

# Electrochemical sensing based on printable temporary transfer tattoos

## †Electronic Supplementary Information

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### *Chemicals and reagents:*

Ascorbic acid (AA), uric acid (UA), 2,4-dinitrotoluene (DNT), potassium ferricyanide ( $K_3Fe(CN)_6$ ), potassium phosphate monobasic ( $KH_2PO_4$ ), and potassium phosphate dibasic ( $K_2HPO_4$ ) were obtained from Sigma Aldrich (St. Louis, MO). 2,4,6-trinitrotoluene (TNT) was obtained from Cerilliant Corp. (Round Rock, TX). Chopped Carbon Fibers (CF) (8  $\mu m$  diameter, 6.4 mm length, 93 % purity) were purchased from Alfa Aesar (Ward Hill, MA) and further processed onsite to reduce the CF length to approximately 0.5 mm. All chemicals were used without further purification or modification. All reagents were prepared in a 0.1 M phosphate buffer solution (pH 7.4). Ultrapure water (18.2 M $\Omega$ -cm) was employed in all of the investigations. All the experiments were performed at room temperature.

An Ag/AgCl conductive ink (E2414), carbon graphite ink (E3449), and insulator ink (E6165) were procured from Ercon Inc. (Wareham, MA). Laser temporary tattoo paper kits were obtained from HPS Papilio (Rhome, TX). For comparison, custom-fabricated carbon screen-printed electrodes (on alumina, 2 mm working electrode diameter) were employed.

Cadaveric porcine skin samples were obtained from the University of North Carolina / North Carolina State University Joint Department of Biomedical Engineering and were immediately refrigerated upon arrival until temporary transfer tattoos were applied.

All test solutions were dispensed on the electrode surface via a micropipette. Volumes of ~50  $\mu L$  were employed in all of the investigations.

### *Instrumentation:*

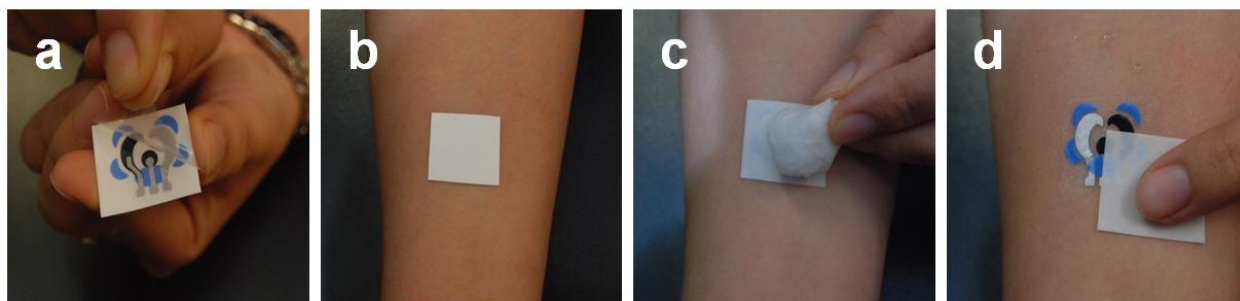
A CH Instruments (Austin, TX) model 660D electrochemical analyzer was employed for the voltammetric, amperometric, and impedimetric experiments. A Keithley (Cleveland, OH) model 6514 system electrometer was used to characterize trace resistance. An Olympus optical microscope with an integrated CCD camera was utilized to investigate the surface morphology of the printed epidermal sensors in greater detail.

Resistance measurements were recorded by multimeter probes at opposite extremities of a 1 cm Ag/AgCl tattoo trace on a GORE-TEX- (CF-reinforced and unreinforced varieties).

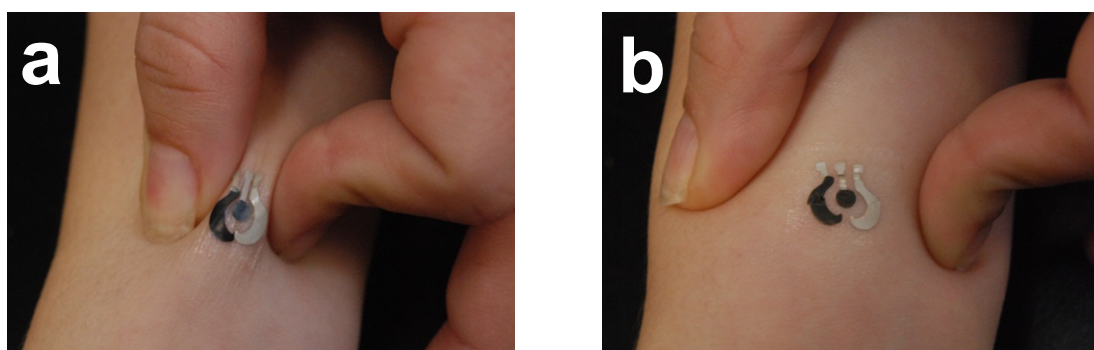
### *Fabrication of the temporary transfer tattoo electrodes:*

The sensor patterns were designed in AutoCAD (Autodesk, San Rafael, CA) and outsourced for fabrication on 75  $\mu m$ -thick stainless steel stencils (Metal Etch Services, San Marcos, CA). A separate stencil pattern was created for each layer (Ag/AgCl, carbon, insulator). An MPM SPM semi-automatic screen printer (Speedline Technologies, Franklin, MA) was employed for the fabrication efforts. A4-sized sheet of temporary transfer tattoo paper (Papilio, HPS LLC, Rhome, TX) was utilized as the substrate. An insulator ink was first printed on the paper. This was followed by screening printing of carbon-based ink

