Ultrahigh Conductivity and Superior Interfacial Adhesion of a Nanostructured, Photonic-Sintered Copper Membrane for Printed Flexible Hybrid Electronics

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ABSTRACT: Inkjet-printed electronics using metal particles typically lack electrical conductivity and interfacial adhesion with an underlying substrate. To address the inherent issues of printed materials, this Research Article introduces advanced materials and processing methodologies. Enhanced adhesion of the inkjet-printed copper (Cu) on a flexible polyimide film is achieved by using a new surface modification technique, a nanostructured self-assembled monolayer (SAM) of (3-mercaptopropyl)trimethoxysilane. A standardized adhesion test reveals the superior adhesion strength (1192.27 N/m) of printed Cu on the polymer film, while maintaining extreme mechanical flexibility proven by 100 000 bending cycles. In addition to the increased adhesion, the nanostructured SAM treatment on printed Cu prevents formation of native oxide layers. The combination of the newly synthesized Cu ink and associated sintering technique with an intense pulsed ultraviolet and visible light absorption enables ultrahigh conductivity of printed Cu (2.3 × 10−6 Ω·cm), which is the highest electrical conductivity reported to date. The comprehensive materials engineering technologies offer highly reliable printing of Cu patterns for immediate use in wearable flexible hybrid electronics. In vivo demonstration of printed, skin-conformal Cu electrodes indicates a very low skin-electrode impedance (<50 kΩ) without a conductive gel and successfully measures three types of biopotentials, including electrocardiograms, electromyograms, and electrooculograms.

KEYWORDS: photonic sintering, printed Cu membrane, enhanced conductivity, interfacial adhesion, flexible hybrid electronics

INTRODUCTION

Over the last few decades, there has been increased interest in low-cost, solution-processed printing technology in various fields, including thin-film transistors, light-emitting diodes, solar cells, and biomaterials.1−9 Especially, conductive metal patterns of electrodes have been intensively studied with printed electronics technology. Among them, printing of conductive copper (Cu) patterns with high electrical conductivity (ρ = 1.72 × 10−6 Ω·cm) have widely been studied for printed flexible electronics using a variety of nanomaterial inks and sintering techniques.7,9 While advances in flexible materials and electronics have shown the possibility of replacing traditional processes, including vacuum processing, chemical deposition, and etching,1−3 they are not ideal methodologies yet due to the lack of interfacial adhesion strength with polymer substrates and low electrical conductivity. As the fabrication of electronic devices on flexible and bendable substrates is widely adopted, the adhesion between the substrate and conductive patterns is important to achieve reliable printed electronics.10

Common methods for enhancing the interfacial adhesion include adding an adhesion promoter, such as a polymer, surfactant, or ceramic frit, to the conductive ink and modifying the morphological and chemical properties of the substrate.11−19 These approaches, however, decrease the electrical conductivity since the remaining organic/inorganic additives hinder electrical flow. Additional disadvantages of the substrate modification include the shortened lifetimes of the functional

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The head and terminal groups have high specific affinity with the polymer substrate and conductive pattern, nanostructured SAM treatment provides high adhesion strength, which is composed of three groups: head, terminal, and spacer.20 Self-assembled monolayer (SAM) is a simple and convenient method of surface engineering in the form of a nanostructured self-assembled monolayer (SAM) is a simple and convenient process that prevents surface damages. The SAM molecules are composed of three groups: head, terminal, and spacer.20−22 If the head and terminal groups have high specific affinity with the polymer substrate and conductive pattern, nanostructured SAM treatment provides high adhesion strength, which is extensively studied in this work. Various advanced sintering techniques have been studied to obtain an electrical pathway of pure metal but have obstacles in mass production and process time.23−28 Recently, an intense pulsed light (IPL) that enables sintering in microseconds under ambient conditions has been proposed.29,30 IPL sintering uses light and thermal energy from a xenon flash lamp and has advantages in large-scale processing and fast manufacturing.

