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# Synchronous Reduction–Oxidation Process for Efficient Removal of Trichloroacetic Acid: H\* Initiates Dechlorination and •OH Is Responsible for Removal Efficiency

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**S** Supporting Information

**ABSTRACT:** Degradation of chlorinated disinfection by-products using the electroreduction process has been considered as a promising approach for advanced water treatment, while the removal efficiency is restricted by a high barrier for dechlorination of intermediates only by reductive atomic hydrogen  $(H^*)$  and excessive cost required for reducing atmosphere. In this paper, we predict that the dechlorination efficiency for trichloroacetic acid (TCA), a typical chlorinated disinfection by-product, can be accelerated via a synchronous reduction—oxidation process, where the dechlorination barrier can be lowered by the oxidation reactions toward the critical intermediates using hydroxyl radicals (·OH). Based on scientific findings, we constructed a synchronous reduction—oxidation platform using a Pd-loaded Cu/Cu<sub>2</sub>O/CuO array as the core component. According to the combined results of



theoretical and experimental analyses, we found that the high dispersion of nano-sized Pd on a photocathode was beneficial for the production of a high concentration of H\* at low overpotential, a perquisite for initiating the dechlorination reaction. Simultaneously, excess H\* has the potential to convert  $O_2$  to  $H_2O_2$  in ambient conditions (air condition), and  $H_2O_2$  can be further activated by a Cu-containing substrate to  $\cdot$ OH for attacking the critical intermediates. In this system, ~89.1% of TCA was completely dechlorinated and ~26.8% mineralization was achieved in 60 min, which was in contrast to the value of ~65.7% and mineralization efficiency of only ~1.7% achieved through the reduction process (Ar condition).

## INTRODUCTION

Chlorinated disinfection by-products, such as trichloroacetic acid (TCA), are known to have potential human carcinogenicity.<sup>1-5</sup> Among numerous TCA removal techniques, the electrochemical dechlorination process has been reported to be the most promising approach for effective removal of the target molecules due to the manageable operation cost.<sup>6-9</sup> In principle, the electrochemical TCA degradation involves multidechlorination processes that are mainly determined by electron transfer from cathode to aqueous solution (direct reduction), as well as a hydrogenation reaction induced by atomic hydrogen  $(H^*)$  under anaerobic reducing atmospheres (indirect reduction).<sup>6,10-12</sup> In stark contrast to the negligible reduction performance of the direct reduction pathway, it was recently proved that the indirect hydrogenation process was responsible for the whole dechlorination process.<sup>10,12-15</sup> However, the degradation of TCA using the conventional electroreduction process was still restricted by the relatively low reduction efficacy and excessive high cost for reducing atmosphere (Ar or N<sub>2</sub>) as well.<sup>6,8,11,16</sup>

To reveal the cause of inefficiency, we looked into the TCA dechlorination pathway via the hydrogenation reaction.

Theoretically, the TCA molecule is first attacked by H\*, and one of the Cl<sup>-</sup> groups in TCA would combine with H\* to form HCl and Cl<sub>2</sub>C–COOH intermediates (Figure 1).<sup>6,10,11,16</sup> Then, another H\* naturally combines with Cl<sub>2</sub>C–COOH to form HCl<sub>2</sub>C–COOH. The above dechlorination process is repeated until all Cl<sup>-</sup> groups are stripped and TCA is



Figure 1. Calculated free energy diagram of TCA dechlorination processes for H\* alone and H\*/ $\cdot$ OH coexisting condition. Cl, O, and H atoms are shown in green, red, and white, respectively.

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converted to H<sub>3</sub>C-COOH. Upon theoretical analyses, we found that the presence of H\* was beneficial for protonation of the critical intermediate of Cl<sub>2</sub>C-COOH to stable HCl<sub>2</sub>C-COOH, with the Gibbs energy change ( $\Delta G$ ) value of -4.17 eV, so that required high energy for dechlorination reactions by another H\* (Path I). Thus, even if there were abundant H\*, the reaction could not continue readily. By contrast, Cl<sub>2</sub>C-COOH will be easily converted into another intermediate (HOCl<sub>2</sub>C-COOH) after accepting the hydroxyl radical (. OH) with the steadier Gibbs energy change, which facilitates the dechlorination process by subsequent oxidation reactions (Path II). This meant that the orderly cooperation of H\* and  $\cdot$ OH could effectively lower the energy requirements and thus significantly improve the TCA dechlorination efficiency. Moreover, ·OH could also partially mineralize intermediate products and achieve thorough TCA removal at the end. In addition to limited dechlorination rate, the generation of large concentration of chlorinated intermediates was the other restriction toward TCA removal only by the reactive oxygen species (ROS)-dominated oxidation reactions.<sup>17-19</sup> Thus, efficient TCA removal required that H\* and ·OH must be generated simultaneously and coexist in the reaction system.

