**Outline (Presentation: Graphene electronic tattoos and biosensor applications):**

<https://pubs.acs.org/doi/10.1021/acsnano.7b02182>

* KEYWORDS:
  + PMMA = Poly(Methyl/Methacrylate)
    - PMMA-coated graphene is made by applying PMMA to CVD graphene on a copper substrate and then removing the “reverse-side graphene”.
    - The PMMA coating on top of the graphene serves to ease the transfer process and helps to avoid contamination.
* Long-term wearable biometric sensors with high fidelity have the potential to be applicable outside of hospital and lab settings to allow for very broad modes of use, including mobile health care, fitness tracking, human–machine interactions, and so on. However, existing medical sensors are too restraining, and the technology is expensive to process the multitude of physiological signals. For example, traditional technologies for electrophysiological measurements use thick, flat electrodes, which are taped to the surface of the skin and have terminal connections to stationary data acquisition facilities.
* The emergence of wearable electronics provides the opportunity for continuous and ambulatory monitoring. However, their functionality and signal quality are still limited. In fact, commercially available wearable devices are still in the form of rigid electrode sensors and chips mounted on bands or straps to be worn on the wrist, chest, *etc*. They are capable of activity tracking, heart rate recording, and even bioimpedance measurements, but the data quality is still far from medical grade.
* As skin is microscopically rough, theoretical analysis has clearly predicted that only ultrathin and ultrasoft tattoos can fully conform to natural skin morphology without artificial adhesives.[(13, 14)](javascript:void(0);) Such conformability enlarges the contact area between the dry electrode and skin and hence lowers the contact impedance, which directly leads to a higher signal-to-noise ratio (SNR) in recorded electrophysiological signals and less susceptibility to motion.
* Gold, a biocompatible and nonirritating material, has been the most popular choice for dry electrodes and interconnects in E-tattoos. Its thickness is often in the range of tens to hundreds of nanometers, and it is supported by translucent polyimide of greater thickness for mechanical robustness.[(15)](javascript:void(0);) However, gold is too pricy to be used in disposable E-tattoos. Moreover, such sensors are obviously visible, which makes it unsuitable to wear on parts of the body such as the face.
* In this work, we have developed a stretchable and transparent graphene based electronic tattoo (GET) sensor that is only sub-micrometer thick but demonstrates high electrical and mechanical performance. We demonstrate that a GET can be fabricated through a simple “wet transfer, dry patterning” process directly on tattoo paper, allowing it to be transferred on human skin exactly like a temporary tattoo, except this sensor is transparent. Due to its ultrathinness, a GET can fully conform to the microscopic morphology of human skin *via* just van der Waals interactions and can follow arbitrary skin deformation without mechanical failure or delamination for an extended period of time. Because of the open-mesh design of the filamentary serpentines, the GET is breathable and has negligible mechanical stiffness. It is, therefore, almost imperceptible both mechanically and optically. GET has been used for various physiological measurements including electrocardiogram (ECG), electromyogram (EMG), electroencephalogram (EEG), skin temperature, and skin hydration, each of which has been validated by a corresponding gold standard sensors.
* The “wet transfer, dry patterning” fabrication process is illustrated in [Figure 1](https://pubs.acs.org/doi/10.1021/acsnano.7b02182#fig1). “Wet transfer” refers to the copper etching step, which retains the high continuity of the large-area graphene grown on copper foil. “Dry patterning” refers to the use of a programmable mechanical cutter plotter to carve out the designed filamentary serpentine shapes on the graphene. Compared with photolithography, the dry patterning process minimizes the chemical contamination of graphene and is significantly more time- and cost-effective.

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**Figure 1.** Fabrication process of GET. (A, B) Graphene was grown on copper foil using atmospheric pressure chemical vapor deposition system (APCVD). (C) Less than 500 nm thick PMMA was spin coated on graphene. (D) Copper was etched away. (E) Graphene/PMMA (Gr/PMMA) was transferred onto tattoo paper with PMMA touching the paper and graphene facing up. (F) Gr/PMMA was cut by a mechanical cutter plotter. (G) Extraneous Gr/PMMA was peeled off from the tattoo paper. (H) Mounting GET on skin like a temporary transfer tattoo. (I) GET on skin.

