Thinnest Transparent Epidermal Sensor System Based on Graphene

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Abstract**—**We report the first demonstration of a graphene-based epidermal sensor system (GESS) with total thickness below 500 nm. The GESS is manufactured by the cost-effective and rapid "cut-and-paste" method on tattoo paper and can be directly laminated on human skin like a temporary transfer tattoo. Without any tape or adhesive, the GESS completely conforms to the microscopic morphology of human skin via van der Waals interaction. The softness and transparency of the GESS, make it the world's first epidermal sensor system that is invisible both mechanically and optically. The GESS has been successfully applied to measure electrocardiogram (ECG), electroencephalogram (EEG) and electromyogram (EMG) with signal-to-noise ratio comparable with commercial electrodes, in addition to skin temperature and skin hydration. The thin and transparent graphene epidermal sensor can be used for the first time enable simultaneous electrical and optical epidermal sensing.

I. Introduction

Skin mounted noninvasive physiological sensors hold the key to the success of mobile health and human machine interaction. Conventional devices such as Holter ECG monitors and emerging wearable systems such as Myo EMG bands are too bulky and too constrained to perform long term, ambulatory measurements. As a result, a new class of wearable electronics named epidermal electronics have been developed [1]. Epidermal electronics are stretchable electronics whose thickness, stiffness, and mass density are well matched with human epidermis. They can be laminated on human epidermis like a secondary skin for sensing, therapy, and wireless communication. Since skin surface is microscopically rough, conformability to skin morphology can help lower skin-electrode impedance and minimize motion artifacts [2]. To enhance conformability, conductive adhesives are often used, buy may lead to skin irritation. Alternatively, a more effective way is to lower the device thickness [3]. As a result, the thickness of epidermal electronics has dropped from the original 30 μm [1] to ~5-6 μm [2, 4]. In those devices, hundreds of nanometers thick gold membranes are used as the conductive electrodes or interconnects. To push the device thickness to the ultimate limit, we turn to atomically thick conductive material, graphene, which is the thinnest nanomaterial in the world [5]. In addition to ultimate thinness (~0.3 nm), graphene is also optically transparent and mechanically robust [5], which is ideal for the construction of optically invisible and mechanically imperceptible bio-electronics. In fact, transparent graphene electrodes have been developed for micro-electrocorticography (ECoG) [6]. In this work, we have developed a nano-scale thin transparent polymethyl methacrylate (PMMA) substrate (~463 nm) for graphene transfer and support purpose. The graphene-PMMA bilayer is placed on a tattoo paper and patterned into stretchable shapes using a low cost, freeform "cut-and-paste" method [7]. After patterning, the graphene based epidermal sensor system (GESS) can be successfully transferred to human skin from the tattoo paper, just like a temporary transfer tattoo, without any tapes or adhesives. The mass density of GESS is dominated by PMMA (1.18 g/cm^3), which is comparable with that of human skin (1.09 g/cm^3). To demonstrate the functionality, we applied GESS to measure EEG, ECG, EMG, skin temperature and skin hydration.

II. Fabrication

The GESS is designed in serpentine ribbons to be stretchable [8]. Following the design guidelines [9], the width of the ribbons is designed to be 0.9 mm and the radius to be 2.7 mm. Fabrication process flow is shown in **Fig. 1**. Graphene was grown on copper foil using atmospheric pressure chemical vapor deposition (APCVD) at 1030°C by flowing hydrogen at 10 sccm for 15 min (copper surface treatment), methane at 2 sccm for 10 min (for graphene growth) and argon with 300 sccm (to maintain atmospheric pressure) (**Fig. 1a&b**). CVD grown graphene was then coated with transparent PMMA by spin coating at 3000 rpm (**Fig. 1c**). The PMMA was then baked for 2 min at 180℃. Thereafter, copper was etched away using copper etchant (**Fig. 1d**) and graphene/PMMA was transferred on Silhouette tattoo paper with graphene faces up (**Fig. 1e**). Graphene/PMMA is cut into the designed pattern using Silhouette Cameo mechanical cutter plotter (**Fig. 1f**). After peeling of the excessive (**Fig. 1g**), water was applied to the tattoo paper to facilitate the release of GESS such that the GESS can be successfully transferred on human skin (**Fig. 1h&i**) without any adhesives on the interface or tapes on the top. The scanning electron microscopy (SEM) image of graphene on copper foil is shown in **Fig. 2a**, where some ad-layers on monolayer graphene are visible. **Figure 2b** displays the characteristic Raman spectrum at different random spots. 2D and G peaks are clearly visible and the variation of the 2D to

G peak ratios at different spots indicates the variation in the number of layers.

