment. Wang et al. suggested that the adsorption energies of O_3 on NiN_4 (–1.65 eV) > CoN_4 (–2.79 eV) > MnN_4 (–2.99 eV), but the interaction type of O_3 on a single Mn site was a head-on configuration (Pauling-type) rather a side-on configuration (Griffiths-type) on Co site [16••]. In this scenario, O_3 would be more readily decomposed into surface-adsorbed $^*O$ on the single Co atom, and meanwhile, generate a free O_2. According to previous literature, the critical species $^*O$ can coordinate several redox reactions, including (1) attacking organics directly, (2) capturing H to form $^\bullet OH$, and (3) reacting with O_3 to form surface-bound $^*O$-O species [47–49]. Although the existence of $^*O$ has been confirmed by *in situ* Raman, the transformation from $^*O$ to other ROS remains controversial.

Metal cations on SACs are also Lewis acid sites, which will introduce surface hydroxyl (-OH) when surrounded by water molecules (H_2O) [45]. However, the adsorption and decomposition of O_3 by -OH on SACs are less discussed and remain debatable. Cui et al. pointed out that H_2O first adsorbed on Na-Pt/TiO_2 and is readily decomposed to OH* due to its low activation barrier [44]. On the contrary, Wang et al. suggested that the role of H_2O should be ignored because there are no obvious changes in the XANES and EXAFS profiles of SACs (Co_1-C_3N_4, Mn_1-C_3N_4, and Ni_1-C_3N_4) in water [16••]. Thus, the genuine role of H_2O in SAC-based HCO should be identified.

Furthermore, the catalytic performance of SACs is governed by different coordination environments. Nitrogen (N) is the most versatile heteroatom for anchoring the central metal and can construct various coordination, including M-N_2, M-N_3, and M-N_4. Among these, Co-N_2 resulted in the elongated O-O bond length (l_{O-O}) to 1.507 Å due to its high electron density, which is significantly longer than Co-N_3 (1.476 Å) and Co-N_4 (1.475 Å) [50••]. In addition, the Fe-pyridinic N_4 moiety with electron-rich Fe single atom exhibited higher activity when compared to Fe-pyridinic N_3 [51]. A robust

Table 1

Application of SACs for pollutant abatement in HCO-based processes.

SACs	Oxidation	Pollutants	Metal Loading (wt%)	Metal Leaching (mg/L)	Cycles (times)	Removal efficiency (%)	Catalytic mechanisms	Ref.
Co_1-C_3N_4	O_3	OA	3.80	0.015	5	100–89	Co-N_4 site promoted $^\bullet OH_{ad}$ and $^\bullet OH_{free}$	[16••]
Mn_1-C_3N_4	O_3	OA	4.00	0.075	5	65–45	Mn-N_4 site promoted $^\bullet OH_{free}$	[41•]
Fe-N-CAF-h	O_3	OA	1.51	0.005	3	70–69	Fe^{III}-N_2O_2-C promoted O_3 decomposition	[42]
Cu-CN	O_3	OA	5.20	0.007	5	93–97	Cu-N site promoted $^\bullet OH$	[43]
Fe_5-NC	O_3	OA, pHBA	0.65	0.117	5	63–59	Fe-N_4 site promoted *O and $^1O_2$.	[44]
Na-Pt/TiO_2	O_3	Isopropanol	0.34	-	-	100	Na-doped Pt promoted $^\bullet OH$	[45•]
Pt/FeO_x	O_3	Toluene	0.15	-	-	73	Synergistic effect between Pt-$(OH)_x$O-Fe and acid sites for O_3 decomposition	
Mn-PSBA	O_3	CH_3SH	2.35	-	-	90	Si-O-Mn activated O_3, (Si-O-)Mn-O adsorbed CH_3SH	[46]
Fe-gCN	O_3/Photo	OA	9.10	0.985	5	100	O_3 captured more photoelectrons than O_2	[27]
Fe-$CeO_{2-\sigma}$	O_3/Photo	4-CP	5.00	-	-	100	Surface OVs promoted O_3 adsorption, bulk OVs promoted O_3 decomposition	[58]
g-C_3N_4/Fe-MCM-48	O_3/Photo	Azithromycin	5.00	-	4	99–97	Single-atom Fe acted as an electron acceptor to promote O_3 decomposition	[59]
Ag-TiO_2	O_3/Photo	Methylparaben	0.50	-	-	70	Photogenerated electrons can react with O_3 adsorbed on the surface	[60]
Ag-g-C_3N_4	O_3/Photo	Acetaminophen	4.00	-	4	83–80	Ag acted as a photogenerated electron acceptor and O_3 decomposition	[61]
Co-C_3N_4	O_3/Photo	OA	8.50	-	5	100–98	Co atoms induced trap states for holes and accelerate O_3 decomposition	[62]
Mn-CN	O_3/H_2O_2	OA	5.20	-	5	100–96	O_3 accelerates HOO-Mn-N_4 to generate $HO_2^\bullet$	[40]
CuSi-BM_{60}	O_3/H_2O_2	Tetracycline	-	0.460	3	72–60	O_3 attacked Si-O…Cu…O-OH* compound	[63]
Co/CMK-3	O_3/PMS	Acetaminophen	3.60	0.050	5	79–75	Co atoms and N-heteroatoms promoted PMS and O_3 decomposition	[56]