To obtain an efficient coexistence system of H\* and ·OH, herein, we designed and precisely constructed a novel Pdloaded Cu/Cu<sub>2</sub>O/CuO (CCC/Pd) array used as a cathode. The addition of Pd not only eliminated corrosion of CCC via fast interfacial charge transfer but also, according to the theoretical and experimental analyses, generated abundant H\* on the surface of Pd in air conditions, which rapidly started the dechlorination reaction of TCA removal. Simultaneously, the excess H\* could efficiently reduce O<sub>2</sub> in solution to form H<sub>2</sub>O<sub>2</sub> concurrently, and the formed  $H_2O_2$  would further be activated by Cu<sup>+</sup>/Cu<sup>2+</sup> to generate abundant ·OH for oxidative degradation of critical dechlorination intermediates. More importantly, the anaerobic environment required for the traditional reduction process (H\* reduction) can be effectively substituted by operation in air, while meeting the requirements for the coexistence of H\* and ·OH at the same time.

With the involvement of  $\cdot$ OH, the reaction activity was greatly improved and the TCA could be removed rapidly and thoroughly through the full cooperation of H\* and  $\cdot$ OH. Meanwhile, the tedious and expensive process for creating an oxygen-free environment could be avoided, and the TCA removal costs were effectively reduced. The TCA removal mechanism of the CCC/Pd photoelectrode was proposed and elucidated, wherein H\* started the dechlorination reaction and  $\cdot$ OH effectively attacked the generated critical intermediates to achieve rapid and thorough TCA removal. Our discovery can be expected to drive great advances in the removal of TCA and even chlorinated disinfection by-products in ambient conditions.

#### EXPERIMENTAL SECTION

Synthesis of Photoelectrodes. The Cu/Cu<sub>2</sub>O/CuO (CCC) heterostructure was synthesized via a one-step calcination process (in Scheme S1). Commercial Cu foils (purity: 99.9% Cu, thickness: 0.1 mm) were cut to a fixed area of 4 cm<sup>2</sup> (2 cm  $\times$  2 cm), successively washed with 1.5 M HCl and deionized water for 5 min, and then dried naturally. The pretreated Cu foils were vertically placed in quartz crucibles and calcined in a muffle furnace by an established program mode (calcination at 300 °C for 1 h followed by treatment at 500 °C for 2 h). The addition of Pd nanoparticles was

conducted by electrochemical deposition in a three-electrode system (CHI 660E, Shanghai Chenhua Instrument Co., China). The as-prepared CCC was used as the working electrode, and a Ag/AgCl electrode and Pt foil acted as the reference and counter electrodes, respectively. A solution composed of 5 mM NH<sub>4</sub>Cl and 0.5 mM PdCl<sub>2</sub> was used as the deposition electrolyte. The applied bias was controlled at -0.8 V (vs Ag/AgCl) and run for 10 min. Then, the obtained CCC/Pd photoelectrode was rinsed with deionized water and dried naturally.

Characterization. Scanning electron microscopy (SEM, SU-8020, Japan), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM) (JEOL JEM-2100F, Japan) were used to investigate the morphology and crystal structure of the as-prepared photoelectrodes. The phase composition of the samples was identified by X-ray diffraction (XRD, Bruker D8, Cu K $\alpha$  ( $\lambda$  = 0.15406 nm), Germany). The surface state and elemental composition analyses were conducted via X-ray photoelectron spectroscopy (XPS, VG ESCALAB210, Al K $\alpha$  (h = 1486.6 eV), Thermo Fisher Scientific, USA). UV-vis diffuse reflection spectra (DRS) were collected on a U-3900 spectrophotometer. Fluorescence spectra were measured on a luminescence spectrometer (F-4500, Hitachi, Japan). Electron spin resonance (ESR) spectra were recorded on a Bruker model ESR E500 spectrometer by using the spin-trap reagent DMPO (5,5-dimethyl-1-pyrroline N-oxide, Sigma Chemical Co., USA) in methanol (for superoxide radical  $(\cdot O_2^{-})$  and water (for H\* and  $\cdot OH$ ).

