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Supplemental Information for:

Chemical Activation of Commodity Plastics for Patterned Electroless Deposition of Robust Metallic Films

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1. Materials

Microfluidic devices were made from PDMS and Ecoflex®. PDMS (Sylgard^{TM} 184) by Dow Corning Co. was purchased from Ellsworth Adhesives, and Ecoflex® 00-30 two-part platinum cure silicone kits by Smooth-On Inc. were purchased from Reynolds Advanced Materials. The polymer films (thickness ranged between 0.25–0.75 mm) purchased from McMasterCarr®. The model materials for 3D printing were ABSplus™ and PR48-Clear Resin purchased from Stratasys Inc. and Autodesk Inc., respectively. Polyethyleneimine (CAS # 9002-98-6) was purchased from Sigma-Aldrich. The electronic surface mount LEDs were purchased from Digi-Key Electronics. The various electronic components were attached to traces using silver paste (purchased from Tedpella, Inc.). The chemicals used for activation solutions and deposition solutions included stannous chloride dihydrate (CAS # 10025-69-1), palladium(II) chloride (CAS # 7647-10-1), and hydrochloric acid (CAS # 7647-01-0), copper sulphate pentahydrate (CAS # 7758-99-8), and 2,2'-dipyridyl (CAS # 366-18-7), nickel chloride pentahydrate (CAS # 7791-20-0), ammonium chloride (CAS # 12125-02-9), sodium citrate tribasic (CAS # 6132-04-3), sodium hypophosphite monohydrate (CAS # 10039-56-2), L-Tartaric acid (CAS #87-69-4), Iron (III) chloride hexahydrate (CAS # 10025-77-01) purchased from Sigma-Aldrich Co. LLC.,

sodium chloride (CAS # 7647-14-5), ethylenediamine tetraacetic acid disodium salt dihydrate (EDTA) (CAS # 6381-92-6), formaldehyde solution (CAS # 50- 00-0), and sodium hydroxide (CAS # 1310-73-2), silver nitrate (CAS #7761-88-8), ammonium hydroxide (CAS # 1336-21-6), potassium hydroxide (CAS # 1310-58-3), ethanol (CAS # XX), hydrogen peroxide (CAS # 7732-84-1), and tetrachloroauric (III) acid trihydrate (CAS # 16961-25-4) purchased from Thermo Fisher Scientific Inc. All chemicals were used as received.

2. Methods

2.1 Surface Functionalization with Metal-Chelating Polymer

The different plastic substrates were cleaned with IPA and deionized water and dried with nitrogen gas. For oxidation of polymeric substrates, they were places under a UVO lamp (Grid Lamp, AssY, 5” × 5” × 0.5” BHK Inc., Claremont, CA) (λ = 184 and 254 nm) with 3 mm separation between the films and the lamp, for 90 s, except for polycarbonate. Substrates were then placed in a solution of 1.0 g PEI dissolved in 50 mL ethanol for 30 min on an orbital shaker at room temperature. Substrates were then removed from the solution and rinsed with DI water and dried with nitrogen.

2.2 Microfluidic Device Fabrication

The microfluidic devices were produced as previsouly reported by replicating 3D printed masters via soft lithography[1,2]. Briefly, we designed the masters using CAD software (Autodesk Inventor) and then printed them using Dimension Elite (by Stratasys Inc.) and Ember (by Autodesk Inc.) 3D printers. The masters printed in acrylonitrile butadiene styrene (ABS) using the Dimension Elite printer were treated with acetone vapor to remove the surface roughness associated with the extrusion based printing process, thus making the surfaces smooth. We mixed PDMS in a 10:1 base to catalyst ratio and degassed the prepolymer for 5 – 10 min in a vacuum desiccator. For replication, we poured the PDMS prepolymer into the master, cured at 60˚C for 1 – 2 hours, and finally demolded the microfluidic stamp. For Ecoflex® 00-30 microfluidic stamps, the same procedure was executed using a prepolymer made by mixing part A and part B of the smooth-on kit in 1:1 ratio and a curing step of 60˚C for 30 min – 1 hour. For microfluidic stamps with soft seals a layer (1 – 2 mm thick) of Ecoflex® prepolymer was poured into the master and partially cured by heating at 60˚C for 10 min. Next PDMS prepolymer (10:1) was layered on top of the partially cured Ecoflex®, filling the master to the desired volume. Finally, we cured the bilayer microfluidic stamps for 1 hour at 60˚C.

2.3 Electroless Deposition

The microfluidic stamps were placed on the polymeric substrates and sealed with compression, creating a microfluidic device. Tubing was used to connect the devices to syringes containing the solutions in syringe pumps (Model NE-4000 by New Era Pump Systems Inc.).

Activation – To activate the surface, both combined and separate activation solutions were made. The combined solution contained tin (II) chloride (30 g/L), palladium (II) chloride (0.5 g/L), sodium chloride (160 g/L) and hydrochloric acid (60 mL/L) in nanopure water. The separate activation solution for tin contained tin (II) chloride (3.12 g/L) and hydrochloric acid (3.12 mL/L) in nanopure water. The separate solution for palladium contained palladium (II) chloride (5 g/L) and hydrochloric acid (5 mL/L) in nanopure water. The surfaces were activated by flowing the combined activation solution (for copper and silver depositions) or separate activation solutions, tin follow by palladium (for nickel deposition), at a rate of 0.2 mL/min for 5 – 30 min. After removal of activation solution(s), the devices were rinsed by flowing DI water through for 30s – 1 min. For deposition of copper and nickel, the devices were removed by releasing compression and the substrates were rinsed with DI water before being placed into the deposition baths.

