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Supporting Information

Abrasion Tolerant, Non-Stretchable and Super-Water-Repellent Conductive & Ultrasensitive Pattern for Identifying Slow, Fast, Weak and Strong Human Motions at Diverse Conditions

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Experimental Section

Materials

Dipentaerythritol pentaacrylate (5Acl, MW ~524.21 g mol⁻¹), (3-aminopropyl)trimethoxysilane (APTMS, MW ~179.29 g mol⁻¹) and octadecylamine (ODA) were purchased from Sigma-Aldrich, Bangalore, India. Ethanol was acquired from TEDIA, USA. Glass slides and abrasive (grit no. 400) sand paper were bought from Jain Scientific Glass Works and Million International, India respectively. Adhesive tape (Johnson tape Ltd. India), Fountain Pen (Legend Executive Fountain Pen) and filter paper (Whatman 42) was supplied by local sources. Hydrochloric acid (~37%), Hydrazine Hydrate (~80%) and ammonia solution (~25%) were purchased from Merck Life Science Pvt. Ltd., Mumbai, India. Graphite fine powder and Methylene Blue dye were acquired from LOBA Chemie, Mumbai, India. MgCl₂, MgSO₄, NaCl, and CaCl₂, all of these salts were bought from Emplura, Mumbai, India.

General Considerations

KRUSS Drop Shape analyser-DSA25 instrument was used to measure all of the water contact angles, which actually contained an auto systematic liquid dispenser. Scanning Electron Microscopy images were obtained by using a Carl Zeiss Field Emission Scanning Electron Microscope (FESEM), prior to imaging a gold sputtered thin layer was prepared on all the samples. PerkinElmer UATR instrument was used to record ATR-FTIR spectrum of all the samples at ambient conditions. The digital images of the samples were taken by using Nikon Coolpix b700 digital camera. Thickness of the material was measured by using stylus surface profilometer (Veeco-Dektak 150). Amino-Graphene Oxide (AGO) Synthesis: A reported procedure was followed to prepare aminographene oxide (AGO),¹ where two consecutive reactions (nitration and reduction) were adopted to synthesize AGO from the freshly prepared GO sheets. In nitration step, 50 mg of air dried GO powder was dispersed in 50% nitric acid (100 mL), and the whole reaction mixture was kept under stirring for 12 hours at ambient condition. After completion of the reaction, obtained product was filtered to be separated and washed thoroughly with acetone followed by vacuum drying. Next, the freshly prepared nitro graphene oxide was dispersed in 50:50 ethanol–water mixture with a concentration of 0.1 mg/mL. Thereafter, adequate amount of ammonium hydroxide (150 μ L) and hydrazine hydrate (50 μ L) were added into the reaction mixture under continuous agitation—such that the reaction temperature maintained at 70 °C.

Preparation of Chemically Reactive Conductive Ink: A reaction mixture was prepared where 1 ml of 5-Acl (concentration of 132.5 mg/ml), 100 mg of AGO and 100 μ L of APTMS were mixed and sonicated for 20 minutes at ambient condition before applying to the selected substrates. The reaction mixture was remained chemically reactive due to presence of residual acrylate groups. The deposition of the chemically reactive interface provided conductive interface with resistance of 3.2 K Ω . The amount of AGO controlled the resistance of the deposited ink.

Fabrication of Superhydrophobic and Conductive Interface: Firstly, a chemically reactive polymeric coating that loaded with residual acrylate groups was developed on a selected paper (filter paper, A4 Paper, tracing paper) following a previous reported procedure,² where the selected papers were individually dip coated in a reaction mixture of 5-Acl/BPEI. Thereafter, the chemically reactive ink was spatially selectively deposited on the chemically reactive paper to develop various pattern interfaces (see Figure S9) following different printing approaches, such as stamp printing, screen printing etc. Then, the chemically reactive ink deposited interface was thoroughly washed with ethanol and air-dried prior to treat with Octadecylamine (ODA) for overnight. The post-chemical modification with ODA allowed to achieve desired water repellency.

Physical Durability of the Superhydrophobic and Conductive Interfaces

The tolerance of the prepared superhydrophobic and conductive pattern interface under various practically relevant challenging environments was examined by adopting widely accepted and standard physical abrasion tests—including adhesive tape peeling test, random scratch test and sand paper abrasion test etc.

Adhesive tape test: First, a freshly exposed adhesive tape $(3 \times 1 \text{ cm})$ was applied on the superhydrophobic and conductive interface $(3 \times 1 \text{ cm})$ with an external load of 100g to facilitate a uniform contact. Thereafter, the adhesive tape was removed from the superhydrophobic and conductive interface. Both the water-wettability and electrical property of the treated interface were examined in details. All of these properties were observed to be intact even after 25 cycles of such abrasions.