* Represents the state of adsorption on the surface.

coordination environment would significantly reduce the leaching of metal ions, improving the stability and reusability of SACs [52]. Therefore, adjusting the coordination environment via controlled pyrolysis can enable the customization of high-activity SACs.

In HCO, shortening the distance between ROS and pollutants and avoiding ROS self-quenching will remarkably improve ozone utilization efficiency and accelerate pollutant removal. Recently, surface hydroxyl radical ($^\bullet OH_{ad}$) has been widely investigated in HCO due to its strong anti-interference [53•]. It has been confirmed that single-atom Co was more conducive to producing $^\bullet OH_{ad}$ compared with Mn in catalytic ozonation. Therefore, the behaviors of O_3 transformation on different single atoms can be different. In summary, the outstanding performance of SACs-based HCO can be attributed to the following two pathways: (1) direct ozonation enhanced by O_3 adsorption on active metal sites, (2) indirect oxidation of surface-confined radicals and non-radicals promoted via in-situ O_3 decomposition.

The density functional theory is frequently employed to visualize the electronic characteristics of SACs and reveal the evolutionary pathway of O_3 to diverse ROS. In addition to the adsorption energy of O_3 on SACs, the intrinsic electronic properties of SACs, such as density of states (DOS), charge/spin density, and D-band structure can provide atomic-level insights into the mechanism of O_3 activation at different SAC sites [10]. For instance, DOS revealed that the strength of single Pt atoms near the Fermi level sharply decreased compared to bulk Pt [54]. While the charge/spin density could reflect the charge accumulation or attenuation region between central metal and C atoms around, where electron-rich sites facilitated O-O bond breakage and ROS generation [55]. Therefore, combining the electronic properties of SAC and its reaction pathway with O_3 can help reveal the transformation pathway of ROS on SACs to initiate diverse reaction pathways.

Performance in combined advanced oxidation process systems

Interestingly, SACs also show excellent catalytic performance in combined AOP systems, where O_3 generally acted as a trigger for ROS production (Figure 2c). Cao et al. proposed that O_3 is more favorable to trap photoelectrons than O_2 due to the higher electrophilicity in the O_3/photosystem, which greatly accelerated the formation of $^\bullet OH$ on Fe-N$_x$ via one-electron reduction pathways ($O_3 \xrightarrow{e^-} {^\bullet}O_3^- /HO_3^\bullet \rightarrow {^\bullet}OH$, or $O_2 \xrightarrow{e^-} {^\bullet}O_2^- \xrightarrow{O_3} {^\bullet}OH$) [27]. A similar role of O_3 has also been discovered in a typical peroxone reaction that O_3 substantially promoted the generation of $HO_2^\bullet$ on the HOO-Mn-N$_4$ site, followed by radical chain reactions to produce $^\bullet OH$ [40]. In terms of the O_3/peroxymonosulfate (PMS) system, single Co atoms promoted the $SO_5^{\bullet-}$ generated, which then reacted with

O_3 to generate $SO_4^{\bullet-}$ [56]. To this end, SACs have broad application prospects in HCO and combined AOP systems for the decontamination of organic micropollutants.

Conclusions and prospects

In summary, single-atom catalysts (SACs) are promising catalysts for environmental remediation via heterogeneous catalytic ozonation. Versatile designated methods render isolated atoms with high dispersion in diverse substrates, providing fine-tuned coordination environment to achieve unique geometric structures and desirable electronic properties for catalytic ozonation. The active metal species and the strong electronic metal-support interactions not only promote the adsorption of ozone (O_3) but also accelerate its decomposition into reactive *O and free O_2 by activating and decomposing the peroxide O-O bond. To fully dissect the oriented interfacial reaction pathways, we proposed the following prospects of SACs-based HCO to enlighten future studies and practical applications.