Copper Deposition – The copper deposition solution contained copper sulfate pentahydrate (15 g/L), EDTA (45 g/L), 2,2 – dipyridil (0.05 g/L) and formaldehyde (27.5 mL/L) in nanopure water. The pH of the solution was brought to 11.5 – 12 using 5 M sodium hydroxide and heated to 60°C in a water bath. The substrates were immersed into the solution for a range of 5 – 20 min. After removal from the deposition bath the substrates were rinsed with DI water and dried with nitrogen.

***Nickel Deposition* –** The nickel deposition solution contained nickel (II) chloride pentahydrate (20 g/L), sodium citrate tribasic (10 g/L), ammonium chloride (35 g/L), and sodium hypophosphite monohydrate (20 g/L) in nanopure water. The solution was heated to 85ºC on a hot plate. The substrates were immersed into the solution for a range of 10 – 50 min. After removal from the deposition bath the substrates were rinsed with DI water and dried with nitrogen.

***Silver deposition* –** The silver was deposited through flow-based deposition in the channels of the microfluidic device. Two separate solutions were made, the first being silver nitrate (6.8 g/L) in nanopure water. The second solution contained L – tartaric acid (16 g/L) dissolved in nanopure water. The tartaric acid solution was brought to a pH range of 9 – 12 using 5 M potassium hydroxide. Then 30% ammonium hydroxide (6 mL/L) and ethanol (20 mL/L) were added. These solutions were then transferred to separate 60 mL syringes. The deposition solutions were flowed through, connected with a Y-junction as the solution entered the device, at a rate of 0.1 mL/min for 30 min – 2 hours. After the deposition was finished, the devices were removed from the substrates by releasing compression and the substrates were rinsed with DI water and dried with nitrogen.

***Gold Deposition* –** A solution of colloid gold nanoparticles was used at the activation solution for gold deposition. Gold nanoparticles were made using the following procedure, 20 mL of 1 μM tetrachloroauric (III) acid trihydrate was heated to 90°C. Once heated, 2 mL of a 1% (w/v) sodium citrate solution was added. The solution was then removed from heat and allowed to cool to room temperature. The color of the solution went from light yellow, to clear, to gray, and finally a dark red, indicating gold nanoparticles were present. Nanoparticles were stored in dark covered containers to avoid photodegradation. We flowed the nanoparticle solution through the device at rate of 0.1 mL/min for 1 – 2 hours to activate the surface. Gold deposition solutions were made in two separate syringes. One syringe contained 0.1 μM gold chloride solution (700 mL/L), the other contained 30% hydrogen peroxide (300 mL/L). The two solutions were connected with a Y-junction as they flowed into the microfluidic device at a rate of 0.1 mL/min for 1 – 2 hours. After the deposition was finished, we removed the devices from the substrates by releasing compression and the substrates were rinsed with DI water and dried with nitrogen.

3. Characterization

3.1 X-Ray Photoelectron Spectroscopy

PET and PC substrates were analyzed during each step of surface preparation using a K-Alpha XPS (Fisher Scientific). The instrument was equipped with a monochromatic aluminum K-alpha X-ray source irradiating the sample at 1486.6 eV. Survey scans as well as elemental scans for carbon, oxygen, and nitrogen were taken.

3.2 Contact Angle

We measured static water contact angle (CA) using an Attension Theta contact angle goniometer (Biolin Scientific, Gothenburg, Sweden). DI water droplets 1 – 3 uL in size were placed on substrates. A total of 7 measurements per sample were taken to give an average static contact angle.

3.3 X-Ray Diffraction

To confirm the identity of the metals, X-Ray Diffraction was used. Each metal was deposited as previously described in a circle pattern 15 mm in diameter. A PANalytical

Empyrean Diffractometer with a 3 kW copper target and theta-theta goniometer was used to obtain XRD patterns for metals.

3.4. Tape Test

To perform the tape test, each metal was scored in a grid pattern using a surgical blade. A piece of Scotch™ tape was placed on the scored area and hand-held pressure was applied to ensure conformal contact with the entire area. The tape was peeled off and microscope images of the grid pattern were taken using Zeiss (Axio Scope) microscope to determine adhesion of metals (Figure S1).

3.5. Interface Adhesion

We masked a PET substrate during functionalization, only allowing a small portion in the middle to be exposed to UVO and PEI. We deposited a nickel trace along the entire substrate including unfunctionalized and functionalized regions of the PET. A scotch tape test was performed, and the nickel trace was peeled from the unfunctionalized region but remained on the functionalized region.

4. Applications

4.1 Circuit Application

We deposited discontinuous copper and nickel traces on a PP and PET substrates. The traces were connected with LEDs and wires, attached with silver paste. A voltage was applied to the traces to light the LEDs. To demonstrate the durability of the traces, the PET substrate was bent to a radius of 10 mm. After 100 bending cycles, we applied a voltage to light the LEDs. To demonstrate the durability of the flexible traces during deformation a copper trace was deposited on a PET substrate. The resistance along the trace was recorded using a data acquisition (DAQ) device (NI cDAQ-9174) and LABVIEW program as the substrate was bent to various radii of curvature. There was a very small change in resistance as the substrate was bent, with a maximum change of 0.145Ω.

4.2 Battery Application

We deposited a copper and silver trace on two different polypropylene substrates in a circle design. A bilayer solution holder, made of PDMS and Ecoflex®, was sealed to each substrate using compression. On the copper substrate, we added 0.1 M copper sulfate pentahydrate solution to the holder, and 0.1 M silver nitrate solution was added to the to the holder on the silver. Each of the metals were connected via alligator clips to the data acquisition (DAQ) device (NI cDAQ-9174). A LabVIEW program to acquire voltage signal from the DAQ was created. A piece of filter paper soaked in 1 M potassium chloride, acting as the salt bridge, was added to the two half cells to turn the battery “on”. We removed the filter paper and disconnected the two half cells to turn the battery “off”. By adding and removing the salt bridge, we cycled the battery in the “on” and “off” states. The expected voltage was calculated using the standard reduction potentials and the Nernst equation.

