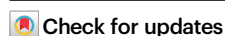


Dynamic oxygen vacancy engineering on CuO via refreshable catalytic surface for high-efficient water decontamination

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Oxygen vacancies (O_v) on metal oxide surfaces exhibit high catalytic activity for activating peroxymonosulfate (PMS) in wastewater decontamination, yet their in-situ regeneration remains a significant challenge. This study successfully achieves in-situ real-time regeneration of O_v on CuO surfaces through simple alkali etching without interrupting the contaminant removal process. The surface hydroxyl groups introduced by alkali treatment significantly reduce the formation energy of O_v on CuO surfaces from 1.60 eV to 0.38 eV. Both experimental results and density functional theory calculations reveal that the high activity of CuO relies on the synergy of surface hydroxyl groups and O_v . This synergy increases the antibonding states below the Fermi level and the electron spin density of Cu near O_v , thereby promoting electron transfer from CuO to PMS. As a result, by just adding an equimolar amount of alkali relative to PMS in CuO/PMS system, the degradation rate constant of sulfamethoxazole (SMX) greatly increases by 42 times. The primary reactive oxygen species in this system are sulfate radicals and hydroxyl radicals. Furthermore, OH/CuO/PMS system exhibits a long-term stability (> 300 h) for SMX removal in a real water matrix. This work provides a highly executable method to in-situ real-time regenerate O_v on CuO surfaces, representing significant progress in the critical yet underappreciated field of catalyst regeneration.

Residual pharmaceuticals in the secondary effluent of wastewater treatment plants constitute a significant source of toxic organic compounds in natural water bodies^{1–4}. Peroxymonosulfate (PMS)-based advanced oxidation processes (PMS-AOPs) have attracted considerable attention due to their effectiveness in eliminating these residual pharmaceuticals^{5–8}. However, the practical application of PMS-AOPs is limited by catalyst deactivation, which results from issues such as coverage by intermediate products, difficulties

in regenerating active sites, and metal leaching^{9,10}. Although significant efforts have been devoted to catalyst regeneration, most current methods involve *off-site* high-temperature treatments or the in-situ addition of cleaning agents after halting the reaction, resulting in complex and costly regeneration procedures^{11–13}. Therefore, addressing the bottleneck of catalyst deactivation is pivotal for the practical application of heterogeneous activation of PMS.

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A primary cause of catalyst deactivation in PMS-AOPs is the adsorption of organic compounds on the catalyst surface, particularly in the case of carbon-based materials¹⁴. These materials inherently exhibit strong adsorption capacities for organic compounds and can activate PMS to initiate the polymerization of organic pollutants, leading to the formation of tenacious adhered layers¹⁵. In contrast, in radical-dominated PMS-AOPs (e.g., $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$), the adsorbed organic compounds can be mineralized and removed, thereby helping to maintain the exposure of active sites^{16,17}.

Compared to carbon-based materials, transition metal oxides demonstrate higher effectiveness in activating PMS to generate $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$, along with advantages in cost efficiency and ease of preparation^{18–20}. The catalytic activity of metal oxides in PMS activation originates from low-valent metals, surface hydroxyl groups, and oxygen vacancies (O_v)^{21–24}. However, regenerating low-valent metals requires consuming a significant amount of oxidant^{7,25}, while the relatively weak activity of surface hydroxyl groups often requires large catalyst dosages^{26,27}. Alternatively, highly active O_v offer a more efficient alternative, requiring reduced amounts of both oxidant and catalyst²⁸. As intrinsic anion defects, O_v are rich in localized electrons and exhibit high activity towards triggering PMS. Nevertheless, these vacancies are susceptible to occupation by external oxygen atoms, which can lead to their deactivation^{29,30}.

Achieving in-situ continuous regeneration of O_v during PMS-AOPs operation, while simultaneously generating highly reactive species to remove organic deposits from the catalyst surface, could substantially lower catalyst regeneration costs. However, current research efforts remain predominantly focused on mitigating O_v poisoning rather than enabling their in-situ continuous regeneration²⁹. Existing methods for generating O_v include high-temperature treatment³¹, chemical reduction^{32,33}, heteroatom doping³⁴, acid/alkali etching³⁵, mechanical treatment³⁶, and ultraviolet irradiation²⁸, etc. Of these, only chemical reduction and acid/alkali etching can be conducted in-situ. However, chemical reduction generally necessitates interrupting the reaction and often involves hazardous reducing agents.

Clearly, acid/alkali etching represents the most promising approach for achieving in-situ continuous regeneration of O_v . Previous studies have reported that surface hydroxyl groups facilitate the formation of O_v ^{30,37}. Thus, the in-situ addition of alkali for the regeneration of O_v during the operation of PMS-AOPs is pre-explored. After screening a series of metal oxides, it is found that even a low alkali addition can significantly increase the number of O_v on the CuO surface. Based on this discovery, our study systematically investigates the effectiveness of the alkali/CuO/PMS system in removing organic pollutants, the mechanism of O_v formation on the CuO surface under alkaline conditions, and the mechanism of PMS activation in this system. The applicability of this system is also evaluated. This research offers particular insights and methodologies for the in-situ continuous regeneration of active sites in PMS-AOPs catalysts, thereby enhancing the practical applicability of PMS-AOPs.

Results

NaOH induced superior performance of CuO in PMS activation

The target CuO was commercial product with monoclinic structure (JCPDS no. 45-0937, Fig. 1a). Combined with additional evidence from the high-resolution transmission electron microscope (HR-TEM) image (Fig. 1b) and the corresponding fast Fourier transform (FFT) pattern (Fig. 1c), CuO was found to possess the main exposed crystal planes of (002), (111), and (311)²⁵. Other characterizations, including scanning electron microscope (SEM, Supplementary Fig. 1), X-ray photoelectron spectroscopy (XPS, Supplementary Fig. 2) and N_2 adsorption-desorption isotherm (Supplementary Fig. 3), provided additional detailed properties of this commercial CuO.

CuO rather than other metal oxides (such as Fe_3O_4 and Co_3O_4 , Supplementary Fig. 4), was selected as the catalyst because only the

performance of CuO in PMS activation could be greatly enhanced in the presence of NaOH. Using the commonly studied sulfamethoxazole (SMX) as the target pollutant, almost 100% of SMX was removed in the $\text{OH}^-/\text{CuO}/\text{PMS}$ system, while in the control groups, the removal rates of SMX were all lower than 20% (Fig. 1d). The poor performance of control groups excluded that the enhancement of SMX removal was due to adsorption or alkali-induced PMS activation. The apparent rate constant (k_{app}) of SMX removal in $\text{OH}^-/\text{CuO}/\text{PMS}$ was $4.2 \times 10^{-3} \text{ s}^{-1}$, which was 210, 70, and 42 times greater than that in the reaction system of PMS alone, OH^-/PMS , and CuO/PMS , respectively (Supplementary Table 1). The dosage influence of alkali, CuO, and PMS was also explored to confirm optimal experimental conditions with the detailed results in Supplementary Fig. 5. Compared to the reported catalysts in recent years (Fig. 1e^{38–49} and Supplementary Data 1), OH^-/CuO showed significant superiority in SMX removal. Apparently, OH^-/CuO has great ability in PMS activation, which was further evidenced by the PMS consumption rate. At 20 min, the consumption rate of PMS in $\text{OH}^-/\text{CuO}/\text{PMS}$ system reached 84.52%, which was remarkably higher than that in OH^-/PMS (3.43%) and CuO/PMS (15.86%) system (Supplementary Fig. 6a).