First, the performance stability and structural robustness of SACs need to be improved in HCO. The catalytic activity of SACs may suffer from significant performance decline during cyclic use or when subjected to water matrix interference, because of the loss/coverage of active metal sites, alteration of coordination environment, structure destruction, and ROS quenching [43]. This is particularly true when the support material is a carbon framework because of the vulnerability in the highly oxidative environment. Thus, deliberate materials engineering design with strong coordination, anti-corrosion support, and stable configuration may address this problem. Meanwhile, as a prerequisite for SACs applications in AOPs, the generation of by-products caused by the complicated water matrix should be taken into considerations. In summary, more effects should be dedicated to the design and synthesis of SACs from low-cost precursors, via facile approaches, and most importantly, with on-demand molecular structures and stable performances in practical catalytic ozonation.

Second, precise identification and rigorous evaluation of active sites in SAC should be conducted. There is no doubt that SACs play an important role in catalytic ozonation, while the structure-activity relationships are poorly understood due to the inherent complexity of SACs and limited studies. Nevertheless, the structural features and chemical environment of carbon (e.g., defects, heteroatoms, functional groups) or metal oxide (e.g., Lewis acid sites, oxygen vacancies) supports also significantly affect the reactant adsorption (O_3 and micropollutants) and reaction pathways. Of particular interest, the role of water molecules in both liquid and gaseous phase reactions should be assessed, which helps understand the evolution of different ROS in HCO.

Third, the interaction mechanism between O_3 and other oxidants (photogenerated electrons, PMS, H_2O_2, etc.) on SACs has not been fully explored. So the different roles of O_3 in combined AOP systems should be deliberately clarified. To evaluate the practical application potential, it is highly imperative to advance granulation and integrated membrane filtration technologies with SACs and investigate its continuous flow reactions for actual decontamination of practical wastewater effluents.

Finally, to gain insights into the transfer and evolution of O_3 into diverse ROS on SACs, designated in-situ experiments should be conducted and advanced analytical instruments should be harnessed to dive into the kinetic features and associated mechanisms. For example, in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and electron paramagnetic resonance (EPR) are advantageous for monitoring the decomposition behavior of O_3 and the generation of surface oxygen species on SACs [57]. In situ XAS technology and Mössbauer spectroscopic technique can help directly monitor the valence/spin state of central metals to elucidate their intrinsic functions and evolution in HCO. The rational design of SACs and in-depth exploration of the associated catalytic ozonation mechanism would lay the foundation for practical application.

Data Availability

Data will be made available on request.

Declaration of Competing Interest

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

Acknowledgements

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest
- of outstanding interest

1. Sun Z, Zhao L, Liu C, Zhen Y, Ma J: **Catalytic ozonation of ketoprofen with in situ N-doped carbon: a novel synergetic mechanism of hydroxyl radical oxidation and an intra-electron-transfer nonradical reaction**. *Environ Sci Technol* 2019, **53**:10342-10351, https://doi.org/10.1021/acs.est.9b02745

2. Liu S, Lai C, Zhou X, Zhang C, Chen L, Yan H, Qin L, Huang D, Ye H, Chen W, *et al*.: **Peroxydisulfate activation by sulfur-doped ordered mesoporous carbon: insight into the intrinsic relationship between defects and $^1O_2$ generation**. *Water Res* 2022, **221**:118797, https://doi.org/10.1016/j.watres.2022.118797

3. Hayyan M, Hashim MA, AlNashef IM: **Superoxide ion: generation and chemical implications**. *Chem Rev* 2016, **116**:3029-3085, https://doi.org/10.1021/acs.chemrev.5b00407

4. Koppenol WH, Stanbury DM, Bounds PL: **Electrode potentials of partially reduced oxygen species, from dioxygen to water**. *Free Radic Biol Med* 2010, **49**:317-322, https://doi.org/10.1016/j.freeradbiomed.2010.04.011

5. Liu H, Wu Z-S, Huang L, Zhang B-W, Yin L-C, Xu C-Y, Zhen L: **Mechanistic insights into interfaces and nitrogen vacancies in cobalt hydroxide/tungsten nitride catalysts to enhance alkaline hydrogen evolution**. *J Mater Chem A* 2021, **9**:11323-11330, https://doi.org/10.1039/D1TA01560E

