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Toward scalable fabrication of electrochemical paper sensor without surface functionalization

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Paper-based electrochemical sensors provide the opportunity for low-cost, portable and environmentally friendly single-use chemical analysis and there are various reports of surface-functionalized paper electrodes. Here we report a composite paper electrode that is fabricated through designed papermaking using cellulose, carbon fibers (CF), and graphene oxide (GO). The composite paper has well-controlled structure, stable, and repeatable properties, and offers the electrocatalytic activities for sensitive and selective chemical detection. We demonstrate that this CF/GO/cellulose composite paper can be reduced electrochemically using relatively mild conditions and this GO reduction confers electrocatalytic properties to the composite paper. Finally, we demonstrate that this composite paper offers sensing performance (sensitivity and selectivity) comparable to, or better than, paper-based sensors prepared by small-batch surface-modification (e.g., printing) methods. We envision this coupling of industrialized papermaking technologies with interfacial engineering and electrochemical reduction can provide a platform for single-use and portable chemical detection for a wide range of applications.

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INTRODUCTION

Cellulose-based paper has attracted considerable attention as a matrix for portable single-use electrochemical sensing because of its low cost, lightweight, and biodegradability^{1–7}. Typical routes for generating paper-based electrochemical sensors use post functionalization methods (e.g., printing) to deposit components that confer conductivity and electrocatalytic activity onto the surface of the paper substrate^{8–13}. These studies have demonstrated impressive performance attributes and suggest an exciting vision forward, however, a key requirement toward the widespread adoption of paper-based electrochemical sensors will be the scalable fabrication of stable, low-cost paper-based electrodes with repeatable properties, which still remains a challenge.

The challenges for advancing the practical application of paper-based electrochemical sensor lie in two aspects: first, the performance of reported paper-based sensors varies in a great extent due to the diversity in substrate features (e.g., porosity, network, and surface), complicated process, and strict conditions in small-batch production, leading to the key concerns for uncertainty in reproducibility and accuracy^{14–16}; second, the surface of paper-based sensors must be specifically designed and modified to meet the requirement for selective detection, and the performance of the paper-based material cannot be controlled on a large scale^{17–19}. Taking screen printing as an example, many factors, including the viscosity and solid content of printing ink, printing strength, and the structure of paper substrate, all affect the sensitivity of paper-based sensor leading to great uncertainty in repeatability. These challenges can hardly be resolved, unless standard paper electrode with well-controlled structure and imbed functionality can be scalably produced and directly used needing no surface treatment. However, it is difficult to integrate functional materials with paper into defined structure and area in

mass production because of the lack of bonding and interaction between cellulose fibers and functional materials.

Here, we realized the scalable production and controlled functionalization of paper, and report the use of this paper for sensitive and selective electrochemical detection based on two findings. First, we adapt conventional papermaking methods to generate a functional composite paper composed of cellulose fibers, carbon fibers (CF), and graphene oxide (GO). As illustrated in Fig. 1a, the successful fabrication of this composite required interfacial engineering to control the interactions between the hydrophilic cellulose fibers, hydrophobic CF, and nanosized GO fillers. Consequently, stable and uniform composite paper with repeatable properties was obtained, which could be further paper-cut into a large number of flexible electrodes with designed patterns. Then, Fig. 1b shows that we used a comparatively mild and efficient electrochemical treatment (<10 min, <1 V) to reduce the GO in the composite into its reduced form (rGO) to create function. As suggested, the CF confers conducting properties that facilitate the reduction of GO to enhance its electrocatalytic activity. Figure 1c suggests that this composite paper can provide a means to realize the vision of low-cost paper-based electrodes for electrochemical detection.

RESULTS

Preparation and characterization of composite paper electrode

A critical requirement for using papermaking technology to prepare stable and uniform composite paper with repeatable properties, is that the cellulose, CF, and GO must be uniformly dispersed in water to make pulp (Fig. 2a). The cellulose fibers and GO are hydrophilic with large negative charges, while the CF fibers are hydrophobic and lightweight with a small negative charge, as