Sand paper abrasion test: An abrasive sand paper $(3 \times 1 \text{ cm})$ was brought in the contact of the superhydrophobic and conductive interface under an external load of 100 g. Next, the abrasive sand paper was manually rubbed with back-and-forth motion (speed of 7 cm/s) for 25 times. During this abrasion, the underlying interior of the material was exposed in air and the top portion was randomly abraded. Thereafter, the water wettability and electrical properties were investigated for the sand paper treated interface.

Scratch test: The superhydrophobic and conductive interface was arbitrarily scratched multiple times by using a sharp-edged knife and then the water-repellent property and conductivity of the interface was examined.

Characterization of Electrical properties

The DC characterization of the synthesized superhydrophobic and conductive pattern interface (denoted as strain sensor) was conducted through the Keithley 4200 SCS pulse parametric analyzer. The prepared strain sensor was studied with 10um Tungsten probes of the Precise's Everbeing BD-6 probe station (generally recognized as Device Under Test, DUT). The connections between the probe station and the pulse parametric analyzer were established through tri-axial cables to obtain low noise and low leakage during the measurements. Moreover, each measurement was done with 4200 SCS (semiconductor characterization system) card combined with a remote preamplifier unit of the analyzer, which on combination have extremely low current measuring capability (~1fA). Different human motions and expressions were monitored in air and under water exposures by employing a tri-axial cable with crocodile clips at the DUT end.

DATA Acquisition system

The data acquisition system comprises of the following three parts:

Arduino Nano Board: The Arduino Nano board (version 3) which has an AVR architecture ATMEGA 328 microcontroller clocking at 16 MHz with an operating voltage of 5 Volts was employed for acquiring the data from the synthesized strain sensor. This board is compact (18 x 45 mm) and light weight (approximately 7 grams) which makes it suitable for wearable applications. The superhydrophobic and conductive pattern interface was integrated in a simple voltage divider circuit with a tunable resistor (to tune and accommodate different patterned sensor strip with different inherent or base resistances). The output of this voltage divider was proportional to the change in the resistance of the strain sensor on bending the pattern interface. This output voltage read through one of the ADC (analog to digital converter) pins of the Arduino Nano and mapped to the corresponding resistance. These values were further supplied to the transceiver (Tx/Rx) pins. Moreover, LCD display allowed to display this data.

Bluetooth Module (HC 05): The data acquisition system was interfaced with the Bluetooth module HC-05 to transmit the data from strain sensor to the receiver, i.e. an android mobile phone. This module was again compact (26.9mm x 13mm x 2.2 mm) and light weight to assure wearable aspects. The module requires 5 Volt DC supply. It utilized Bluetooth V2.0+EDR which operated at 2.4 GHz ISM band and has improved data rate of 2Mbps. The obtained values from the transceiver (Tx/Rx) pins of the Arduino microcontroller were transmitted with a baud rate of 9600 over 2.4 GHz ISM bandwidth. The emission power of the module was below 4dBm which

provided a working range of 10 meters between the receiver and transmitter with either Android Mobile or Laptop with Bluetooth connectivity.

A display device (Smart Phone/ Laptop): Any android mobile or laptop with Bluetooth connectivity can be used to receive the transmitted data over the Bluetooth bandwidth through the proper pairing of the Bluetooth modules and setting up the baud rate of 9600. In our demonstration, an android mobile phone was used to obtain the data through serial data display programs or apps.

References:

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Materials	Method	Wettability	Response time	Recovery time	Gauge factor	References
					(GF)	
SWCNT film strain sensor	Water-assisted chemical		14 ms	~5000 ms.	0.82 at	Nature Nanotech, 2011, 6 , 296
	vapour deposition				~40% strain	
Pt-coated polymeric nanofibres	Ultraviolet exposure and		< 50 ms		8.53	Nature Mater, 2012, 11 , 795
supported on thin PDMS layers	interlocking				(<5%)	
Graphene woven fabrics (GWFs)	CVD method				≈10 ³ under 2–6% strains	Adv. Funct. Mater., 2014, 24 , 4666
MASK/PDMS/CNT	Solution based self- pinning method				161 (ε < 2%)	Adv. Mater., 2015, 27 , 6230
FGF/PDMS	CVD grown method, fragmentation and drop casting				21 at less than 1% strain	Adv. Funct. Mater. 2015, 25 , 4228
Low-density microcracked graphite thin films/ Ecoflex elastomer films/ (high-density graphite thin films/ Ecoflex elastomer and dental polymer	Air spray, peeling-off and flipping, plasma exposure followed by bar coating				82.8 below 50 % tensile strain	ACS Appl. Mater. Interfaces 2016, 8, 5618.
Reduced graphene oxide	Stretching/releasing				150 at 82% strain	ACS Nano, 2016, 10 , 7901
Channel cracks-based gold	Electron-beam evaporation				5000 at a strain of 0.7- 1%.	Mater. Horiz., 2016, 3, 248
Graphene woven fabric or,	Template-based CVD		~72 ms		223 at a	Mater. Horiz.,2017, 4 , 477
GWF/PDMS composites	method and Spin coating				strain of 3%	
Fragmented and carbonized melamine sponges (FCMS)	Carbonization and fagmentation		240 ms		18.7	Nanoscale, 2017, 9 , 17948
Au microwire network/PDMS matrix	solution-processed crackle templating method		30 ms		180 below 2% tensile strain	ACS Appl. Mater. Interfaces 2018, 10, 44126.
Ti3C2Tx MXene/carbon nanotube (CNT)	Layer-by layer (LBL)				4.4-772.6 sensing	ACS Nano, 2018, 12 , 56
composites	op. ay coanny conniquor				range of 30-130%	
Laser scribed graphene (LSG) with cracks	Laser scribe with water lift-off				673 at 10% strain	ACS Nano, 2018, 12 , 8839
GO–AgNW–C ₆₀	Screen-printing and drying				25 at 0–3%;	<i>Adv. Funct. Mater.</i> , 2018, 28 , 1800850