Here, we develop advanced materials processing technologies that combine an IPL-based method and nanostructured SAM treatment with (3-mercaptopropyl)trimethoxysilane (MPTS) to improve the electrical conductivity of printed Cu patterns and interfacial adhesion with a polymer membrane. Novel surface engineering technique of printed Cu provides a blocking surface oxidation as well as removal of the native oxide layer of Cu traces. Consequently, Cu traces, printed on a flexible polymer, show ultrahigh conductivity (2.3 × 10^{-6} Ω cm), superior mechanical strength (level, 4B; peel, 1192.27 N m^{-1} from ASTM D3359), and great mechanical flexibility (negligible resistance change after 100 000 bending cycles). To explore a possible application, flexible Cu electrodes are printed and mounted on the human skin for electrophysiological monitoring of electromyograms (EMG), electrocardiograms (ECG), and electrooculograms (EOG). Device demonstrations with Cu conductive patterns illuminate their potential in wearable flexible hybrid electronics.

### RESULTS AND DISCUSSION

Figure 1 shows the overview of a new class of technologies developed in this work. We utilized a Cu ink to print on a polymer film for a flexible hybrid electronic system (Figure 1a). Chemical bonds of −OH and C==O, formed on an oxygen treated PI film, react with the silane functional groups of the SAM solution (Figure 1b; details of the material processing appear in Figure S1 and Note S1). In the meantime, the opposite functional groups bond with the Cu ink, resulting in silanol and Cu−S bonds with a small contact angle (30.1°), shown in Figure 1b. The printed Cu patterns are processed with IPL sintering and nanostructured SAM treatment (Figure 1c). Cu is easily combined with thiol groups and the trimethoxysilane functional groups are exposed to the air to serve as a barrier to oxidation because of its hydrophobic property, proven by the contact angle of 132.3° (Figure 1c). All the chemical bonds, functionalized with the nanostructured SAM treatment, were verified by XPS analysis (see details in Figure S2−3, Table S1−2, and Note S2−3). Figure 1d (left) captures a photo of a set of printed flexible Cu traces on a PI film. Scanning electron microscope (SEM) images (top view; middle and side view; right in Figure 1d) show a microstructure with great packing density, which is the key indication of high sinterability. The thickness of the printed Cu layer is ~130 nm.

Figure 2 summarizes material properties and mechanical characteristics of the printed Cu on a flexible PI membrane. We explored various IPL powers (1600, 1800, 2000, 2200, and 2400 kW) and times (8000, 9000, 10000, 11000, and 12000 μs) to sinter the printed Cu (Figure 2a and b). This study revealed that low power with limited time is not sufficient for sintering Cu complex ion ink, as also indicated by the Cu2O phase (case 1 in Figure 2c and Table S3). However, a high photonic energy (power = 2400 kW and time =12000 μs) was also not suitable because of sample damage (case 5 in Figure 2c). If the IPL sintering parameters (power = 2400 kW and time = 12000 μs) were not suitable because of sample damage. Therefore, a low power with limited time is necessary for Cu ink sintering. As a result, we investigated the Cu ink sintering process at low power and limited time to achieve the desired Cu film properties.
2c). SEM investigation captures specific phase and morphology of the sintered Cu (Figure 2d). Low sintering energy (1600 kW/8000 μs) makes black colored surface (left, Figure 2d), which corresponds to a Cu$_2$O phase, while an increased energy (1800 kW/9000 μs) produces greater reduction of Cu$_2$O to a Cu phase. Optimum condition appears with the power and time of 2000 kW and 12000 μs that yields a pure Cu phase with a bright appearance (middle, Figure 2d). The microstructure, shown in the SEM image, clearly show dramatically increased necking of conductive Cu patterns and captures a distinct grain boundary with sufficient density. A higher power and time of 2400 kW at 12000 μs than the optimal case makes surface damage and burning (right, Figure 2d) because of excessive photonic energy. For verification of deposited materials on the surface with nonoptimal cases, we explored energy-dispersive X-ray spectroscopy (Table S4). The conductive Cu pattern, prepared with low power (1800 kW/12000 μs), shows 90 atomic percentage (at%) of Cu, while the sample sintered with excess energy (2400 kW/12000 μs) has 63.5 at% of elemental carbon (C) with only 8.4 at% of Cu. This result indicates that ash from the damaged PI film during sintering was deposited onto the Cu pattern. Collectively, a set