OH^-/CuO showed a more significant performance than most of the studies in Fig. 1e and Supplementary Data 1 in terms of reusability and mineralizing SMX. In the $\text{OH}^-/\text{CuO}/\text{PMS}$ system, the TOC removal rate of SMX was as high as 65.9% after 20 min of treatment (Supplementary Fig. 7). In the presence of alkali, CuO exhibited satisfactory reusability, and specifically, the degradation rate of SMX decreased by only 5.28% in the fifth cycle (Fig. 1f). Besides, the k_{app} of SMX removal and PMS consumption rate also remained a high level during the reuse experiment (Supplementary Figs. 8 and 9). The introduction of alkali significantly reduced the leaching of Cu ions from 2.68 mg/L to below 0.05 mg/L, a concentration far lower than the standard limit of 1.0 mg/L set in China (GB 3838-2002) (Fig. 1g). After five cycles, the CuO had no significant change based on the characterization by SEM (Supplementary Fig. 10a, b) and XRD (Supplementary Fig. 10c), indicating the good structural stability of CuO in the $\text{OH}^-/\text{CuO}/\text{PMS}$ system.

The $\text{OH}^-/\text{CuO}/\text{PMS}$ system demonstrated exceptional performance in removing a variety of organic pollutants, including known refractory compounds such as ibuprofen (IBP), quinoline (QNL), carbamazepine (CBZ), and atrazine (ATZ), implying that this was a radical-dominated system. As displayed in Fig. 1h, the removal efficiency of IBP, QNL, CBZ, and ATZ reached 94%, 100%, 100%, and 99%, respectively. The corresponding fitted first-order kinetic curves yielded apparent rate constants of $2.5 \times 10^{-3} \text{ s}^{-1}$, $4.0 \times 10^{-3} \text{ s}^{-1}$, $7.4 \times 10^{-3} \text{ s}^{-1}$, and $3.3 \times 10^{-3} \text{ s}^{-1}$ (Supplementary Fig. 11). In addition, when treating simulated wastewater containing 10 types of organic pollutants, all of them exhibited removal rates greater than 95% (Supplementary Fig. 12).

Active sites: surface oxygen vacancy from alkali in-situ etching

The enhancement of alkali on the performance of $\text{OH}^-/\text{CuO}/\text{PMS}$ system was not attributable to alkali activation and electrostatic adsorption (Supplementary Figs. 13 and 14). Although OH^- in-situ etching increased BET surface area of CuO (Supplementary Fig. 3b–f), the enhanced activity of CuO did not originate from the change of BET surface area, as even after increasing the CuO dosage from 0.1 g/L to 0.3 g/L to increase the total BET surface area, CuO (0.3 g/L) still exhibited much lower activity than OH^-/CuO (0.1 g/L) in triggering PMS to remove SMX (Supplementary Fig. 15). In addition, 0.2 mM OH^- in-situ etching bring about similar BET surface area improvement for CuO with 0.4 mM OH^- . These two points indicate that OH^- enhanced activity of CuO was not due to the change of BET surface area.

In the presence of alkali, surface hydroxyl groups ($-\text{OH}$) tend to form on metal oxides, which are capable of activating PMS^{50,51}. For the alkali-etched CuO, the Fourier transform infrared spectroscopy (FTIR) analysis revealed a positive correlation between the intensity of the $-\text{OH}$ stretching vibration band (observed at approximately 3400 cm^{-1})

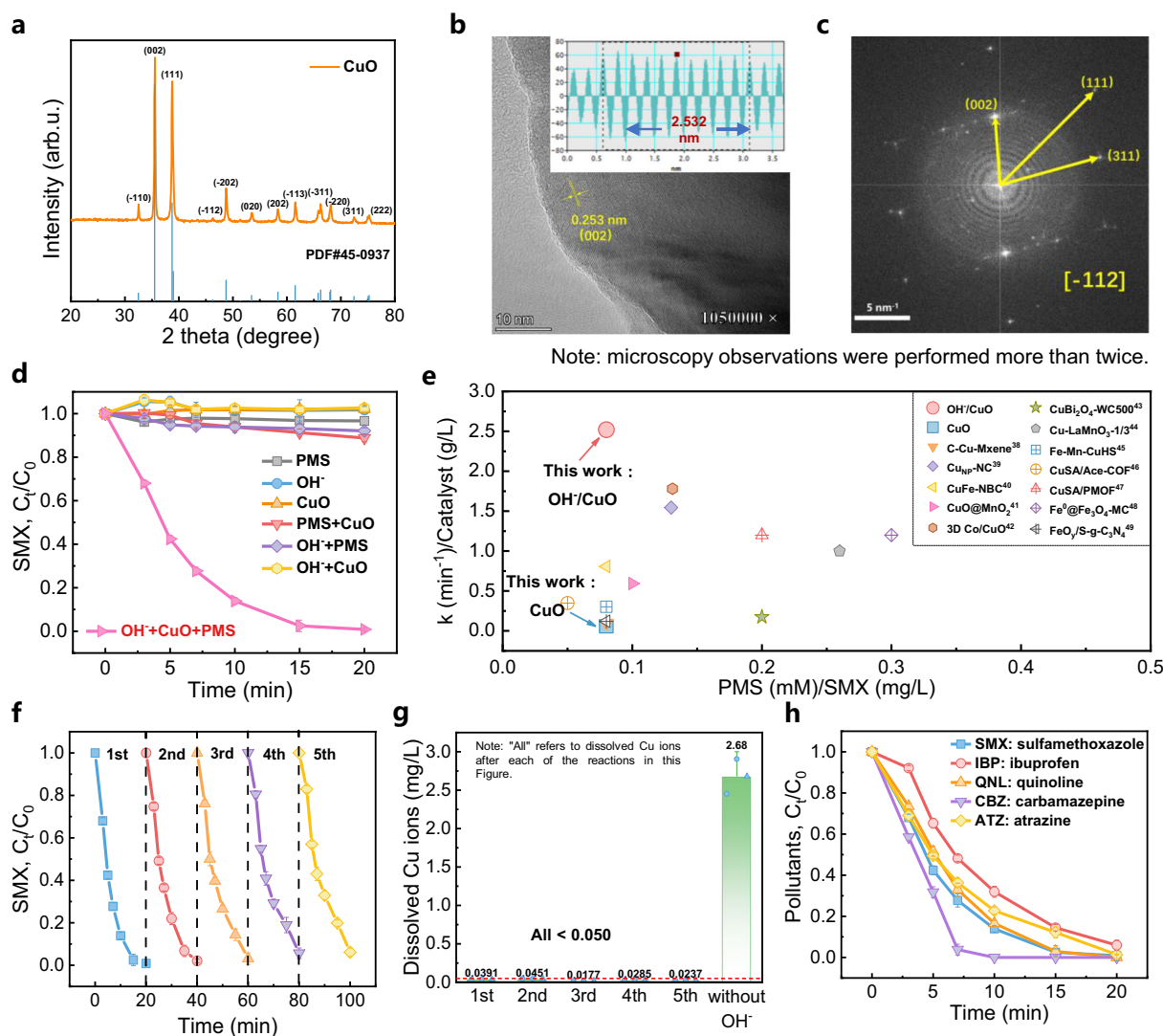


Fig. 1 | Characterization of target CuO and its remarkable catalytic performance with OH⁻ in-situ etching. **a** XRD pattern, **b** HR-TEM image with corresponding, **c** FFT analysis of target CuO. **d** Degradation efficiency of SMX across catalytic systems. **e** Comparative performance benchmarking against

representative catalyst/PMS systems^{38–49}. **f** Cyclic stability tests showing (g) concomitant Cu ion leaching. **h** Broad-spectrum removal efficiency for diverse organic contaminants. Experiment conditions: [Pollutants]₀ = 5 mg/L, [NaOH]₀ = 0.4 mM, [PMS]₀ = 0.4 mM, [Catalyst]₀ = 100 mg/L, T = 25 °C.

and the increasing alkali concentration (Fig. 2a). A strong positive correlation was observed between the signal intensity of surface –OH and the degradation rate constant (k_{app}) of SMX, suggesting that surface –OH likely serve as the primary active sites for PMS activation (Fig. 2c Left). However, despite its abundant hydroxyl groups, Cu(OH)₂ (characterized by XRD, Supplementary Fig. 16a, b) demonstrated significantly lower catalytic activity compared to OH⁻/CuO (Supplementary Fig. 16c). This observation strongly suggests the existence of additional crucial active sites beyond surface hydroxyl groups in OH⁻/CuO.