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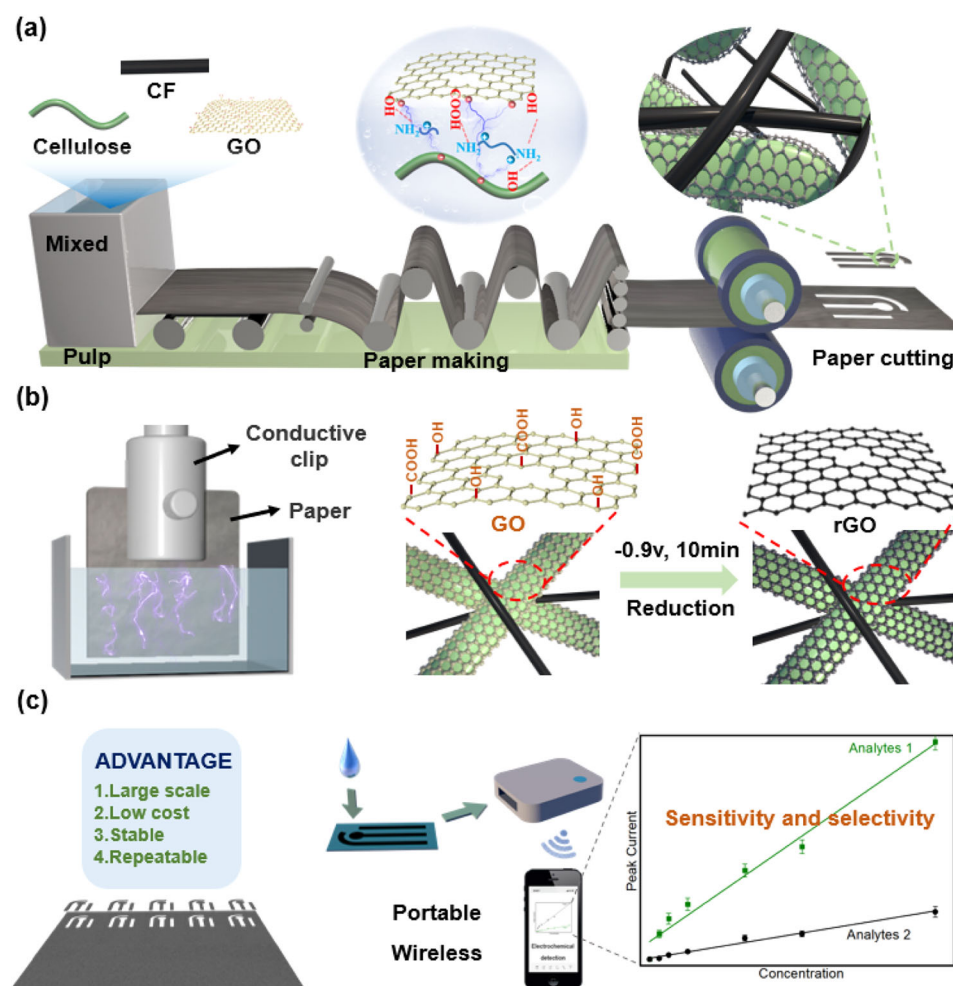


Fig. 1 Large-scale preparation of high-performance paper-based electrochemical sensors. **a** Large-scale papermaking. By controlling interfacial interactions, composite paper was prepared composed of cellulose, carbon fibers (CF, confers conductivity) and graphene oxide (GO, confers electrocatalytic activities). **b** Electrochemistry reduction of GO. Electrochemistry provides a simple scalable approach to GO reduction. **c** Vision of paper-based electrochemical sensor. The vision for high-performance and sustainable paper-based sensors for portable electrochemical detection.

determined by the zeta-potential measurements in Fig. 2b²⁰. The diversity in the properties of fibers increases the difficulty of pulping and following papermaking. An interface-engineering approach was employed to address this problem. The series of photographs in Fig. 2a indicate that the addition of a small amount of cationic polyacrylamide (CPAM) promotes the association and aggregation of cellulose and GO, while the low-density and hydrophobic CF could be well dispersed within these GO/cellulose aggregates. The resulting CF/GO/cellulose “pulp” could then be processed into composite paper and a very fast processing time is confirmed (further details of the pulping and processing steps are provided in Supplementary Fig. 1 of Supporting Information). By studying the electrochemical sensing and mechanical properties of different raw material ratios, the optimal ratio of CF/cellulose/GO was determined as 1/1/0.17 (further details of the electrochemical sensing and mechanical properties are provided in Supplementary Fig. 2 and Supplementary Fig. 3 of Supporting Information).

We employed three independent measurements to provide molecular and microstructural evidence for the effective integration of components into the composite paper. First, we use energy dispersive X-ray spectroscopy (EDS) to provide evidence for the location of the CPAM (as measured by elemental nitrogen) in the composite paper. The addition of

CPAM to CF/GO/cellulose led to a significantly increased N-content (compared with the CF/cellulose control without CPAM addition; Supplementary Fig. 4 of Supporting Information), and Fig. 2c shows that this N-containing component was uniformly assembled onto the surface of the cellulose fiber. Second, we used micro-computed tomography (micro-CT) to examine the distribution of the carbon and cellulose fibers within the CF/GO/cellulose composite (note: micro-CT can discern these different fibers based on their different densities). Figure 2d shows that the two fiber networks are uniformly distributed and interpenetrating throughout the network. Third, we used scanning electron microscopy (SEM) to observe the microstructure of the composite paper. Figure 2e shows that GO/cellulose interweaves with CF to form a uniform network structure and GO sheets can be observed on the surface of cellulose fibers (further analysis is provided in Supplementary Fig. 5d of Supporting Information). The above results show that we have successfully prepared uniform and stable CF/GO/cellulose paper.