4.3 Electrochemical Application

Integrated gold, silver, and silver/silver chloride electrodes were deposited on an ABS substrate to function as an electrochemical cell, containing a working, counter, and reference electrode, respectively. To create the silver/silver chloride reference electrode, a 0.1 M iron (III) chloride hexahydrate solution was used to convert the top layer of deposited metallic silver to silver chloride. We flowed the iron chloride solution through a microfluidic device sealed on to previously deposited silver at a rate of 0.2 mL/min for 5 min. XRD was taken to confirm conversion of the top layer of the silver into silver chloride (Figure S2). A bilayer solution holder, made of PDMS and Ecoflex®, was sealed to the ABS substrate allowing the three electrodes to be exposed to the solution. A solution of 5 mM ferricyanide dissolved 0.1 M potassium chloride was added to the holder. The electrodes were connected to the potentiostat (CH Instruments Inc. CHI660C) using copper tape, silver paste, and wires. A cyclic voltammetry experiment was run using standard parameters for ferricyanide including 100 mV/s scan rate, and potential range of -0.4V to 0.7 V. The same experimental set up was used to run electrochemical impedance spectroscopy (EIS) with an initial E = 0.17 V, frequency range of 10^5 Hz – 0.01 Hz, and amplitude of 0.01 V.

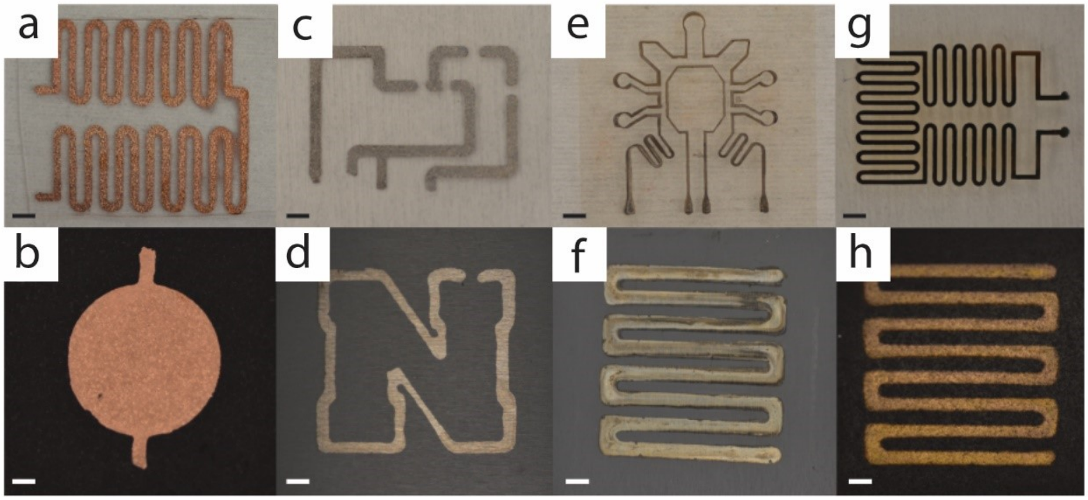

Figure S1. Representative images of metals deposited on various substrates using uDMD: (a,b) copper on PC and PP, (c,d) nickel on PC and PVC, (e,f) silver on PET and PVC, (g,h) gold on PET and PP. All scale bars are 3mm.

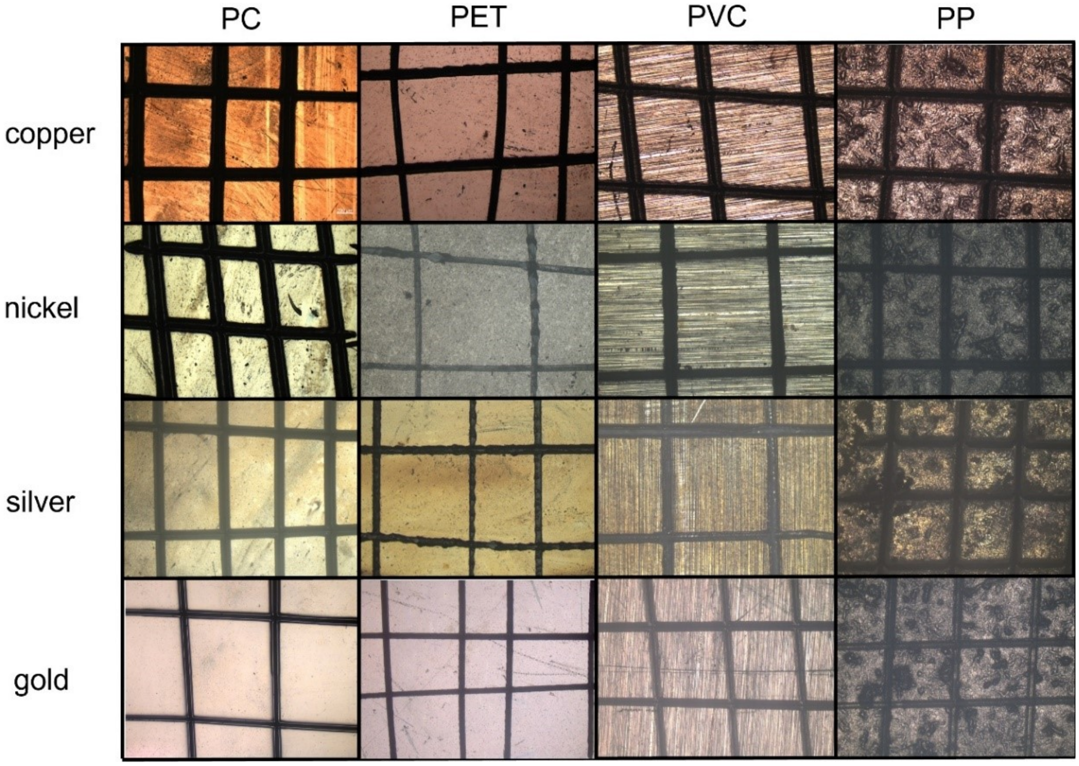

Figure S2. Microscope images of each type of metal on each type of plastic after tape test was performed.