Previous studies have shown that surface –OH could help in the generation of O_v on the TiO₂ surface³⁰. Therefore, solid electron paramagnetic resonance (EPR) spectroscopy was carried out to detect O_v on CuO surface, revealing a positive correlation between the signal intensity of O_v ($g = 2.003$) and alkali dosage (Fig. 2b)³⁴. To quantify the relative concentration of O_v on the CuO surface, XPS analysis was further employed (Supplementary Fig. 17). The relative ratio of O_v was summarized in Supplementary Fig. 18 Left²⁴. As the alkali concentration increased, the relative content of O_v increased from 24.62% (for 0 mM OH⁻) to 25.24% (for 0.2 mM OH⁻), 28.93% (for 0.3 mM OH⁻), and

37.58% (for 0.4 mM OH⁻), respectively. The ratio of low-valence copper increased from 65.26% to 66.90%, 73.43% and 74.37%, respectively (Supplementary Fig. 19), which is attributed to the loss of lattice oxygen in the formation of O_v^{28,52}. Furthermore, the formation of O_v was also evidenced by thermogravimetric analysis that the mass loss of CuO decreased along with the OH⁻ concentration (Supplementary Fig. 20), since the oxidation process of O_v in O₂ atmosphere under high-temperature would reduce the mass loss^{53–55}.

The strong positive correlation between the k_{app} of SMX removal and O_v content provides further evidence of O_v as the primary active site for PMS decomposition (Fig. 2c Right and Supplementary Fig. 18 Right). In contrast, Cu(OH)₂ with no observed O_v (Supplementary Fig. 21), had much lower activity than OH⁻/CuO (Supplementary Fig. 16c). However, the above evidence was still insufficient to fully establish the key role of O_v. Thus, an O_v quenching experiment was further carried out. After pre-aerating O₂ for 2 h to consume O_v in OH⁻/CuO system, the removal of SMX was significantly inhibited (Fig. 2d), proving that O_v was indeed the main active site. This also indicates that surface –OH alone was not the active site, since its concentration remained unchanged while O_v was significantly reduced under an O₂

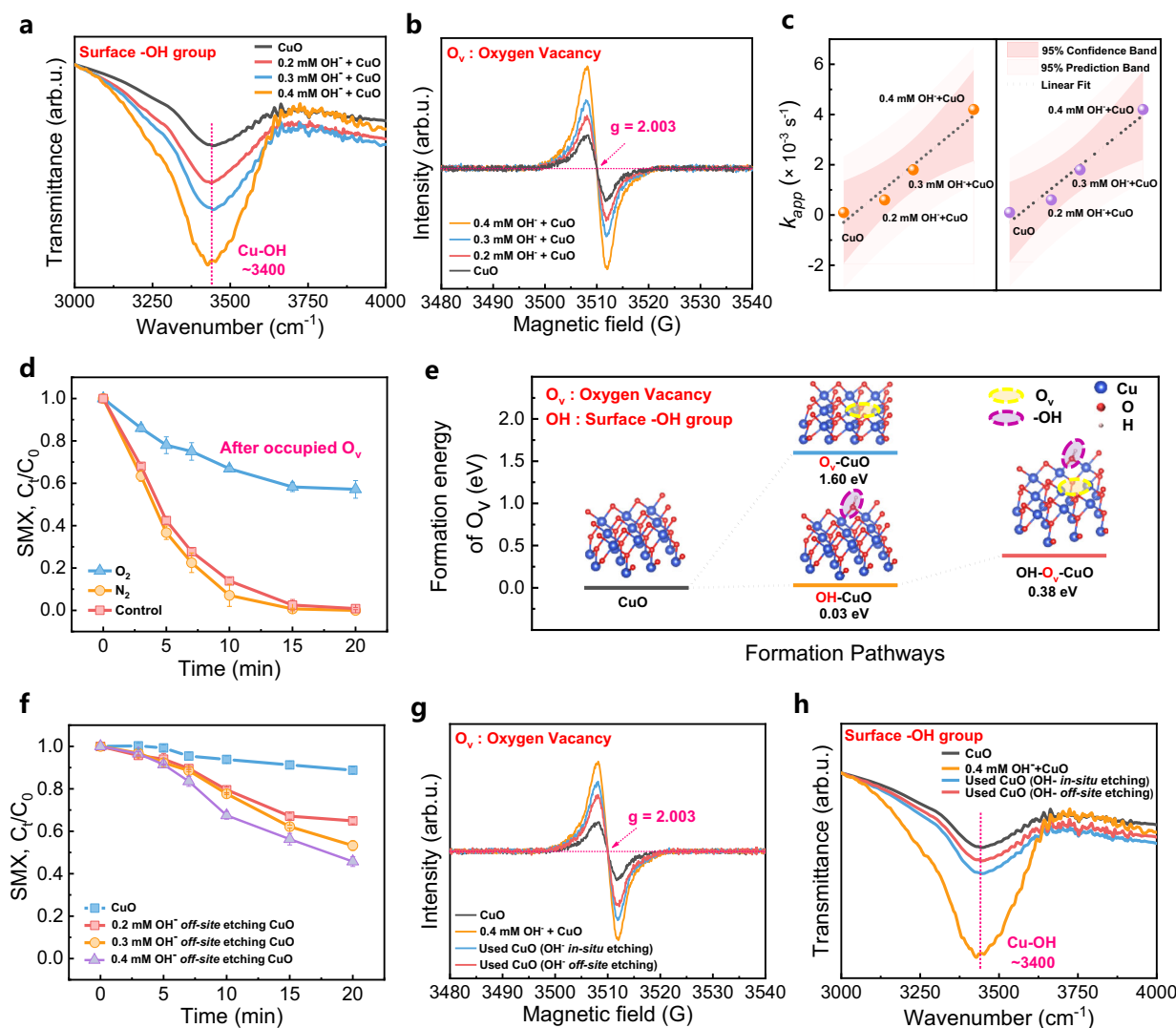


Fig. 2 | Refreshable oxygen vacancies induced by in-situ alkali etching acted as the main active site. a FTIR spectra and **b** EPR spectra of CuO with OH⁻ in-situ etching of different concentrations. **c** Correlation between SMX degradation rate and surface -OH (Left), O_v (Right) of various CuO in PMS activation process (For details on fitting methods, see “Statistics and Reproducibility”). **d** The degradation

efficiency of SMX with adequate O₂/N₂ exposure. **e** The formation energy of O_v in different pathways. **f** The degradation efficiency of SMX with PMS activated by fresh CuO and OH⁻ off-site etching CuO. **g** EPR spectroscopy and **h** FTIR spectra of fresh CuO and used CuO with OH⁻ in-situ etching and off-site etching. Experiment conditions: [SMX]₀ = 5 mg/L, [PMS]₀ = 0.4 mM, [Catalysts]₀ = 100 mg/L, T = 25 °C.