Electrochemical reduction of GO

The electrocatalytic activity of GO is often improved by reduction, and a variety of methods have been used to convert GO into its reduced rGO form^{21,22}. As illustrated in Fig. 3a, we used a comparatively mild electrochemical method in which the

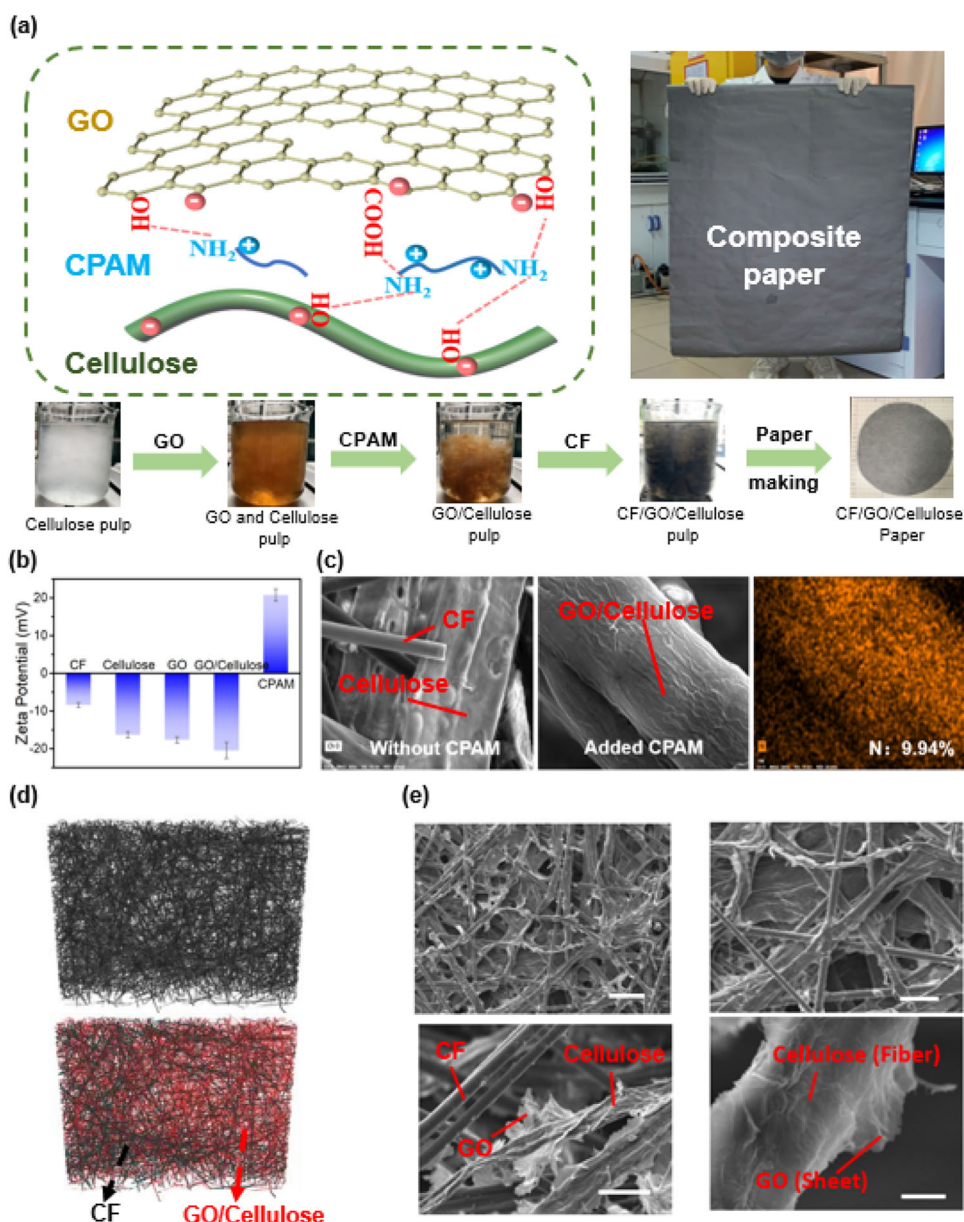


Fig. 2 Preparation and characterization of CF/GO/cellulose paper. **a** Fabrication of CF/GO/cellulose paper. Cationic polyacrylamide (CPAM) was used to control the interfacial interactions to enable the assembly of GO sheets onto the surface of the cellulose fibers. **b** Electrostatic interaction. Zeta-potential measurements indicate the electrostatic charge of the components. **c** The distribution of CPAM was detected by EDS. EDS shows that CPAM (determined by nitrogen) is localization on the surface of cellulose. **d** 3D structure by micro-CT. Micro-CT shows a homogeneous distribution of the CF and cellulose fibers in the CF/GO/cellulose composite. **e** Surface morphology by SEM. Scanning electron microscopy images show the composite's homogeneous distribution and also the assembly of the GO sheets on the cellulose surface. Scale bar is: top left 50 μm , bottom left 10 μm , top right 10 μm , and bottom right 1 μm .

composite paper was immersed in an electrolyte solution (1 M KCl, pH 7) and a cathodic voltage (-0.9 V vs the Ag/AgCl reference electrode) was applied. Figure 3b shows current-time ($i-t$) curves for the current drawn by several composite paper formulations. The leftmost plot shows that a control GO/cellulose (lacking CF) draws little current that demonstrates the importance of the carbon-fiber network for conferring conductivity to the composite. This plot also shows little current drawn for the CF/cellulose control (lacking GO), which suggests the current is being drawn to reduce the GO component. The rightmost plot in Fig. 3b shows the $i-t$ curves for CF/GO/cellulose composites prepared with differing amounts of GO. The inset in this plot indicates a nearly linear increase in electron transfer (charge; $Q = \int i dt$) with GO content. These electrochemical results indicate that the electrons

transferred are reducing the GO component of the composite paper (additional electrochemical evidence for this conclusion is provided in Supplementary Fig. 6 of the Supporting Information).