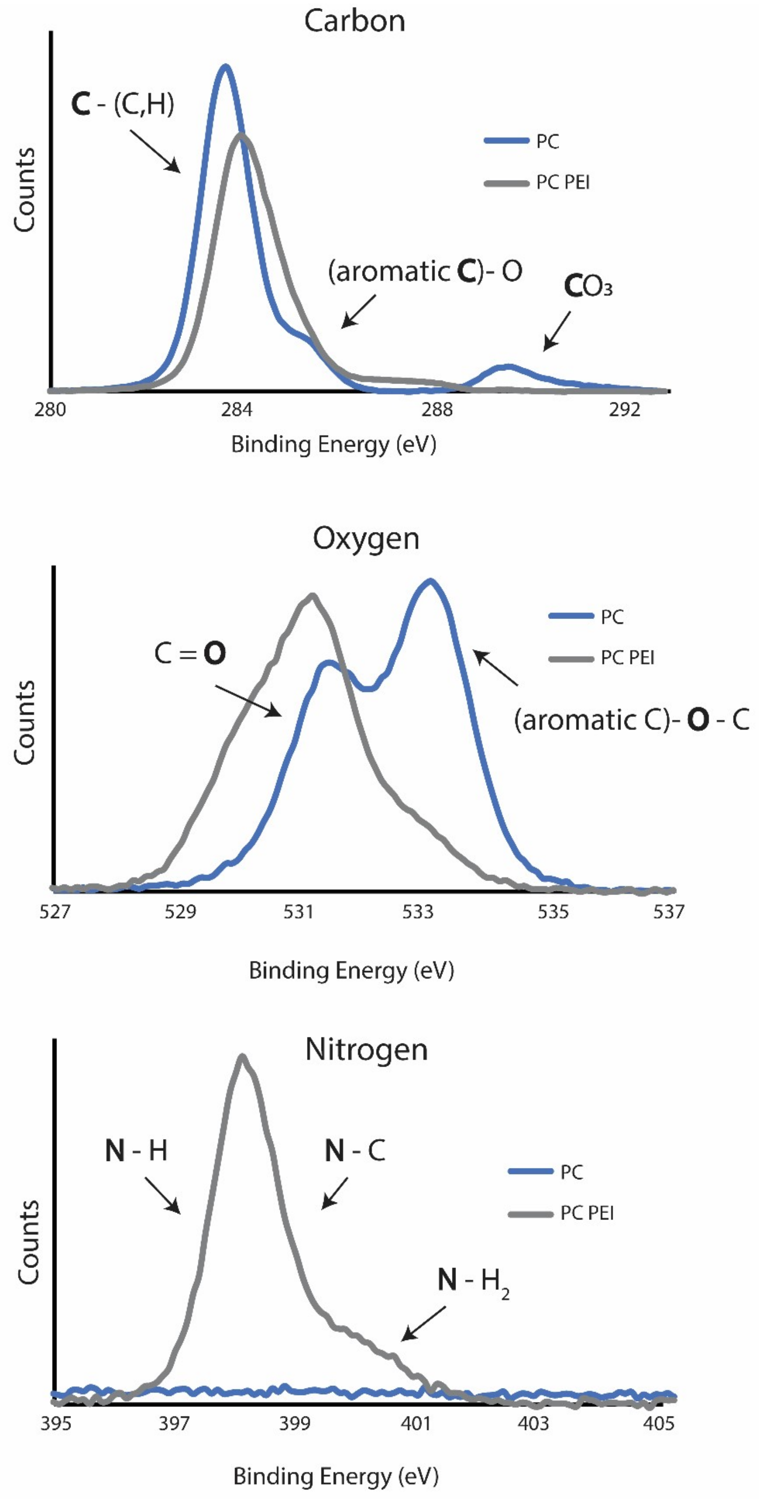

Figure S3. XPS data of PC before and after PEI functionalization. PC treated with PEI showed a shift in the primary carbon (C-C) peak towards ~285 eV and a corresponding decrease in the relative intensity of the -COO peak at 289 eV, consistent with the formation urethane bonds.

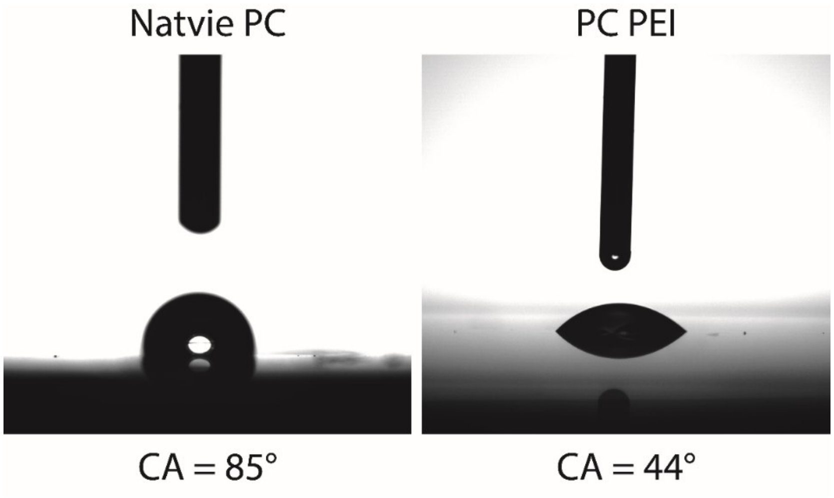

Figure S4. Static water contact angle of PC substrate before and after PEI functionalization.

