Dechlorination of Trichloroacetic Acid Using a Noble Metal-Free Graphene–Cu Foam Electrode via Direct Cathodic Reduction and Atomic H*

Ran Mao,^{†,‡} Ning Li,^{†,‡} Huachun Lan,[†] Xu Zhao,[†] Huijuan Liu,[†] Jiuhui Qu,^{*,†} and Meng Sun^{†,‡}

[†]Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, P. R. China

[‡]University of Chinese Academy of Sciences, Beijing, 100049, P. R. China

S Supporting Information

ABSTRACT: A three-dimensional graphene–copper (3D GR–Cu) foam electrode prepared by chemical vapor deposition method exhibited superior electrocatalytic activity toward the dechlorination of trichloroacetic acid (TCAA) as compared to the Cu foam electrode. The cyclic voltammetry and electrochemical impedance spectra analysis confirmed that GR accelerated the electron transfer from the cathode surface to TCAA. With the applied cathode potential of -1.2 V (vs SCE), 95.3% of TCAA ($500\text{ }\mu\text{g/L}$) was removed within 20 min at pH 6.8. TCAA dechlorination at the Cu foam electrode was enhanced at acidic pH, while a slight pH effect was observed at the GR–Cu foam electrode with a significant inhibition for Cu leaching. The electrocatalytic dechlorination of TCAA was accomplished via a combined stepwise and concerted pathway on both electrodes, whereas the concerted pathway was efficiently promoted on the GR–Cu foam electrode. The direct reduction by electrons was responsible for TCAA dechlorination at Cu foam electrode, while at GR–Cu foam electrode, the surface-adsorbed atomic H* also contributed to TCAA dechlorination owing to the chemical storage of hydrogen in the GR structure. Finally, the potential applicability of GR–Cu foam was revealed by its stability in the electrocatalytic dechlorination over 25 cycles.

INTRODUCTION

Chloroacetic acids (CAAs), including mono-, di-, and trichloroacetic acids (MCAA, DCAA, and TCAA, respectively) are commonly detected disinfection byproducts in chlorinated water and known to have suspected human carcinogenicity.^{1,2} The U.S. Environmental Protection Agency proposed a maximum contaminant level of $60\text{ }\mu\text{g/L}$ for the sum of five haloacetic acids (HAAs), i.e., MCAA, DCAA, TCAA, mono-(MBAA) and dibromoacetic acid (DBAA).³ Reductive dehalogenation which usually requires an addition of reducing agents such as zerovalent iron, hydrogen and sodium sulphite has been considered as an attractive option to remove HAAs in water.^{4–7} For example, Hozalski et al. reported that HAAs were susceptible to reduction by zerovalent iron (Fe^0) and in compounds containing chlorine, the final product of reactions with Fe^0 was MCAA.⁴

Application of the electrochemical reductive process in the removal of halogenated organic compounds (HOCs) is receiving growing interest. The electrochemical reduction may ensure the selective removal of halogen atoms from HOCs without producing toxic byproducts or adding any toxic chemicals.^{8,9} For instance, Sonoyama et al. reported an efficient electrochemical dehalogenation of several regulated trihalo-

methanes using metal electrodes, while Li and Farrell demonstrated the reductive dechlorination of trichloroethene at iron and palladized-iron electrodes.^{10,11} Electrochemical reduction could be easily applied as a continuous treatment using a flow-through reactor and the pollutants present at low concentrations could be efficiently decomposed using electrodes with a large surface area.

The cathode materials play an important role in the electrochemical reduction process.^{12,13} Some researchers have reported that palladium (Pd) and gold (Au) modified electrodes showed good activities for the reduction of CAAs.^{14,15} Pd has been explored for catalytic contaminant reduction due to the property to retain atomic H*, a highly activated intermediate hydrogen atom produced from water reduction which would serve as a strong reducing agent.^{16,17} However, it is desirable to design cathode materials free from noble metal catalysts for the efficient dechlorination of CAAs.