Density Functional Theory (DFT) Calculation. The first principles calculations in the framework of density functional theory, including structural and electronic performances, were carried out based on the Cambridge sequential total energy package known as CASTEP. The exchange-correlation functional under the generalized gradient approximation (GGA) with norm-conserving pseudopotentials and Perdew-Burke-Ernzerhof functional were adopted to describe the electron-electron interaction. An energy cutoff of 750 eV was used and a k-point sampling set of  $7 \times 7 \times 1$  was tested to be converged. A force tolerance of 0.01 eV Å<sup>-1</sup>, energy tolerance of  $5.0 \times 10^{-7}$  eV per atom, and maximum displacement of 5.0  $\times$  10<sup>-4</sup> Å were considered. The vacuum space along the z direction was set to be 15 Å, which was enough to avoid interaction between the two neighboring images. The Grimme method for DFT-D correction was considered for all calculations. The detailed descriptions for each unit were further listed in the Supporting Information.

Experimental Setup. All photoelectrochemical experiments were carried out on the CHI 660E electrochemical workstation. A 150 W xenon lamp was utilized as the visible light source with a cutoff filter ( $\lambda > 400 \text{ nm}$ , 100 mW cm<sup>-2</sup>), and the spectrum of the lamp is shown in Figure S1. A doublechamber electrolysis cell was used as the reactor for TCA removal. The scheme of the reaction unit is given in Figure S2. The anode cell (50 mL) and cathode cell (50 mL) were separated by a proton exchange membrane (PEM, Nafion 117, Du Pont). The effective working area of as-prepared photoelectrodes was 4 cm<sup>2</sup> (2 cm × 2 cm). A Ag/AgCl electrode and Pt foil  $(2 \text{ cm} \times 2 \text{ cm})$  acted as the reference and counter electrodes, respectively. In the process of the experiments, a given volume of catholyte was sampled and filtered by a 0.45  $\mu$ m membrane before detection. The stability and repeatability of photoelectrodes were measured by repeating the experiment under identical conditions 10 times.



Figure 2. Characterizations. (a) TEM and (b) EDX mapping images of the CCC/Pd photoelectrode. (c) XRD patterns and (d-f) high-resolution XPS spectra of CCC/Pd and CCC photoelectrodes.

The scavenger quenching experiments were carried out via adding different scavengers. In detail, the scavengers were tertiary butanol (TBA, 0.5 mM, Sigma, 99.5%) for atomic H<sup>\*</sup>, · OH, Fe(II)-EDTA for H<sub>2</sub>O<sub>2</sub>, and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPOL) for  $\cdot$ O<sub>2</sub><sup>-</sup>.

Analytical Methods. The concentrations of trichloroacetic acid (TCA), dichloroacetic acid (DCA), monochloroacetic acid (MCA), and the products (including acetic acid and Cl<sup>-</sup>) were measured by an ion chromatograph (IC, ICS-5000, Thermo Fisher Scientific, USA). The Pd and Cu elemental analyses were carried out via an inductively coupled plasma source mass spectrometer (ICP-MS, Thermo Fisher iCAP Q, USA). The dissolved organic carbon (DOC) of the solution was investigated via a total organic carbon analyzer (TOC-L, Shimadzu, Japan). The generated H<sub>2</sub>O<sub>2</sub> content was determined by the iodometric method, with the potassium iodide solution (KI) and ammonium molybdate solution (H<sub>8</sub>Mo<sub>2</sub>N<sub>2</sub>O<sub>7</sub>) added in advance.<sup>20</sup> Formation of ·OH was detected via the fluorescence method with benzoic acid (BA) as a probe molecule.<sup>21</sup> The photoelectrochemical analyses were performed in a standard three-electrode configuration. The specific tests included cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronoamperometry (I-T curve), electrochemical impedance spectroscopy (EIS), incident photon conversion efficiency (IPCE), and Mott-Schottky curves.

## RESULTS AND DISCUSSION

**Characterization of As-Prepared Electrodes.** The SEM images (Figure S3) indicated that irregularly shaped Cu<sub>2</sub>O thin films were grown on smooth-faced Cu foils, and CuO nanowire arrays (~100 nm in diameter) were further grown in situ on the surface of Cu<sub>2</sub>O. Pd nanoparticles were uniformly distributed on the surfaces of CuO, and the particle diameters ranged from 2 to 10 nm. The TEM and HRTEM images (Figure 2a) further depict the intimate contact between Pd and CuO. The lattice spacing of 0.224 nm matched well with the (111) plane of palladium.<sup>22–24</sup> Pd was only decorated on the surfaces of the CuO rather than entering into the internal lattice. This hierarchical structure was beneficial to vectorial transfer of electrons and then enhanced the electronic

utilization.<sup>25,26</sup> The EDX mapping images (Figure 2b) further confirmed the uniform distribution of Pd over the CuO surfaces.