6. Li X, Yang X, Huang Y, Zhang T, Liu B: **Supported noble-metal single atoms for heterogeneous catalysis**. *Adv Mater* 2019, **31**:1902031, https://doi.org/10.1002/adma.201902031

7. Zhu W, Chen Z, Pan Y, Dai R, Wu Y, Zhuang Z, Wang D, Peng Q, Chen C, Li Y: **Functionalization of hollow nanomaterials for catalytic applications: nanoreactor construction**. *Adv Mater* 2019, **31**:e1800426, https://doi.org/10.1002/adma.201800426

8. Huang G-X, Wang C-Y, Yang C-W, Guo P-C, Yu H-Q: **Degradation of bisphenol a by peroxymonosulfate catalytically activated with $Mn_{1.8}Fe_{1.2}O_4$ nanospheres: synergism between Mn and Fe**. *Environ Sci Technol* 2017, **51**:12611-12618, https://doi.org/10.1021/acs.est.7b03007

9. Chen Y-Z, Zhou Y-X, Wang H, Lu J, Uchida T, Xu Q, Yu S-H, Jiang H-L: **Multifunctional PdAg@MIL-101 for one-pot cascade reactions: combination of host–guest cooperation and bimetallic synergy in catalysis**. *ACS Catal* 2015, **5**:2062-2069, https://doi.org/10.1021/cs501953d

10. Shang Y, Xu X, Gao B, Wang S, Duan X: **Single-atom catalysis in
•• advanced oxidation processes for environmental remediation**. *Chem Soc Rev* 2021, **50**:5281-5322, https://doi.org/10.1039/D0CS01032D.
This work offers an atomic-level correlation of the isolated metal density and photocatalytic properties, and can scientifically guide the design of high-performance photocatalysts for organic synthesis and water purification.

11. Xu H, Jiang N, Wang D, Wang L, Song Y, Chen Z, Ma J, Zhang T: **Improving PMS oxidation of organic pollutants by single cobalt atom catalyst through hybrid radical and non-radical pathways**. *Appl Catal B: Environ* 2020, **263**:118350, https://doi.org/10.1016/j.apcatb.2019.118350

12. Xi J, Jung HS, Xu Y, Xiao F, Bae JW, Wang S: **Synthesis strategies, catalytic applications, and performance regulation of single-atom catalysts**. *Adv Funct Mater* 2021, **31**:2008318, https://doi.org/10.1002/adfm.202008318

13. Yuan L, Shen J, Yan P, Chen Z: **Interface mechanisms of catalytic ozonation with amorphous iron silicate for removal of 4-chloronitrobenzene in aqueous solution**. *Environ Sci Technol* 2018, **52**:1429-1434, https://doi.org/10.1021/acs.est.7b04875

14. Zhang T, Li C, Ma J, Tian H, Qiang Z: **Surface hydroxyl groups of synthetic α-FeOOH in promoting·OH generation from aqueous ozone: property and activity relationship**. *Appl Catal B Environ* 2008, **82**:131-137, https://doi.org/10.1016/j.apcatb.2008.01.008

15. Asghar A, Lutze HV, Tuerk J, Schmidt TC: **Influence of water matrix on the degradation of organic micropollutants by ozone based processes: a review on oxidant scavenging mechanism**. *J Hazard Mater* 2022, **429**:128189, https://doi.org/10.1016/j.jhazmat.2021.128189

16. Wang J, Xie Y, Yu G, Yin L, Xiao J, Wang Y, Lv W, Sun Z, Kim J-H,
•• Cao H: **Manipulating selectivity of hydroxyl radical generation by single-atom catalysts in catalytic ozonation: surface or solution**. *Environ Sci Technol* 2022, **56**:17753-17762, https://doi.org/10.1021/acs.est.2c06836.

This work reveals the role of a key intermediate species (*OO) of ozone decomposition at metal sites, which is collectively responsible for the observed differences in oxidation mechanisms and kinetics.