Two chemical methods were used to provide molecular evidence for electrochemical GO-reduction. First, Raman spectroscopy was used as the D and G peaks in the Raman spectra are often correlated to graphene structure and the ratio of D- to G-peak intensity is often correlated to structural defects that are believed to be important to electrocatalytic activities^{23,24}. The Raman spectra and summary bar chart in Fig. 3c show the results for CF/GO/cellulose composites that had been electrochemically reduced for various times along with the results from controls. This bar chart shows that electrochemical reduction led to an increase on the D- to G-peak ratio for the composite. Second, X-ray

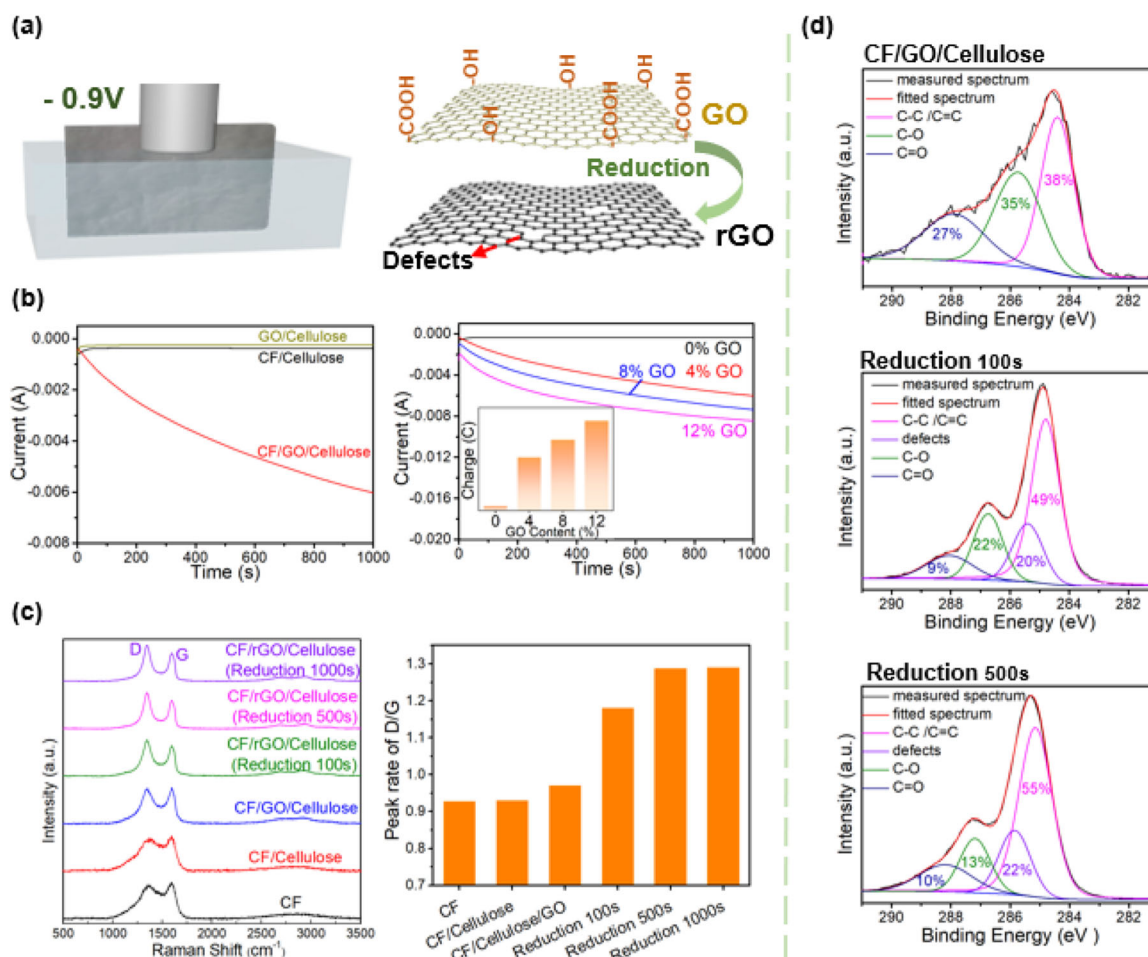


Fig. 3 Electrochemical reduction of GO in the composite paper. **a** Electrochemical reduction of graphene oxide. Schematic of electrochemical conversion of GO to reduced GO (rGO). **b** Controllable electrochemical reduction of GO in paper. Electrochemical measurements of current vs time (i-t) show that CF is required for reduction (CF provides the conducting network) and the reducing charge transferred ($Q = \int i dt$) increases with GO content (GO is the species being reduced). **c** Raman evidence on GO electrochemical reduction. Raman spectroscopy provides molecular evidence for GO reduction and the generation of defects (indicated by D band) is believed to be important for electrocatalytic activity. **d** High-resolution XPS spectra of C 1s. The high-resolution C 1s peaks of XPS provide further molecular evidence for electrochemical reduction.