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The three-dimensional graphene (3D GR) emerged as an ideal cathode material due to its large specific surface area, porous structure and excellent electrical conductivity.^{18,19} Compared with the 2D GR which is vulnerable to cracks, wrinkling, defective sites, and some other mechanical problems, 3D GR is structurally a well-defined material which offers mechanical robustness in all three directions.²⁰ 3D GR has been used for oxygen reduction reaction, electrochemical sensing of dopamine and glucose, and electrodeposition of heavy metal ions.^{18,21–23} It can be typically fabricated by chemical vapor deposition of carbon containing gas on the 3D metal foam substrate.^{24,25} Besides, Cu foam is considered as a good candidate for electrode materials in water treatment due to the low cost and extensive specific surface area. Hence, the 3D GR–Cu foam electrode is expected to show a high electrocatalytic activity toward the dechlorination of CAAs. As far as we know, there have been no studies of such material for the treatment of HOCs. Furthermore, it is recognized that the electrochemical reduction of contaminants may occur through both direct and indirect mechanisms.^{11,15,16} Direct reduction may occur by electron tunneling or by the formation of a chemisorption complex for target compounds with cathode materials.¹¹ Indirect reduction occurs via the surface-adsorbed atomic H*.^{15,16} It was deduced that the indirect reduction was responsible for the dechlorination of CAAs by Pd modified electrodes.¹⁵ However, the mechanism of the electrocatalytic dechlorination of CAAs at the GR–Cu foam cathode is unknown.

In the present work, the noble metal-free 3D GR–Cu foam electrode was fabricated through chemical vapor deposition method and its performance for TCAA dechlorination in the electrochemical reduction process was systematically investigated. The results showed that the 3D GR on Cu foam significantly facilitated the reductive transformation and promoted the concerted dechlorination pathway. The difference with a Pd-containing electrolytic system concerning the direct and indirect reduction mechanism, the feasibility of the electrochemical reductive treatment of HAAs-contaminated drinking water, and stability of the electrode in the repeated applications were also discussed.

■ EXPERIMENTAL SECTION

Synthesis of Electrodes. The 3D GR–Cu foam electrode was fabricated by chemical vapor deposition method in a quartz tube furnace. For the synthesis of 3D GR–Cu foam, Cu foam (pore density 100 ppi, thickness 1.2 mm) was first ultrasonically cleaned by aqueous acetic acid solution, alcohol, and acetone, respectively, to remove oxides and organic pollutants. Then the substrate was placed in the middle of the quartz tube. Fed with mixed gas of 300 sccm Ar and 35 sccm H₂ under about 300 mTorr, the furnace was heated to 940 °C for 2 h. Subsequently, methane (10 sccm, purity >99.99%) was introduced into the system, and then cracked and deposited on Cu foam. The furnace was naturally cooled down to room temperature, and the 3D GR–Cu foam electrode can thus be obtained. The Pd modified carbon fiber (Pd–C) electrode was prepared via our previously reported electrodeposition method.²⁶ The carbon fiber paper substrate (thickness 0.28 mm, bulk density 0.44 g cm^{−2}, TGP-H-090, Toray) is a graphitic sheet of the randomly arranged short carbon fibers.

Experimental Setup. All electrochemical experiments were performed with an EG&G model 263A workstation (Princeton Applied Research, U.S.A.). A divided three-electrode system

batch reactor was employed for TCAA reduction, which was separated into cathode cell (50 mL) and anode cell (50 mL) by the proton exchange membrane (Nafion-117, Du Pont). The scheme of the experimental setup is given in Figure S1 of the Supporting Information (SI). The as-prepared electrodes with a geometric surface area of 10 cm² (2.5 × 4 cm²) served as the working electrode. A platinum wire with 72 mm in length and 1.5 mm in diameter was used as the counter electrode, and a saturated calomel electrode (SCE) was employed as the reference electrode. The system was magnetically stirred at a rate of 700 rpm. A constant potential on the cathode was controlled using the amperometric *i-t* technique with the electrochemical workstation throughout the reduction experiments. The conductivity of the tested tap water and 2 mM Na₂SO₄ background electrolyte was 398 and 443 μS/cm, respectively. The initial pH of the catholyte was adjusted to 6.8 by H₂SO₄ and NaOH before electrolysis unless otherwise specified and was not adjusted during the process. In order to investigate the effect of pH on the electrochemical reduction of TCAA, the initial conductivity of the catholyte at different pH values was adjusted to 5820 μS/cm using 0.5 M Na₂SO₄. All the experiments were carried out in triplicate. For clarity of presentation, only mean values of three experiments are presented in some cases, while standard deviations are less than 5% of the calculated mean.

