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Pulsed Electrocatalysis Enables Efficient 2-electron Oxygen Reduction Reaction for H_2O_2 Production

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1. The influence on the structure of the electrocatalyst

It was found that the morphology, hydrophilicity and defect degree had changed to a certain extent, among which the surface of graphite felt carbon fiber was etched seriously and its surface roughness increased continuously (Figure S1), the contact angle of graphite felt was changed from 139.5° to 26.3° (Figure S2), and the ratio of I_D/ I_G also increased (Figure S3), indicating the enhancement of the surface disorder of graphite felt with more defects. All these show the possibility of dynamic regulation of the electrocatalyst structure by the application of pulse potential, but it is worth discussing that hydrogen peroxide produced by 2eORR may have similar effects on the catalyst and therefore decoupling this effect will be necessary in the future.

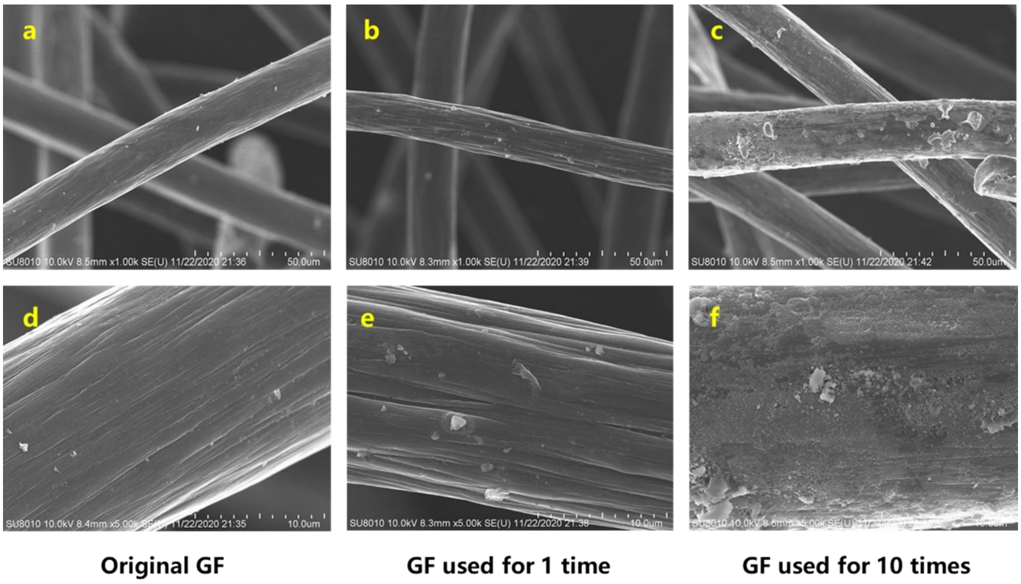

Figure S1. SEM images of graphite felt with different reaction times in pulsed-potential electrocatalytic system. (a), (d) the original graphite felt; (b), (e) the graphite felt reacted for 1 time; (c), (f) the graphite felt reacted for 10 times.

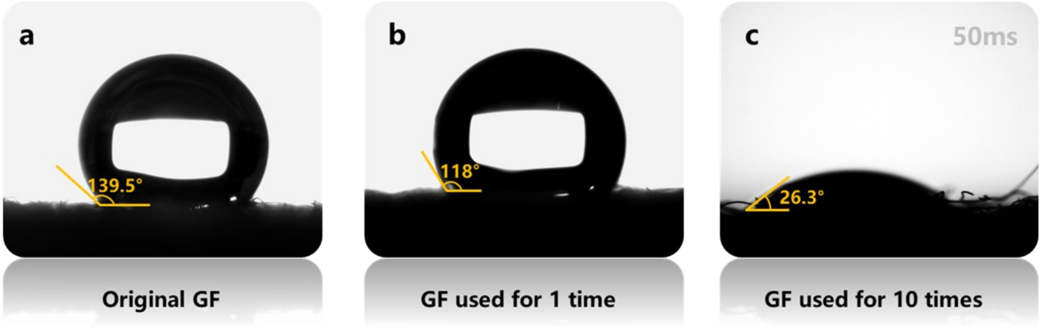

Figure S2. Hydrophilicity of graphite felt in pulsed-potential electrocatalysis system with different reaction times. (a) the original graphite felt; (b) the graphite felt reacted for 1 time; (c) the graphite felt reacted for 10 times.