photoelectron spectroscopy (XPS) was used and the C 1s region of the spectra was analyzed for chemical modification. The spectra in Fig. 3d show that electrochemical reduction resulted in decreases in the peaks for C/O single and double bonds consistent with expectations. These chemical and electrochemical measurements both indicate that the CF/GO/cellulose composite paper can be reduced electrochemically.

Flexibility and stability of composite paper electrode

To illustrate the macroscopic electrical properties of our composite paper, we used conventional cutting operations to create patterned “sensors” (Fig. 4a). The photographs in Fig. 4b provide a simple illustration that these composites possess conducting properties. We measured the sheet resistance of composite paper ($9 \Omega \text{ sq}^{-1}$) and calculated its conductivity as 1389 S m^{-1} . The schematic in Fig. 4c shows that these composites could also serve as working electrodes in a three-electrode electrochemical cell. In this experiment, the composite paper was tested using a standard electrochemical mediator potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$) in cyclic-voltammetry (CV) experiments. As illustrated, the CV curves were similar for electrodes that had been folded at different angles and even cut. These illustrations provide initial evidence for the electrochemical properties of the composite paper.

One functionally important feature of this composite paper is its stability in water. To illustrate this water stability, Fig. 4d shows we immersed the composite electrode in water and after 60 hours, this composite paper showed no evidence of swelling or leaching of the GO components. To quantify this stability, we removed this composite paper from the water every 12 hours and tested it by CV using the $\text{K}_3\text{Fe}(\text{CN})_6$ (5 mM). The bar chart of Fig. 4d shows that the oxidation-peak current in this CV remains nearly constant over this 60 hour experiment. Another functionally important feature that results from the fabrication method is repeatability. To illustrate repeatability, we cut several sensors from different locations of the composite paper and we tested each cut sensor by performing CV measurements with the $\text{K}_3\text{Fe}(\text{CN})_6$. The bar graph in Fig. 4e shows that the oxidation-peak current for these five different electrodes was similar (relative standard deviation among these five electrodes is less than 3.5%). These results indicate that the composite paper offers important practical features for paper-based electrochemical sensing.

Electrochemical sensing of phenols

While CF confers conductivity to the composite paper, the reduced GO (rGO) confers electrocatalytic activities (additional electrochemical evidence for this conclusion is provided in