atmosphere (Supplementary Fig. 22). Furthermore, no significant inhibition of SMX removal was observed after the pre-aeration of N₂, reflecting that the generation of reactive oxygen species (ROS) for SMX removal did not depend on the dissolved oxygen in water⁵⁶. Based on the results of density functional theory (DFT) calculations, the surface -OH significantly reduced the formation energy of O_v from 1.60 to 0.38 eV (Fig. 2e). Therefore, based on the experimental and theoretical results, it is reasonable to conclude that alkali in-situ etching leads to the formation of surface -OH groups (Fig. 2a), which in turn facilitates the generation of O_v (Fig. 2e). Additionally, another CuO sample, denoted as CuO(002) with a higher (002)/(111) crystal plane intensity ratio in the XRD pattern than the original CuO, was prepared (Supplementary Fig. 23a). CuO(002) exhibited similar activity with the present CuO in the removal of SMX (Supplementary Fig. 23b), indicating that the ratio decreases of (111) plane did not significantly change the activity of CuO. The addition of OH⁻ also enhanced the formation of surface -OH and O_v for CuO(002) (Supplementary Fig. 24), and OH⁻ can enhance the formation of O_v on (111) plane as well (Supplementary Fig. 25), indicating that both the (002)

and (111) planes interact effectively with OH⁻. Consequently, the simple addition of alkali enables the in-situ continuous regeneration of O_v, ensuring the high activity of CuO. Based on the quantitative analysis of O_v concentrations (Supplementary Table 2), the O_v concentration at 0.4 mM OH⁻ was about 1.6-fold than that without OH⁻. Furthermore, the O_v formation energy on CuO surface with the assistance of OH⁻ was just 0.38 eV (Fig. 2e), while it was 1.69 and 1.60 eV for Fe₃O₄ (Supplementary Fig. 26) and Co₃O₄ (Supplementary Fig. 27), respectively. EPR tests also confirmed that O_v was much easier to form on the surface of CuO than on the surface of Fe₃O₄ and Co₃O₄ (Supplementary Fig. 28 and Supplementary Table 2), which should be the reason that the activity of Fe₃O₄ and Co₃O₄ cannot be enhanced by OH⁻ (Supplementary Fig. 4).

The pre-treated CuO, namely alkali off-site etching, could enhance the removal of SMX as well, but its activity was much lower than that of alkali in-situ etching (Fig. 2f). This could be attributed to the fact that after the consumption of pre-formed surface -OH and O_v, there was no alkali to regenerate O_v and surface -OH (Fig. 2g, h). It is noteworthy that the used CuO (OH⁻ off-site etching) still had relative EPR signal

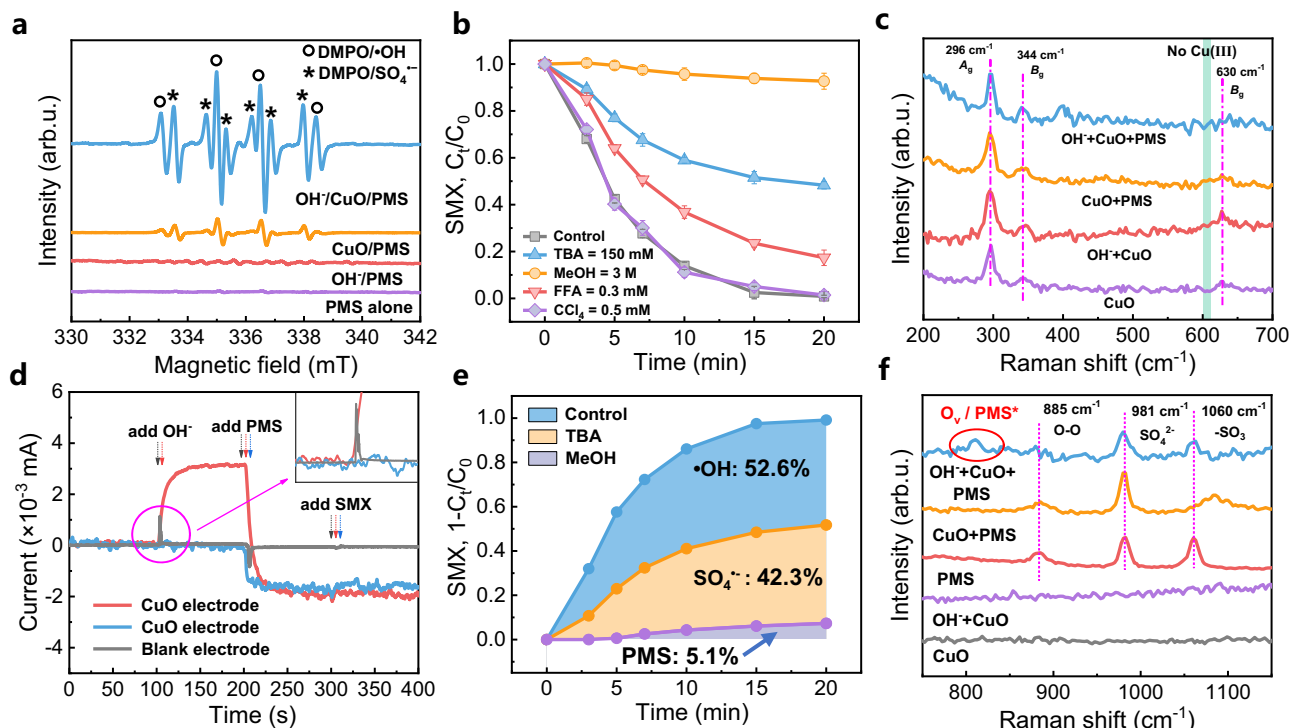


Fig. 3 | Mechanistic investigation of reactive oxygen species (ROSs) generation and PMS activation pathways. **a** EPR spectra of DMPO-trapped radicals ($\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$) across different catalytic systems. **b** Quenching experiments identifying dominant reactive species in $\text{OH}^-/\text{CuO}/\text{PMS}$ system. **c** Identifying the existence of

Cu(III) by in-situ Raman spectra in the $\text{OH}^-/\text{CuO}/\text{PMS}$ system. **d** Electrochemical i-t response curves tracking interfacial electron transfer processes. **e** The contribution of PMS, $\bullet\text{OH}$, and $\text{SO}_4^{\bullet-}$ to SMX removal. **f** In-situ Raman spectroscopic monitoring of PMS activation in various situations.

intensity of O_v , which was similar to that of CuO subjected to 0.3 mM OH^- in-situ etching, but the latter achieved a significantly higher removal rate of SMX (Supplementary Fig. 29). The results of the XPS assay and analysis further verified the above conclusion (Supplementary Figs. 30 and 31). Compared to the remarkable residual of O_v (Fig. 2g), the surface $-\text{OH}$ of the used CuO (both OH^- in-situ etching and OH^- off-site etching) was almost consumed (Fig. 2h). It seemed that although O_v served as the key active site, its high catalytic activity required the synergistic assistance of surface $-\text{OH}$. This mechanism will be further elucidated in the DFT-based mechanistic study of PMS activation. In addition, higher OH^- dosage bring about higher surface $-\text{OH}$ and O_v on CuO (Supplementary Fig. 32), but resulted in relative lower activity, as evaluated by k_{app} (Supplementary Fig. 5a) and PMS consumption (Supplementary Fig. 6b). This is likely due to the electrostatic repulsion, since PMS (HSO_5^-) is negative charged, and more OH^- on the CuO surface imparts a more negative charge to it.