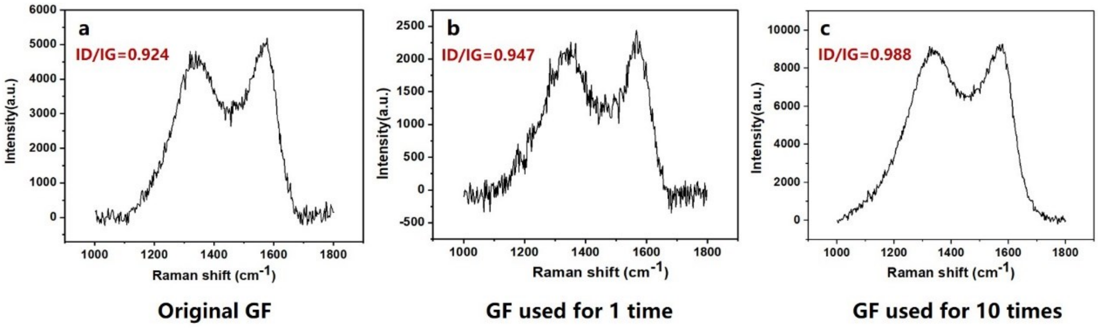

Figure S3. Raman spectra of graphite felt in pulsed-potential electrocatalysis system with different reaction times. (a) the original graphite felt; (b) the graphite felt reacted for 1 time; (c) the graphite felt reacted for 10 times. The peaks at 1350 cm^{-1} and 1580 cm^{-1} correspond to the disordered D-band and graphitic G-band in GF, respectively. The intensity ratio between D-band and G-band ($I_D/I_G = 0.988$) indicated that the existence of defective structure. This is the reason why we choose to construct a graphene model with defects for DFT calculation, which can accurately reflect the adsorption capacity of GF for ORR intermediates.

2. DFT simulation details

All the density functional theory (DFT) calculations were carried out by Gaussian 09 D. 01 [1]. The structures of defective carbon surface and adsorbed intermediates were optimized using M06-2X[2] functional in conjunction with 6-31 G(d, p) basis set, and their stability were further confirmed by frequency analyses at the same level. To analyze the effect of EDL discharging process on the ORR, electric field in Z direction was applied to simulate the electric field intensity of the double layer. According to Che's study [3], the thickness of Helmholtz layer was about 3-8Å when applying potential on the electrode, thus 0.2V/Å was set to be the initial electric field intensity of EDL. Besides, The adsorption energy E_{ad} of reactants as well as reaction intermediates (H, O_2, OOH) under external electric field was calculated by $E_{ad} = E_{[X + graphene,\vec{E}]} - (E_{[graphene,\vec{E}]} + E_{[X = H,O_2,\ OOH]})$, where $E_{[X + graphene,\vec{E}]}$, $E_{[graphene,\vec{E}]}$ and $E_{[X = H,O_2,\ OOH]}$ referred to the energy of adsorption complexes, bare graphene and adsorbates X (X=H, O_2, OOH), respectively. All the models in the manuscript were plotted by VMD 1.9.3 program [4].

3. The H_2O_2 yield via 2eORR under the optimal pulse condition

We successfully increased the production of H_2O_2 by 138.12% by applying a pulsed potential with a pulsed width of 1 s, a duty ratio of 30%, and a pulsed potential of -1.0V vs. Ag/AgCl.

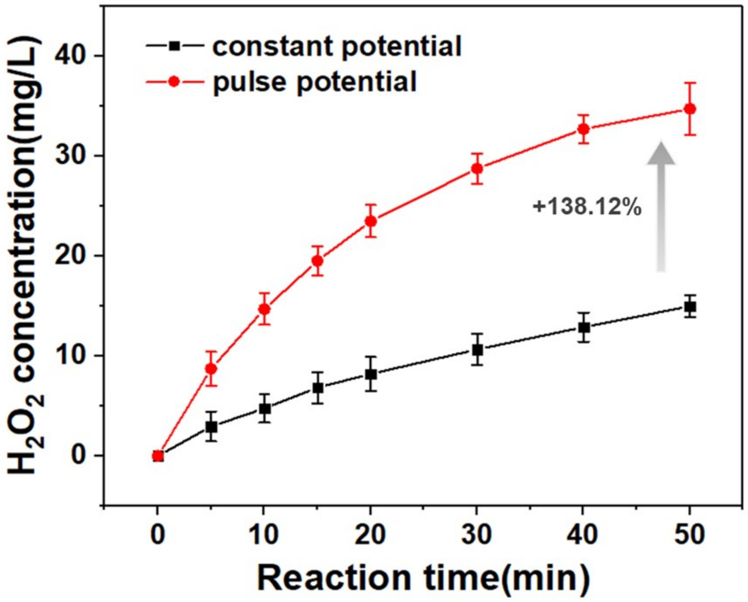

Figure S4. The H_2O_2 yield via ORR under the optimal pulse condition (Ec = -1.0V vs. Ag/AgCl, D = 30%, t_r+t_c = 2s)

