

Supporting Information

Highly Stretchable Fully-Printed CNT-based Electrochemical Sensors and Biofuel Cells: Combining Intrinsic and Design-induced Stretchability

*Amay J. Bandodkar[#], Itthipon Jeerapan[#], Jung-Min You, Rogelio Nuñez-Flores, Joseph Wang**

Department of NanoEngineering, University of California, San Diego La Jolla, CA 92093, USA.

[#] Equal Contribution

**E-mail: josephwang@eng.ucsd.edu; Fax: +1 (858) 534 9553; Tel: +1 (858) 246 0128*

Figures

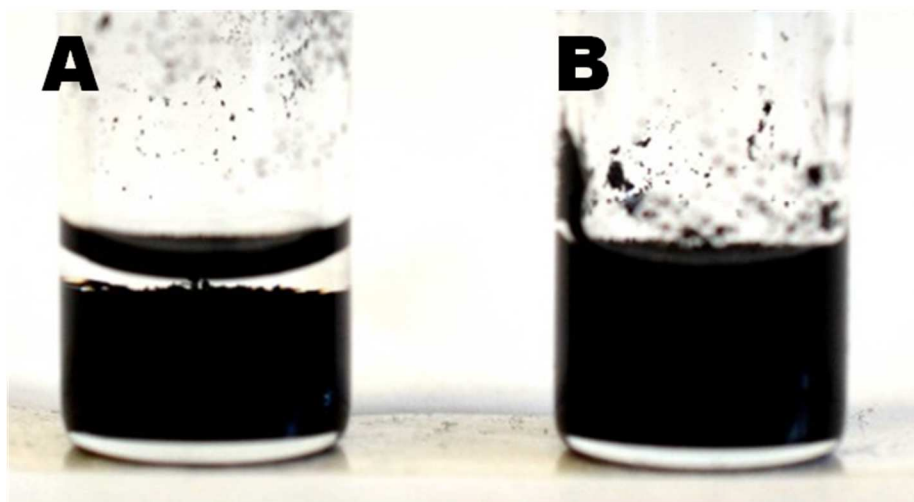


Figure S1: Images of suspension of (A) CNT in THF and (B) CNT-mineral oil in THF.

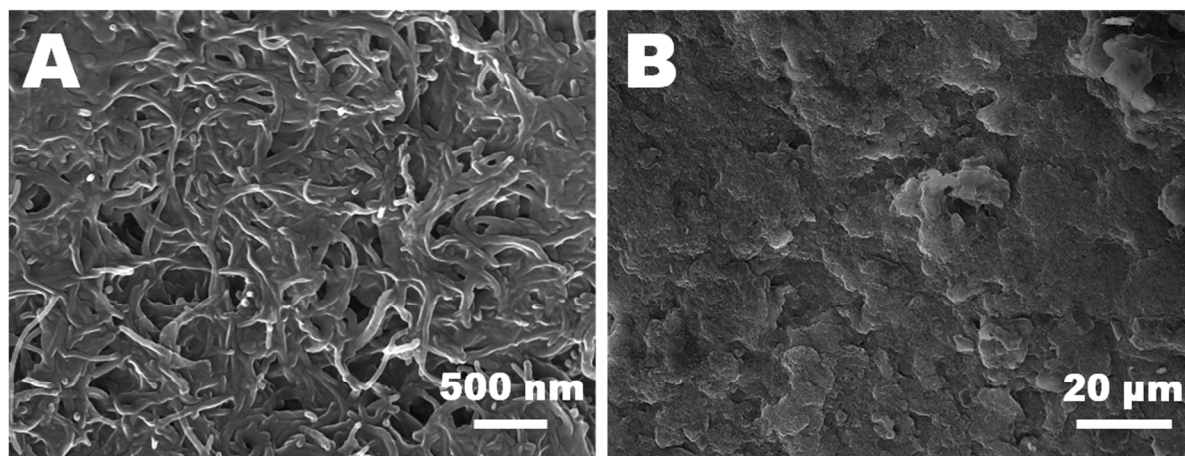


Figure S2: SEM images of printed stretchable CNT ink-based trace at different magnifications.