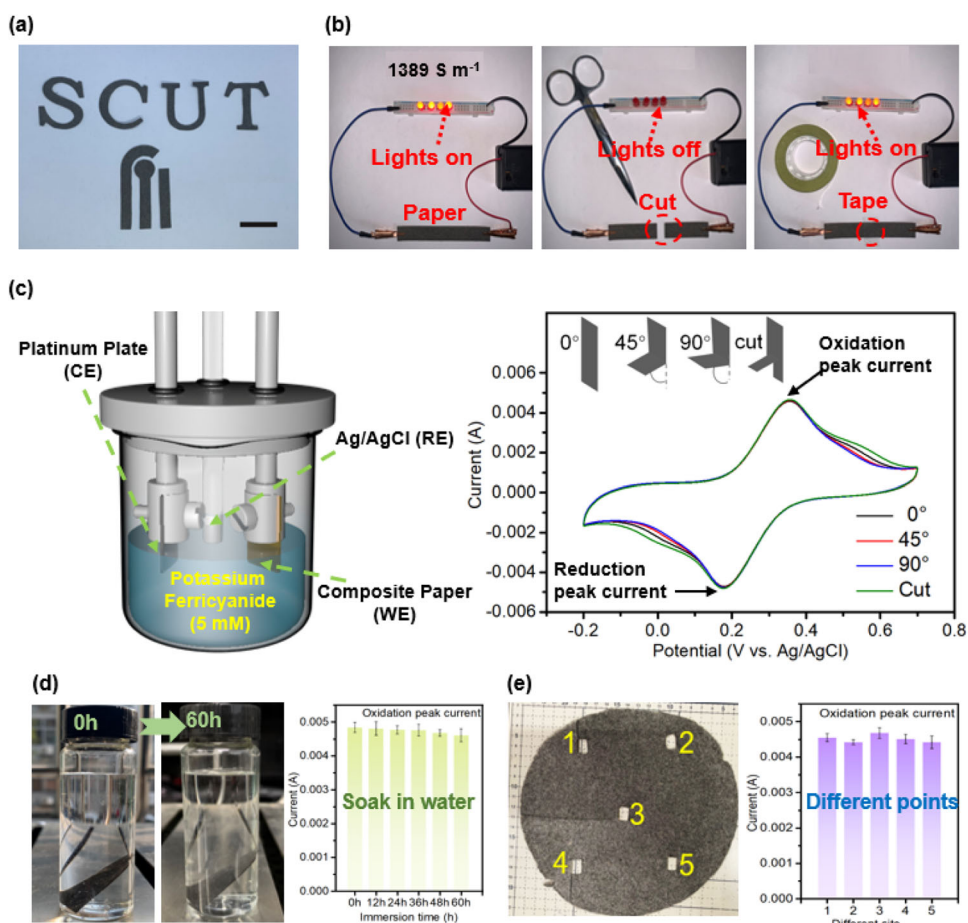


Fig. 4 Important features of CF/GO/cellulose composite paper. **a** Cut paper. Paper cutting allows reproducible generation of different patterns. Scale bar is 2 cm. **b** Repairability. The composite paper is conducting (conductivity value is 1389 S m^{-1}). Electrochemical measurements (of $\text{K}_3\text{Fe}(\text{CN})_6$) demonstrate that the CF/GO/cellulose composite is (c) flexibility (CV of potassium ferricyanide). Electrochemically active and flexible. **d** Stability. Structurally and functionally stable in water, and (e) repeatability. Repeatable in that different samples (i.e., different sensors) taken from different locations show the same functional performance.

Supplementary Fig. 7 and Supplementary Fig. 8 of the Supporting Information). To illustrate the importance of GO reduction on the composite's electrocatalytic activity, we prepared sensors that had been reduced to different extents by varying the electrochemical reduction time (and therefore the reductive charge transfer). As illustrated in Fig. 5a, these sensors were evaluated by performing CV measurements with $\text{K}_3\text{Fe}(\text{CN})_6$. Sensors prepared from a CF/GO/cellulose composite that were not electrochemically reduced show no peaks for oxidation or reduction. Sensors prepared from composites that were electrochemically reduced show peak currents for $\text{K}_3\text{Fe}(\text{CN})_6$ and these peak currents were larger for composites prepared with increasing reduction times²⁵. The bar chart summarizes these results and demonstrates the importance of GO reduction for the composite's electrocatalytic activity.

As a proof-of-concept demonstration, we considered the analysis of three phenols that are commonly present in the environment^{26,27}. As illustrated in Fig. 5b, hydroquinone (HQ) can be oxidized under mildly oxidative voltages, while p-chlorophenol (CP) and p-nitrophenol (NP) require more positive voltages for their oxidation. For this demonstration study, we prepared composite paper from CF (45.9% w/w), GO (8% w/w), cellulose (45.9% w/w), and CPAM (0.2% w/w), electrochemically reduced this composite (-0.9 V , 10 min), and then cut rectangular sensors (surface area 1 cm^2). Electrochemical measurements were performed using a commonly used method of differential pulse voltammetry (DPV). When solutions containing a single phenol (10 mg L^{-1}) were measured, the DPV curves in Fig. 5b show that

an oxidation peak was observed, and these oxidation peaks occurred at different voltages. When a solution was prepared containing all three phenols (10 mg L^{-1} for each phenol), Fig. 5c shows that three separate oxidation peaks were observed and the voltages where these peaks appeared are consistent with those for the individual phenols. The DPV curve for a control sensor prepared from a composite that was not electrochemically reduced shows no discernable oxidation peaks when tested with the mixture containing all three phenols. These results illustrate that the reduced graphene oxide (rGO) confers electrocatalytic properties to the composite paper: electrocatalytic properties are generally believed to improve sensitivity by amplifying detection currents and improve selectivity by separating peaks to avoid interference^{28–30}.

To test the detection sensitivity of the composite paper sensors, we analyzed solutions containing three phenols all present at the same concentration. The DPV curves in Fig. 5c show that oxidation peaks are observed for all three phenols and each of the peak currents was larger for solutions prepared with higher phenol concentrations. Each of these peak currents was quantified and the correlations between peak current and concentration are also shown in Fig. 5c. The estimated detection limits of HQ, CP, and NP were 0.045 , 0.093 , and 0.571 mg L^{-1} , respectively. The results from this demonstration study indicate that the composite paper offers appropriate electrocatalytic activities to serve as an electrochemical sensor.