17. Shokuhi Rad A, Zareyee D: **Adsorption properties of SO₂ and O₃ molecules on Pt-decorated graphene: a theoretical study**. *Vacuum* 2016, **130**:113-118, https://doi.org/10.1016/j.vacuum.2016.05.009

18. Cai T, Teng Z, Wen Y, Zhang H, Wang S, Fu X, Song L, Li M, Lv J, Zeng Q: **Single-atom site catalysts for environmental remediation: recent advances**. *J Hazard Mater* 2022, **440**:129772, https://doi.org/10.1016/j.jhazmat.2022.129772

19. Wei Y-S, Zhang M, Zou R, Xu Q: **Metal–organic framework-based catalysts with single metal sites**. *Chem Rev* 2020, **120**:12089-12174, https://doi.org/10.1021/acs.chemrev.9b00757

20. Liang X, Fu N, Yao S, Li Z, Li Y: **The progress and outlook of metal single-atom-site catalysis**. *J Am Chem Soc* 2022, **144**:18155-18174, https://doi.org/10.1021/jacs.1c12642

21. Singh B, Sharma V, Gaikwad RP, Fornasiero P, Zbořil R, Gawande MB: **Single-atom catalysts: a sustainable pathway for the advanced catalytic applications**. *Small* 2021, **17**:2006473, https://doi.org/10.1002/smll.202006473

22. Wang Q, Ina T, Chen W-T, Shang L, Sun F, Wei S, Sun-Waterhouse D, Telfer SG, Zhang T, Waterhouse GIN: **Evolution of Zn(II) single atom catalyst sites during the pyrolysis-induced transformation of ZIF-8 to N-doped carbons**. *Sci Bull* 2020, **65**:1743-1751, https://doi.org/10.1016/j.scib.2020.06.020

23. Zhou C, Liang Y, Xia W, Almatrafi E, Song B, Wang Z, Zeng Y, Yang Y, Shang Y, Wang C, *et al*.: **Single atom Mn anchored on N-doped porous carbon derived from spirulina for catalyzed peroxymonosulfate to degradation of emerging organic pollutants**. *J Hazard Mater* 2023, **441**:129871, https://doi.org/10.1016/j.jhazmat.2022.129871

24. Zhou Z, Shen Z, Song C, Li M, Li H, Zhan S: **Boosting the activation of molecular oxygen and the degradation of tetracycline over high loading Ag single atomic catalyst**. *Water Res* 2021, **201**:117314, https://doi.org/10.1016/j.watres.2021.117314

25. Fei H, Dong J, Chen D, Hu T, Duan X, Shakir I, Huang Y, Duan X: **Single atom electrocatalysts supported on graphene or graphene-like carbons**. *Chem Soc Rev* 2019, **48**:5207-5241, https://doi.org/10.1039/C9CS00422J

26. Li X, Huang X, Xi S, Miao S, Ding J, Cai W, Liu S, Yang X, Yang H, Gao J, *et al*.: **Single cobalt atoms anchored on porous N-doped graphene with dual reaction sites for efficient fenton-like catalysis**. *J Am Chem Soc* 2018, **140**:12469-12475, https://doi.org/10.1021/jacs.8b05992

27. Cao H, Wang J, Kim J-H, Guo Z, Xiao J, Yang J, Chang J, Shi Y, Xie Y: **Different roles of Fe atoms and nanoparticles on g-C₃N₄ in regulating the reductive activation of ozone under visible light**. *Appl Catal B: Environ* 2021, **296**:120362, https://doi.org/10.1016/j.apcatb.2021.120362

28. Liu P, Zhao Y, Qin R, Mo S, Chen G, Gu L, Chevrier DM, Zhang P, Guo Q, Zang D, *et al*.: **Photochemical route for synthesizing atomically dispersed palladium catalysts**. *Science* 2016, **352**:797-800, https://doi.org/10.1126/science.aaf5251

29. Huang D, de Vera GA, Chu C, Zhu Q, Stavitski E, Mao J, Xin H, Spies JA, Schmuttenmaer CA, Niu J, *et al*.: **Single-atom Pt catalyst for effective C–F bond activation via hydrodefluorination**. *ACS Catal* 2018, **8**:9353-9358, https://doi.org/10.1021/acscatal.8b02660

30. Yan H, Cheng H, Yi H, Lin Y, Yao T, Wang C, Li J, Wei S, Lu J: **Single-atom Pd1/graphene catalyst achieved by atomic layer deposition: remarkable performance in selective hydrogenation of 1,3-butadiene**. *J Am Chem Soc* 2015, **137**:10484-10487, https://doi.org/10.1021/jacs.5b06485

31. Yang M, Allard LF, Flytzani-Stephanopoulos M: **Atomically dispersed Au–(OH)ₓ species bound on titania catalyze the low-temperature water-gas shift reaction**. *J Am Chem Soc* 2013, **135**:3768-3771, https://doi.org/10.1021/ja312646d