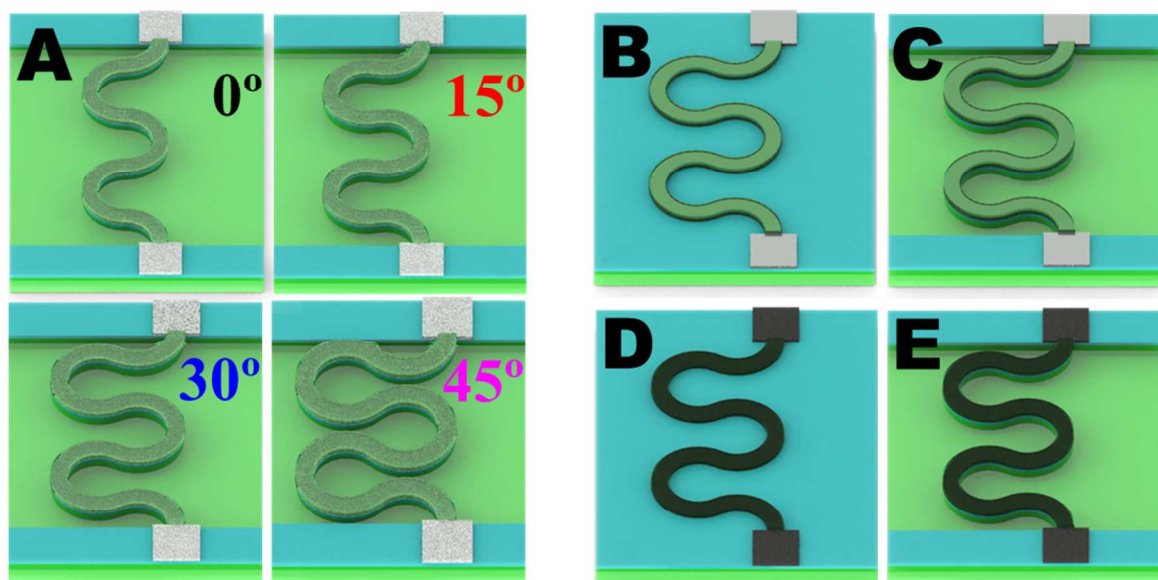


Figure S3: Pictorial representation of (A) free-standing serpentine interconnects having different connecting angles (θ). Schematic showing (B) surface-bound (C) free-standing Ag/AgCl-based serpentine interconnect ($\theta = 30^\circ$) and (D) surface-bound (E) free-standing CNT-based serpentine interconnect ($\theta = 30^\circ$).

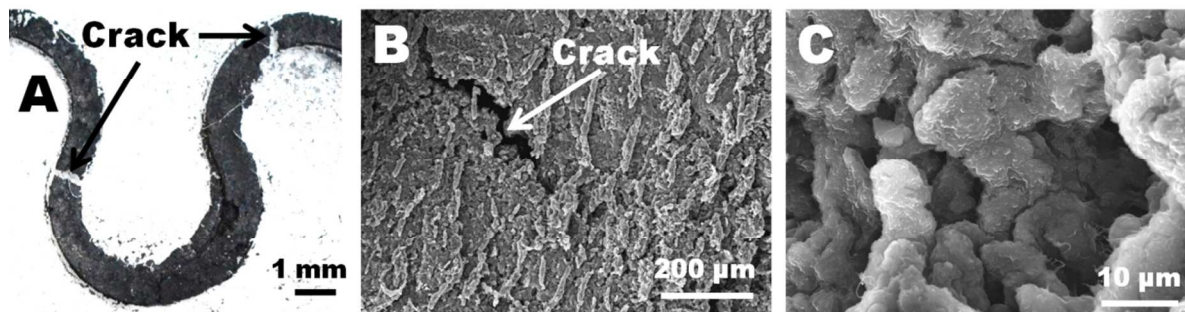


Figure S4: (A) Optical and (B, C) SEM images showing macroscopic and microscopic cracks and morphology of the printed trace fabricated using non-stretchable CNT ink.