Identification of major reactive oxygen species and their contributions

In $\text{OH}^-/\text{CuO}/\text{PMS}$ system, $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ were identified as the key ROS. The potential roles of other ROS commonly involved in PMS-based advanced oxidation processes (AOPs) were systematically excluded through a series of experiments. No EPR signal of $\text{O}_2^{\bullet-}$ was found in all conditions, and there were similar EPR signal intensities of $^1\text{O}_2$ for all conditions (including background value, namely PMS itself without catalyst) (Supplementary Figs. 33 and 34), indicating that $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$ were not the key ROS for SMX removal. Even in the atmosphere of O_2 , there was no signal of $\text{O}_2^{\bullet-}$ and no enhanced signal of $^1\text{O}_2$, indicating that O_2 indeed did not contribute the ROS formation (Supplementary Fig. 35). In the presence of alkali, there was a much stronger EPR signal intensity of $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ (Fig. 3a). To further verify the role of $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$, quenching experiments were carried out, in which, the

dosage of quenchers was calculated based on Eq. (1) to achieve completely quenching²³.

$$k_{\text{quencher, ROS}} \times C_{\text{quencher}} \geq 500 \times k_{\text{antibiotic, ROS}} \times C_{\text{antibiotic}} \quad (1)$$

Tertbutyl alcohol (TBA, quencher of $\bullet\text{OH}$) and methanol (MeOH, quencher of both $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$) could make the degradation rate of SMX decrease from near 100% to 51.8% and 7.4%, respectively, indicating that both $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ contributed a lot in the removal of SMX. Although furfuryl alcohol (FFA, quencher of $^1\text{O}_2$) had a certain degree of inhibition on SMX removal, this inhibition effect should be ascribed to the consumption of $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ by FFA since the high reaction rate between FFA and these two radicals (Supplementary Table 3). Tetrachloromethane (CCl_4), as a quencher of $\text{O}_2^{\bullet-}$ ($k_{\text{O}_2^{\bullet-}, \text{CCl}_4} = 1.1 \times 10^9$)⁵⁷, did not affect the reaction rate, further excluding the involvement of $\text{O}_2^{\bullet-}$ (Fig. 3b). In the studied range of OH^- dosage (0.2–0.6 mM), the main ROSs had no change based on the results of quenching experiments (Supplementary Fig. 36) and EPR tests (Supplementary Fig. 37). The generation of $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ increased along with the OH^- concentration from 0 to 0.4 mM. A further increase in OH^- concentration resulted in a slight decrease in SMX removal and a reduction in the generation of $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$. This decline may be attributed to enhanced electrostatic repulsion between the negatively charged PMS and the CuO surface, as higher OH^- concentrations lead to a more negatively charged surface of CuO^{58–60}.

Besides the aforementioned ROS ($\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$, $^1\text{O}_2$ and $\text{O}_2^{\bullet-}$), high-valent metal and adsorbed PMS (PMS^*) are often proposed as important contributors in PMS-based AOPs^{23,61}. As the possible high-valent metal in $\text{OH}^-/\text{CuO}/\text{PMS}$ system, Cu(III) was detected by periodate colorimetric method (Cu(III) -periodate complex: 400–450 nm)^{62,63} and in-situ Raman spectroscopy (Cu(III) : 600–620 cm^{-1})^{64,65}, but the

related characteristic peak was not observed (Supplementary Fig. 39 and Fig. 3c). Thus, the generation of Cu(III) could be ruled out. Regarding the electron transfer process (ETP) mediated by PMS*, this pathway was also excluded based on pre-mixing experiments, since the pre-mixing of OH⁻, CuO, and PMS led to significant inhibition of SMX removal (Supplementary Fig. 40). In this process, OH⁻, CuO, and PMS were pre-mixed at different times, and then SMX was added to initiate the reaction. ETP-dominated process usually does not consume the PMS in the absence of target pollutants; thus, the removal rate of pollutants will not decrease in the pre-mixing test^{66–70}. The observed rapid decrease in SMX removal with increasing pre-mixing time indicates that ETP did not contribute to SMX degradation in the OH⁻/CuO/PMS system. This point was further verified by the i-t curve (Fig. 3d) since there was no observable current change after SMX addition. In fact, the quenching effect of methanol could rule out the role of Cu(III) and PMS*, but the above results provided more solid evidence.

To quantify the contribution of •OH, SO₄^{•-} and PMS direct oxidation to SMX degradation, the integral areas under the reaction kinetic curves—plotted as 1-C_t/C₀ (Y axis) versus time (X axis)—were calculated and compared based on quenching experiment results. Herein, •OH, SO₄^{•-}, and PMS contributed 52.6%, 42.6%, and 5.1% to the removal of SMX, respectively (Fig. 3e).

The activation mechanisms of PMS in OH⁻/CuO/PMS system

The formation of O_v on the CuO surface through OH⁻ etching constitutes a reduction process, while the consumption of O_v during PMS activation represents an oxidation process. Thus, the addition of alkali and PMS would cause an opposite current, which was proved well by i-t curves in Fig. 3d. The introduction of defect sites was usually favourable for electron transfer at the material surface⁷¹. The arc radius of Nyquist curves of CuO after being in-situ etched by alkali were all smaller than that of the initial CuO, in the order of CuO > 0.2 mM OH⁻ + CuO > 0.3 mM OH⁻ + CuO > 0.4 mM OH⁻ + CuO (Supplementary Fig. 41a). According to the fitted equivalent circuit model, the main electrical resistance was from the charge transfer resistance of the electrode, which decreased in the range of OH⁻ concentrations from 0 to 0.4 mM (Supplementary Fig. 41b and Supplementary Table 4). It could be inferred that the existence of O_v attenuated the charge transfer resistance and boosted carrier transport⁷². A related key intermediate was further found at about 809 cm⁻¹ in in-situ Raman tests (Fig. 3f). This new characteristic peak corresponded to the vibration of the O–O bond belonging to metastable O_v–•OOSO₃, and this metastable species would be readily decomposed to produce SO₄^{•-}^{73,74}. Noting that, although O_v existed in the untreated CuO, O_v–•OOSO₃ was not observed. It should be that in the absence of OH⁻, O_v cannot efficiently regenerate after being consumed. It is noteworthy that although O_v sites were present in the untreated CuO, the O_v–•OOSO₃ intermediate was not detected. This is likely because, in the absence of OH⁻, O_v cannot be efficiently regenerated once consumed.

The above points consolidated the important role of O_v and surface –OH. To further investigate their synergistic effect, four configurations (CuO, OH-CuO, O_v-CuO, OH-O_v-CuO in Supplementary Fig. 42) were employed in the DFT calculations. According to the projected crystal orbital Hamiltonian preoccupation (pCOHP) without adsorption of PMS (Fig. 4a Top), OH-O_v-CuO had the most antibonding states under Fermi level. This means that OH-O_v-CuO is prone to lose electron for reducing the antibonding states to get stable state. In other words, OH-O_v-CuO is expected to have the strongest interaction with PMS, since PMS is an electron-deficient molecule that tends to accept electrons. This point was well reflected after PMS adsorption (Fig. 4a Bottom) because there was highest absolute value of integrated pCOHP (IpCOHP) (–1.32 eV) and shortest Cu–O (Cu and the O of PMS) bond length (1.82 Å). These results clearly demonstrate that OH-O_v-CuO has the strongest interaction with PMS.

As is well known, the d-band center is a robust descriptor for evaluating the interaction between a catalyst and an adsorbed molecule. Therefore, the d-band center of Cu was calculated to further analyze the interaction between the catalyst and PMS (Fig. 4b). In the absence of PMS, the Cu d-band center of OH-O_v-CuO was located closest to the Fermi level (–1.49 eV), indicating that the combination of surface –OH and O_v enhances the interaction between Cu sites and PMS (Fig. 4b Left)⁷⁵. Upon PMS adsorption, the d-band center of the Cu atom in OH-O_v-CuO shifted the farthest, decreasing to –2.211 eV (Fig. 4b Right), demonstrating that both of surface –OH and O_v are responsible for the enhanced interaction of catalyst and PMS. In the presence of both surface –OH and O_v, there were the highest PMS adsorption energy (–4.13 eV) and the longest O–O bond of PMS (1.481 Å) (Fig. 4c), which were much higher than that being triggered by O_v or surface –OH itself. This further indicated that the synergy of surface –OH and O_v played key roles in PMS activation.