32. Chen X, Yu L, Wang S, Deng D, Bao X: **Highly active and stable single iron site confined in graphene nanosheets for oxygen reduction reaction**. *Nano Energy* 2017, **32**:353-358, https://doi.org/10.1016/j.nanoen.2016.12.056

33. Wang H, Wang Q, Cheng Y, Li K, Yao Y, Zhang Q, Dong C, Wang P, Schwingenschlögl U, Yang W, *et al*.: **Doping monolayer graphene with single atom substitutions**. *Nano Lett* 2012, **12**:141-144, https://doi.org/10.1021/nl2031629

34. Gao C, Low J, Long R, Kong T, Zhu J, Xiong Y: **Heterogeneous single-atom photocatalysts: fundamentals and applications**. *Chem Rev* 2020, **120**:12175-12216, https://doi.org/10.1021/acs.chemrev.9b00840

35. Li Y, Chen G, Mou J, Liu Y, Xue S, Tan T, Zhong W, Deng Q, Li T, Hu J, *et al*.: **Cobalt single atoms supported on N-doped carbon as an active and resilient sulfur host for lithium–sulfur batteries**. *Energy Storage Mater* 2020, **28**:196-204, https://doi.org/10.1016/j.ensm.2020.03.008

36. Chen W, Pei J, He C-T, Wan J, Ren H, Wang Y, Dong J, Wu K, Cheong W-C, Mao J, *et al*.: **Single tungsten atoms supported on MOF-derived N-doped carbon for robust electrochemical hydrogen evolution**. *Adv Mater* 2018, **30**:1800396, https://doi.org/10.1002/adma.201800396

37. Wang L, Chen M-X, Yan Q-Q, Xu S-L, Chu S-Q, Chen P, Lin Y, Liang H-W: **A sulfur-tethering synthesis strategy toward high-loading atomically dispersed noble metal catalysts**. *Sci Adv* 2019, **5**:eaax6322, https://doi.org/10.1126/sciadv.aax6322

38. Li J, Guan Q, Wu H, Liu W, Lin Y, Sun Z, Ye X, Zheng X, Pan H, Zhu
• J, *et al*.: **Highly active and stable metal single-atom catalysts achieved by strong electronic metal–support interactions**. *J Am Chem Soc* 2019, **141**:14515-14519, https://doi.org/10.1021/jacs.9b06482.
This work emphasizes the strong electronic metal-support interactions between Pt single atom and Co₃O₄ in the dehydrogenation of ammonia borane for room-temperature hydrogen generation.

39. Lim S, Shi JL, von Gunten U, McCurry DL: **Ozonation of organic compounds in water and wastewater: a critical review**. *Water Res* 2022, **213**:118053, https://doi.org/10.1016/j.watres.2022.118053

40. Guo Z, Xie Y, Xiao J, Zhao Z-J, Wang Y, Xu Z, Zhang Y, Yin L, Cao H, Gong J: **Single-atom Mn–N₄ site-catalyzed peroxone reaction for the efficient production of hydroxyl radicals in an acidic solution**. *J Am Chem Soc* 2019, **141**:12005-12010, https://doi.org/10.1021/jacs.9b04569

41. Ouyang C, Wei K, Huang X, Gamal El-Din M, Zhang X: **Bifunctional
• Fe for induced graphitization and catalytic ozonation based on a Fe/N-doped carbon–Al₂O₃ framework: theoretical calculations guided catalyst design and optimization**. *Environ Sci Technol* 2021, **55**:11236-11244, https://doi.org/10.1021/acs.est.1c00728.
This work reveals that higher Fe valence promoted ozone decomposition, which provides a novel solution for designing ozonation catalysts.