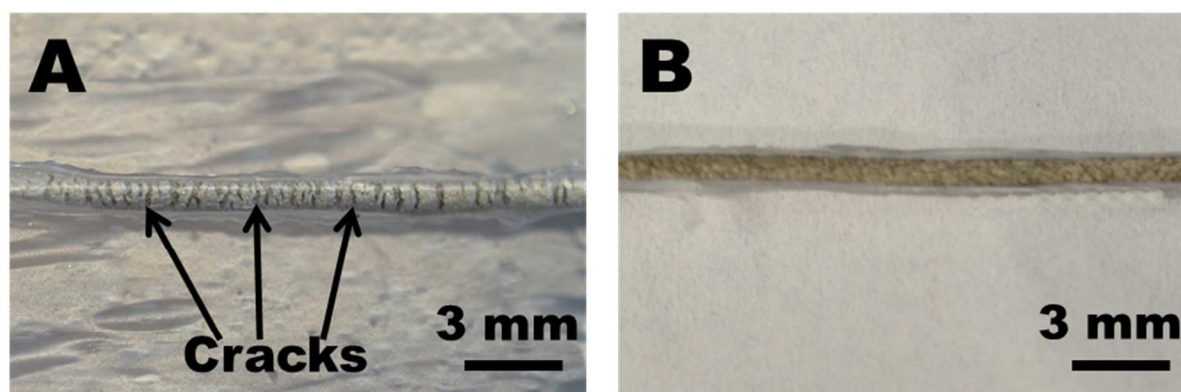


Figure S5: Images showing (A) non-stretchable and (B) stretchable Ag/AgCl ink-based trace under 200% strain.

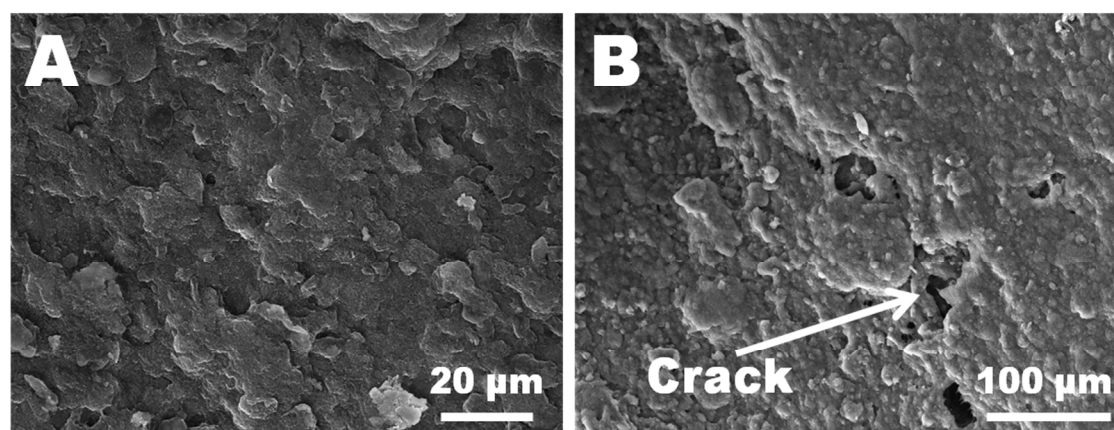


Figure S6: SEM image of stretchable CNT ink-based trace (A) before and (B) after being stretched by 500%.

