Supplementary Information (SI) for Industrial Chemistry & Materials.

# Supporting Information

## Carboxylated Cotton Fiber-Integrated PPy/PANI Composites for High-Performance Flexible Supercapacitor Electrodes via TEMPO Oxidation

*Meijuan Cao, Xiaopei Wu, Dongdong Qiu, Shouzheng Jiao*, Jian Sun, Jie Zong*

M. C., X. W., D. Q., S. J., J. Z.
Beijing Engineering Research Center of Printed Electronics, School of Printing and Packaging Engineering, Beijing Institute of Graphic Communication, Beijing 102600, P. R. China
E-mail: sz.jiao@outlook.com
J. S.
Key Laboratory of Molecular Medicine and Biotherapy in the Ministry of Industry and Information Technology, School of Life Science, Beijing Institute of Technology, Beijing 100081, China.

# 1. Experimental Section

## 1.1 Modification of Cotton Fibers via TEMPO Oxidation

Sodium hypochlorite (NaClO) solutions with different concentrations (1 M, 2 M, 3 M, 4 M, and 5 M) were freshly prepared by dilution with deionized water. In each reaction, 0.032 g of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and 0.2 g of sodium bromide (NaBr) were dissolved in 200 mL of deionized water under continuous stirring at room temperature. Then, 2.0 g of cotton fiber (CF) was immersed in this solution, followed by the addition of NaClO.

During the oxidation process, 0.5 M NaOH solution was used to maintain the pH between 10.0 and 10.5. The reaction was maintained under mild agitation for 3 h, after which 10 mL of absolute ethanol was added to quench the reaction. The oxidized product, referred to as **carboxylated cotton fibers (C-CFs)**, was washed thoroughly with deionized water until the pH was neutral. The resulting C-CFs were dried in an oven at 35 °C and then cut into uniform pieces (5 cm × 5 cm) for further use.

## 1.2 Preparation of PANI/C-CFs Electrode Materials

### 1.2.1 Effect of Oxidant Concentration

Polyaniline (PANI) was deposited onto the C-CFs via in situ chemical oxidative polymerization. Aniline (ANI), ammonium persulfate (APS), and hydrochloric acid (HCl) were used at a fixed molar ratio of 1:1:1. APS was dissolved in 30 mL of 0.075 M HCl to prepare APS/HCl solutions of varying concentrations (0.05, 0.10, 0.15, 0.20, and 0.25 mol/L). All solutions were pre-cooled before use.

Meanwhile, ANI was dissolved in 30 mL of 0.075 M HCl to obtain a 0.15 mol/L ANI/HCl solution, followed by 20 min sonication. C-CFs were immersed in the ANI/HCl solution for 30 min, then the pre-cooled APS/HCl solution was added dropwise. The polymerization was carried out under ice bath conditions (<4 °C) for 3 h. After the reaction, the samples were washed thoroughly and dried at 35 °C for 4 h to yield **PANI/C-CFs**.

### 1.2.2 Effect of Aniline Monomer Concentration

To examine the effect of ANI concentration, ANI was dissolved in 30 mL of 0.075 M HCl at varying concentrations (0.05, 0.10, 0.15, 0.20, and 0.25 mol/L). After 20 min of sonication, C-CFs were soaked in these ANI solutions for 30 min. The oxidant APS was prepared at a fixed concentration of 0.15 mol/L in 30 mL of 0.075 M HCl. Polymerization was conducted under the same conditions as described above.

### 1.2.3 Effect of Acid Concentration

To evaluate the influence of acidity, ANI was dissolved in 30 mL of HCl solutions with different concentrations (0.025, 0.050, 0.075, 0.100, and 0.125 mol/L), followed by 20 min of sonication. C-CFs were soaked in each ANI/HCl solution for 30 min. The corresponding APS solutions (matching HCl concentrations, with APS:ANI = 1:1) were prepared and added dropwise. The polymerization protocol was consistent with Section S2.1.