42. Guo Z, Wei J, Wu Z, Guo Y, Song Y: **Stabilized N coordinated Cu site in catalytic ozonation: the efficient generation of OH induced by surface hydroxyl groups based on the Lewis acid site**. *Sep Purif Technol* 2023, **304**:122215, https://doi.org/10.1016/j.seppur.2022.122215

43. Ren T, Yin M, Chen S, Ouyang C, Huang X, Zhang X: **Single-atom Fe-N₄ sites for catalytic ozonation to selectively induce a nonradical pathway toward wastewater purification**. *Environ Sci Technol* 2023, **57**:3623-3633, https://doi.org/10.1021/acs.est.2c07653

44. Cui J, Hao Z, Wang Y, Xue L, Xue H, Tu L, Hao L, Tian M, Guo J, Zhao D, *et al*.: **Mechanism of ozone-assisted catalytic oxidation of isopropanol over single-atom platinum catalysts at ambient temperature**. *Chem Eng J* 2022, **446**:136989, https://doi.org/10.1016/j.cej.2022.136989

45. Liu R, Liu S, Ding H, Zhao D, Fu J, Zhang Y, Huo W, Li GK:
• **Unveiling the role of atomically dispersed active sites over amorphous iron oxide supported Pt catalysts for complete catalytic ozonation of toluene at low temperature**. *Ind Eng Chem Res* 2021, **60**:3881-3892, https://doi.org/10.1021/acs.iecr.0c05549.

This work suggests that surface hydroxyl groups and highly dispersed Pt species are the two determining factors for the exceptional catalytic performance at a low temperature.

46. Ma D, Liu W, Huang Y, Xia D, Lian Q, He C: **Enhanced catalytic ozonation for eliminating CH₃SH via stable and circular electronic metal–support interactions of Si–O–Mn bonds with low mn loading**. *Environ Sci Technol* 2022, **56**:3678-3688, https://doi.org/10.1021/acs.est.1c07065

47. Wang Y, Chen L, Cao H, Chi Z, Chen C, Duan X, Xie Y, Qi F, Song W, Liu J, *et al*.: **Role of oxygen vacancies and Mn sites in hierarchical Mn₂O₃/LaMnO₃-δ perovskite composites for aqueous organic pollutants decontamination**. *Appl Catal B Environ* 2019, **245**:546-554, https://doi.org/10.1016/j.apcatb.2019.01.025

48. Cheng Y, Wang B, Yan P, Shen J, Kang J, Zhao S, Zhu X, Shen L, Wang S, Shen Y, *et al*.: **In-situ formation of surface reactive oxygen species on defective sites over N-doped biochar in catalytic ozonation**. *Chem Eng J* 2023, **454**:140232, https://doi.org/10.1016/j.cej.2022.140232

49. Zhang T, Li W, Croue JP: **Catalytic ozonation of oxalate with a cerium supported palladium oxide: an efficient degradation not relying on hydroxyl radical oxidation**. *Environ Sci Technol* 2011, **45**:9339-9346, https://doi.org/10.1021/es202209j

50. Liang X, Wang D, Zhao Z, Li T, Gao Y, Hu C: **Coordination number
•• dependent catalytic activity of single-atom cobalt catalysts for fenton-like reaction**. *Adv Funct Mater* 2022, **32**:2203001, https://doi.org/10.1002/adfm.202203001
This work proposed that the catalytic specific activity of Co-Nₓ is found to be dependent on the coordination number of single atomic Co sites, where the lowest-coordinated Co-N₂ catalyst exhibits the highest specific activity.

51. Gao Y, Zhu Y, Li T, Chen Z, Jiang Q, Zhao Z, Liang X, Hu C: **Unraveling the high-activity origin of single-atom iron catalysts for organic pollutant oxidation via peroxymonosulfate activation**. *Environ Sci Technol* 2021, **55**:8318-8328, https://doi.org/10.1021/acs.est.1c01131

52. Yan H, Zhao M, Feng X, Zhao S, Zhou X, Li S, Zha M, Meng F, Chen X, Liu Y, *et al*.: **PO₄³⁻ coordinated robust single-atom platinum catalyst for selective polyol oxidation**. *Angew Chem Int Ed* 2022, **61**:e202116059, https://doi.org/10.1002/anie.202116059

53. Zhang S, Quan X, Zheng J-F, Wang D: **Probing the interphase
• "HO·zone" originated by carbon nanotube during catalytic ozonation**. *Water Res* 2017, **122**:86-95, https://doi.org/10.1016/j.watres.2017.05.063.
This work validates that hydroxyl radical was accumulated within a surface region of the CNT, which emphasizes the importance of surface hydroxyl radicals.