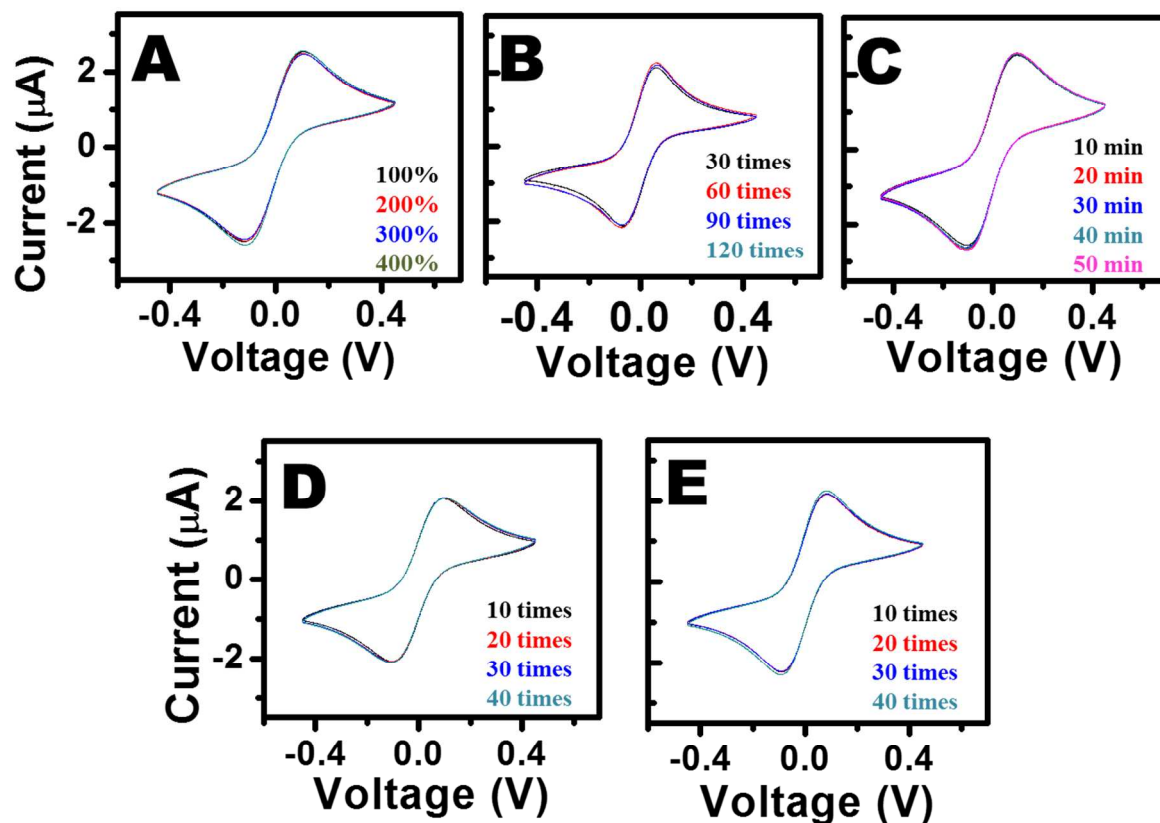


Figure S7: Intermediate CVs recorded after applying (A) increasing linear strain (B) repeated strain of 300% (C) a continuous strain of 300% (D) repeated indentation stress (E) repeated torsional stress.

Experimental Section

1. Chemicals and reagents

Carboxylic acid functionalized multi-walled carbon nanotubes (CNTs) (purity >95%, diameter = 10-20 nm, length = 10-30 μm), polyurethane (PU) (Tecoflex SG-80A), Ecoflex® 00-

30 (Smooth-On, Inc., PA), ferricyanide, mineral oil, tetrahydrofuran (THF), polyvinyl butyral (PVB), NaCl, methanol, nonactin (NAT), 2-nitrophenyl octyl ether (*o*-NPOE), potassium tetrakis(4-chlorophenyl)borate (KTCIPB), chitosan, glucose oxidase (GOx) from *Aspergillus niger*, Type X-S (EC 1.1.3.4), 1, 4-naphthoquinone (NQ), D (+)-glucose, bovine serum albumin (BSA), glutaraldehyde, potassium phosphate dibasic (K₂HPO₄), potassium phosphate monobasic (KH₂PO₄), and Nafion®, ethanol, and tetrathiafulvalene (TTF) were purchased from Sigma-Aldrich. All other chemicals were of analytical grade and were used without further purification. Ultra-pure deionized water was used in the preparation of the aqueous electrolyte solutions. Ecoflex® 00-30 was prepared in-house by mixing equal volumes of pre-polymer A with pre-polymer B provided by the supplier.