4. The adaptability to different electrocatalysts in pulsed-potential electrocatalysis

A low-cost activated coke (AC-CO_2B) electrocatalyst with size-tailored amorphous carbon clusters doped by oxygen functional groups, which could achieve high activity and high H_2O_2 selectivity (~90%) [5], was selected to explore the adaptability to different electrocatalysts for H_2O_2

generation through two-electron ORR in the pulsed electrocatalytic system. Specifically, we loaded the carbon powder (AC-CO_2B) on a carbon cloth (1.5*2.5 cm) through spraying process, with a catalyst loading density of 0.04 mg/cm^2, and set the pulse parameters as $t_{rest} = t_{cathode} = 1$ s, $E_{cathode} = -1.0$ V vs Ag/AgCl to carry out the H_2O_2 electroproduction. It was found that the yield of H_2O_2 increased by 123.12% when applying the pulse potential, which also proved that the pulsed electrocatalysis has a high adaptability to various carbon-based catalysts.

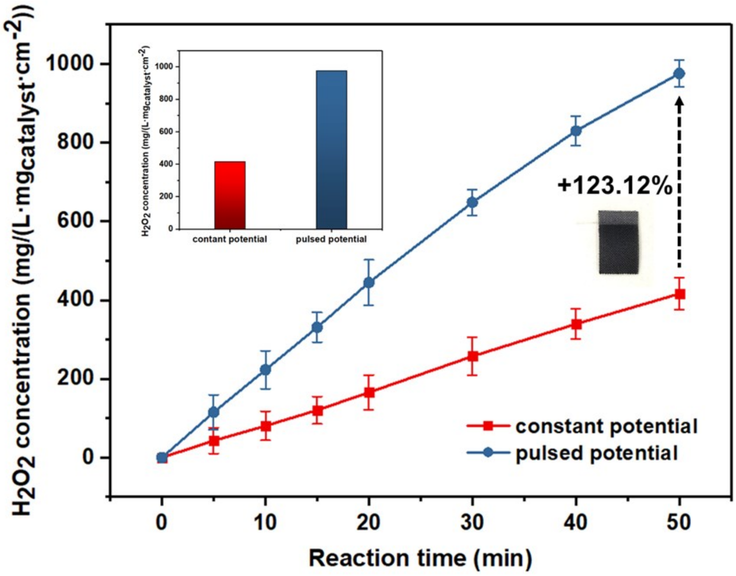

Figure S5. H_2O_2 production in pulsed potential electrocatalysis (blue line) and constant potential electrocatalysis (red line) through AC-CO_2B electrocatalyst. Reaction condition: 0.05 M Na_2SO_4, t_a=t_c=1 s, E_c= -1.0 V vs. Ag/AgCl, E_r=0 V vs. AgCl.

5. The adaptability to different pH in pulsed-potential electrocatalysis

Sulfuric acid (H_2SO_4, 98wt%) and sodium hydroxide (NaOH) were used to adjust the pH, and the pulse parameters were set as $t_{rest} = t_{cathode} = 1$ s, $E_{cathode} = -0.4$ V vs. RHE (Conversion from -1.0 V vs Ag/AgCl in pH = 6.95). The results in the figure below showed that the pulsed electrocatalysis method is suitable for both acidic and alkaline conditions. However, it can also be seen that the application of pulsed potential differs in the degree of promotion of the ORR at different pH. Although the H_2O_2 yield under strong acid and strong base conditions is very high, reaching nearly 50mg/L, the yield can only be increased by 40.97% (pH = 0.7) and 40.59% (pH = 13), respectively, compared with the constant potential electrocatalysis conditions. On the contrast, the pulsed potential electrocatalysis method can increase H_2O_2 production by 91.42% in neutral system (pH = 6.95). Therefore, the application of pulse electrocatalysis under the neutral system seems to possess greater industrial and market prospects, no matter from the perspective of environmental protection or economic benefits.