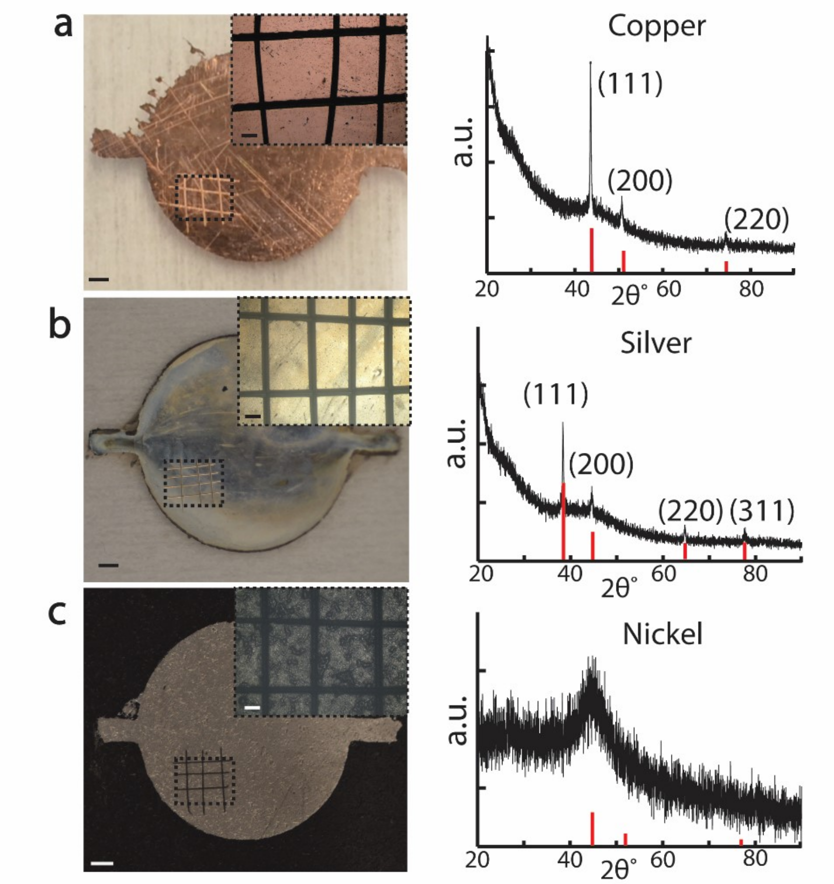

Figure S5. Representative optical micrographs of µDMD metals after the tape test where the annotated test regions are given as high magnification insets (left). Representative XRD data with each primary peak indexed to the appropriate metal (right) (PDF no. Cu 00-0836, Ag 04-0783, Ni 04-0850). Inset scale bars are 250µm, all other scale bars are 1.5mm.

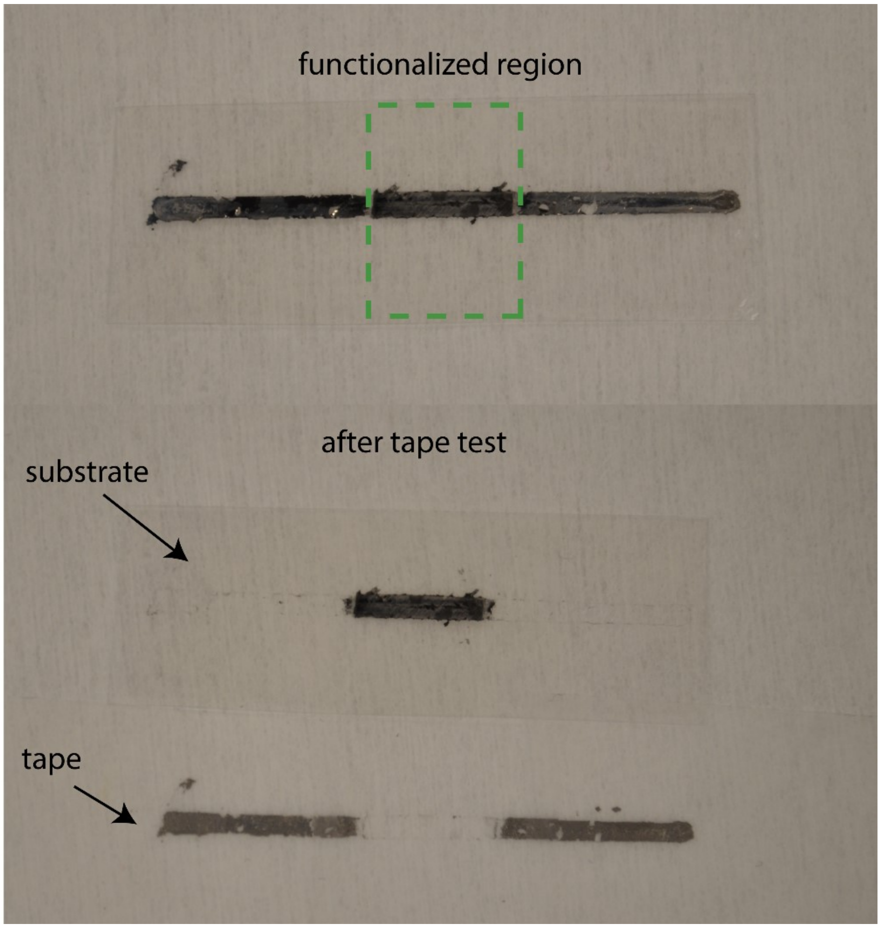

Figure S6. Nickel deposited on a PET substrate with small area of functionalized region and subsequent peeling of trace on unfunctionalized regions.