The electrochemical analyses including cyclic voltammetry (CV), electrochemical impedance spectra (EIS) and amperometric analysis were performed in an undivided conventional three-electrode cell with the same counter electrode and reference electrode as in reduction experiments. CV curves was conducted with reference to the open circuit potential. EIS was recorded by applying an AC voltage with 10 mV amplitude in a frequency range 0.1–100 kHz at open circuit voltage.

Analytical Method. All solutions were prepared using analytical grade reagents and Millipore water (specific conductivity of 18.2 MΩ). The concentrations of HAA and chloride in the solution were measured using ion chromatograph (IC, ICS-2000, Dionex, Sunnyvale, CA). The detection limits of MCAA, DCAA, TCAA, MBAA, DBAA, acetic acid, and chloride are 1.5, 1.0, 1.8, 2.5, 1.7, 0.6, and 2.0 μg/L, respectively. The concentration of Cu²⁺ was measured by the inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Co.) with the detection limit of 10 μg/L.

The morphology of the electrodes was investigated using a scanning electron microscope (SEM, Zeiss SUPRA 55) equipped with an energy dispersive X-ray (EDX) analyzer. SEM image of the Pd–C electrode is given in Figure S2. Transmission electron microscopy (TEM) images were collected on an FEI Tecnai G2 F20 S-Twin working at 200 kV. X-ray powder diffraction (XRD) patterns of the samples were obtained with an X'Pert PRO Powder diffractometer (PANalytical Co.) with Cu K_α radiation. The specific surface area measurement was performed by the Brunauer–Emmett–Teller (BET) method. Raman spectra were recorded on a Bruker Senterra Raman spectrometer and microscope through a 20X objective lens using a 20 mW and a 514 nm laser excitation. X-ray photoelectron spectra (XPS) was performed using a PHI Quantera SXM (PHI-5300/ESCA, ULVAC-PHI, Inc.). The electron spin resonance (ESR) signals of radicals spin trapped by spin-trap reagent 5,5'-dimethyl-1-pyrroline-N-oxide (DMPO, purchased from Sigma Chemical Co.) were detected on a Bruker model ESR 300E spectrometer equipped

Figure 1. (a) Low- and (b) high-magnification TEM images of GR, where a SAED pattern recorded from the center of the domains is shown in the inset, (c) XRD patterns, and (d) Raman spectra of the Cu foam and GR–Cu foam electrodes.

with a quanta-Ray Nd:YAG laser system as the irradiation source.

RESULTS AND DISCUSSION

Characterization of the electrodes. The low- and high-magnification TEM images of the GR transferred onto the TEM grids are shown in Figure 1a and b. The GR with 10 layers (indicated by the arrow) can be identified clearly through the folded edge, along with the selected area electron diffraction (SAED) pattern shown in inset, revealing the typical hexagonal crystalline nature of GR. It is found that GR sheets are composed of graphite layers and most of them have 8–10 layers. The EDX mapping analysis provides clear information about the uniform distribution of GR throughout the whole structure of Cu foam (Figure S3). XRD patterns of the Cu foam and GR–Cu foam electrodes are recorded in Figure 1c, where diffraction peaks assigned to (111), (200), (220), and (310) of metallic Cu are observed. On the basis of the analysis of Raman spectroscopy, the two prominent bands observed in the GR–Cu foam around 1586 and 2682 cm^{-1} are assigned to the G and 2D bands of carbon, respectively, proving that GR were successfully synthesized on the Cu foam substrate (Figure 1d). The I_{2D}/I_G intensity ratio was known to strongly correlate with the number of GR layers.²⁷ This value is low in the synthesized GR–Cu foam, which is consistent with the TEM observation of the multilayered GR. The weak defect-related D peak reflects the high quality of the 3D-GR.