III. RESULTS AND DISCUSSION

An optical micrograph of the GESS is offered in **Fig. 3a**. Three different sensors are integrated on the GESS: electrophysiological sensor (EPS), resistance temperature detector (RTD), and skin hydration sensor (SHS). The transparency of GESS can be well demonstrated when laminating the GESS over University of Texas at Austin longhorn silhouette in **Fig. 3b**. The photo of laminated device on forearm skin is shown in **Fig. 3c**. **Figure 3d** is macroscopic zoom in photo of GESS laminated on human skin. After zooming in under optical microscope, **Figs. 3e&f** show the ultimate conformability of GESS on human skin with just van der Waals interaction as the adhesive force. The deformability of GESS is tested by stretching and compressing the skin as shown in **Figs. 3g** and **3h**. The resistance of the EPS and RTD was measured before and after all skin deformation and **Fig. 3i** confirms that there was almost no change in resistance after all kinds of skin tolerable deformation.

Impedance results are given in **Fig. 4**. GESS-skin interface impedance was measured by connecting the two probes of the LCR meter to the two SHS as labeled in **Fig. 3a**. Due to the ultimate conformability between GESS and skin, GESS-skin interface impedance is found to be very close to that between commercial Ag/AgCl solid gel electrodes and skin. Although gold based epidermal electrodes have also demonstrated interface impedance similar to gel electrodes [2] the gold thickness (200 nm) was orders of magnitude larger than monolayer graphene. The total thickness of GESS is measured by profilometer to be ~463 nm as shown in **Fig. 5**.

The impedance value shows a clear variation with skin hydration. To calibrate the SHS, hydration level of skin was tuned by applying body lotion. As the lotion gets absorbed, skin hydration decayed gradually. During this process, impedance was measured through the SHS and skin hydration was simultaneously measured by a commercial corneometer as shown in **Fig. 6**. It shows that the magnitude of impedance increases with decreasing hydration level and the sensitivity of SHS increases when frequency is lower. Based on the calibration curves in **Fig. 6b**, we can convert future impedance measurements at a given frequency into hydration readings.

The electrophysiological measurement results are presented in **Fig. 7**. Figure 7a compares the ECG signals measured by EPS (red curve) and gel electrodes (black curve) on human chest using AvatarEEG, which is equipped with build in amplifier. A 60 Hz digital notch filter was applied to both data after downloading from AvatarEEG. Characteristic P, Q, R, S and T peaks are captured using both EPS and gel electrodes. The P peak is more pronounced and the U peak is only visible in the ECG recorded by EPS suggesting that the ultimate contact between graphene and skin is desirable for reading small signals. **Figure 7b** shows the EMG signals recorded by placing EPS (red curve) and gel electrodes (black curve) next to each other on forearm muscles while the subject is squeezing handgrip. AvatarEEG was used to record the signal and 60 Hz digital notch filter was applied to both signals. We also recorded EEG signal by placing EPS and gel electrodes on the forehead of human subject. The signal was recorded using one of the EPS electrodes as a recording electrode a shared reference and a shared ground gel electrode placed behind the ear and on forearm, respectively. The electrodes are connected to an amplifier and recorded using brain vision recorder software. Subject was asked to keep eyes open for 1 min and closed for another minute. The signal was filtered using a high pass filter with a cutoff frequency of 0.1 Hz and a 60 Hz notch filter. The Fourier transform function was applied to the recorded signal in real time. The frequency-time plot of the EEG recorded by both EPS and gel electrodes are given in **Fig. 7c**. The two spectra are highly identical and both show the α signal (~10 Hz) during rest (eyes closed). **Figure 8a** shows skin temperature sensing using RTD and thermocouple before and after an ice bag was placed on the forearm in vicinity to both sensors. The RTD was connected to a digital multimeter to measure its change in resistance. It is clear that the resistance of RTD decreased with temperature reduction but the mechanism of graphene RTD remains a topic for further investigation. Finally, the SHS was used to measure real time change in skin hydration after applying body lotion to the skin. The results are shown in **Fig. 8b**. Gradual decay of skin hydration was observed in recorded data using both SHS and corneometer.