## 2. More Characterization Data for SLC

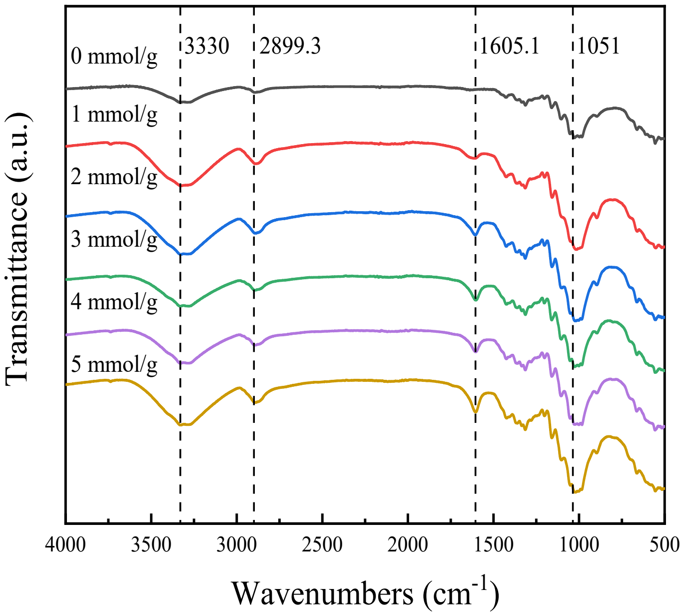

**Figure S1.** Fourier-transform infrared (FTIR) spectroscopy was employed to evaluate the chemical structure of cotton fibers (CFs) subjected to TEMPO-mediated oxidation with varying concentrations of sodium hypochlorite (NaClO). In this system, TEMPO acts as a catalytic mediator while NaClO serves as the primary oxidant, selectively converting the C6 primary hydroxyl groups on cellulose chains into carboxyl groups (–COOH), yielding carboxylated cotton fibers (C-CFs).

The FTIR spectrum of unmodified CFs (0 M NaClO) displays characteristic absorption bands at 3330 cm$^{-1}$ (O–H stretching), 2899.3 cm$^{-1}$ (C–H stretching), and 1051 cm$^{-1}$ (C–O stretching). Notably, the band at 1051 cm$^{-1}$ lies within the typical range for cellulose C–O vibrations (1030–1060 cm$^{-1}$), but may also reflect contributions from ring-breathing modes or C–O–C linkages, as reported in previous studies. Following oxidation, a new absorption band emerges at ~1605.1 cm$^{-1}$, corresponding to the asymmetric stretching vibration of carboxylate (COO$^{-}$) groups. The intensity of this band increases monotonically with increasing NaClO concentration, indicating a higher degree of surface carboxylation. Interestingly, the predominant presence of COO$^{-}$ rather than protonated COOH peaks—even after extensive washing to near-neutral pH—suggests partial deprotonation of the carboxyl groups or a persistent ionic environment on the fiber surface. This behavior may reflect incomplete neutralization or strong ionic association with residual counterions, warranting further investigation. Collectively, these FTIR results confirm the successful introduction of carboxyl functionalities onto the cellulose surface, and demonstrate that the extent of chemical functionalization is positively correlated with the NaClO oxidant concentration.