Performance of the GR–Cu Foam Electrode for Dechlorination of CAAs. First, the electrocatalytic dechlorination of TCAA at the Cu foam and GR–Cu foam electrodes was performed under the same experimental conditions. The removal efficiency of TCAA through GR–Cu foam electrode

achieves 95.2% at 20 min; meanwhile, the value is 48.9% for Cu foam electrode (Figure 2). It is also shown that the

Figure 2. Electrocatalytic dechlorination of TCAA at the Cu foam and GR–Cu foam electrodes ($[TCAA]_0 = 3.06 \mu\text{M}$, applied potential = -1.2 V vs SCE, $2 \text{ mM Na}_2\text{SO}_4$, initial pH = 6.8).

dechlorination of TCAA follows a pseudo-first order kinetic model, which is expressed as $-\ln(C_t/C_0) = kt + b$, where t is the reaction time (min), k is the reaction rate constant (min^{-1}), b is a constant, and C_t and C_0 are the TCAA concentrations (μM) at times of $t = t$ and $t = 0$, respectively. The observed reaction rate constants (k_{obs}) of TCAA through Cu foam and GR–Cu foam cathode are found to be 0.038 and 0.137 min^{-1} ,

respectively. The results indicate that the GR–Cu foam electrode shows a much higher electrocatalytic activity in contrast to Cu foam electrode for TCAA dechlorination.

The electrocatalytic activities of the two cathodes toward TCAA dechlorination were further characterized by CV scan and EIS. When TCAA was added, the peak current of -0.95 mA appeared at the potential of -1.19 V on the Cu foam (Figure 3a). By contrast, on the GR–Cu foam, the peak current

Figure 3. (a) CV spectra of TCAA reduction on Cu foam and GR–Cu foam (scan rate: 10 mV/s), (b) Nyquist diagrams obtained at Cu foam and GR–Cu foam in 2 mM Na₂SO₄ and 0.1 mM TCAA. Inset is the equivalent electrical circuit used to fit the EIS data (R_e is the electrolyte resistance, R_{ct} is the charge-transfer resistance, CPE is the constant phase-angle element, and R_{SEI} and C_{SEI} are the pseudocapacitance and resistance of solid/electrolyte interface, respectively).

was significantly decreased to be -2.64 mA at a less negative potential around -0.89 V. The reduction peaks can be attributed to the electron transfer from cathodes to TCAA since they did not appear in the absence of TCAA. This result indicates that TCAA reduction is more kinetically favorable at GR–Cu foam cathode. In EIS, the arc radius on the Nyquist plot corresponds to the electron transfer limiting process.²⁸ When GR was loaded, the size of the arc radius was reduced, revealing that GR decreased the interface impedance and accelerated the electron transfer (Figure 3b). On the basis of the results, it was speculated that 3D GR in the hybrid materials set up a fairly conductive network, which may facilitate the charge-transfer and mass-transfer processes. Due to its unique

electronic structure, the GR works as a highly conductive matrix for quickly providing electrons which might be favorable for TCAA dechlorination. Additionally, according to the results of the BET test, the specific surface area of the GR–Cu foam (3.3844 m² g⁻¹) is larger than that of the Cu foam (1.3229 m² g⁻¹). The increased surface area may also lead to enhanced reactions at the reactive sites, thus facilitating the electrocatalytic dechlorination of TCAA.