Figure 2. Electrical, morphological and optical properties of printed Cu traces and Cu ink. (a, b) Characterization of printed Cu, showing sheet resistance (a) and electrical resistivity (b) of IPL sintering with various light powers and duration times (gray 10 < $R_s$, 100 < $\rho$; blue 2 < $R_s$, 10, 30 < $\rho$ < 100; yellow 0.5 < $R_s$, 3 < $\rho$, red $R_s$, 0.5, $\rho$, < 3). (c) XRD data and corresponding pictures of Cu, sintered with different photonic conditions: 1600 kW/8000 μs for (1), 1800 kW/9000 μs for (2), 2000 kW/12000 μs for (3), 2200 kW/11000 μs for (4), and 2400 kW/12000 μs for (5). (d) Sequential SEM images of a Cu film with increased sintering energy from 1600 kW/8000 μs (left) to 2000 kW/12000 μs (middle) and 2400 kW/12000 μs (right). Scale bars: 500 nm. (e) Photographs of Cu complex ion ink undiluted and diluted with methanol. (f) UV-vis spectra of Cu complex ion ink. (black = Cu ink, red = 2%, blue = 1%, 0.5%, green = 0.1% dilution) (g) The wavelength spectrum of IPL equipment.
of material processing tests optimized the IPL sintering method; with 2000 kW and 12000 μs for power and exposure time, we achieved the best electrical resistivity of $2.3 \times 10^{-6}$ Ω·cm (even 1.33 times higher than bulk copper; $1.72 \times 10^{-6}$ Ω·cm). Table 1 compares measured electrical resistivity from various types of conductive Cu patterns with optimized processing conditions.\textsuperscript{24,30} To reveal the main reason for the lowest resistivity, we further examined the Cu ink via UV−vis spectroscopy. As shown in Figure 2e, Cu complex ion inks were diluted in methanol and the absorbance of light was investigated in the UV−visible region (400−800 nm; Figure 2f). Cu ink with a dark blue color was composed of formate and acetate ligand, explained by Jahn−Teller distortion.\textsuperscript{39−41} It was found that the absorbance wavelength between the Cu ink (Figure 2f) and IPL light (Figure 2g) matched. Therefore, the Cu ink could fully use the light energy for sintering, which made the sintered Cu patterns have the lowest resistivity. Even though, types of Cu sources and sintering methods decided the electrical resistivity, our study showed that the optimized IPL sintering methodology could offer the ideal condition for an ultrahigh conductivity. Figure 3 demonstrates another important property of the adhesion strength between metal traces and polymer film substrate. We characterized the quality of adhesion of printed Cu via a tape test and a bending-induced peeling test by following the guidelines of ASTM D3359.\textsuperscript{42} The focus of this study lies on the advantage of surface modification through nanostructured SAM treatment on a PI film. Figure 3a shows the result from a tape test that quantifies the adhesion grade based on the remaining area after tape peeling of printed Cu on a substrate. The nanostructured SAM treatment enhances the adhesion grade up to 4B from 3B of untreated surface (scale = 0 lowest−5B highest). SAM functionalization provided a highly dense surface structure, while the untreated sample had many voids in a porous structure (Figure S4). Bending-induced 180° peeling test in Figure 3b captures the outstanding adhesion property with the SAM modification. According to the ASTM, adhesive strength is classified as five levels: excellent removable (<40 N·m\textsuperscript{−1}), removable (80−160 N·m\textsuperscript{−1}), semiremovable (240−320 N·m\textsuperscript{−1}), permanent (400−560 N·m\textsuperscript{−1}), and excellent permanent (>560 N·m\textsuperscript{−1}).\textsuperscript{43} Without SAM treatment, the measured sample shows a peel strength of 422.58 N·m\textsuperscript{−1}, which is significantly enhanced up to 1192.27 N·m\textsuperscript{−1} with SAM treatment (Figure 3b; details in Experimental Section). The main reason for the improved adhesion comes from chemical bonds created through MPTS-based SAM treatment. In addition, a bending test evaluates the mechanical stability of a printed Cu with cyclic bending (Figure 3c). A mechanical bending tester controls radius of curvature (10, 12.5, and 15 mm) and number of cycles (details in Figure S5a−c). The result in Figure 3c shows that a sample with nanostructured SAM treatment has negligible change in electrical resistance, even with 100 000 bending cycles (initial