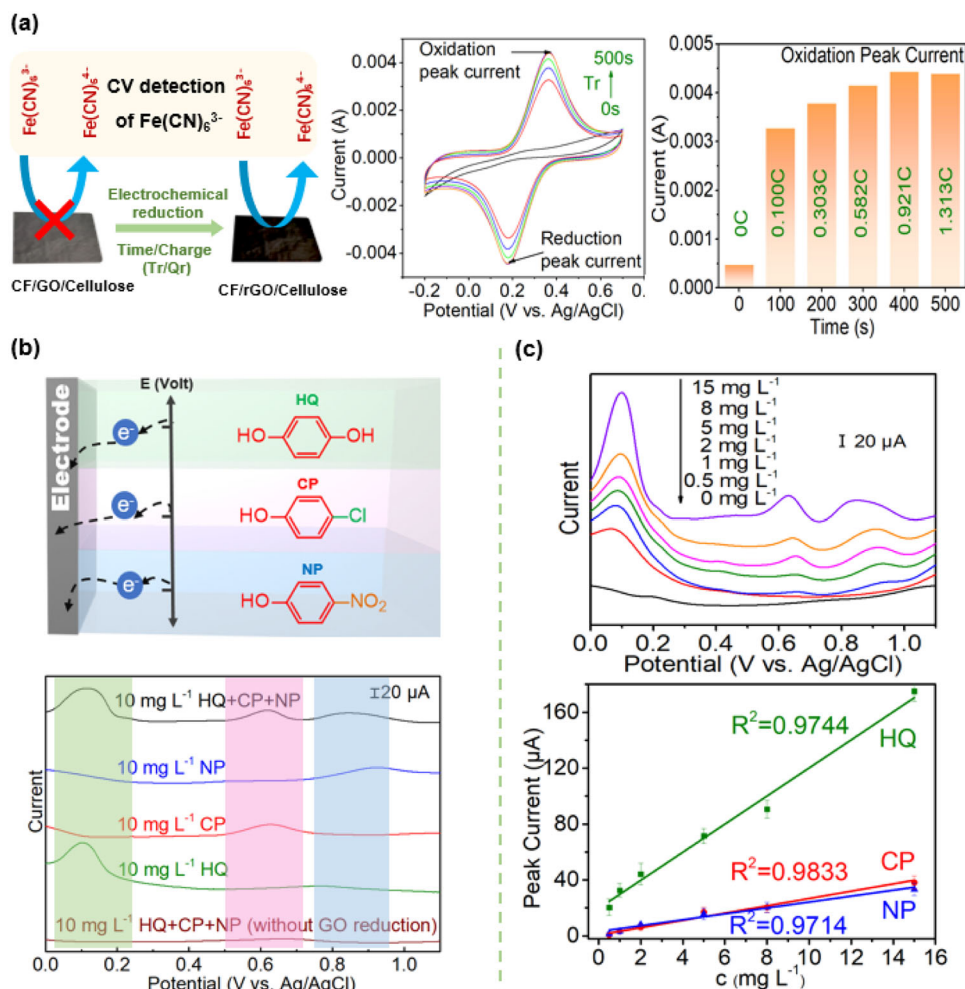


Fig. 5 Electrochemical detection by composite paper. **a** Electrocatalytic activities. Electrochemical reduction of CF/GO/cellulose confers electrocatalytic activity to the composite (as measured by CV measurements of $\text{Fe}(\text{CN})_6^{3-}$). Differential pulse voltammetry (DPV) measurements with three phenols (hydroquinone, chlorophenol, and nitrophenol) illustrate that the electrocatalytic properties enhance **(b)** selectivity of electrochemical sensing. Detection selectivity (DPV-peak separation) and **(c)** sensitivity of electrochemical sensing. Detection sensitivity (peak amplification; error bars show the standard deviation from three measurements and are generally small relative to symbol size).

Comprehensive evaluation

We prepared the radar chart in Fig. 6 to provide a multivariate comparison of our composite paper with other representative electrochemical sensors that have been considered for hydroquinone (HQ) analysis (the specific scoring criteria and values are provided in the Supporting Information). The two metrics at the upper left (limit of detection and R^2) are quantitative values that characterize sensor performance, and these metrics show that our composite paper is comparable to other reported electrochemical sensors. For the ease of operation metric at the lower left, the two paper-based electrodes and screen-printed carbon electrodes (SPCE) were scored more highly because they would be disposed after a single use, while the glassy-carbon electrodes (GCE) would need to be reused (GCE's cost is relatively high). For the cost metric at the lower right, the composite paper was more favorable because sensors made from ball-milled graphene or gold incur significant additional raw material costs, and SPCE requires a high cost of substrate and conductive ink. Finally, the large-scale processability metric at the upper right shows a higher score for the composite paper as we envision the use of scalable-paper manufacturing and electrochemical-processing technologies for the fabrication of this composite. In contrast, GCE is more difficult to manufacture at a large scale, while surface modification with

nanoparticles (gold or graphene) will likely require slower serial manufacturing steps (e.g., printing). Thus, as indicated in Fig. 6, we envision that our composite paper provides a low-cost and scalable approach to generate single-use electrodes with the necessary performance to realize the vision for portable electrochemical analysis.