Meantime, the k_{obs} of TCAA, DCAA, and MCAA by the Cu foam and GR–Cu foam electrodes are illustrated in Figure S4. The GR–Cu foam electrode shows higher rate constants of the CAAs dechlorination, which are 3–6 times larger than those at the Cu foam electrode. Besides, Table S1 suggests an increased dechlorination rate with the chlorination degree (TCAA > DCAA > MCAA). It was recognized that the strong electron withdrawing ability of the chlorine atom caused the carbon center electron deficient, which was more amenable to electrophilic attack.^{29,30} Thus, the highly chlorinated CAAs would be more prone to be reduced during the dechlorination process, which is consistent with previous studies.^{31,32}

Effect of Cathode Potential and Initial TCAA Concentration. The electrochemical reduction of TCAA on the GR–Cu foam electrode at different cathode potentials was investigated, and the results are presented in Figure 4a. Nearly no loss of TCAA is observed at the applied potential of -0.3 and -0.5 V (vs SCE) within 40 min. 89.2% removal of TCAA is attained with the rate constant of 0.063 min⁻¹ at -0.7 V,

Figure 4. (a) Effect of cathode potential on TCAA reduction at the GR–Cu foam electrode ($[TCAA]_0 = 3.06$ μ M, 2 mM Na₂SO₄, initial pH = 6.8) and (b) effect of initial TCAA concentration on TCAA reduction at the GR–Cu foam electrode (applied potential = -1.2 V vs SCE, 2 mM Na₂SO₄, initial pH = 6.8).

Figure 5. Effect of initial pH on TCAA reduction at the (a) Cu foam and (b) GR-Cu foam electrode, (c) chronoamperometric profiles of the electrodes at pH 2.1 and 6.8, and (d) the released Cu²⁺ after reaction at different pH ([TCAA]₀ = 3.06 μM, applied potential = −1.2 V vs SCE). The initial conductivity of the catholyte at different pH values is kept constant.

which is more positive than the cathodic peak potential in the CV scan (−0.89 V). It has been recognized that the characteristic shape of the CV is a result of the potential-dependent changes in the surface concentrations of the redox system and the simultaneous diffusion processes.³³ The cathodic peak potential is reached when all of the substrate exposed to the surface of an electrode has been reduced.³⁴ Accordingly, TCAA in solution can undergo electrochemical conversion before the reduction current peak during the cathodic scan. The obtained result of the reduction experiment is in accord with the CV behavior of the GR-Cu foam electrode. Similar phenomena can be found in previous studies.^{35–37} The reaction rate then gradually rises to 0.113 and 0.137 min^{−1} when the applied bias potential is decreased to −1.0 and −1.2 V, respectively. However, further decrease of the potential to −1.5 V results in a decrease in the reaction rate. This can be attributed to the numerous hydrogen bubbles evolved at −1.5 V which would influence the electron conduction at the electrode surface.¹⁵ The result also indicates that the role of TCAA adsorption is negligible and the electrocatalytic reduction is the primary process for TCAA removal. The change of pH during the electrochemical process at various cathode potentials is provided in Figure S5. When decreasing potentials from −0.7 to −1.5 V, the difference in the final pH value is less than 0.5. The pH effect on the dechlorination would be analyzed subsequently.

Initial concentration of the target TCAA is an important factor for the removal efficiency during electrocatalytic process.⁹ The reduction rate of TCAA at the GR-Cu foam electrode increases successively with increasing the initial TCAA concentration (Figure 4b). The k_{obs} versus logarithm of TCAA concentration curve shows a certain linear relationship ($R^2 = 0.989$), which probably can be used for the prediction of k_{obs} at the GR-Cu foam electrode for a given

TCAA concentration within a specific range. Combined with the effect of cathode potential and initial TCAA concentration on the reduction rate of TCAA, it could be deduced that electron transfer and TCAA diffusion were simultaneously responsible for controlling the electrochemical reduction process under tested conditions.

Effect of Solution pH and Dissolved Oxygen. A comparison of TCAA dechlorination at Cu foam and GR-Cu foam electrodes with various pH values under the same initial conductivity was performed. TCAA dechlorination is promoted with decreasing pH from 9.6 to 2.1 at the Cu foam electrode (Figure 5a), whereas it is only slightly enhanced with a decrease of pH at the GR-Cu foam electrode (Figure 5b). The corresponding kinetic constants at the two electrodes are provided in Figure S6. The electrons coupled with H⁺ are considered to take part in the dechlorination process on the cathode surface.²⁹ Therefore, acidic solution facilitates the dechlorination of TCAA on Cu foam electrode as it is an H⁺ consumption process. Meanwhile, the lowered electrostatic repulsion between the negatively charged TCAA and cathode due to the shielding effect of protons at lower pH could also contribute to the higher dechlorination efficiency. As for the GR-Cu foam electrode, the weaker pH effect reflects that the electrocatalytic dechlorination of TCAA with the electrode can be performed under a wide pH range. The hydrolysis effect on the removal can be excluded as the measured concentrations of TCAA, DCAA, and MCAA are identical to the initial concentrations in the pH range from 2.1 to 11.2 without applying any electrochemical potential (Figure S7).