IV. CONCLUSIONS

In conclusion we have demonstrated a submicron thick, transparent GESS for electrophysiology, skin temperature and skin hydration sensing. The GESS features unprecedented softness and transparency that it is a truly imperceptible wearable device. This work opens the possibility of building epidermal sensors with atomically-thin materials for maximum opto-electro-mechanical compliance.

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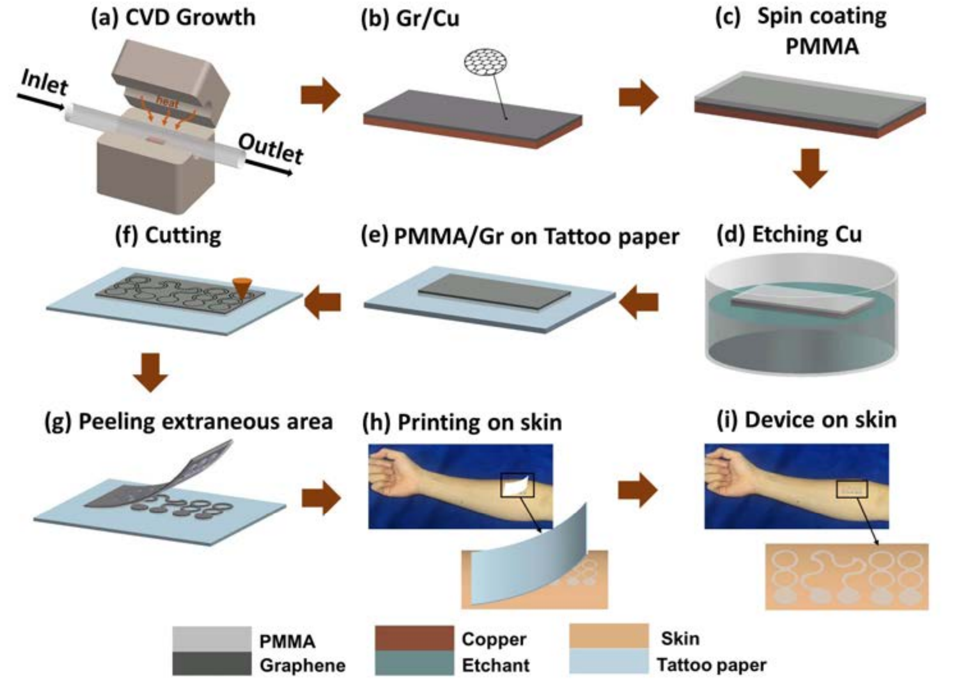

Fig. 1. Fabrication process of graphene electrode; (a) Graphene is grown by APCVD; (b) Graphene grown on copper foil; (c) PMMA is spin-coated; (d) Copper is etched away; (e) Graphene on PMMA is transferred on to tattoo paper; (f) Graphene on PMMA are cut by Silhouette Cameo electronic cutting tool; (g) Extraneous area is peeled off; (h) Illustration of GESS mounted on skin; (i) Illustration of the attached device on skin.

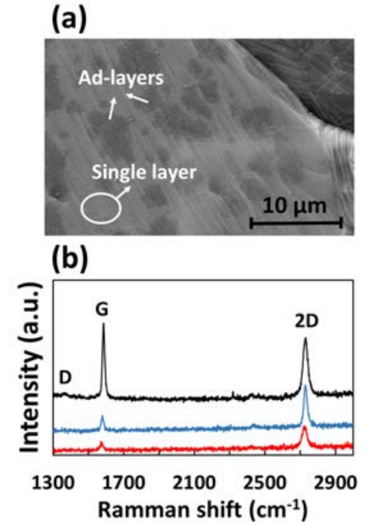

Fig. 2. Scanning electron microscopy images and Raman spectroscopy of graphene grown on copper foil using APCVD; (a) SEM of graphene on copper, darker regions represent ad-layers; (b) Raman spectroscopy of graphene from random spots on a large area graphene shows the existence of G and 2D peak signatures. D peak was observed at some spectrums spots.