DISCUSSION

We report the fabrication of a low-cost composite paper that offers conducting and electrocatalytic properties appropriate for electrochemical sensing. In contrast to other paper-based sensors prepared by surface modification (i.e., printing), the composite is prepared using conventional papermaking technologies and thus offers advantages in terms of repeatability and scalability. We believe that there are three important features of this work. First, controlling interfacial interactions is essential for generating a composite from equal quantities of the cellulose and carbon fibers, and also for assembling the GO sheets onto the cellulose fibers. Second, reduction of the GO confers electrocatalytic activities to the composite and we performed this reduction using an electrochemical step that is mild ($<1\text{ V}$ for several minutes) and scalable. Third, the composite paper has several

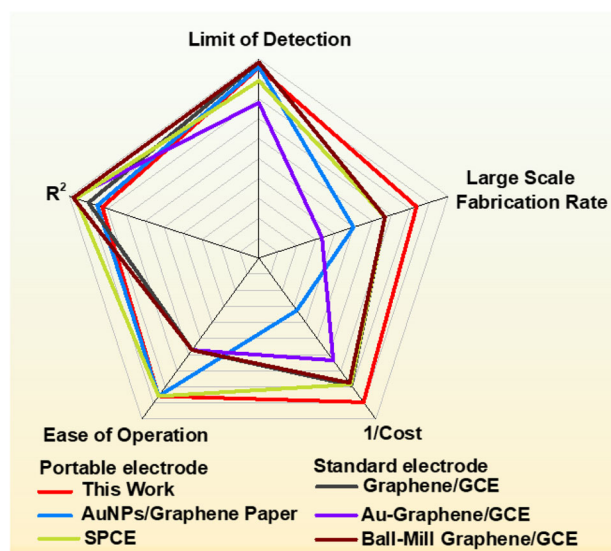


Fig. 6 Comparison of CF/GO/Cellulose paper - based sensors with other sensors. Radar chart compares the manufacturability and performance of CF/GO/Cellulose paper-based electrochemical sensor with sensors from other studies^{23,31–37}.

useful characteristics: it can be patterned using simple cutting operations, it is flexible and stable in water, and its electrocatalytic activities enable sensitive and selective chemical analysis. We envision that these characteristics of the composite provide the opportunity to realize the dream for portable, low-cost, and sustainable paper-based electrochemical detection.

METHODS

Materials

Graphene oxide (GO) (piece of diameter 20 μm , thickness <5 nm) was purchased from Xiwang Company (Shanghai, China). Cellulose pulp (Poplar chemical pulp) was purchased from Huatai Paper Industry Co., Ltd (Dongying, China). Carbon fiber (CF) (diameter 6 μm , length 4.5 mm) was purchased from Shenzhen Yataida Science & Technology Co. Ltd (Shenzhen, China). Cationic polyacrylamide (CPAM) was purchased from Tianjin Zhiyuan Chemical Reagent Co. Ltd (Tianjin, China). Hydroquinone (HQ), p-chlorophenol (CP), p-nitrophenol (NP), and other chemicals were purchased from Sigma-Aldrich. All reagents were used as received without further purification. Ultrapure water (>18 M Ω) prepared by Super Milli-Q water system was used for experiments.

Preparation of CF/GO/cellulose paper

A 0.3% GO slurry in water was obtained after 1 h of ultrasonic treatment with a cell crusher. Preparation of mixed pulp: softwood pulp board (1 g), which is 99% cellulose, was dispersed into 1 L of water, after which a specific amount of the GO slurry was added and stirred evenly, and then a specific amount of CPAM was added and stirred until the water became clear. CF (1 g) was dispersed in 100 ml of water and then poured into the freshly prepared GO/cellulose slurry and mixed well. Finally, this mixed pulp was poured into the Kaiser paper making machine (RK3AKWT, Austria) and diluted with 5 L of water, and then make the CF/GO/Cellulose paper. Although the concentrations varied between experiments a typical pulp was composed of 45.9% cellulose, 45.9% CF, 8% GO, and 0.2% CPAM. All test samples were prepared in the laboratory; scalable fabrication of composite paper (Fig. 1a) is prepared by a pilot-scale paper machine in the same proportion using 50 kg of softwood pulp.

Electrochemical reduction of GO

GO of the CF/GO/cellulose paper was electrochemically reduced using a three-electrode system, in which the counter electrode was a platinum

plate, the reference electrode was Ag/AgCl, the electrolyte was 1 M KCl solution, the reaction condition was -0.9 V , and the reaction time was varied, depending on the experiment 100–1000 s.

Electrochemical measurements

Cyclic voltammograms (CV) were performed using a three-electrode system (platinum counter electrode and a Ag/AgCl reference electrode), a scan rate of 100 mV s^{-1} , and a potential range between -0.2 V and 0.7 V ; and a 1 M KCl electrolyte containing 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$. Electrochemical-impedance spectroscopy was performed using 5 mM $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ and a frequency range of 100 kHz to 0.01 Hz.

Electrochemical sensing

The phenols HQ, CP, and NP were dissolved in 0.1 M phosphate buffer (pH 7) and then detected using composite paper as the working electrode in a three-electrode system. Measurements were performed using differential pulse voltammetry (DPV) with the potential range of 0–1.1 V.

DATA AVAILABILITY

All relevant data that support the findings of this study are available from authors upon reasonable request.

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AUTHOR CONTRIBUTIONS

X.W. and C.W. conceived and designed the work. C.W. prepared paper electrodes and carried out characterization and electrochemical sensing detection. R.W. and H.L. optimized and repeated the experiment. Z.L., W.H., X.S., and G.P. analyzed and interpreted the data. All authors discussed the results and commented on the final paper. X.W. and G.P. supervised the project.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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