XRD analyses showed the well-crystallized nature of CCC and CCC/Pd. In Figure 2c, the phases of Cu, Cu<sub>2</sub>O, and CuO could be observed simultaneously, revealing the step-by-step phase transition from Cu to CuO during the thermal treatment process.<sup>25</sup> Due to the low content and fine particle size, only one characteristic diffraction peak (41.7°) of Pd was observed in the XRD pattern of CCC/Pd.<sup>6,8,11</sup> The addition of Pd would slightly decrease the peak intensities due to its shielding effect, further confirming the successful synthesis of the CCC/Pd photoelectrode.

EDX and survey spectra (Figure S3f,g) showed the coexistence of Pd, O, and Cu elements in CCC/Pd. In Figure 2d, the peaks at 335.5 and 340.7 eV corresponded to the spinorbit coupling of Pd  $3d_{5/2}$  and Pd  $3d_{3/2}$ , respectively, which could be assigned to metallic palladium.<sup>11,13,22</sup> The other two peaks located at 336.3 and 341.7 eV were identified as the characteristic peaks of  $PdO_{x}$ , which is also named as "electrodeficient" Pd species.<sup>6,10</sup> This result indicated that the Pd would combine with the oxygen existing on the surface of CuO, which could further promote the formation of Pd nanoparticles. In Cu 2p spectra (Figure 2e) of CCC and CCC/Pd, eight distinct peaks showed the coexistence of Cu,  $Cu_2O$ , and CuO.<sup>21,27,28</sup> It is worth noting that the Cu 2p peak position in CCC/Pd had a slight blue shift in comparison to that in CCC, which is most likely caused by the attraction of Pd to the oxygen atoms. This result further confirmed the existence of  $PdO_r$  in CCC/Pd. The broad peaks in the O 1s spectra (Figure 2f) could be resolved into two peaks centered at 531.8 and 530.2 eV, belonging to O=C and O-Cu bonds, respectively.<sup>29–32</sup> In the O 1s spectra of CCC/Pd, a new peak appearing at 536.7 eV was ascribed to Pd-O bond.<sup>6,8,11</sup> After the addition of Pd, the peak intensity of the O-Cu bond was reduced significantly, which was attributed to the shielding effect of Pd nanoparticles.

**Photochemical Properties.** After identifying the hierarchical structure, the photochemical properties of the CCC/ Pd electrode was further investigated using various measurements. As shown in Figure S4, the CCC showed good

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absorption in the visible light region, which was in agreement with intrinsic absorption properties of Cu<sub>2</sub>O and CuO.<sup>33–35</sup> However, the introduction of Pd could further improve the visible light absorption, probably owing to the strong light absorption capacity of Pd nanoparticles. Under intermittent light irradiation, the CCC/Pd electrode exhibited the strongest photocurrent responses in all of cathode potentials, which was almost ~2 times larger than that of CCC, indicating the effective photocarriers separation efficiency in the presence of nano-sized Pd clusters (Figure 3a). Moreover, there was a



Figure 3. Photoelectrochemical properties. (a) LSV curves, (b) IPCE spectra, (c) EIS curves, and (d) PL spectra of Cu, CCC, and CCC/Pd photocathodes. Experimental conditions: temperature (25 °C), electrolyte (50 mM Na<sub>2</sub>SO<sub>4</sub>), LSV scan rate = 10 mV s<sup>-1</sup>, applied voltage (-0.5 V vs RHE), frequency range (0.1 Hz–100 kHz), disturbance voltage (10 mV), and in visible light irradiation.

sharp photocathodic current spike in the J-V curve of CCC, while the transient peaks almost disappeared after depositing Pd on the surface of CCC. The disappeared current spike was ascribed to rapid electron depletion, implying the fast charge transfer after loading of Pd.

Moreover, in contrast to the value of ~39% for the pristine CCC, the incident photo-to-current conversion efficiency (IPCE) for CCC/Pd increased to ~50%, further indicating that the addition of Pd could effectively convert photons into electrons (Figure 3b).<sup>25</sup> As for CCC/Pd, the smaller arc radius in EIS indicated that faster interfacial charge transfer would efficiently promote spatial charge separation (Figure 3c). In contrast to the pristine CCC, the weak PL signal when using the CCC/Pd clearly showed that Pd could quickly trap electrons that accumulated on the surface of CuO to participate in the subsequent reduction reactions, thereby effectively inhibiting the recombination of photogenerated charge carriers (Figure 3d).<sup>36,37</sup>