Ag nanoparticles/ Polyurethane- based stretchable fibers	Absorption and Reduction				182 below 50 % tensile strain	ACS Nano 2018, 12 , 4259.
Ti3C2Tx/graphene/PDMS	Vacuum filtration and polymerization		130 ms		190.8in strain ranges of 0–52.6%	Nano Energy, 2019, 66 ,104134
Micro-/nano-voids guided two- stage film	Hierarchical assembly of interfacial nanowires				107.45 (10%)	Nat Commun, 2019, 10 , 3862
Crumpled & cracked RGO	Balloon-assisted mechanically driven process				205 in the strain range of 0–130% tensile strain	ACS Appl. Mater. Interfaces 2019, 11, 18645.
Hf-SiO2/CB/CNT paper	Dip coating	WCA= 154°			7.5 (0.7%)	ACS Appl. Mater. Interfaces, 2019, 11 , 21904
SiC-based array	Laser Direct Writing		200 ms		854.7 (below 3.5 %)	Adv. Funct. Mater. 2019, 29 , 1806786
MXene/PANIF	Layer-by-layer spreading coating		0.6s sunder a tiny strain of 1%	800 ms	97.6 within 10% strain	Nano Energy, 2020, 78 , 105187
PAM/gelatin/PEDOT: PSS (MGP) CHs	Radical polymerization		200 ms		1.58	Nano Energy, 2020, 7 6, 105035
Poly(acrylamide) (PAAm) hydrogel	Under UV light		150 ms	400 ms	1.94 at 100% strain	Nano Energy, 2020, 76 , 105064
TPU/BNNSs/ GNRs	Vacuum filtration				35.7	Nat Commun, 2020, 11 , 3530
Platinum (Pt)/superaligned carbon nanotube (SACNT) hybrid conducting films	Dry spinning and metal sputtering techniques		~257.7 ms		~12 274 at 50% strain	Mater. Horiz., 2020, 7, 2662
F/Ag/MWCNT/G-PDMS	Spray coating	WCA= 157°	150 ms		1989 (170%)	Adv. Funct. Mater., 2020, 30 , 2000398
PDMS/rGO gradient wrinkle film	Pre-stretching, ion- sputtering followed by curing	WCA>154°	90 ms		19.24 (8%)	<i>J. Mater. Chem. A</i> , 2021, 9 , 9634
nWPU-rGO/ CNTs (6:4)	Solution processing (Drop cating, Drying, peel off)		50 ms		7.2 at 60% Strain	Adv. Funct. Mater., 2021, 31 , 2007495
HMDS/SiO2/MWCNT paper	Spray coating	WCA= 164°	78 ms		263.34 (0.098%)	ACS Appl. Mater. Interfaces, 2021, 13 , 1967
Chemically Reactive ink	Printable chemically reactive conductive ink	WCA = 155.6°	8 ms	21 ms	18,300 (0.2% strain)	Our work

Table S1. Comparing the performance of the recently reported strain sensor with the currentlyprepared pattern interface in terms of response time, recovery time and Gauge factor.



Fig.S1 (A-F) Digital images depicting the impact of simple finger wiping test on different conductive coatings—that were derived from AGO (A-B), reaction mixture 1 (5-Acl and AGO; B-C) and reaction mixture 2 (5-Acl, APTMS and AGO; E-F). Only, the coating that prepared from reaction mixture 2 remained efficient to survive the finger wiping test. (G) The bar graph accounting the change in resistance of the above mentioned conductive coatings before and after incurring the finger wiping test.