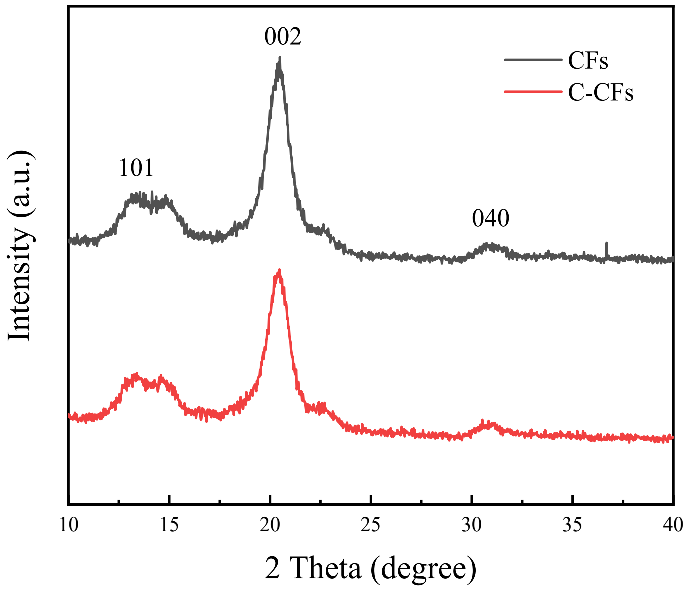

**Figure S2.** X-ray diffraction (XRD) patterns of cotton fibers before and after TEMPO-mediated oxidation.

The crystallinity and phase structure of CFs before and after TEMPO oxidation were characterized by X-ray diffraction (XRD), as shown in Figure S2. The CFs substrate displays characteristic cellulose I peaks at 2θ = 14.7° and 16.5° (assigned to the (101) plane), 22.6° ((002) plane), and 34.2° ((040) plane). The XRD pattern of C-CFs remains essentially unchanged, indicating that TEMPO oxidation does not disrupt the cellulose crystalline structure.

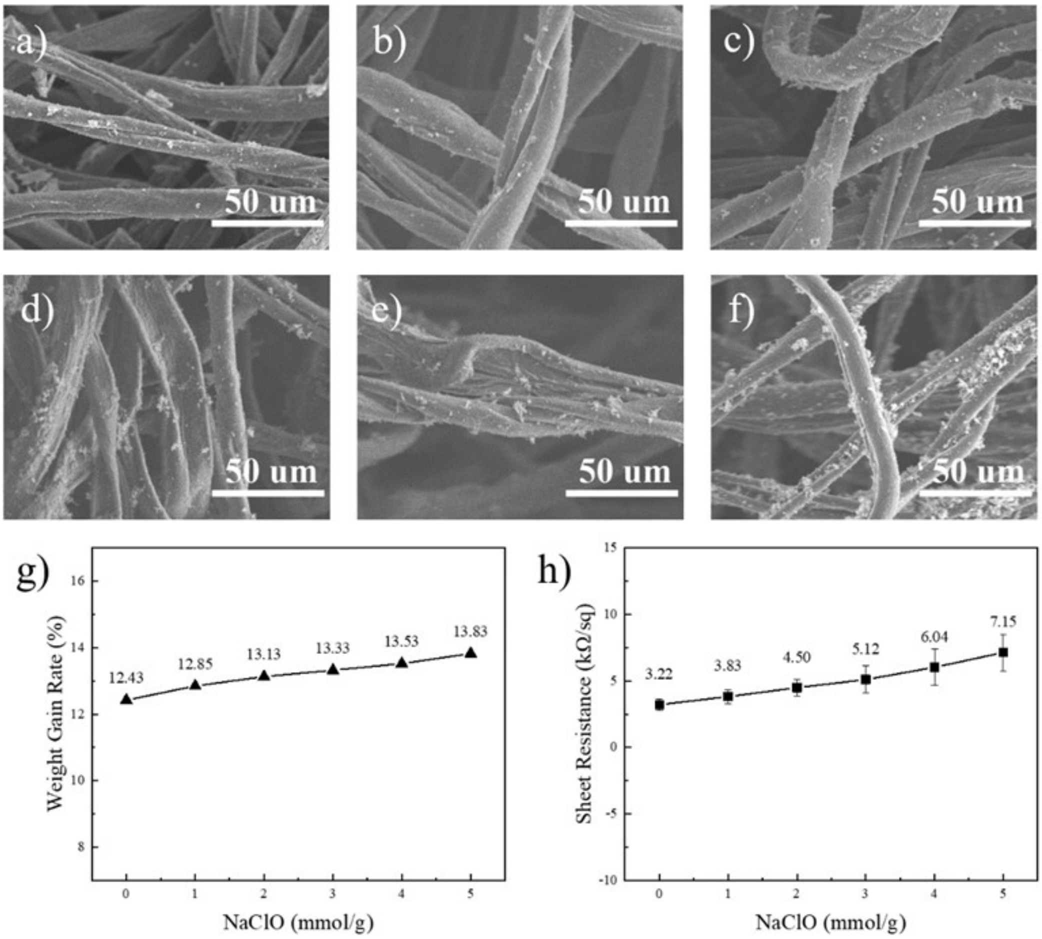

**Figure S3.** SEM images of PANI/C-CFs electrode materials prepared with different NaClO concentrations during TEMPO oxidation: (a) 0 M (unmodified CFs), (b) 1 M, (c) 2 M, (d) 3 M, (e) 4 M, and (f) 5 M. (g) Weight gain of the electrodes as a function of oxidant concentration, indicating increased PANI loading with higher carboxyl content. (h) Sheet resistance of PANI/C-CFs electrodes showing the effect of oxidation level on electrical conductivity.