### Table 1. Comparison of Electrical Resistivity from Various Cu Patterns

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Figure 3. Mechanical characteristic and oxidation stability of printed Cu traces. (a) Remaining area (%) after the tape test, showing better adhesion with SAM treatment. (b) Peel strength (N/m) of Cu patterns on PI without (black) and with SAM treatment (red). (c) Change of electrical resistance of Cu upon cyclic bending (different bending radii) without (blue) and with SAM treatment (black, red, and green). (d) XPS scans of printed Cu, showing the different binding energy, caused by nanostructured SAM treatment. (e) Oxidation stability of printed Cu, measured by resistivity change (%) according to time (up to 15 days).
resistance = 2.35 $\Omega$ and final resistance = 2.37 $\Omega$. On the other hand, untreated sample shows gradual increase of the resistance from 2.55 to 10.75 $\Omega$ with cyclic bending, which is caused by microcracks on the Cu pattern (SEM images in Figure S5d–e). Table 2 summarizes the studied materials and mechanical characteristics of the SAM treated Cu film, along with reported values from prior works. Overall, the flexible Cu film, prepared by surface engineering, has superior properties to other works, which shows a great potential of the advanced material for building various types of flexible hybrid electronics.

Subsequently, we explored the advantage of the surface treatment technology in the reduction of Cu oxidation. Before SAM treatment, the O 1s spectra (Figure 3d) of a printed Cu has peaks at 530.3 eV (metallic oxide, Cu–O), 531.8 eV (–C=O), and 533.5 eV (H2O), indicating the presence of native oxide on the surface. Interestingly, nanostructured SAM treatment removes the metallic oxide (“blue” curve in Figure 3d) with remained peaks of Si(OMe)3 and C–O–C at 532.8 and 534.1 eV. This result suggests that the thiol (or mercapto) functional group eliminates the Cu oxide layer based on the reaction for CuO or Cu2O reduction by MPTS.
2HSC₃H₂Si(OCH₃)₃ + 2CuO
→ Cu₂O + RS − SR + H₂O  \hspace{1cm} (1)

2HSC₃H₂Si(OCH₃)₃ + Cu₂O
→ 2Cu(SC₃H₅Si(OCH₃)₃) + H₂O  \hspace{1cm} (2)

where R corresponds to C₆H₅Si(OCH₃)₃, CuO is gradually reduced to Cu₂O (eq 1) and Cu−S (eq 2).

To validate the reaction, we measured oxidation stability of Cu patterns at ambient temperature and humidity and monitored the change of electrical resistivity up to 15 days (Figure 3e). As clearly shown in the graph, the SAM treated sample shows negligible change in resistivity for 15 days, while untreated Cu has a dramatic increase (~58%) of resistivity after 7 days (details of the resistance values in Table S5). Collectively, this result suggests that the nanostructured SAM layer, especially trimethoxysilane function groups, protects the printed Cu film against oxidation under ambient conditions.