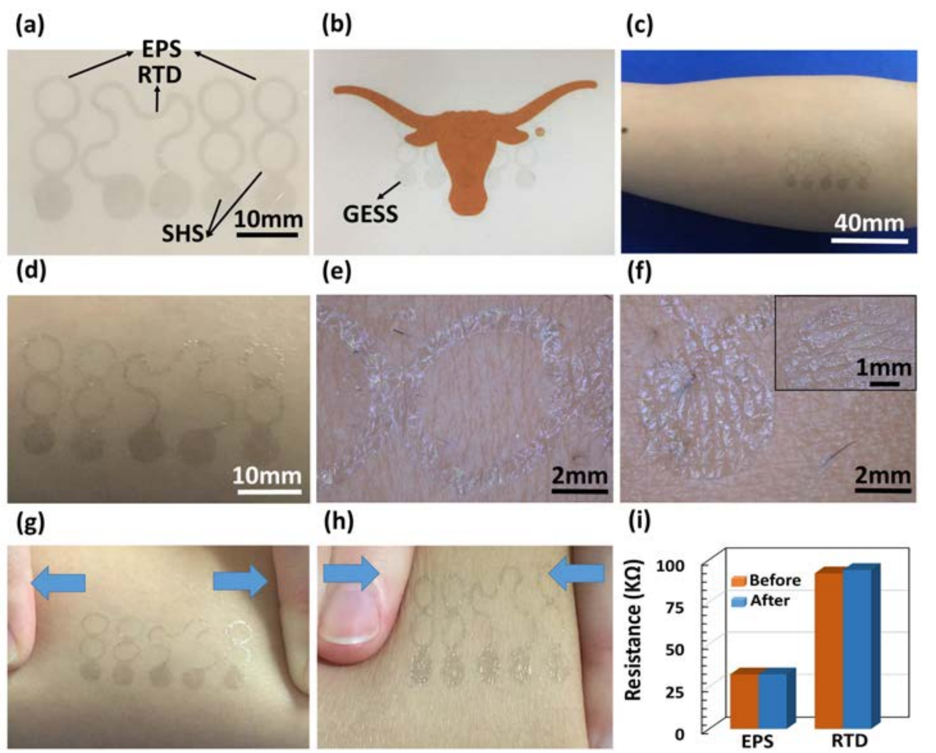

Fig. 3. Graphene-based epidermal electronic sensor (GESS); (a) Fabricated GESS on white background; (b) GESS mounted on tegaderm on top of UT Austin logo showing high transparency. (c) GESS on forearm and (d) close-up view. (e) and (f) Magnified photo of GESS on skin shows intimate conformability to skin; (g) and (h) Tattooed GESS on skin was stretched and compressed; (i) Resistance change of GESS after skin deformation.

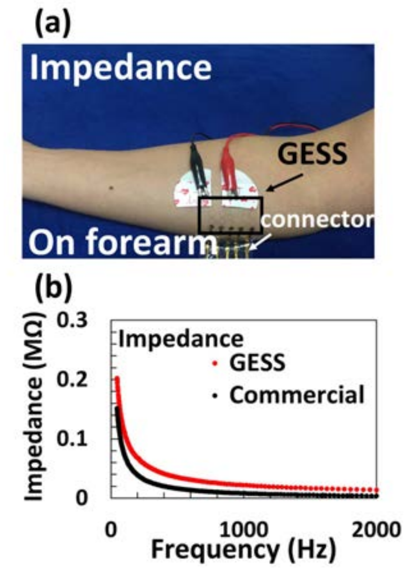

Fig. 4. The comparison of GESS-skin interface impedance with Commercial dry gel electrode-skin interface impedance; (a) Photo of GESS and commercial electrodes mounted on the forearm next to each other; (b) The impedance versus frequency for GEES and commercial dry conductive gel, the gel-skin and GESS-skin interface impedance are comparable.