Fig.S2 FTIR spectra of APTMS in solution (black) and after depositing (red, air-dried) on selected substrate. The characteristic IR peaks for Si-O-Si and Si-O-C appeared at 1028 cm⁻¹ at 1076 cm¹. After air-drying, an intense IR peak for Si-O-Si at 1028 cm⁻¹ revealed the self-polymerization of APTMS on air-drying.



Fig.S3 The plot accounting the impact of change in the concentration of used AGO in the reaction mixture-2 on lowering the resistance of the deposited ink.



Fig.S4 (A-F) Digital images and static contact angle images of the beaded water droplets on the deposited chemically reactive ink on both bare paper (A-D) and chemically reactive coated paper (E-H), before (A,C; E,G) and after (B,D; F,H) the post covalent modification with ODA.



Fig.S5 FTIR data demonstrating the successful post-chemical modification of the deposited chemically reactive conductive ink with ODA, where the characteristic acrylate peak at 1408 cm⁻¹ was significantly depleted after the post modification with ODA.



Physical Abrasions

Fig.S6 (A-B, D-E, G-H) Digital images showing the change electrical resistance of the superhydrophobic and conductive interface before and after performing physical abrasions

including adhesive tape tests (A-B); scratch tests (D-E); and sand paper abrasions test (G-H) respectively. C,F,I) Water contact angle images illustrated the existence of superhydrophobicity after exposing the prepared superhydrophobic and conductive interface to different physical abrasions including adhesive tape tests (C); scratch tests (F); and sand paper abrasions test (I) respectively.



Fig.S7 The bar plot comparing the change in the resistance of deposited chemically reactive ink with (red bars) and without (black bars) ODA modification after exposing to air, DI water, artificial sweat, pH~1 and pH~11.



Figure S8. A-B) Illustrating the impact of changes in the temperature (°C; A) and relative humidity (RH%; B) on the resistance of the conductive interface.



Figure S9. Accounting the changes in the number of cracks (per mm²) and their width on the conductive and superhydrophobic interfaces with increasing the bending angle.



Figure S10. Demonstrating the successful deposition of superhydrophobic and conductive coating on various flexible interfaces—including PDMS film, plastic film and paper. The change in resistance remained same on incurring bending of 60°. The water contact angle (WCA) of beaded droplet on the coated substrates remained well above 150°.



Fig.S11 (A-B, E-F) Schematic (A,E) and digital images (B,F) illustrating different patterning methods, i.e., stamp printing (A-B) and screen printing (E-F) for developing pattern conductive interfaces. (C, G) External circuit that connected to LED was integrated with the prepared patterns to depict the conductive behaviour. (D, H) Digital images accounting the presence of superhydrophobicity of the pattern interface, where the jet of tap water immediately bounced off from the pattern interface that post modified with ODA.



Fig.S12 Schematic representation of various conductive patterns—including, linear, pattern-1 (P-1), pattern-2 (P-2), pattern-3 (P-3), pattern-4 (P-4) and pattern-5 (P-5); maintaining the end to end distance (ETED) of the deposited ink was gradually changed from 3 cm (linear) to 20.6 cm (P-5). The apparent length of each pattern remained 3 cm.



Figure S13. A) Illustrating the essential parameters that involved in calculation of gauge factor (GF) of the patterned interface., where the thickness of the sensor (i.e. coated tracing paper; h) is $30 \mu m$. B) The change of chord length (C) with radius of curvature (R) for a fixed arc length (L) of 3 cm.



Fig.S14 The plot accounting the response and recovery time of the prepared sensor (P-3) in response on bending the pattern interface at 30° .



Figure S15. Depicting the changes of resistance of the prepared coating with dynamic changes (forwards/backwards) of bending.



Figure S16. Accounting the hysteresis of the change of resistance of the prepared interface on application and releasing of external strain—i.e. bending.



Figure S17. A) The plot accounting the durability of the flexible superhydrophobic and conductive interface (FSCI) after incurring repetitive bending (at 30°) for 15000 cycles, where the changes in resistance were recorded at regular interval. The change in resistance remained unaltered even after 15,000 cycles of bending the FSCI. B) Illustrating the change in resistance at each and every step during the repetitive bending of the same interface for 1000 cycles, and insets displayed some subsets of them.



Fig.S18 (A-B) Graph demonstrates the detection of coughing (A) and uttering of different words (B).



Fig.S19 Forward and reverse bending of neck was successfully monitored using the flexible superhydrophobic and conductive interface (FSCI), the inset image revealed the position of FSCI on the neck of a volunteer. During forward bending a positive change in resistance was noted and a negative change of resistance appeared due to backward bending of the FSCI (sensor). The backward bending makes the interface more conductive.



Figure S20. (A-B) Schematic demonstrating localized deformation of FSCI against the applied pressure (A-B), where the beaded water droplet on the FSCI is responsible for elevating the resistance of the pattern interface. (C) Graph accounting the change in resistance on increasing the volumes of beaded water droplets.