Figure 4 summarizes high-fidelity biopotential recording via a set of inkjet-printed, Cu electrodes on a thin, soft elastomeric membrane. The schematic illustration in Figure 4a shows a multilayered electrode (details of the fabrication process appear in Figure S6). The flexible and ultrathin structure (total thickness is ~10 μm) ensures adequate skin contact of an electrode to collect reliable biopotential signals, which is quantitatively proved by the measurement of skin-electrode impedance. It should be noted that the top PI/Cu side makes the contact with the skin where Cu electrode detects the biopotentials while top PI only shields the interconnects. The bottom PI layer was used to promote the adhesion between the Cu and soft membrane. The printed Cu electrodes allow noninvasive, biopotential recording of EMG, ECG, and EOG on the forearm (Figure 4b), the chest (Figure 4c), and around the eye (Figure 4d), respectively. A recording of biopotentials from the conventional gel electrodes, placed adjacent to the printed ones, compares the Cu electrode performance simultaneously. Overall, the measured quality of biopotentials from the flexible electrodes and conventional sensors agree qualitatively well, supported by a similar level of the contact impedance (Figure 4e−g). The measured impedance values for EMG, ECG, and EOG recording are 50.1, 55.2, and 23.4 kΩ for Cu electrodes and 32.5, 32.2, and 8.8 kΩ for gel electrodes. The impedance values with Cu electrodes are low enough to acquire high-quality biopotentials, comparable to the gel electrodes (Figure 4e−g). The discrepancy of impedance levels is caused by small gaps between the Cu electrode and skin, which will be addressed as a future work by designing the electrode in an open-mesh configuration.

EMG signals in Figure 4e clearly distinguish different gestures of a hand, while ECG graphs in Figure 4f capture the most important biometrics of PQRSST waves (marked in the graph) with only single set of electrodes. Three separate electrodes (“G” for recording, “T” for reference, and “tower symbol” as ground in Figure 4d) measure distinctive EOG signals from two eye movements (“up” and “down” in Figure 4g).

Experimental Section

Materials. A copper plate (2.5 cm × 5 cm × 0.1 cm, 99.9%) and (3-mercaptopropyl)trimethoxysilane (MPTS, HS(CH₂)₃Si(OCH₃)₃, 95%) were purchased from Sigma-Aldrich. Formic acid (HCOOH, 99.5%) was obtained from Junssei Chemical. Ammonia−water (NH₃·H₂O, 25−28%), acetic acid (CH₃COOH, > 99%), and ethanol (EtOH, 95%) were purchased from Dae-Jung Chemical. All of the reagents were used as received without further purification.

Surface Modification of a PI Film. Before nanostructured SAM treatment of a PI film, oxygen plasma (ICP-PIE, Standard Asher RIE System, SNTEK) treatment was performed to form hydroxyl functional groups for combining with the trimethoxysilane of MPTS. Afterward, the plasma-treated PI film was immersed in a 50 mM solution of MPTS and deionized (DI) water for 30 min at a controlled temperature of 30 °C. The PI film was then sonicated in ethanol for removal of residual MPTS solution and dried in a stream of nitrogen gas.

Preparation of Cu Complex Ion Ink, Inkjet Printing, and IPL Sintering. Preparation of the Cu complex ion ink and an inkjet printer setup were conducted using the process we reported in our previous research. For generation of the Cu complex ion ink, a direct voltage of 40 V was applied between Cu plate electrodes in an electrolyte solution consisting of formic acid, acetic acid, and ammonia−water, as shown in Figure S7. The resulting complexing solution was concentrated to achieve a Cu ion content of 15 wt %. Inkjet printing was conducted with a piezoelectric inkjet Dimatix (DMP 2800, Fujifilm). The inkjet printer used the nozzles of 10-pl (DNC-11610) cartridges and ran at an operating frequency of 60 kHz and a firing voltage of 16 V. The inkjet-printed patterns were sintered with IPL equipment (IPL-45 kW, 2100, PSTEK Co.) equipped with a xenon lamp (Heraeus). In order to optimize the IPL conditions with our Cu complex ink, the irradiation power and on-time were varied as shown in Figure 2a and b.

Surface Modification of Cu Conductive Pattern. To deposit the oxidation protective layer on the Cu surface, the sintered Cu conductive patterns were immersed in a SAM solution (50 mM) of MPTS in ethanol. The nanostructured SAM treatment was performed at a constant temperature of 30 °C for 10, 30, 60, 90, and 120 min. Then, the samples were cleaned with ethanol and dried in a stream of nitrogen gas.