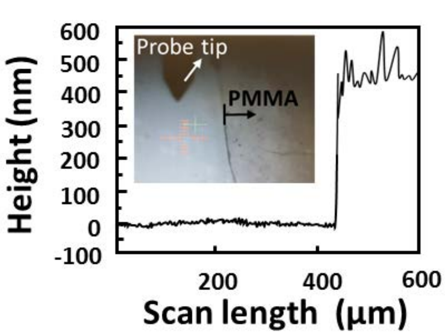

Fig. 5. Thickness measurement of PMMA; The inset shows microscopic image of PMMA with the profilometer probe. The thickness of PMMA was measured to be 463 nm ± 27nm.

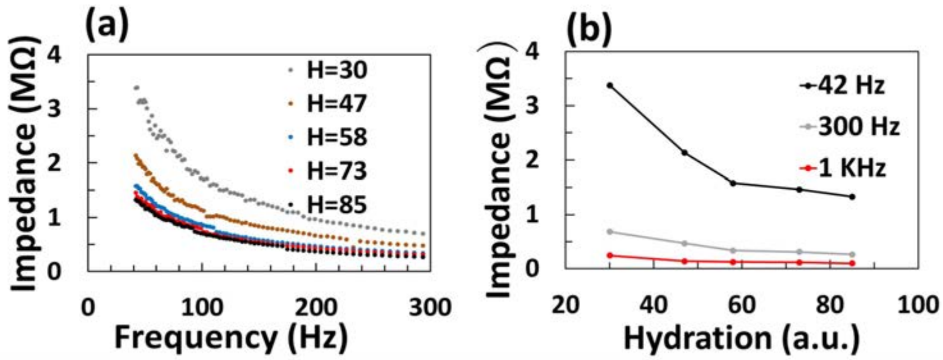

Fig. 6. Skin hydration sensor calibration; (a) Magnitude of impedance was measured at different skin hydration level for different frequencies; (b) Magnitude of impedance was measured versus frequency at different skin hydration level. The impedance of GESS-skin interface decreases with increasing skin hydration and the sensitivity of SHS increases with decreasing frequency.