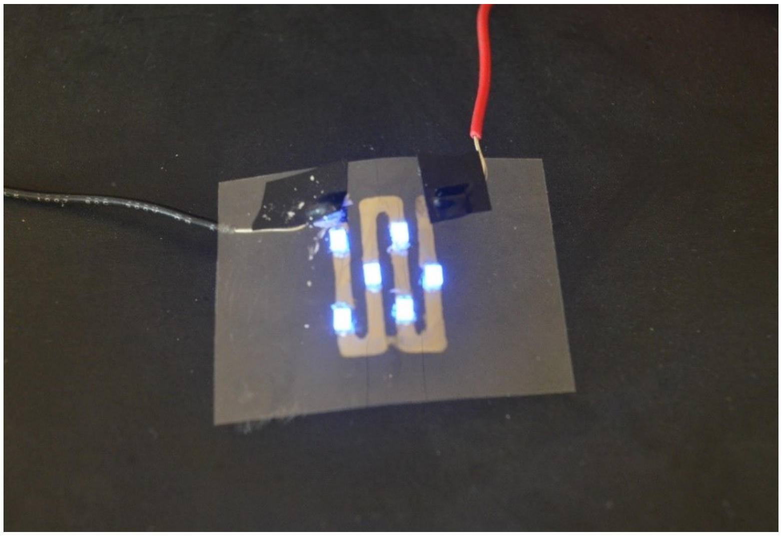

Figure S7. LEDs connected to nickel trace on PET substrate, lit up with applied voltage after 100 cycles of bending to radius of curvature of 10mm.

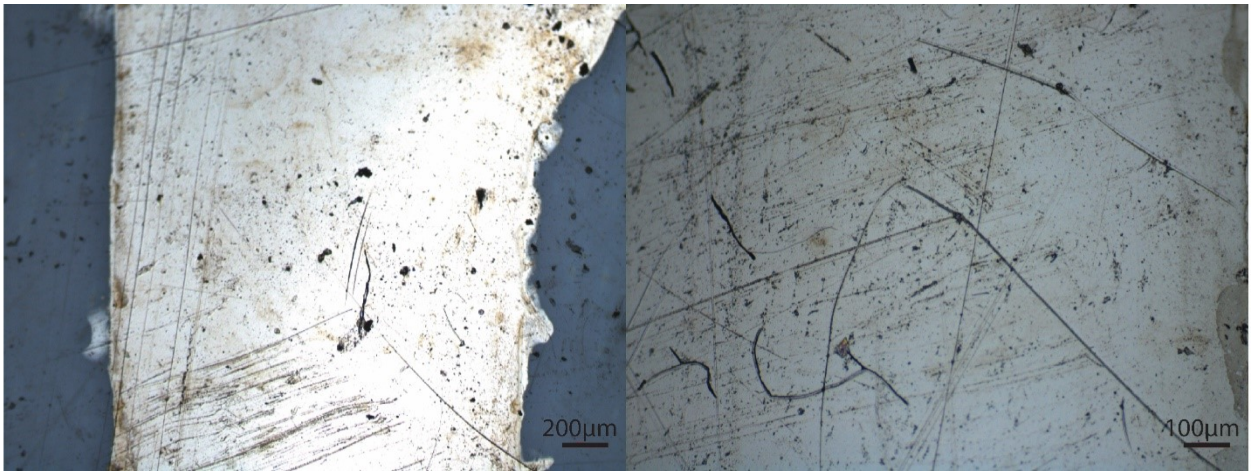

Figure S8. Microscope images of nickel trace used as flexible electronic device after 100 bending cycles.