2. *Synthesis of stretchable CNT and Ag/AgCl inks*

Stretchable CNT ink was prepared by mixing 100mg of CNTs with 70mg of mineral oil. This composition was dispersed in THF for 1 h in an ultrasonic bath and then homogenized in a shaker for 5h. Thereafter, 113mg of PU was added and the resulting mixture was shaken overnight. A solid-to-solvent ratio of 1mg: 9μL was maintained for printing purpose. The stretchable Ag/AgCl ink was prepared by thoroughly mixing 177.2mg Ag/AgCl ink (E2414, Ecron Inc., Wareham, MA) with 26.5mg Ecoflex.

3. *Fabrication of stretchable electrochemical device array*

The fabrication process employed an MPM-SPM semi-automatic screen printer (Speedline Technologies, Franklin, MA). Sensor patterns were designed in AutoCAD (Autodesk, San Rafael, CA) and outsourced for fabrication on stainless steel through-hole 12" x 12" framed stencils of 125μm thickness (Metal Etch Services, San Marcos, CA). The printing process comprised of first screen printing a 75μm thick layer of Ecoflex on a supporting surface (Laser temporary transfer tattoo paper kits from HPS Papilio, Rhome, TX). While the Ecoflex layer was still uncured, it was carefully placed on a 26μm thick PU sheet (DelStar Technologies Inc., Middletown, DE) and allowed to bond with the PU layer while curing overnight at ambient room temperature. Precaution was taken to avoid entrapment of air bubbles while placing the Ecoflex layer onto the PU sheet. Thereafter, the protective paper on top of the PU sheet was gradually peeled off to expose the PU layer. Subsequently, a sequence of stretchable Ag/AgCl, stretchable

CNT and Ecoflex ink was printed to realize the complete electrochemical device array. The printed stretchable Ag/AgCl and CNT patterns were cured at 120°C for 6min, and 85°C for 10min in a convection oven, respectively. The final Ecoflex layer, used to define the electrode area and contact pads, was cured at room temperature for 1h. Subsequently, the free-standing serpentine interconnects were realized by excising the printed pattern, followed by placing it on an Ecoflex supporting base (75µm thick). The contact pads of the printed device array were firmly adhered to the underlying Ecoflex base by using freshly prepared liquid Ecoflex as a glue. The step involving excising the printed pattern was avoided in order to obtain traces with surface-bound interconnects. The device array was subsequently modified with specific reagents and biomolecules for achieving electrochemical sensors and biofuel cells.

4. *Fabrication of stretchable ion-selective potentiometric ammonium sensor*

The ammonium-selective membrane cocktail was prepared by mixing 2wt% NAT, 35wt% *o*-NPOE, 1wt% KTCIPB and 27wt% PU. The membrane solution was prepared by dissolving 100 mg of the above mixture in THF (1 mL). The cocktail was vigorously shaken for 1.5 h in an ultrasonic bath. The cocktail for making reference membrane was prepared by dissolving PVB (78.1 mg) and NaCl (50 mg) in methanol (1 mL). The cocktail was then vigorously shaken for 1h in an ultrasonic bath.

To fabricate the stretchable ammonium-ion sensor, 1.5µL of the reference membrane cocktail was drop-casted twice onto the Ag/AgCl reference electrode, and the ammonium sensitive electrode was modified by dropping 1.5µL of the ammonium-selective membrane cocktail three times onto CNT indicator electrode. The sensor was left to dry overnight before use.

5. *Fabrication of stretchable amperometric glucose sensor*

The stretchable glucose sensor was fabricated by functionalizing the CNT-based stretchable electrode with TTF mediator and GOx enzyme. This was achieved by first preparing a solution of 1% Nafion and TTF (50mM) in ethanol and a separate solution of GOx (40mg/ml) with BSA (10mg/ml) in 0.1M phosphate buffer (pH 7). The TTF solution and the GOx solution were then subsequently mixed in 1:1 v/v ratio and drop-casted onto the CNT-based stretchable electrode. The electrode was left to dry for at least 2h. Finally, 1µL of 3wt% PVC in THF was casted onto the electrode and dried at ambient temperature for at least 2h before use.