Radical Analysis. The excellent photoelectric conversion performance of CCC/Pd has the potential to supply electrons continuously, thereby generating sufficient H\* in the CCC/Pd system. As shown in Figure 4a, the nine characteristic peaks of DMPO-H\* were clearly observed at the CCC/Pd electrode, while no signals were detected for the CCC or Cu electrodes. For H\* formation, H\* generally is generated in the first step of the hydrogen evolution reaction (Volmer step), which is followed by electrochemical desorption (Heyrovsky step) or chemical desorption (Tafel step).<sup>38</sup> <sup>40</sup> In principle, the H\* would appear on the electrode at an appropriate cathode potential. In contrast to the potential of -0.5 V vs RHE for the CCC/Pd electrode, the potential for the production of the comparable amount of H\* was markedly retarded when using the CCC or Cu electrodes. This indicated that addition of Pd could significantly minimize the overpotential for H\* production and improve electrochemical activity. Moreover, the noble metal Pd acted as an excellent catalyst for hydrogen storage, which could effectively inhibit the conversion from H\* to H<sub>2</sub> (Heyrovsky or Tafel steps) and ensured a higher steadystate concentration of adsorbed hydrogen on the electrode surface. Pd also possessed a unique property of adsorbing and storing H\* via the formation of Pd-H bonds based on multiple  $\sigma$ -bonding between the hydrogen atoms and d orbitals of Pd atoms.<sup>8,11,13,41</sup> Even if H<sub>2</sub> molecules had formed, they would be easily dissociated on the Pd surface and thus provide sufficient H\*. H\* evolution on the surface of Pd also could be



Figure 4. Radical generation mechanism. (a, b) DMPO spin-trapping ESR spectra recorded for different radicals in the Cu-based photochemical reaction system under different atmospheres. (c, d) Calculated free energy diagram for the formation of  $H^*$ ,  $O_2^-$ ,  $HO_2$ , and  $H_2O_2$  on surfaces of CuO and CuO/Pd, respectively.



Figure 5. TCA removal performance. TCA dechlorination rate constants for Cu, CCC, and CCC/Pd electrodes at different cathode potentials in the (a) absence and (b) presence of visible light irradiation. Experimental conditions:  $TCA_0$  (5 mg L<sup>-1</sup>), electrolyte (5 mM Na<sub>2</sub>SO<sub>4</sub>), initial pH (5.1), reaction time (60 min), and temperature (25 °C).

further investigated by CV curves.<sup>13</sup> It was clearly seen that an oxidation peak of H\* appeared in the potential ranges of 0.5-0.7 V, and the peak area gradually increased with decreasing starting potential (from 0.37 to -0.03 V vs RHE) (Figure S5a).

In addition, the excess H\* also could effectively reduce dissolved oxygen to form ·OH simultaneously. ESR analyses were conducted to detect the coexistence of H\* and ·OH in the CCC/Pd system. In the presence of oxygen (ambient condition), ESR spectroscopy exhibited that some additional signals attributed to reactive oxide species (ROSs) coexisted in this system, while the weak signals can be recorded in both other systems (Figure 4b). The results indicated that  $H^*$  and  $\cdot$ OH could coexist in the CCC/Pd system under natural conditions. Meanwhile, we further compared CV curves of CCC/Pd with and without O2 under the same starting and fixed ending potentials (Figure S5b). The H\* evolution peak sharply decreased after adding O2, which implied that the H\* generated on the surface of Pd could effectively reduce O2 simultaneously. In addition, negligible difference from LSV curves before and after O2 saturation can be observed, indicating the absence of direct electron transfer between the cathode and O<sub>2</sub> molecules (Figure S5c), which can be further confirmed by EIS in Figure S5d. Based on the combination with band structure analyses (Figure S6), it was reasonable to conclude that ROS was generated via O<sub>2</sub> reduction by H\* instead of originating from oxygen or H<sub>2</sub>O reduction reactions.44

Moreover,  $\cdot$ OH generation pathways were then explored using the theoretical calculations. In principle, the traditional routes for the  $\cdot$ OH generation were mainly through the  $\cdot$ O<sub>2</sub><sup>-</sup> dominant process by the way of  $O_2 \rightarrow \cdot O_2^- \rightarrow H_2O_2 \rightarrow \cdot OH$  and other possibility as follows:  $O_2 \rightarrow HO_2 \rightarrow H_2O_2 \rightarrow \cdot OH$ . As the critical intermediates, the thermodynamic and kinetic properties of proton reduction into H\* and O<sub>2</sub> reduction into  $\cdot$ O<sub>2</sub><sup>-</sup> on the CCC and CCC/Pd electrodes were compared via DFT calculations with CuO and CuO/Pd as models (Figure 4c,d). On CuO, the H\* formation was exothermic by ~1.19 eV. Similarly, on CuO/Pd, the H\* formation was exothermic by ~3.05 eV. As such, the H\* formation on CuO/Pd and CuO was all preferred over  $\cdot O_2^-$  generation.