The chronoamperometry profiles show that the electroreduction currents on GR-Cu foam electrode are higher than those on Cu foam electrode in both neutral and acidic solutions (Figure 5c). The higher currents on GR-Cu foam may be due to the conductive multilayered GR in the porous and

interconnected structure, which is advantageous for the efficient diffusion and transport of electrons or intermediates. This result is in agreement with its behavior in the electrocatalytic reduction. Additionally, the current at pH 2.1 on either electrode is higher than that at pH 6.8, which is probably attributed to the enhanced hydrogen evolution reaction at pH 2.1. Furthermore, the leaching of Cu after reaction at different pH under the same conductivity is presented in Figure Sd. The concentration of released Cu^{2+} with the Cu foam electrode is determined to be 0.583 and 0.128 mg/L at pH 2.1 and 4.3, respectively. While for the GR–Cu foam electrode, the concentration of Cu^{2+} under the same conditions is significantly reduced to 0.057 and 0.044 mg/L, respectively, suggesting a significant inhibition for Cu dissolution by the GR–Cu foam electrode.

Dissolved oxygen may compete with TCAA for the reaction sites at the cathode. By purging the solution with N_2 , the concentration of dissolved oxygen was reduced from 7.98 to 0.56 mg/L. The reduction rate at the GR–Cu foam electrode is observed to be 0.269 and 0.137 min^{-1} with and without N_2 sparging, respectively (Figure S8). It was reported by Xie et al. that dissolved oxygen may compete with trichloroethylene for both the electrons and atomic H^* on the cathode surface, thus suppressing trichloroethylene reduction.¹⁶ In this study, the enhancement of the reaction rate in the presence of N_2 indicates the competition effects with oxygen for reactive sites on the cathode.

Reaction Pathway and Mechanism. The intermediates and final products generated from the electrocatalytic dechlorination of TCAA on Cu foam and GR–Cu foam electrodes are compared in Figure 6. TCAA is degraded within the first 90 min at the Cu foam electrode, with the concomitant rise of DCAA as the major product (Figure 6a). While at the GR–Cu foam electrode, the completely dechlorinated product acetic acid is efficiently generated as TCAA is rapidly consumed within the first 20 min (Figure 6b). The higher generation of chloride at the GR–Cu foam electrode is consistent with its higher production of acetic acid. Further, accompanied by the sequential dechlorination of TCAA, MCAA, and acetic acid are immediately detected in both reaction systems, indicating the direct dechlorination pathways from TCAA to MCAA or acetic acid and from DCAA to acetic acid.⁷ Thus, the electrocatalytic dechlorination of TCAA may be implemented via a combined stepwise and concerted pathway as depicted in Figure S9. The respective rate constants of the dechlorination of CAAs on both electrodes are obtained by fitting the kinetic data (see details in Section S1 and Figure S10), and the results are summarized in Table S2. Notably, for TCAA the ratio of the rate constants of the concerted pathways ($k_2 + k_3$) to that of the stepwise pathway (k_1) is 0.13 and 0.26 for Cu foam and GR–Cu foam, respectively, indicating that the TCAA dechlorination on both electrodes is mainly controlled by the stepwise pathway. As for DCAA, the ratio of the rate constant of the concerted pathway (k_5) to that of the stepwise pathway (k_4) is 0.29 and 1.19 for Cu foam and GR–Cu foam, respectively, reflecting that the concerted pathway is predominant on the GR–Cu foam electrode. On the basis of the above results, it can be concluded that the concerted pathway is efficiently promoted on the GR–Cu foam electrode as compared to the Cu foam electrode, especially for the DCAA produced by the dechlorination of TCAA.