Carboxylated cotton fibers (C-CFs) possess a higher density of active functional groups compared to unmodified CFs, thereby enabling stronger interactions with the functional groups in polyaniline (PANI). This enhanced interfacial interaction significantly improves the adhesion between PANI and the fiber substrate, contributing to improved structural integrity and uniformity in the composite electrodes. Figure S3a–f shows SEM images of PANI/C-CFs prepared with varying concentrations of NaClO. As the oxidant concentration increases, the PANI coating becomes more continuous and uniform. At the highest concentration (5 M, Fig. S3f), the surface of the C-CFs is densely covered with a homogeneous PANI layer, indicating effective polymer deposition. This improvement is attributed to the formation of hydrogen bonds between the amino groups of ANI and the –COOH groups introduced onto the fiber surface during TEMPO oxidation. Figure S3g presents the weight gain of the fibers after PANI deposition, which increases proportionally with the degree of carboxylation. This indicates that the presence of –COOH groups promotes higher PANI loading. However, as shown in Figure S3h, the electrical conductivity of the resulting PANI/C-CFs composites decreases with increasing NaClO concentration. This trend may be explained by structural changes in the fiber substrate: while –COOH enhances chemical reactivity and polymer adhesion, it also weakens interfiber cohesion, resulting in a more porous and disordered substrate that impedes the formation of effective conductive pathways, thereby increasing sheet resistance.

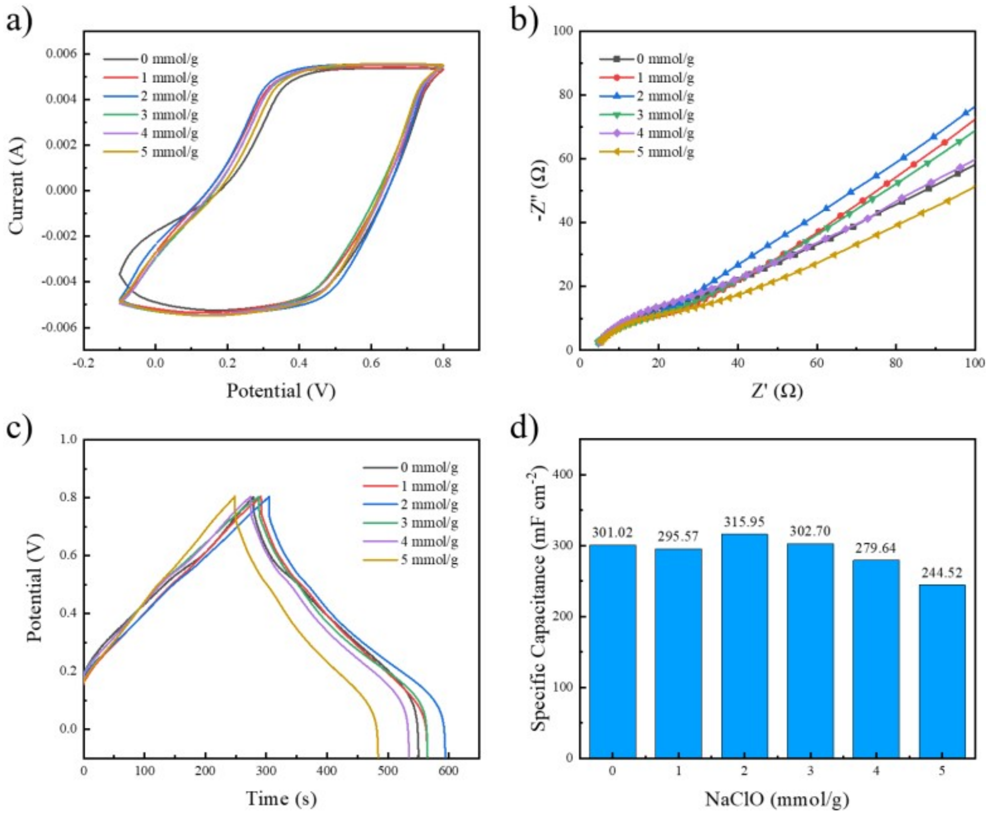

**Figure S4.** Electrochemical performance of PANI/C-CFs electrodes prepared with different NaClO concentrations: (a) Cyclic voltammetry (CV) curves at a scan rate of 50 mV s$^{-1}$; (b) Electrochemical impedance spectroscopy (EIS) curves; (c) Galvanostatic charge–discharge (GCD) curves at a current density of 0.8 mA cm$^{-2}$; (d) Specific capacitance values derived from GCD data, showing the dependence on oxidant concentration.