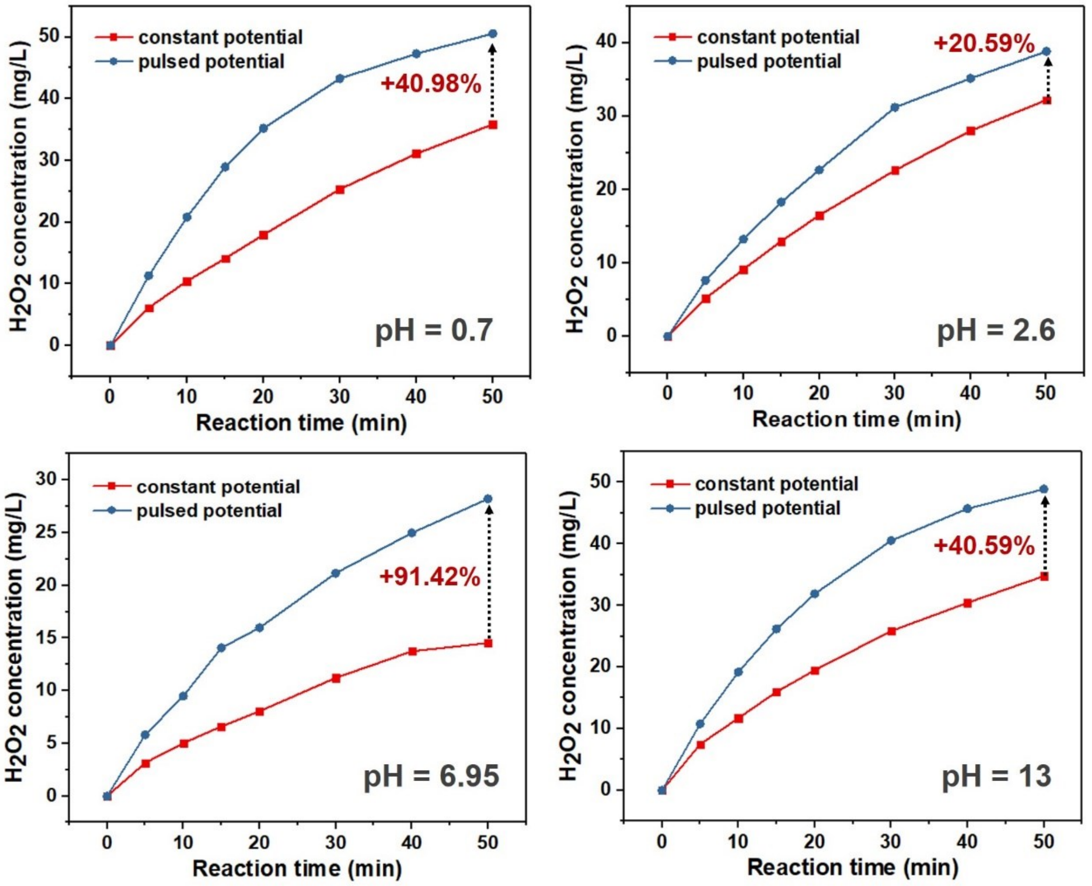

Figure S6. The production of H_2O_2 via ORR by pulsed electrocatalysis at different pH values. Reaction condition: 0.05 M Na_2SO_4, t_r=t_c=1 s, $E_{cathode}$ = -1.0 V vs. Ag/AgCl, and the reference electrodes were Ag/AgCl and Hg/ HgO in acidic and alkaline conditions, respectively.

6. The stability test of GF in pulsed-potential electrocatalysis.

We tested the stability of the electrocatalyst (GF) for 10 times under the condition of pulsed electrocatalysis, and found that the graphite felt can basically maintain a relatively stable ORR activity and obtain a relatively similar H_2O_2 yield.

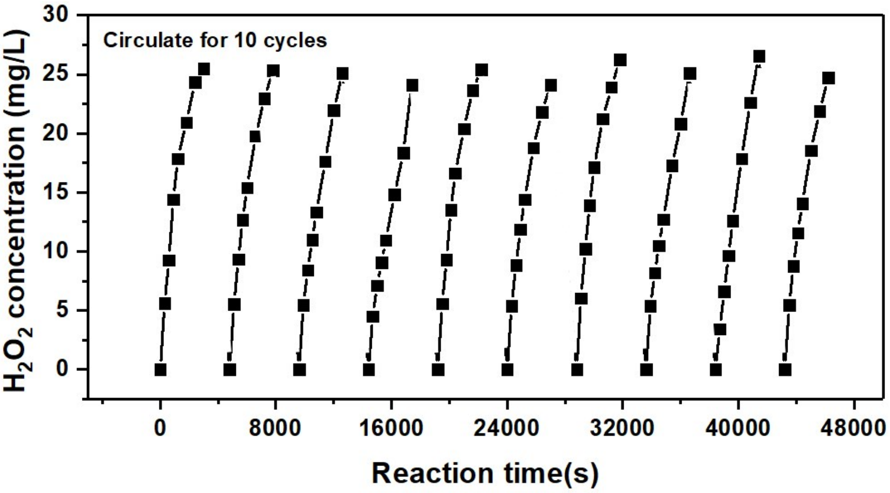

Figure S7. The stability test of GF in pulsed-potential electrocatalysis. Reaction condition: 0.05 M Na_2SO_4, t_a=t_c=1 s, E_c= -1.0 V vs. Ag/AgCl, E_r=0 V vs. AgCl.

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