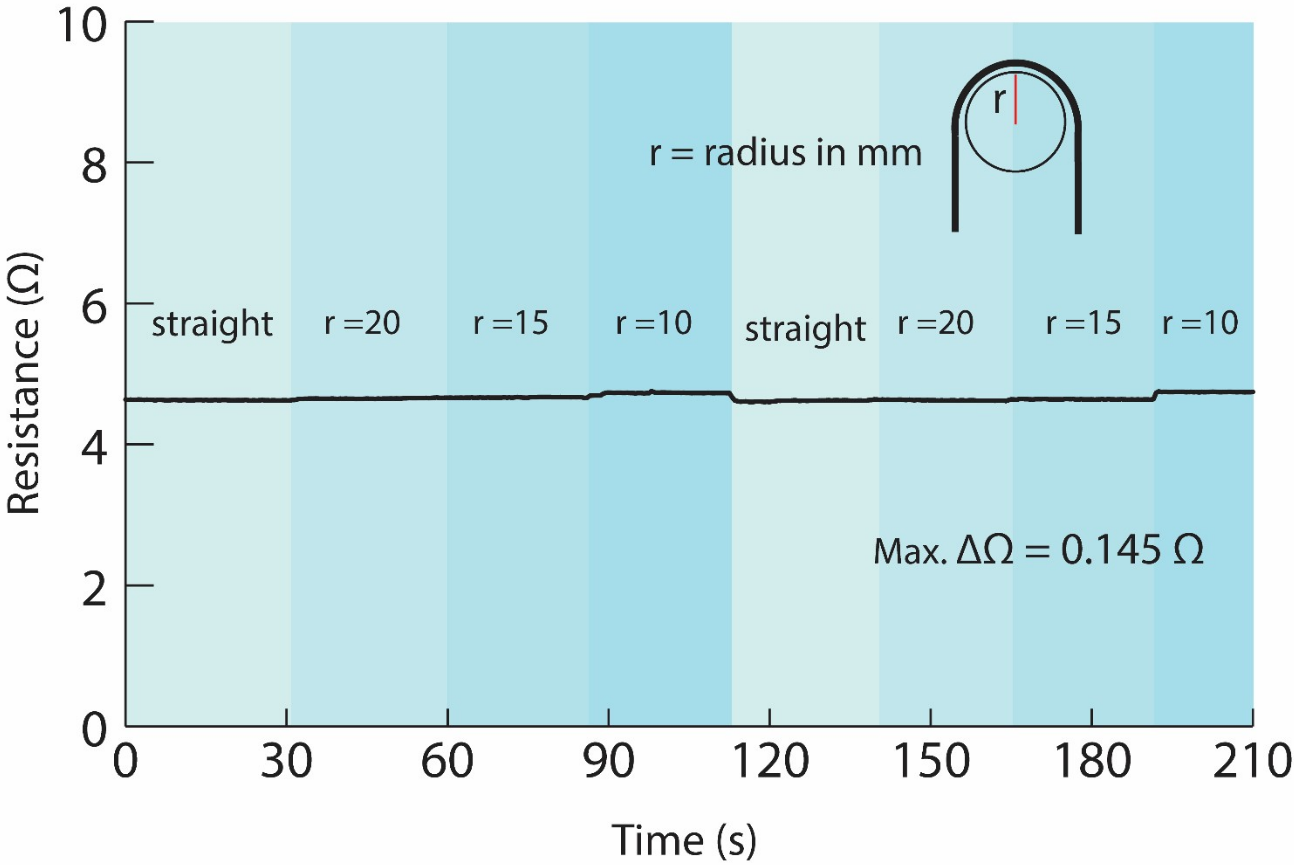

Figure S9. Graph of change in resistance while bending a PET substrate with copper trace to various radii of curvature.

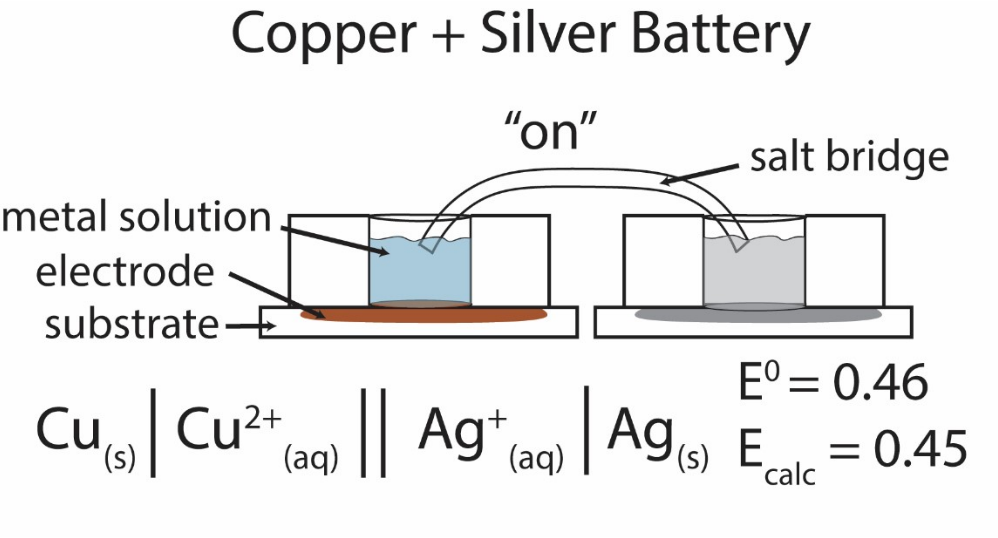

Figure S10. Schematic diagram of battery experiment using copper and silver electrodes with salt bridge connected turning battery "on". Expected voltage from standard reduction potentials and calculated voltage using Nernst equation.

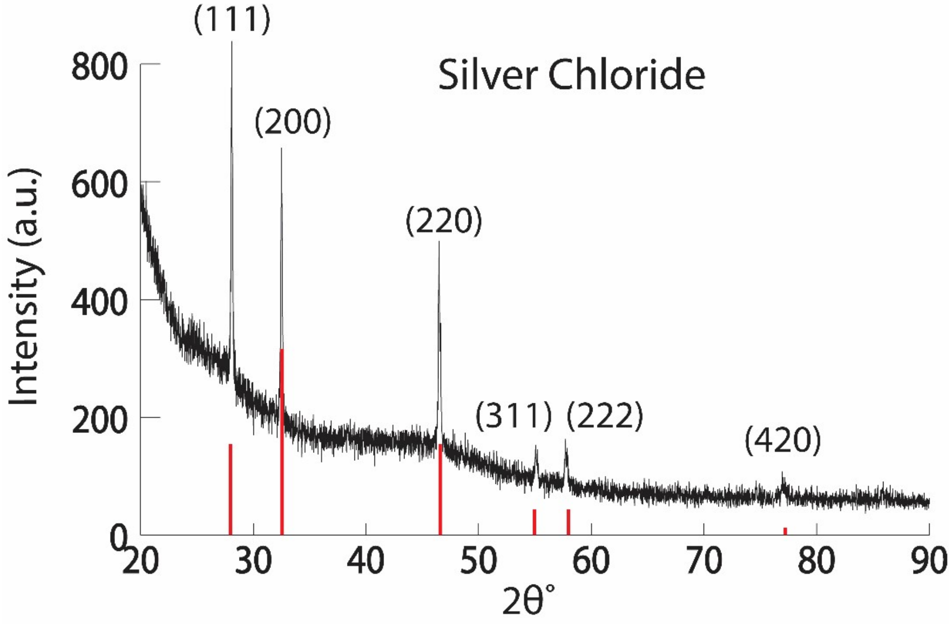

Figure S11. XRD pattern of silver trace after being converted to silver chloride to use as reference electrode. (PDF no. 31-1238)