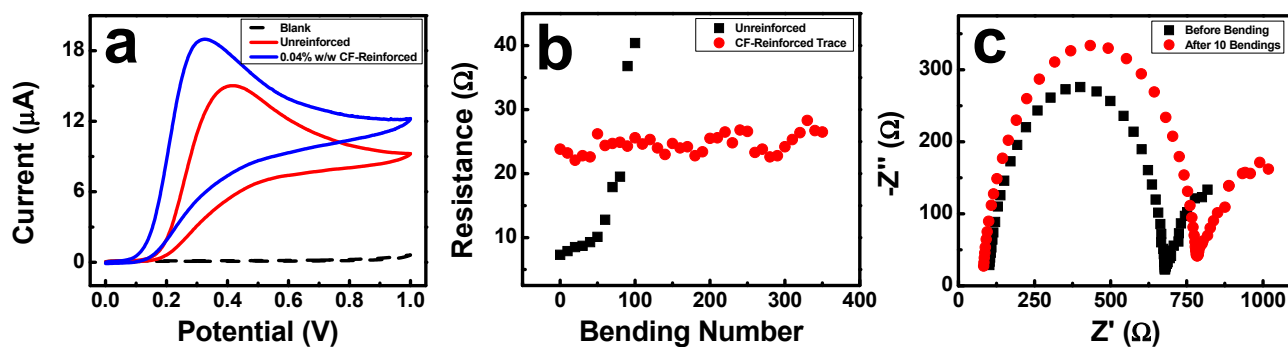
on the insulator design to define the working and counter electrode geometry. Finally, an Ag/AgCl-based ink was employed to define the connection points as well as the reference electrode. After each printing process, the patterned substrate was cured in a temperature-controlled convection oven (SalvisLab Thermocenter, Renggli AG, Industrie-Ost, Switzerland) at 60 °C for 40 min and finally cut into individual sensor tattoos for single use. In order to conduct electrochemical experiments, a tattoo pattern containing a circular working electrode was designed and possessed a 3 mm radius. In order to increase the tensile strength of the printed electrodes, 100 mg of chopped CFs were dispersed in 30 mL of ink and homogenized thoroughly. It should be noted that the loading level cannot be adjusted arbitrarily high. Exceeding the 0.04 % level compromised the viscosity of the ink and the ability to generate well-defined printing patterns. Therefore, the 0.04 % CF reinforcement level was employed in all the studies.



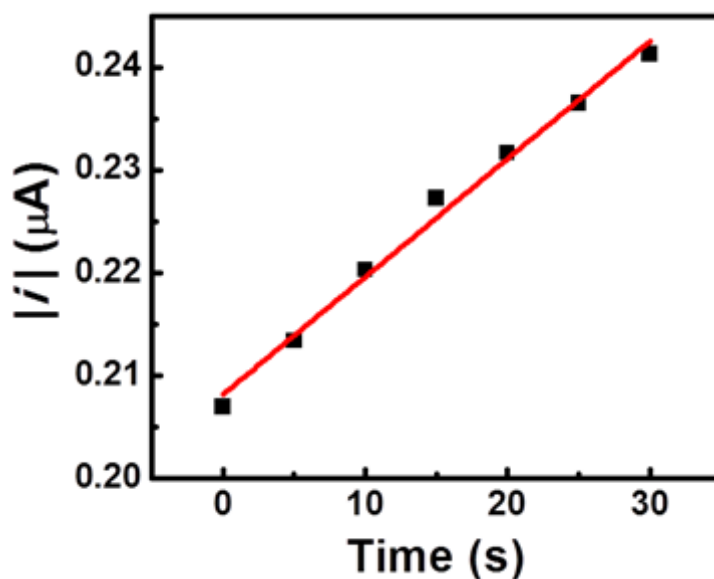
**Fig. S1:** Transfer of the T3 sensor onto the epidermis: (a) The protective sheet is peeled from the patterned T3 paper. (b) The paper is flipped and applied to the skin and subsequently dabbed with water (c). Finally, the paper is gently removed (d), exposing the sensor contingent.



**Fig. S2:** Photographic evaluation of the CF-reinforced T3 sensor on human skin during (a) pinching and (b) stretching.



**Fig. S3:** (a) Cyclic voltammograms illustrating the enhanced response generated by the dispersion of CF segments into the ink matrix; scan rate, 10 mV/s. (b) Resistive profile of a normal (black) and carbon fiber-reinforced (red) 1 cm Ag/AgCl tattoo trace on porcine skin. (c) Nyquist complex-valued impedance curves generated by a T3 sensor before (black) and after 10 bending operations (red) on porcine skin; potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ) was employed as the redox probe. Impedance spectrogram parameters: frequency, 0.1 Hz – 10 kHz; applied potential, 0.4 V vs Ag/AgCl; amplitude, 10 mV<sub>pp</sub>.



**Fig. S4:** SWV plot for detection of 100 mg DNT in a sealed 15 mL container on porcine skin by CF-reinforced T3 sensor. The inset illustrates the repeatability of the vapor-phase response over successive voltammetric scans ( $n = 6$ ). Square wave voltammetry (SWV) parameters: frequency, 20 Hz; amplitude, 25 mV; step, 4 mV (C). The system was allowed to reach vapor pressure equilibrium for 30 min prior to recording measurements.

**Note:** Fig. 2 cyclic voltammetry scan rate, 10 mV/s (a,b). SWV parameters: frequency, 20 Hz; amplitude, 25 mV; step, 4 mV (c).

References:

- <sup>1</sup> *M. C. Chuang, J. R. Windmiller, P. Santhosh, G. V. Ramirez, M. Galik, T. Y. Chou, J. Wang, Electroanal., 2010, 22, 2511-2518.*