Furthermore, we compared Gibbs free energy ( $\Delta G$ ) profiles and reaction pathways among CuO and CuO/Pd to understand the H<sub>2</sub>O<sub>2</sub> generation activity (Figure 4 and Figure S7). As shown in Figure 4c, negative  $\Delta G$  value ( $\sim$ -2.73 eV) for formation of H\* on CuO implied that the reduction of H<sup>+</sup> can be proceeded spontaneously. Meanwhile,  $\Delta G$  for protonation of HO<sub>2</sub>· and  $*H_2O_2$  were ~0.07 and ~-0.98 eV, respectively, and thereby, the potential-limiting step of  $H_2O_2$  desorption on CuO in this mechanism was ~3.64 eV. At zero electrode potential (U = 0), an energy barrier of ~3.64 eV was required for H<sub>2</sub>O<sub>2</sub> production on CuO. In contrast, when H<sub>2</sub>O<sub>2</sub> production proceeds via another reaction path, the energy barrier of only  $\sim 2.33$  eV was required for H<sub>2</sub>O<sub>2</sub>. desorption. By contrast, the introduced Pd possessed a unique property of adsorbing and storing of H\* via the formation of Pd-H bond.<sup>11</sup> As for CuO/Pd, a weak chemical bonding effect toward H\* ( $\Delta G \sim -0.66$  eV) was beneficial for subsequent protonation reactions so that the following desorption process can be proceeded preferably, with an energy barrier of only ~1.71 eV, which was in sharp contrast to the value of ~3.05 eV when proceeding in the  $\cdot O_2^-$ -dominated path. Theoretical predictions were subsequently verified using the radical quenching experiments. After introduction of TBA (a trapping agent for H\*) in the CCC system (Figure S8), it was clearly observed that the concentration of H<sub>2</sub>O<sub>2</sub> remained at the same level, unambiguously indicating H<sub>2</sub>O<sub>2</sub> in CCC was produced via the  $\cdot O_2^{-}$ -dominated path. By contrast, the rapid decreased H<sub>2</sub>O<sub>2</sub> in the CCC/Pd system implied that H\* should be the dominated species during the H<sub>2</sub>O<sub>2</sub> production process. Furthermore, we compared the changes of the concentrations of H<sub>2</sub>O<sub>2</sub> before and after the introduction of the  $O_2^-$  trapping agent. Conversely, the concentration of  $H_2O_2$ when using the CCC catalyst was remarkably decreased in the presence of quencher. Overall, based on these results analyses, it was reasonably speculated that the ROSs in CCC/Pd were coming from the H\*-dominated  $O_2$  reduction, and the  $H_2O_2$ production on CuO was preferred through the ·O2-dominated pathway.

TCA Removal Performance. The TCA removal performance in the coexistence of H\* and ·OH was investigated in detail. In the absence of light illumination, the CCC/Pd electrode always showed optimal TCA dechlorination performance compared to Cu and CCC electrodes at cathode potentials in the range of 0.0 to -0.7 V vs RHE (Figure 5a). The apparent reaction rate constant ( $k_{obs}$  value) of the three cathodes increased with the decrease in potential (from 0.0 to -0.7 V). In particular, at -0.5 V, CCC/Pd possessed the highest apparent reaction rate constant ( $k_{obs} = 1.48 \text{ min}^{-1}$  $g_{Pd}^{-1}$ ), and ~83.4% of TCA was dechlorinated within 60 min. For CCC and CCC/Pd, the  $k_{obs}$  at -0.7 V decreased slightly compared to  $k_{obs}$  at -0.5 V, which was mainly due to the inhibition from excessive H<sub>2</sub> evolution.<sup>10,11,13</sup> After turning on the light (Figure 5b), the dechlorination performance was greatly enhanced for both of CCC and CCC/Pd photoelectrodes, with  $k_{\rm obs}$  increasing ~2 times at -0.5 V vs RHE. As



**Figure 6.** TCA removal mechanism. (a) TCA removal for the CCC/Pd photocathode under Ar,  $O_2$ , and air atmosphere. Inset: dechlorination and DOC removal efficiency. (b, c) Intermediates, final products, and carbon balance of TCA removal in the CCC/Pd system under Ar and air atmosphere. (d) TCA removal performance using the Cu, CCC, and CCC/Pd systems in the absence/presence of TBA. Experimental conditions: TCA<sub>0</sub> (5 mg L<sup>-1</sup>), electrolyte (5 mM Na<sub>2</sub>SO<sub>4</sub>), initial pH (5.1), photocathode potential (-0.5 V vs RHE), temperature (25 °C), and in visible light irradiation.

shown in Figure S9a, the photoelectrocatalytic (PEC) efficiency for the TCA dechlorination was much higher than photocatalysis (PC) or electrocatalysis (EC) alone.