As reported, high electron spin density can facilitate PMS activation to produce radicals^{76,77}. Analysis of the electron spin density distribution (Fig. 4d) revealed that the introduction of surface –OH significantly increased the electron spin density on Cu atoms near O_v sites. Metal centers with high spin electron density, characterized by delocalized unpaired electrons, promote electron transfer between the metal and PMS^{76,77}. Based on charge density difference and Bader charge analysis (Fig. 4e), the synergy of surface –OH and O_v indeed promoted the electron transfer (0.237 e⁻) from catalyst to PMS. The results of transition state calculations showed that the synergy of OH-O_v-CuO had the lowest free energy barrier in triggering PMS to form radicals (Fig. 4f and Supplementary Fig. 43), which strongly indicate the synergistic effect of surface –OH and O_v in PMS activation. Increasing the number of surface –OH and O_v can result in lower energy barrier of •OH and SO₄^{•-} formation (Fig. 4f and Supplementary Fig. 44), which had a similar tendency to experimental results, namely the positive correlation between the activity of CuO and the content of surface –OH and O_v in the range of 0 to 0.4 mM OH⁻. Based on all of the results of DFT calculations, it is reasonably to deduce the process of PMS activation as that after grabbing electron from CuO, the O–O bond of PMS would be broken with the formation of •OH or SO₄^{•-} (Fig. 4g). On the whole, there were four steps in the process of OH⁻ enhanced •OH and SO₄^{•-} formation, including OH⁻ adsorption, O_v formation, PMS adsorption, and •OH and SO₄^{•-} formation, namely the combination of Figs. 2e and 4f. Compared to the other three steps, the energy barrier of •OH and SO₄^{•-} formation was highest, which can be regarded as the rate limited step.

Evaluation of application feasibility of OH⁻/CuO/PMS system

As known, •OH and SO₄^{•-} dominated AOPs usually deserve low efficiency to remove target pollutants in the application. In OH⁻/CuO/PMS system, HCO₃⁻ and NOM had significant inhibition on SMX removal among the studied coexisting substances (Cl⁻, SO₄²⁻, NO₃⁻, HPO₄²⁻, HCO₃⁻, Ca²⁺, Mg²⁺, and NOM) (Supplementary Fig. 45a–i). To guarantee the efficient removal of SMX in the practical application, the dosage of PMS (0.4–0.5 mM), OH⁻ (0.4–0.5 mM) and CuO (100–400 mg/L) was increased (Supplementary Fig. 46). The need for remarkably higher CuO dosage suggested that the inhibition of HCO₃⁻ and NOM on SMX removal was due to their coverage of catalytic sites. Under the updated condition, the degradation rate of SMX could be up to 100%, 99.7%, and 99.1% within 40 min in tap water, Qinghe River water (surface water of Beijing), and secondary effluent of waste water treatment plant (WWTP), respectively (Supplementary Fig. 47a and Supplementary Table 5). In these three waters, the consumed PMS were 78.09%, 67.58%, and 69.89%, respectively (Supplementary Fig. 47b), and concentrations of leached Cu ions were all below 0.1 mg/L (Supplementary Fig. 47c). In addition, OH⁻ itself (0.5 mM) or CuO itself (400 mg/L) still could not efficiently trigger PMS to remove SMX (Supplementary Fig. 48).

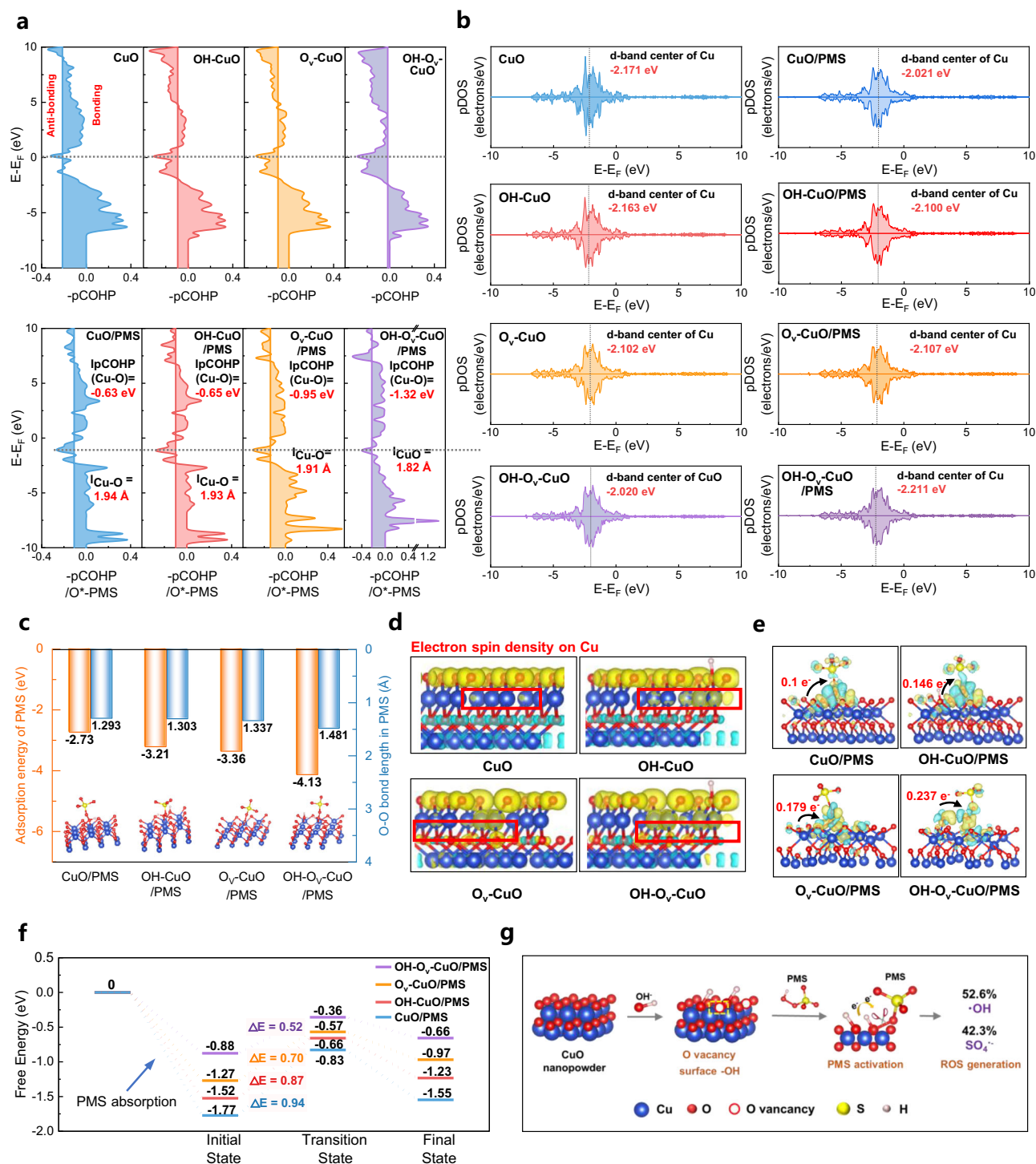


Fig. 4 | Mechanistic insights based on DFT calculation into enhanced PMS activation via the synergy of oxygen vacancy (O_v) and surface hydroxy (OH). **a** Top: The pCOHP diagrams of CuO, OH-CuO, O_v-CuO, and OH-O_v-CuO. Bottom: The pCOHP between the central Cu atoms and the O atoms as PMS adsorption. Relative IpCOHP values and Cu-O bond lengths were display in the figures. **b** The pDOS for CuO, OH-CuO, O_v-CuO, and OH-O_v-CuO (Left) before and (Right) after PMS adsorption. **c** The adsorption energy and O-O bond length of PMS on the

surface of catalysts. **d** The electron spin density distribution of various structure surfaces (blue means negative value, yellow means positive value). **e** Charge density difference and Bader charge change in CuO/PMS, OH-CuO/PMS, O_v-CuO/PMS, and OH-O_v-CuO/PMS system (blue means positively charged, yellow means negatively charged). **f** The reaction energy barriers for PMS activation to produce •OH and SO₄^{•-} on CuO, OH-CuO, O_v-CuO, and OH-O_v-CuO. **g** Schematic illustrations for the catalytic mechanism of OH⁻/CuO/PMS system.