* The serpentine ribbons were designed with a width of 0.9 mm and a radius of 2.7 mm to ensure the GET has a stretchability greater than that of skin.
* The fabricated GET sensor can then be transferred onto any part of the glabrous or less-hairy skin, regardless of its curvature or shape, simply by bringing the graphene side in contact with the skin and wetting the backside of the tattoo paper to detach the GET from the paper ([Figure 1](https://pubs.acs.org/doi/10.1021/acsnano.7b02182#fig1)H), exactly like a temporary transfer tattoo.
* In addition to transparent PMMA, a popular substrate often used in flexible electronics, polyimide (PI), was also applied to support graphene following a procedure similar to Gr/PMMA. As the PI thickness was 13 μm, the Gr/PI sensors cannot stay attached to human skin by just van der Waals interactions. Therefore, the Gr/PI sensors were transferred onto a 3M Tegaderm tape with graphene facing up and then taped onto the skin for measurements.

Stretchability and compliance of freestanding serpentine-shaped ribbons: <https://te7fv6dm8k.search.serialssolutions.com/?url=http://te7fv6dm8k.search.serialssolutions.com?sid=achs&sid=achs&iuid=4417024&date=2014&dbid=16384&volume=51&aulast=Lu&doi=10.1016/j.ijsolstr.2014.07.025&atitle=Stretchability+and+Compliance+of+Freestanding+Serpentine-Shaped+Ribbons&genre=simple&spage=4026&title=Int.+J.+Solids+Struct.&epage=4037&suffix=cit30&aufirst=N.+S.>

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**Figure 2.** Mechanical and optical characterization of the GET. (A) Picture of the as-fabricated GET with a white background, labeled with different sensors including graphene-based electrophysiological sensors (GEPS), a resistance temperature detector (GRTD), and a skin hydration sensor (GSHS). (B) The thickness of PMMA was measured by a profilometer to be 463 ± 30 nm. (C) Optical transparency of bare PMMA and Gr/PMMA. (D) Normalized resistance of the GET *versus* applied tensile strain. The linear GET ribbon ruptures at 20%, whereas the serpentine-shaped GET can be stretched up to 50%. (E) Less than 6% change in GRTD resistance after 1300 cycles of 15% stretching. (F) GET mounted on skin. (G, H) GET on skin compressed and stretched by 25%, respectively. (I) Change in GEPS and GRTD resistance after all kinds of skin-tolerable deformations. (J to L) Magnified photographs of a GET on relaxed, compressed, and stretched skin, which demonstrate its full conformability even under skin deformation.

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**Figure 3.** Electrical performance of the GET on skin. (A) Without any skin preparation, GET–skin contact impedance is almost on par with that between commercial gel electrodes and skin. (B) EEG sensing on the forehead with both the GET and gel electrodes (left). When the eyes were closed, an α rhythm of 10 Hz is visible in both spectrograms. (C) ECG measured synchronously by the GET and gel electrodes. Characteristic ECG peaks can be measured by both electrodes. (D) EMG sensing on the forearm with the GET and gel electrodes when the subject squeezed the hand exerciser three times.

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**Figure 4.** Comparison of motion artifacts in GET and gel electrodes. (A, B) The motion was induced by poking the chest using a glass rod. (C) ECG synchronously recorded by a GET and gel electrodes shows comparable susceptibility to motion.

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**Figure 5.** Demonstration of a GET as a skin hydration and skin temperature sensor. (A) Skin hydration sensing right after the application of body lotion, using both a GSHS and a commercial corneometer. GSHS calibration curves are provided in [Supporting Information](https://pubs.acs.org/doi/suppl/10.1021/acsnano.7b02182/suppl_file/nn7b02182_si_005.pdf) Figure S10. (B) Skin temperature sensing with an ice bag placed in the vicinity of the GRTD and a thermocouple. GRTD calibration curves are provided in [Supporting Information](https://pubs.acs.org/doi/suppl/10.1021/acsnano.7b02182/suppl_file/nn7b02182_si_005.pdf) Figure S11.

**CONCLUSION:**

We invented a sub-micrometer-thick transparent GET that can function as a stretchable and noninvasive electronic tattoo for multimodal biometric sensing. It is manufactured by a low-cost “wet transfer, dry patterning” process on tattoo paper, which can minimize the chemical contamination of the GET. The GET can be directly transferred on human skin from tattoo paper. Although no adhesive is applied, the GET can fully conform to the microscale morphology of skin and follow arbitrary skin deformation without any fracture or delamination for an extended period of time. The GET was used to measure EEG, ECG, EMG, skin hydration level, and skin temperature. As dry electrodes, the GET–skin interface impedance is almost as low as that of Ag/AgCl gel electrodes, which can be attributed to its ultimate conformability. As a result, the GET has achieved comparable SNR with gel electrodes and also demonstrated similar susceptibility to motion. As tattoo-like wearable skin hydration and temperature sensors, the GET has been validated by state of the art gold standards. We believe that the GET has opened a door for two-dimensional materials to be applied in biosensing electronic tattoos, as well as many other applications.