It was clear that the reduction rate of TCA increased with increasing initial TCA concentration for the three cathodes (Figure S10a). The  $k_{obs}$  showed a linear relationship with the logarithm of the initial TCA concentration within a specific range (Figure S11a). This indicated that both of the diffusion and electron transfer were responsible for the dechlorination process. In addition, an acidic condition was beneficial to TCA dechlorination for the CuO-based cathode (Figure S10b), which was primarily due to the fact that the shielding effect of H<sup>+</sup> could effectively lower the electrostatic repulsion between TCA and cathode. Moreover, the sufficient H<sup>+</sup> not only facilitated the charge transfer but also enhanced hydrogen evolution reaction (Figure S11b), whereby high concentration of H\* can be achieved for the efficient TCA removal performance. In this optimal condition, we noted that the  $k_{\rm obs}$  of TCA dechlorination in ambient conditions was obviously larger than those in Ar-saturated and O2-saturated conditions (Figures S10c and S11c). This indicated that TCA was more easily dechlorinated and mineralized with the coexistence of H\* and ·OH.

**Redox Synergistic Effects.** The experimental results demonstrated that the presence of H\* (reduction) and  $\cdot$ OH (oxidation) in the system could remarkably enhance the TCA dechlorination rate. To further reveal the mechanism of redox synergistic effects of H\* and  $\cdot$ OH, we compared the TCA removal performance in the case of various conditions (Ar, O<sub>2</sub>, and air conditions) (Figure 6a and Figure S12). In contrast to Ar conditions with the highest concentration of H\*, a faster TCA conversion rate can be observed in the coexistence of  $\cdot$  OH and medium H\* (air condition), with the dechlorination efficiency increased from 65.7 to 89.1%. Under O<sub>2</sub> conditions, the lowest concentration of H\* corresponded to the slowest dechlorination rate, emphasizing the role of H\* in initiating the dechlorination process. To achieve the agreeable circumstance,

the compromise formula was acceptable to the air condition, where the concentration of H\* can be well preserved for initiating the dechlorination process, and the presence of ·OH can accelerate the reaction efficiency. During the TCA removal process, the critical intermediates, including DCA, MCA, acetic acid, and Cl-, can be detected in both Ar and air conditions (Figure 6b,c), implying that H\* initiated the dechlorination reaction. However, different from those in the reduction process alone, the critical intermediates DCA and MCA exhibited much lower concentrations in air conditions, which might be ascribed to the different dechlorination pathways induced by ·OH. In addition, when proceeding in the complete dechlorination reaction, the stoichiometric ratio of Cl<sup>-</sup> production and TCA consumption should be 3:1. Under air conditions, the stoichiometric ratio of Cl<sup>-</sup> and TCA was 2.6:1 (with coexistence of H\* and ·OH), almost approximating to the ideal dechlorination process, while the corresponding stoichiometric ratio of Cl<sup>-</sup> and TCA was only ~1.9:1 in Ar conditions. While calculating the mass balance during TCA dechlorination at the CCC/Pd photocathode, we confirmed that the total carbon of three chloroacetic acids decreased from  $\sim$ 30.9 to  $\sim$ 8.8  $\mu$ M and the mineralization efficiency is  $\sim$ 26.8%, which was in sharp contrast to the DOC removal efficiency of only ~1.7% in the counterpart system. Thus, we proposed that a synchronous reduction-oxidation process should be involved toward the efficient TCA removal under air conditions.