In the absence of externally added pollutants, various pharmaceutical and personal care products (PPCPs) were detected in the secondary effluent of a WWTP. Nearly all of these compounds were completely removed after treatment with the OH⁻/CuO/PMS system (Fig. 5a1 and a2). The characterization with 3D excitation-emission-matrix (EEM)

spectra showed that proteins (IV region) and humic acid (V region) were the main organics in the secondary effluent of WWTP, which were effectively removed by the treatment of OH⁻/CuO/PMS system but not by other systems (OH⁻/PMS, CuO/PMS) (Supplementary Fig. 49). The TOC removal rate of secondary effluent was up to 60.9%

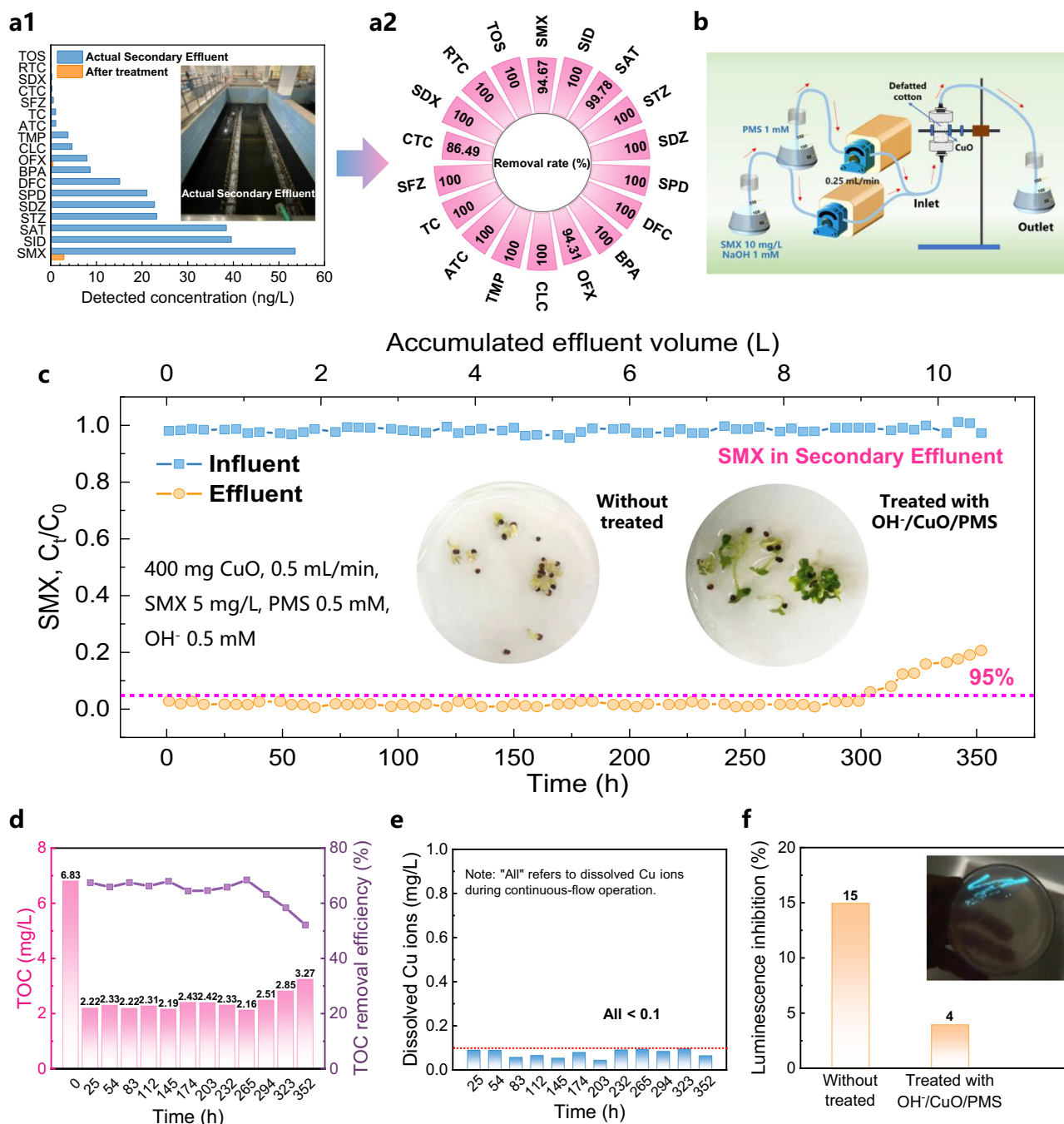


Fig. 5 | Practical performance evaluation and environmental impact assessment of the OH⁻/CuO/PMS system. a Treatment effect on residual pharmaceutical and personal care products (PPCPs) in secondary effluent from waste water treatment plant (WWTP) with OH⁻/CuO/PMS system, including sulfamethoxazole (SMX), sulfaisodimidine (SID), sulfamethazine (SAT), sulfathiazole (STZ), sulfadiazine (SDZ), sulfapyridine (SPD), diclofenac (DFC), bisphenol A (BPA), ofloxacin (OFX), clindamycin (CLC), trimethoprim (TMP), azithromycin (ATC), tetracycline (TC), sulfafurazole (SFZ), clarithromycin (CTC), sulfadimethoxine (SDX), roxithromycin (RTC), tylosin (TOS). **a1** The detected concentration of PPCPs in

secondary effluent before and after treatment. **a2** The removal rate of PPCPs in secondary effluent after the treatment. Experiment conditions: [NaOH]₀ = 0.5 mM, [PMS]₀ = 0.5 mM, [Catalyst]₀ = 400 mg/L, T = 25 °C. **b** Schematic representation of continuous-flow reactor configuration. **c** Long-term SMX removal efficiency over 15-day operation (inset: phytotoxicity assessment using *Brassica juncea* growth assay). **d** The change and removal efficiency of TOC. **e** Associated Cu ion leaching during continuous running. **f** Ecotoxicity evaluation using *Vibrio fischeri* bioluminescence inhibition test (inset: corresponding optical images) before/after the continuous-flow treatment.

(Supplementary Fig. 50a), and the indicator UV₂₅₄, representing the natural humic macromolecules and aromatic compounds with C=C double bonds and C=O double bonds⁷⁸, reduced by 51.67% (Supplementary Fig. 50b). In summary, the organics in secondary effluent could be well removed by OH⁻/CuO/PMS system. Furthermore, the leached Cu ions and consumed PMS were about 0.08 mg/L and 71.1%, respectively (Supplementary Fig. 50c). OH⁻/CuO/PMS system can efficiently remove

the trace organics from other three actual secondary effluents of municipal WWTPs, without extra addition of organic pollutants as well (Supplementary Figs. 51, 52, and 54), even using a lower concentration of PMS (0.25 mM) (Supplementary Fig. 53). In addition, OH⁻/CuO/PMS system also perform well in treating actual secondary effluent from an industrial park (Supplementary Fig. 55). Thus, OH⁻/CuO/PMS system had good applicability in treating actual wastewaters.

To further evaluate the practical applicability of OH⁻/CuO/PMS system for treating the secondary effluent of WWTP, a continuous-flow reactor was employed (hydraulic residence time, HRT ≈ 40 min) (Fig. 5b). In the secondary effluent, an extra 5 mg/L SMX was added. The results showed that this reactor operated stably for about 300 h, during which more than 95% removal of SMX was achieved (Fig. 5c) with average 64.3% TOC removal rate (Fig. 5d) and lower than 0.1 mg/L of leached Cu ions (Fig. 5e). The consumption rate of PMS was maintained at more than 84% (Supplementary Fig. 56), and the pH of the effluent was stabilized at around 7 (Supplementary Fig. 57). Obviously, OH⁻/CuO/PMS had the desired performance in treating the secondary effluent of WWTP. The used CuO for 15 d in a continuous-flow reactor was characterized. The micro-morphology and phase structure of used CuO did not change significantly, but the O_v and surface -OH groups were heavily depleted. (Supplementary Fig. 58 and Supplementary Table 2).