To assess the influence of surface carboxylation on electrochemical performance, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge–discharge (GCD) measurements were performed on PANI/C-CFs electrodes synthesized with different oxidant dosages. As shown in Figure S4a, the CV curves of PANI/C-CFs exhibit enlarged enclosed areas and more symmetric voltage profiles compared to PANI/CFs, confirming improved capacitive behavior. Notably, the CV area increases with oxidant concentration up to 2 M, then declines at higher dosages. This suggests that moderate carboxylation (2 M) provides the optimal balance between polymer adhesion and ion transport, resulting in superior charge storage capability. EIS analysis (Figure S4b) further supports these findings. In the high-frequency region, the semicircle radius—which corresponds to charge transfer resistance—initially decreases and then increases with rising oxidant concentration. The electrode prepared with 2 M NaClO shows the smallest semicircle radius, indicating the lowest charge transfer resistance. In the low-frequency region, this sample also exhibits the steepest slope in the Warburg region, reflecting enhanced ion diffusion. Figures S4c and S4d present the GCD curves and corresponding specific capacitance values. The discharge time follows the same trend as CV and EIS results, reaching a maximum at 2 M oxidant concentration. Under this condition, the electrode delivers the highest area-specific capacitance, confirming that moderate carboxylation leads to optimal electrochemical performance.

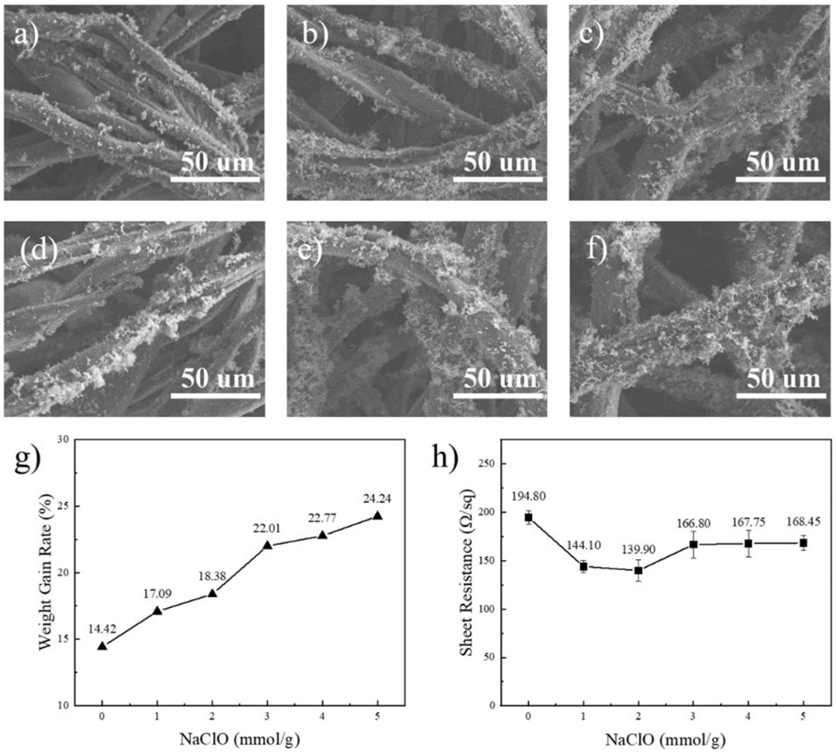

**Figure S5.** SEM images of PPy/PANI/C-CFs electrode materials prepared with different NaClO concentrations: (a) 0 M, (b) 1 M, (c) 2 M, (d) 3 M, (e) 4 M, and (f) 5 M. (g) Weight gain of the composite materials as a function of oxidant concentration, indicating increasing polymer loading with higher degrees of carboxylation. (h) Sheet resistance of PPy/PANI/C-CFs, showing the variation in electrical conductivity with different oxidation levels.