Regarding the electrochemical reduction process, two mechanisms that have been proposed involve direct electron

Figure 6. Intermediates and final products of reductive dechlorination of TCAA through (a) Cu foam electrode and (b) GR–Cu foam electrode ($[\text{TCAA}]_0 = 12.24 \mu\text{M}$, applied potential = -1.2 V vs SCE, $2 \text{ mM Na}_2\text{SO}_4$, initial pH = 6.8). The dashed line represents the observed chloride mass balance.

transfer and indirect reduction via atomic H^* .^{11,15,16} Tertiary butanol ($t\text{-BuOH}$) which can scavenge the hydrogen atoms was used to identify the role of atomic H^* for TCAA dechlorination at different electrodes.^{38,39} The efficiency of TCAA dechlorination at the Cu foam electrode remains nearly constant with the addition of incremental levels of $t\text{-BuOH}$ from 0 to 5.0 mM (Figure 7a). While on the GR–Cu foam electrode, the dechlorination rate decreases gradually when $t\text{-BuOH}$ is increased from 0 to 1.0 mM, and then keeps constant with further increasing $t\text{-BuOH}$ amount (Figure 7b). In the presence of 5.0 mM $t\text{-BuOH}$, up to 96.8% of TCAA can still be removed within 20 min at the GR–Cu foam electrode. However, at the Pd–C electrode (Pd loading amount 0.75 mg/cm^2 , $S_{\text{BET}} 1.2906 \text{ m}^2 \text{ g}^{-1}$), the reduction rate of TCAA decreases obviously with the increase of the $t\text{-BuOH}$ concentration (Figure 7c). Furthermore, the atomic H^* involved in the electroreduction process was detected by the ESR spin trapping, which was first reported in our previous research.⁴⁰ As shown in Figure 7d, nine characteristic peaks of DMPO–H are observed at all of the three electrodes; no such signals are detected in the black electrolyte. The peak intensity for the GR–Cu foam electrode is nearly identical to that of the Pd–C electrode, which is larger than that of the Cu foam electrode.

The discharge of water through the Volmer step with the formation of surface-adsorbed atomic H^* , the electrochemical desorption (Heyrovsky step) and the recombination of the atomic H^* (Tafel step) are generally accepted as the steps of

Figure 7. Removal of TCAA by (a) Cu foam electrode, (b) GR-Cu foam electrode and (c) Pd-C electrode in the electroreduction process with various $\text{C}_4\text{H}_{10}\text{O}$ concentrations ($[\text{TCAA}]_0 = 122.4 \mu\text{M}$, applied potential = -1.2 V vs SCE , $2 \text{ mM Na}_2\text{SO}_4$, initial pH = 6.8), (d) DMPO spin-trapping ESR spectra with Cu foam, GR-Cu foam and Pd-C electrodes (applied potential = -1.2 V vs SCE).

the kinetic mechanism of the hydrogen evolution reaction, as given by⁴¹

Atomic H^* would accordingly be generated first by Volmer mechanism, which can explain the DMPO-H adducts observed at the three electrodes. However, in the absence of normally required noble metal catalysts (e.g., Pd and Ag) for hydrogen storage, atomic H^* would turn to H_2 quickly by Heyrovsky and Tafel routes during the TCAA reduction process.^{16,42–44} Thus, the role of atomic H^* in the dechlorination of TCAA at the barely Cu foam electrode can be ignored and the direct electron transfer is responsible for TCAA dechlorination. In contrast, Pd is well-known to have the unique property of adsorbing large amounts of nascent H^* via the Pd-H bonds based on multiple σ -bonding between the hydrogen atoms and the d orbitals of the Pd atoms.^{45,46} Even if H_2 molecules are formed, they would be readily dissociated on the Pd surface.⁴⁷ Therefore, the electrocatalytic dechlorination of TCAA at the Pd-C electrode mainly proceeds via the indirect H^* reduction due to the ability of Pd to maintain a high surface concentration of atomic H^* . It has been shown that hydrogen can also be adsorbed on GR and the reaction of GR with hydrogen atoms generates $\text{sp}^3 \text{ C-H}$ bonds on the basal plane.^{48–50} The hydrogenation of GR was considered to be more feasible with multilayer GR than that with single-layer GR.⁵¹ At the GR-Cu foam electrode, a certain amount of surface-adsorbed atomic H^* derived from such chemical storage of hydrogen in the GR nanostructure turns to be active species, which is in part responsible for the effective