The toxicity of the effluent of the continuous-flow reactor was detected via luminescent bacteria (*Vibrio fischeri*), some plants (*Brassica napus*, *Mung bean*, *Rice*), and *zebrafish embryos*. Compared to the untreated one, the effluent behaved much lower inhibition to luminescent intensity of *Vibrio fischeri* (Fig. 5f) and the growth of plants (Fig. 5c inset for *Brassica napus*, and Supplementary Fig. 59 for *Mung bean* and *Rice*). As for *zebrafish embryos*, the untreated actual wastewater had no inhibition on its growth (Supplementary Fig. 60). Thus, there was no significant difference cultured in the untreated and treated actual wastewater, but which can indicate that the toxicity had no increase at least. Owing to the complex components of the secondary effluent of WWTP, it was hard to detect the degradation products of SMX. Thus, the analysis of the degradation products was carried in the simulated wastewater, namely, with a background of ultrapure water. According to electrospray ionization quadrupole time-of-flight mass spectrometry (ESI Q TOF MS) qualitative analysis results (Supplementary Data 2 and Supplementary Table 6), 12 possible intermediates were detected, and three different degradation pathways were deduced according to the reaction sites (N-atom, aniline group, and S-N sites) (Supplementary Fig. 61). The toxicity of these intermediates was predicted by the Toxicity Estimation Software Tool (T.E.S.T.). All the intermediates of SMX have reduced developmental toxicity, while most of them were of negative mutagenicity (Supplementary Fig. 62a, b). And all the intermediates had lower bioaccumulation factors as well (Supplementary Fig. 62c). In brief, OH⁻/CuO/PMS system could significantly reduce the toxicity of SMX.

Discussion

In this study, an innovative alkali in-situ etching strategy was developed for the sustainable generation of oxygen vacancies (O_v) on low-cost commercial CuO, enabling highly efficient peroxymonosulfate (PMS) activation for degrading refractory pollutants. The key scientific and technological advancements include: (i) The alkali in-situ etching approach achieved cost-effective and continuous O_v replenishment on CuO surfaces, effectively preventing catalyst deactivation through dynamic vacancy regeneration. (ii) The constructed OH⁻/CuO/PMS system demonstrated exceptional catalytic performance, attaining complete SMX removal ($k_{app} = 4.2 \times 10^{-3} \text{ s}^{-1}$, representing a 42-fold enhancement compared to pristine CuO) with 65.9% mineralization efficiency and remarkably low metal leaching (<0.05 mg/L), significantly surpassing conventional catalytic systems. (iii) The synergy of O_v and surface -OH is the origin of enhanced catalytic activity of CuO with alkali in-situ etching, promoting electron transfer from CuO to PMS and reducing the formation energy barriers of radicals (SO₄^{•-} or •OH). (iv) A corresponding continuous-flow system maintained SMX removal efficiency of >95% over 300 h (HRT ≈ 40 min) with 64.3% mineralization and significant toxicity reduction in the secondary effluent from WWTP, demonstrating the super stability. This work established a promising paradigm for active site regeneration engineering in advanced

oxidation. However, the current alkali in-situ etching approach is limited to Cu-based material. Future research should focus on developing more universally applicable regeneration strategies, particularly for environmentally friendly iron-based catalysts.

Methods

Chemicals

The target CuO (≥99.0%, CAS: 1317-38-0) used in this study was purchased from Macklin Biochemical Technology Co., Ltd. more details about characterization methods were described in Supplementary Text 1. PMS (Peroxymonosulfate, KHSO₅•0.5KHSO₄•0.5K₂SO₄), sodium thiosulfate pentahydrate (Na₂S₂O₃•5H₂O), tertiary butyl alcohol (TBA), methanol (MeOH), ethanol (EtOH), furfuryl alcohol (FFA), tetrachloromethane (CCl₄), 5,5-dimethyl-1-pyrrolidinium N-oxide (DMPO), 2,2,6,6-tetramethyl-4-piperidinol (TEMP) were provided by Aladdin Reagent Co., Ltd. Sulfamethoxazole (SMX), atrazine (ATZ), ibuprofen (IBP), carbamazepine (CBZ), quinoline (QNL), potassium iodide (KI), and naphthol were purchased from Sinopharm Chemical Reagent Co., Ltd. For details of other reagents, please refer to Supplementary Text 2. All reagents used in the experiments were of analytical grade without further purification, which were prepared with ultrapure water (18.2 MΩ·cm) as solvent within the validity period. Stock solutions of PMS (0.1 M) and Na₂S₂O₃ (0.1 M) were reconstituted once a week.

Catalytic activity experiments

Batch experiments were conducted with mechanical stirring (350 rpm) in a 100 mL beaker at 25 °C. The initiation of the reaction involved the sequential addition of NaOH, CuO, and PMS with predetermined concentrations to the solution containing the target contaminants. Samples were taken at given time intervals and filtered through polyethersulfone membranes (0.22 μm), quenched with excess Na₂S₂O₃ (2 mM). The CuO after use was separated by a solvent filter, collected, and washed three times each with ultrapure water and ethanol, followed by drying for subsequent repeat experiments.

Statistics and reproducibility

All experiments and characterizations, including microscopy analyses, were performed in duplicate to ensure reproducibility and obtain reliable mean values with standard deviation. The linear relationship between the active site detection signal intensity and the catalytic reaction activity was fitted within a 95% confidence interval using a linear function of the form “y = ax + b”. The direction of the correlation (positive or negative) was determined by the coefficient “a”.

Corresponding analytical methods

The concentrations of the compounds of interest were determined on a high-performance liquid chromatography (HPLC, 1260 infinity III, Agilent, USA) equipped with an XDB-C18 chromatography column (4.6 × 150 mm, 5 μm), the specific assays were listed in Supplementary Table 7. The PMS concentration was determined according to the method recorded in Supplementary Text 3, and Cu ion dissolution was determined by a high-resolution inductively coupled plasma emission spectrometer (ICP, Plasma Quant PQ9000). Mineralization of contaminants was determined by a TOC meter at a reaction temperature of 850 °C and an oxygen pressure setting of 0.1 MPa. Detailed information on pollutant degradation efficiency and reaction kinetics calculations was provided in Supplementary Text 4. Other experimental procedures, including in-situ Raman tests, electrochemical measurements, reactive oxygen species identification, quantification and contribution calculations, and identification of intermediates, could be searched in Supplementary Text 5–14.

Calculation and DFT models

All the density functional theory (DFT) calculations were conducted using the Vienna Ab initio Simulation Package (VASP)^{79,80} to obtain

relaxed geometries and total energies. The projector augmented wave (PAW) method was implemented to describe nuclei–electron interactions^{81,82}. For exchange–correlation energy calculations, we employed the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) framework with a kinetic energy cutoff of 420 eV^{83–85}. The computational model consisted of a four-layer p (3 × 3) CuO slab with periodic boundary conditions, where the two uppermost layers were allowed to relax during structural optimization. A 15 Å vacuum layer along the Z-axis was incorporated to minimize inter-slab interactions. Convergence criteria were established as follows: the electronic self-consistent field (SCF) iterations were terminated when energy differences fell below 1 × 10^{−5} eV/atom, while atomic positions were optimized until residual forces became less than 0.04 eV/Å. Charge density difference analysis was subsequently performed using the VESTA software package. The calculation method for formation energy of surface O_v, projected electronic structure analysis, and transition state reaction energy barrier were offered in Supplementary Text 15–17.

Data availability

The data that support the findings of the study are included in the main text and supplementary information files. Raw data can be obtained from the corresponding author upon request. Source data have been deposited in the Figshare repository⁸⁶. Source data are provided with this paper.

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X.Z. and L.W. designed research; X.Z. and X.L. performed research; X.Z., L.W., and Z.G. analyzed data; L.W. and L.D. language polishing and visualization; J.W., H.Z., and Y.S. supervised research; and X.Z. and L.W. wrote the paper.

Competing interests

The authors declare no competing interests.

Additional information

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