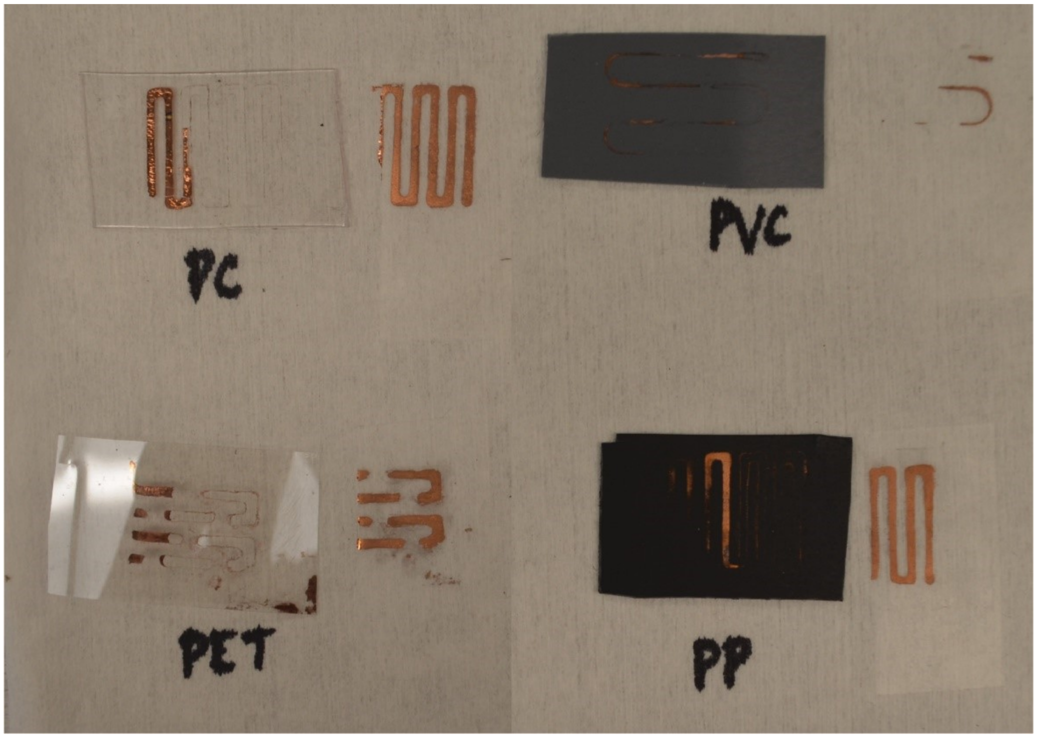

Figure S12. Tape test of copper deposited on all substrates without UVO and PEI treatment.

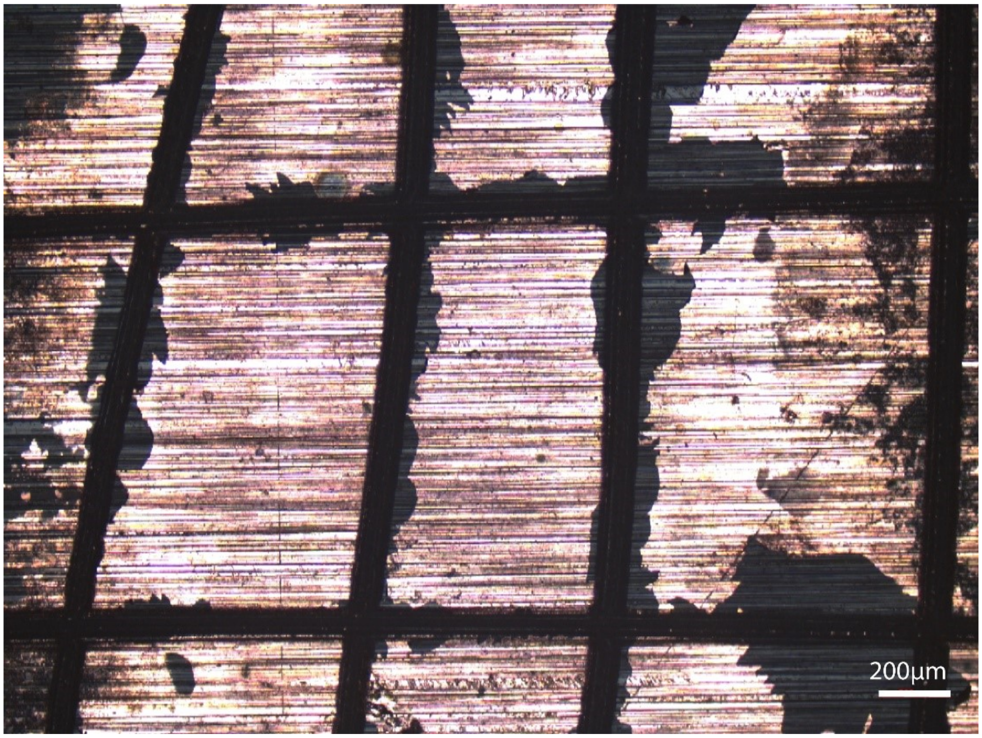

Figure S13. Micrograph image of copper on PVC with only 60 s of UVO exposure after tape test

References

1. A. Konda, J. M. Taylor, M. A. Stoller and S. A. Morin, *Lab Chip*, 2015, **15**, 2009-2017.
2. A. Konda, A. Rau, M. A. Stoller, J. M. Taylor, A. Salam, G. A. Pribil, C. Argyropoulos and S. A. Morin, *Adv. Funct. Mater.*, 2018, **28**, 9.