To gain deep insight into synergetic role of the H\* and  $\cdot$ OH, radical quantification and quenching experiments were thereafter performed. We primarily applied the PL technique to analyze the amount of  $\cdot$ OH in the CCC/Pd system (Figure S12),<sup>21,43</sup> and the high fluorescence signal corresponded to the high concentration of  $\cdot$ OH in CCC/Pd. Meanwhile,  $\cdot$ OH generation was due mainly to the activation of H<sub>2</sub>O<sub>2</sub> by the Cu substrate, which is demonstrated and revealed in Figure S13. After the addition of tertiary butanol (TBA), a scavenger for H\* and  $\cdot$ OH (Figure 6d),<sup>6,11,43</sup> the TCA dechlorination rate



**Figure 7.** Stability and reusability. (a) Recycling runs of TCA dechlorination for Cu, CCC, and CCC/Pd electrodes. (b) Concentrations of released Cu and Pd after each cyclic use. Experimental conditions:  $TCA_0$  (5 mg  $L^{-1}$ ), electrolyte (5 mM  $Na_2SO_4$ ), initial pH (5.1), reaction time (60 min), photocathode potential (-0.5 V vs RHE), temperature (25 °C), and in visible light irradiation.

obviously decreased by ~3.5 times. In view of that it was extremely hard to respectively scavenge the H\* and ·OH radicals, TCA removal through the oxidation and electron transfer processes (only the CCC system) was compared in the absence/presence of TBA. However, after quenching of ·OH radicals, the  $k_{obs}$  only decreased by ~1.3 times in this electron transfer-dominated process, which also emphasized the role of H\* during the removal process.

As we all know, the H\* initiated the dechlorination process; however, the reaction efficiency of which was mainly limited by the energy barrier for the dechlorination process in the critical intermediates. We further investigated and found that the C atom attached to the Cl atom in Cl<sub>2</sub>C-COOH showed a negative charge number (-0.19 eV), meaning that Cl<sub>2</sub>C-COOH would preferably attract H\* to form HCl<sub>2</sub>C-COOH, which was detrimental to the subsequent dechlorination reactions (Figure \$14). However, after conversion of some portion of the H\* into ·OH, the key intermediate of Cl<sub>2</sub>C-COOH was more readily to be captured by the ·OH, with the accumulation of other intermediate (HOCl<sub>2</sub>C-COOH), whereby the conventional hydrogenation-dechlorination process might be substituted by the oxidation-removal process. Meanwhile, in contrast to the intermediate of HCl<sub>2</sub>C–COOH by the hydrogenation process, the production of HOCl<sub>2</sub>C-COOH was beneficial for the thorough removal of TCA in the subsequent reactions due to the higher electron density of Cl atoms (from -0.05 to -0.08 eV). In addition, the Cl-C bond in HOCl<sub>2</sub>C-COOH had a longer bond length than that in HCl<sub>2</sub>C-COOH, indicating that the Cl-C bond in HOCl<sub>2</sub>C-COOH was easier to break, which was also beneficial for further reduction or oxidation process. Overall, the H\* and ·OH coexisting system has the potential to convert the traditional dechlorination process into a more energy consumption path; thereby both highly effective dechlorination and mineralization processes can be eventually achieved in this platform.

**Stability of As-Prepared Electrodes.** The stability and reusability of as-prepared electrodes were compared via their performance over 10 cycles and the release of Cu and Pd (Figure 7). The activities of Cu and CCC/Pd remained almost unchanged after 10 cycles, and the released Cu and Pd in the CCC/Pd system were all below 0.02 and 0.01 mg  $L^{-1}$ , respectively. In contrast, the CCC electrode exhibited gradually reduced TCA dechlorination after cycling and the final efficiency was only ~43.7%, but the content of released Cu was in the range of 0.01–0.02 mg  $L^{-1}$  similar to that of the CCC/Pd electrode. In addition, according to chronoamperometric currents in Figure S15, the current magnitudes of Cu and CCC/Pd electrodes were almost remaining unchanged in

each cycle, while the current of CCC gradually decline with the growth of cycle times.

In sharp contrast to severe corrosion for pristine CCC electrode, the low-magnification SEM image of the used CCC/Pd electrode almost maintained the same structure in contrast to the fresh one (Figures S16 and S17). Further, the physicochemical properties of the used CCC/Pd electrode were almost unchanged from the comparison results of XPS, XRD, DRS, and J-V and current-time curves. This implied that the CCC/Pd electrode possessed excellent anticorrosion ability, which might be ascribed to the fast electron transfer from CCC to Pd. Thus, in the CCC/Pd electrode, CCC heterostructure realized space-charge separation, and the Pd acted as an electron reservoir to further enhance the electron transfer and utilization efficiency.

### ASSOCIATED CONTENT

## **S** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b05389.

Schematic of photoelectrode synthesis and charge transfer and redox in photoelectrocatalysis; SEM images, DRS spectra; band structure analysis; CV curves, I-T curves; analyses of influencing factors; DFT calculations; and stability test (PDF)

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## Notes

The authors declare no competing financial interest.

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