54. Duchesne PN, Li ZY, Deming CP, Fung V, Zhao X, Yuan J, Regier T, Aldalbahi A, Almarhoon Z, Chen S, *et al*.: **Golden single-atomic-site platinum electrocatalysts**. *Nat Mater* 2018, **17**:1033-1039, https://doi.org/10.1038/s41563-018-0167-5

55. Li Z, Li K, Ma S, Dang B, Li Y, Fu H, Du J, Meng Q: **Activation of peroxymonosulfate by iron-biochar composites: Comparison of nanoscale Fe with single-atom Fe**. *J Colloid Interface Sci* 2021, **582**:598-609, https://doi.org/10.1016/j.jcis.2020.08.049

56. Liao G, Xu P, Lu P, Qing X, Yu Z, Chang Y, Chen W, Tang Y, Wang J, Wang X, *et al*.: **Dramatic enhancement of mineralization capability for ozone/peroxymonosulfate process by single atom Co/CMK-3 catalyst**. *Sep Purif Technol* 2022, **287**:120582, https://doi.org/10.1016/j.seppur.2022.120582

57. Wu J, Su T, Jiang Y, Xie X, Qin Z, Ji H: **In situ DRIFTS study of O₃ adsorption on CaO, γ-Al₂O₃, CuO, α-Fe₂O₃ and ZnO at room temperature for the catalytic ozonation of cinnamaldehyde**. *Appl Surf Sci* 2017, **412**:290-305, https://doi.org/10.1016/j.apsusc.2017.03.237

58. Chen X, Zhan S, Chen D, He C, Tian S, Xiong Y: **Grey Fe-CeO₂₋σ for boosting photocatalytic ozonation of refractory pollutants: roles of surface and bulk oxygen vacancies**. *Appl Catal B: Environ* 2021, **286**:119928, https://doi.org/10.1016/j.apcatb.2021.119928

59. Ling Y, Liu H, Li B, Zhang B, Wu Y, Hu H, Yu D, Huang S: **Efficient photocatalytic ozonation of azithromycin by three-dimensional g-C₃N₄ nanosheet loaded magnetic Fe-MCM-48 under simulated solar light**. *Appl Catal B: Environ* 2023, **324**:122208, https://doi.org/10.1016/j.apcatb.2022.122208

60. Gomes JF, Leal I, Bednarczyk K, Gmurek M, Stelmachowski M, Diak M, Emília Quinta-Ferreira M, Costa R, Quinta-Ferreira RM, Martins RC: **Photocatalytic ozonation using doped TiO₂ catalysts for the removal of parabens in water**. *Sci Total Environ* 2017, **609**:329-340, https://doi.org/10.1016/j.scitotenv.2017.07.180

61. Ling Y, Liao G, Xu P, Li L: **Fast mineralization of acetaminophen by highly dispersed Ag-g-C₃N₄ hybrid assisted photocatalytic ozonation**. *Sep Purif Technol* 2019, **216**:1-8, https://doi.org/10.1016/j.seppur.2019.01.057

62. Wang J, Yu G, Wang Y, Liu S, Qiu J, Xu Y, Wang Z, Wang Y, Xie Y, Cao H: **Surface density of cobalt single atoms manipulating hydroxyl radical generation via dual pathways: electrons supply and active sites**. *Adv Funct Mater* 2023, **33**:202215245, https://doi.org/10.1002/adfm.202215245

63. Li S, Huang J, Wang Y, Yu G: **Role of in-situ electro-generated H₂O₂···bridge in tetracycline degradation governed by mechanochemical Si-O anchoring Cu²⁺ as electron shuttle during E-peroxone process**. *Appl Catal B Environ* 2022, **304**:120930, https://doi.org/10.1016/j.apcatb.2021.120930

64. Yin Y, Shi L, Li W, Li X, Wu H, Ao Z, Tian W, Liu S, Wang S, Sun H: **Boosting fenton-like reactions via single atom Fe catalysis**. *Environ Sci Technol* 2019, **53**:11391-11400, https://doi.org/10.1021/acs.est.9b03342

65. Yi L, Lan F, Li J, Zhao C: **Efficient noble-metal-free Co-NG/TiO₂ photocatalyst for H₂ evolution: synergistic effect between single-atom Co and N-doped graphene for enhanced photocatalytic activity**. *ACS Sustain Chem Eng* 2018, **6**:12766-12775, https://doi.org/10.1021/acssuschemeng.8b02001

66. Han A, Chen W, Zhang S, Zhang M, Han Y, Zhang J, Ji S, Zheng L, Wang Y, Gu L, *et al*.: **A polymer encapsulation strategy to synthesize porous nitrogen-doped carbon-nanosphere-supported metal isolated-single-atomic-site catalysts**. *Adv Mater* 2018, **30**:e1706508, https://doi.org/10.1002/adma.201706508