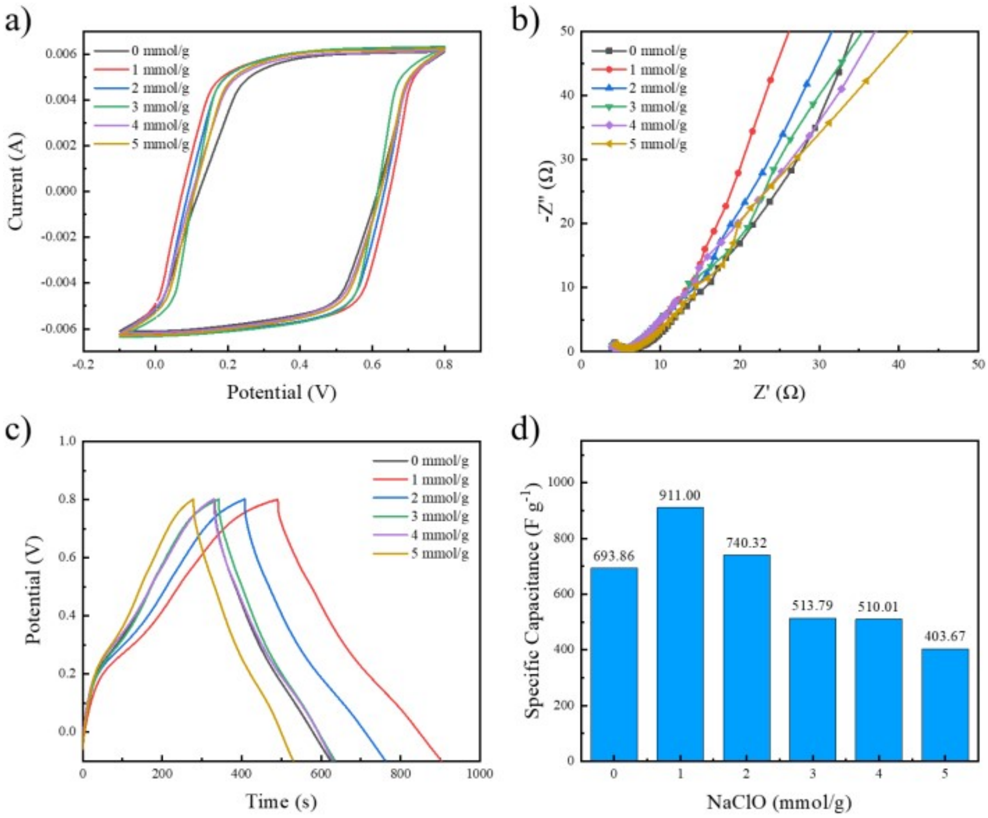

**Figure S6.** Electrochemical performance of PPy/PANI/C-CFs electrodes prepared with different NaClO concentrations: (a) Cyclic voltammetry (CV) curves at a scan rate of 50 mV s$^{-1}$; (b) Electrochemical impedance spectroscopy (EIS) curves; (c) Galvanostatic charge–discharge (GCD) curves at a current density of 2 mA cm$^{-2}$; (d) Specific capacitance values calculated from GCD data, demonstrating the dependence on oxidant concentration.

Table S1. Surface elemental composition (C, O, N; at.%) determined from XPS survey spectra.

| **Sample** | **C (at.%)** | **O (at.%)** | **N (at.%)** |
|---|---|---|---|
| CF | 63.52 | 35.27 | 1.21 |
| C-CF | 63.55 | 35.05 | 1.40 |
| PPy/PANI/C-CF | 75.90 | 13.04 | 11.06 |

Table S2. Electrochemical Test Parameters and Calculation Notes

| **Parameter** | **Value / Description** |
|---|---|
| Geometric area of working electrode | 4.0 cm² |
| Areal mass loading of active electrode material | 1.2 mg/cm$^2$ |
| Mass fraction of active polymer (PPy/PANI) | 48% |
| Current Density | 2 mA/cm $^2$ |
| Definition of mass *m* in $C_{sp}$ formula | only to the mass of active polymer (PPy/PANI) |