6. *Fabrication of stretchable glucose biofuel cell*

The bioanode was realized by modifying the stretchable CNT-based electrode with NQ mediator and GOx enzyme. 0.2 M NQ was first dispersed in ethanol and acetone (9:1 v/v) solution and sonicated for 1h. After sonication, 5 μL of NQ solution was drop casted onto the electrode at room temperature. The enzyme solution was prepared by mixing GOx (40 mg/mL) with BSA (10 mg/mL) in 0.2 M phosphate buffer. Subsequently, a 6 μL aliquot of the enzyme solution and 1 μL glutaraldehyde (1%) were casted on the electrode and dried under ambient conditions, and then covered with 2 μL of a 1 wt% chitosan solution. The cathode was obtained by electrodepositing platinum (Pt) on the other CNT-based stretchable electrode from a commercial platinum plating solution (Platinum RTP; Technic Inc, Anaheim, CA) for 600 s at -0.65 V (vs Ag/AgCl, 3M KCl). Finally, the cathode was covered with 1 μL Nafion® (5 %). Each electrode had a surface area around of 0.04 cm².

7. *Resistance studies*

The resistance studies comprised of connecting the free-standing and surface-bound stretchable Ag/AgCl and CNT-based serpentine traces to a multimeter interfaced with a personal computer with a computer for real-time data acquisition. The in-situ variation of the resistance was recorded as the traces were subjected to increasing levels of applied stress.

8. *Electrochemical studies*

Electrochemical characterization of the printed device was performed using a CH Instruments (Austin, TX) model 630C electrochemical analyzer. The preliminary studies focusing on the effect of applied strain on the device's electrochemical properties were performed using an electrolyte consisting of 10mM ferricyanide in 0.1M phosphate buffer (pH 7.0). Cyclic voltammograms (CV) were recorded over the -0.45V to 0.45V voltage range with a scan rate of 0.1V/s. The ammonium ion potentiometric sensor studies were performed using an electrolyte comprising varying concentrations of NH₄Cl in deionized water. Glucose sensor and biofuel cell experiments employed 0.1M phosphate buffer (pH 7.0) containing varying glucose concentrations. The glucose concentration was measured by the stretchable sensor by applying a constant voltage of +0.05V and measuring the current for 50s after a 1min incubation. The electrocatalytic activity of the anode and cathode of the biofuel cell were examined with a

platinum-wire counter electrode, and an Ag/AgCl (3.0 M KCl) reference electrode. Polarization curves were recorded by applying linear sweep voltammetry with a scan rate of 1 mV/s in 0.2M phosphate buffer solution (pH 7.0).

9. *Mechanical resiliency studies*

The preliminary study aimed at studying the effect of mechanical stress on the stretchable device array was analyzed by recording variation in the resistance of Ag/AgCl and CNT-based free-standing and surface-bound serpentine traces. A typical test involved measuring the resistance of an un-stretched trace. Thereafter a desired level of external stress was applied followed by release of the applied stress and measurement of the resistance.

The subsequent electrochemical approach to study the effect of applied stress on the electrochemical properties of the printed device was performed in a fashion similar to the resistance study. Cyclic voltammograms (CV) was first obtained for an unstretched device followed by stretching it to a desired strain and then gradually bringing it back to its unstretched position. Subsequently, CV was recorded to identify any variation in the electrochemical properties of the device. In case of the study for repeated 300% stretching study, the device was stretched for a total of 150 times and the CV was measured after every 30 cycles. In order to study the effect of applied stress in real-time, the printed device was maintained at a strain of 300% and CV were recorded after every 10 min for a total of 60 min. Throughout the entire study, the device was strained to 300%. The effect of mechanical stress on the stretchable potentiometric ammonium ion sensor, amperometric glucose sensor and glucose biofuel cell was also studied in a manner similar to the preliminary electrochemical studies (discussed above).

Supplementary Movie Caption

Video V1: Video showing application of repeated linear and multi-dimensional external strain to the all-printed CNT-based electrochemical device array.