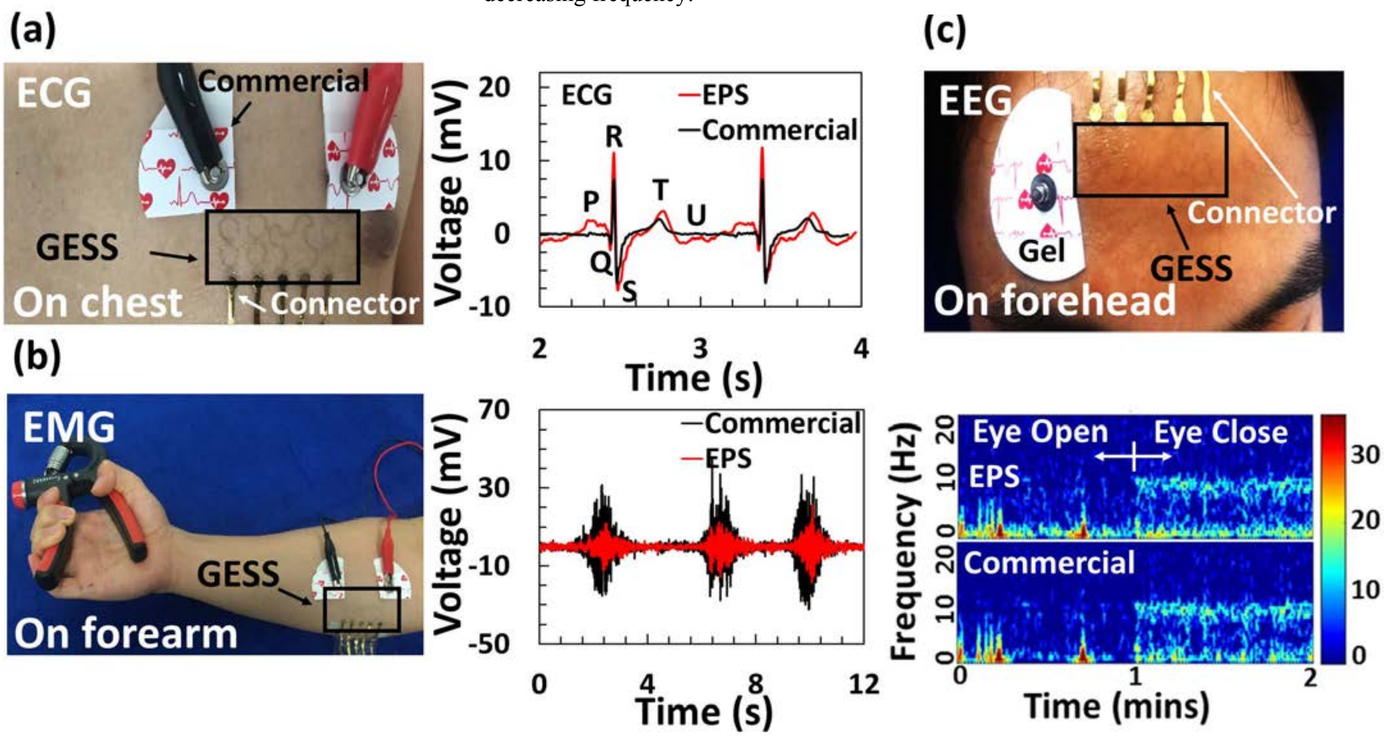

Fig. 7. First demonstration of graphene epidermal sensor for measuring ECG, EMG and EEG. (a) ECG using GESS; commercial electrode (black) and EPS (red). The ECG signal measured with the ultra-thin EPS shows characteristic peaks similar to commercial electrodes, with the advantage of detecting the U peak that is not observed in commercial electrode. (b) EMG sensing on the forearm. The EMG signal captured with both commercial electrode and EPS when the subject squeeze the handgrip; (c) EEG sensing on the forehead when eye is opened and closed; The α signal at 10 Hz was recorded using both EPS and commercial electrode.

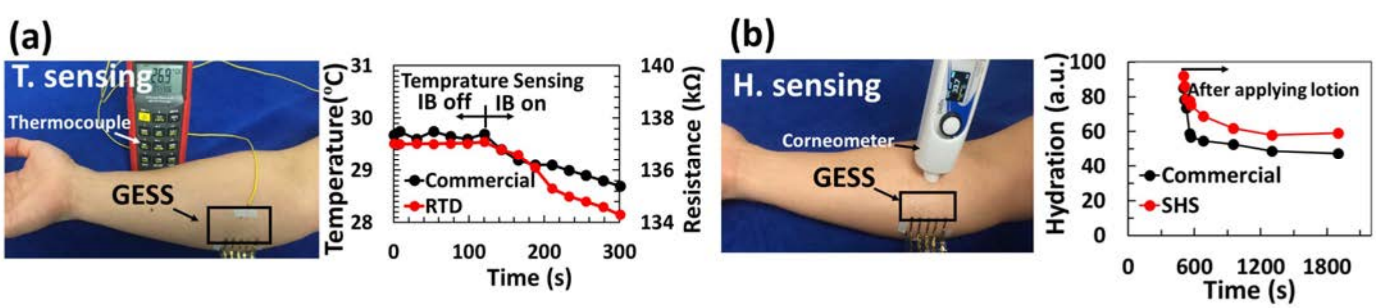

Fig. 8. Graphene epidermal sensor for skin temperature and hydration measurement. (a) Temperature sensing on the forearm, skin temperature was tuned by placing ice bag (IB) in vicinity of EPS and thermocouple. The resistance of the RTD dropped with decreasing skin temperature. The RTD shows very similar trend as a thermocouple. (b) Skin hydration sensing; the change in skin hydration after applying body lotion was measured versus time, using both SHS and commercial sensor. Measurements with SHS and commercial electrodes were performed simultaneously. Result shows the skin hydration level gradually decreases with time after applying lotion. The plots presented in figure 6 were used as the calibration plots to plot the real time skin hydration measurement presented in fig. 8b