Material Characterization. PI films, modified by oxygen plasma and SAM treatment, were characterized by water contact angle analysis (SmartDrop, SDLab-200TEZD, FEMTOFAB Co.) and X-ray photoelectron spectromicroscopy (XPS; Kratos Analytical Ltd.). UV−visible spectrophotometry (UV−vis, UV-2600, JEOL) was used to confirm light absorption of the Cu complex ion ink. The crystallinity and morphology of the sintered Cu conductive patterns were observed with an X-ray diffractometer (XRD; Ultima IV CuKα, Rigaku), field-emission scanning electron microscope (FE-SEM; S-4800, Hitachi), and scanning electron microscope (SEM) equipped with a focused ion beam (FIB; LYRAI, Tescan). In addition, the sheet resistance of Cu conductive patterns was measured by a four-point probe (CMT-82000N, AIT), and the resistivity was calculated from the measured sheet resistance and thickness of the pattern. Adhesion between the PI film and Cu conductive patterns was evaluated by scratch and cross-cut tape tests of the American Society for Testing

Conclusion

Collectively, this work summarizes that the combination of IPL sintering technique and surface engineering significantly improves key material properties of the printed Cu on a PI film. We demonstrate that Cu ink with high light absorption is suitable for IPL sintering, which results in a superior electrical resistivity (2.3 × 10⁻⁶ Ω cm), the best value up to date. The surface modification with nanostructured SAM treatment enhances the interfacial adhesion strength (level = 4B and peel = 1192.27 N/m from ASTM D3359), mechanical stability (negligible resistance change with 100 000 bending cycles), and oxidation prevention of a printed Cu over 15 days. Examples of flexible hybrid electronics, demonstrated as skin-mounted electrodes, show potentials of the new class of metal printing, processing, and manufacturing technologies for a reliable biopotential sensor in human health monitoring and human−machine interfaces.
and Materials (ASTM D3359). In addition, for measurement of precise adhesive strength, a 180° peel tester (MCT-2150, AND Korea) was used. The specimen of the peel test was prepared as follows. Rectangular patterns of 30 mm × 5 mm were fixed on a slide glass with Epoxy 3 M DP420, and then the samples were cured at 80 °C for 2 h. The slide glass and PI films were attached on the bottom stage and the grip of a load cell, and the samples were pulled at a speed of 10 mm-min⁻¹. The measurement was repeated three times. A bending property was performed using the homemade IPC sliding tester for investigating the mechanical properties of printed Cu conductive patterns. The samples prepared with the size of 20 mm wide and 150 mm long (Figure S5a) were loaded into the bending system consisting of lower and upper plates. The upper plate is fixed, and the lower plate moves forward and backward with stroke of 180 cycles/min. The resistance change of samples is measured during the bending test of 100,000 cycles.

Fabrication of Skin-Wearable Electrodes. A glass was cleaned with acetone, IPA, and DI water, and dehydrated on a hot plate at 150 °C for 30 s. After oxygen plasma treatment at 50 W for 60 s, a mixture of polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning) and curing agent (PDMS/curing agent = 4:1) was spin-coated on the glass at 3000 rpm for 30 s. The sample was then baked on a hot plate at 150 and 250 °C for 5 min and spin-coated PI (PI-2545, HD MicroSystems) at 2000 rpm for 1 min. Prebaking and hard baking were performed at 200 °C for 3 min and 5 min, respectively. A set of nanostructured SAM treatment, the inkjet printing, and photonic sintering were conducted on the prepared glass, and PI layer by dry etching (RIE at 150 W for 20 min) was removed. The copper electrodes were connected with an anisotropic conductive cable (ACF, Elform) and picked up with water-soluble tape (3M). After the device transfer from the water-soluble tape to an elastomeric membrane (Ecoflex 00–30), the electrodes were washed away water-soluble tape. Lastly, the sensor was connected and measured with a data acquisition system (BioRadio; Great Lakes Neurotechnologies) at a sampling rate of 1 kHz. Signals of the EMG and the ECG were processed and filtered using Matlab software (high-pass filter with a cutoff of 1 and 30 Hz). For human study, two volunteers (males, ages 22 and 30) were recruited by following the approved protocol (H17212) at Georgia Institute of Technology.

Author Contributions

Notes
The authors declare no competing financial interest.

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