TCAA dechlorination. However, atomic H^* plays a relatively minor role and the primary dechlorination of TCAA at the GR-Cu foam electrode is achieved by the direct mechanism.

Potential Application. In the current work, the efficient and rapid dechlorination of chlorinated compounds was achieved in the electrochemical reduction process using a 3D GR-Cu foam cathode. The use of expensive Pd or Au catalyst was avoided. Treatment of HAAs-contaminated tap water by the electroreduction process with the GR-Cu foam cathode was conducted to check its applicability in a realistic water matrix. The water quality of Beijing tap water was provided in Table S3. The initial concentration of HAAs was adjusted to $120 \mu\text{g/L}$, including $20 \mu\text{g/L}$ for DBAA, $50 \mu\text{g/L}$ for DCAA and TCAA, respectively. As presented in Figure 8a, HAAs are reduced below $60 \mu\text{g/L}$ at 15 min, indicating that the electrochemical dechlorination of HAAs has the potential for application to drinking water treatment in some specific cases because of its rapid reduction rate. The 25-cycle dechlorination reaction experiment shows a first increased and then nearly constant activity at the Cu foam and GR-Cu foam electrodes (Figure 8b). Further insights on the XPS spectrum of $\text{Cu } 2\text{p}_{3/2}$ (Figure S11), and $\text{C } 1\text{s}$ (Figure S12) indicate that CuO is partly reduced to Cu^0 by cathodic current on the two electrodes, and the GR maintains stability during the dechlorination reaction. XRD and Raman spectra further demonstrate the stability of the electrodes (Figure S13). Thus, the electrocatalytic activities could be first enhanced due to the decrement of CuO content by cathodic polarization and then maintain nearly constant with durations. The energy consumption for the GR-Cu foam electrode is calculated to be 0.067 against 0.159 kWh g^{-1} TCAA for the Cu foam electrode at -1.2 V (Figure S14 and Table S4). Because of its high effectiveness and stability, low cost, and environmental

Figure 8. (a) HAAs concentration in tap water during the electrochemical reductive process with the GR-Cu foam electrode ($[TCAA]_0 = [DCAA]_0 = 50 \mu\text{g/L}$, $[DBAA]_0 = 20 \mu\text{g/L}$, applied potential = -1.2 V vs SCE) and (b) 25-cycle dechlorination reaction of TCAA by Cu foam and GR-Cu foam electrodes ($[TCAA]_0 = 3.06 \mu\text{M}$, applied potential = -1.2 V vs SCE , $2 \text{ mM Na}_2\text{SO}_4$, initial pH = 6.8).

friendliness, the 3D GR-Cu foam electrode would play a beneficial role as a promising cathode in the electroreduction process for efficient removal of HOCs in water, especially for a point-of-use drinking water treatment.

■ ASSOCIATED CONTENT

Supporting Information

Experimental setup; SEM and EDX mapping images of electrodes, fitted rate constants, change of pH at different cathode potentials, hydrolysis test, effect of dissolved oxygen, reaction pathway, and fitting of the kinetic data; water quality of the Beijing tap water, XPS, XRD, and Raman spectra of the electrodes before and after the dechlorination, and energy cost analysis. The Supporting Information is available free of charge on the [ACS Publications website](https://doi.org/10.1021/acs.est.5b05006) at DOI: 10.1021/acs.est.5b05006.

(PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +86-10-62849151; fax: +86-10-62923558; e-mail: jhqu@rcees.ac.cn (J.Q.).

Notes

The authors declare no competing financial interest.

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