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Lignin-derived Porous Graphene for Wearable and Ultrasensitive Strain Sensors

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Abstract

This study aimed to explore lignin as a naturally occurring aromatic precursor for the synthesis of LIG and further fabrication of ultrasensitive strain sensors for the detection of small deformations. One-step direct laser writing (DLW) induced high quality porous graphene, so called laser induced graphene (LIG), from kraft lignin under the conditions optimized for laser power, focus distance, and lignin loading. An electrode based on the resulting LIG was facilely fabricated by transferring LIG onto an elastomeric substrate (i.e., Dragon Skin™). The novel LIG transfer was facilitated by spinning coating followed by water lifting, leading to full retention of porous graphene onto the elastomeric substrate. The strain sensor was shown to be highly sensitive to small human body motions as well as tiny deformations caused by vibrations. It had a working range of up to 14% strain with a gauge factor of 960 and showed high stability as evidenced by repetitive signals over 10,000 cycles at 4% strain. The sensor was also successfully demonstrated for detecting human speaking and movement of pulse and eye. Overall, the lignin-derived LIG can serve as excellent piezoresistive materials for wearable,

stretchable, ultrasensitive strain sensors with applications in human body motion monitoring and sound-related applications.

Keywords: laser-induced graphene, direct laser writing, lignin, strain sensor, human body motion, vibration detection.

1. Introduction

Strain sensors can be used as wearable and healthcare-oriented electronics for human health monitoring. In general, there are two main categories of human body motion detections, including large scale (bending, jumping, movements of arms and legs, etc.) and small scale (pulse, breath, and other tiny muscle movements).[1-6] A high-performance strain sensor would require large working range, high sensitivity, long durability, low fabrication cost, etc. Numerous methods, such as carbon nanotube (CNT),[7-9] nanoparticles,[10] graphene,[1, 11] and laser-induced graphene (LIG),[12-17] have been reported for developing high-performance strain sensor to fulfill the increasing demands for human health monitoring. However, most strain sensors have limitations in sensing. For example, a CNT-based strain sensor with PDMS as an elastomeric substrate had a low gauge factor (0.82~14) although it exhibited excellent stretchability.[8, 9] Similarly, the strain sensor based on CVD-grown graphene showed high sensitivity in detection of small-scale human motions, but it can only be stretched at 7% strain or below, with a gauge factor only up to 35.[1] Sensor configuration like sandwiched structure can significantly improve gauge factors,[18, 19] but correlation between signals and applied strains would need to be further improved. Therefore, further efforts would be needed to explore new piezoresistive materials and advance sensor fabrication techniques for developing ultrasensitive, wearable, and stretchable strain sensors with low cost.

LIG has been explored as active materials for strain sensor fabrication, as aforementioned. LIG can be facilely synthesized from various precursors using single-step direct laser writing (DLW), exhibiting excellent electrical, chemical, and mechanical properties.[14, 16, 20, 21] More strikingly, it has intrinsic porous structures which typically cannot be achieved by traditional techniques for graphene synthesis. Such attribute makes LIG a unique active element for strain sensor fabrication. The LIG-based strain sensors particularly derived from polyimide (PI) have been reported to outperform CVD-grown graphene sensors,[22] and show high sensitivity to capture various human body motions (e.g., speaking, pulse detection, arm movements).[12, 16, 17, 23, 24] However, those sensors had the limited detection strain ranges (below 1% strain) and gauge factors below 30 if the LIG-embedded PI film was used for a substrate for sensor fabrication.[12] While stretchable strains can be realized by transferring PI-derived LIG onto an elastomer, the gauge factors were still below 200 with significantly decreased sensitivity in small strain detection. One major reason for comprised sensitivity should be drastically increased sheet resistance (>20 kΩ) associated with LIG transfer.[15] LIG synthesized from other precursors such as cellulose paper was also used to fabricate on-chip, flexible strain sensors; however, the as-prepared sensors had poor stretchability and a very low working range (0~0.3% strain) as well as low gauge factors (only up to 42).[25] To fully explore the potential of LIG to be an active material for strain sensors, technical barriers like LIG quality, sensitivity, and transferability would need to be tackled.

Among various precursors (polyimide, wood, etc.) explored for LIG,[25-29] lignin stands out to a unique natural precursor for graphene synthesis given its high-carbon and aromatic structures. Compared to cellulose and hemicellulose, lignin is the most favorable constituent in lignocellulosic biomass for LIG formation. Lignin separated from biomass, so called technical

lignin, is more processable than raw biomass like wood to form a suitable substrate for DLW and yield higher quality of LIG. On the other hand, in puling mills and biorefinery facilities lignin is generated at large quantities (>100 million dry tons annually) as waste streams.[30] Therefore, upgrading lignin into graphene-based materials can add additional revenues and be of great significance to paper and pulp and biorefinery industries. As lignin is typically recovered in a powder form from biorefinery, lignin-based films can be made using a binder such as PVA, PEO, and cellulose nanofibers (typically not contributing to LIG formation) to well suit direct laser writing.[31-33] This strategy would enable mass production of lignin derived LIG as renewable advanced carbon materials via roll-to-roll manufacturing process. Prior studies reported that lignin derived LIG has high potential in energy storage and sensing applications.[26, 28, 32] However, research on lignin to LIG and subsequent applications is still limited compared to PI, a synthetic polymer precursor. For strain sensing, little research has been done to explore lignin derived LIG as an active material. A recent study reported a strain sensor based on lignin derived LIG/PDMS for human motion monitoring but with low sensitivity as reflected by a quite low gauge factor of 20 because of low LIG quality.[34] Therefore, more research efforts are needed for tailoring properties of lignin derived LIG as an excellent piezoresistive material. Further exploration of lignin-to-LIG upgrading pathway would need to address technical barriers to both LIG and lignin-specific precursor. For example, for sensing application, the sensor fabrication could involve LIG transfer from a lignin-based substrate (e.g., film); however, carbon loss, a common issue with LIG regardless of precursors, should be mitigated. Another consideration is to obtain high quality LIG like crystalline graphene since abundant oxygen-containing functionalities in lignin and biomass would contribute to noticeable defects in LIG. To this end, it would be very necessary to tune lasing conditions to ensure LIG quality.

In this study, we demonstrated the feasibility to fabricate a stretchable and wearable strain sensor using lignin derived LIG. The LIG was synthesize from kraft lignin by DLW and further transferred onto Dragon Skin™ for sensor fabrication. The LIG transfer was facilitated by a novel technique based on spinning coating coupled with water lifting, without noticeable modification on 3D structure of LIG. The key parameters optimized for lasing included precursor loading, laser power, and defocus distance. The resultant LIG was characterized for microstructure and graphene domains. The fabricated strain sensor showed ultrasensitive response to external stimuli including strains up to 14% and vibrations (5-135 Hz) with high stability. The excellent sensing performance underscored that lignin derived LIG can serve as a highly promising piezoresistive material for detecting tiny deformations induced by strains (below 6%) and vibrations.

2. Methods

2.1. LIG synthesis

A lignin-based film was prepared by mixing kraft lignin with polyvinyl alcohol (PVA). In brief, PVA (Mw=146,000-186,000) was first dissolved at 9 wt% in deionized (DI) water with continuous stirring at 90 ºC for 40 min. Kraft lignin of 0.5, 1.0, or 1.5 g was dissolved in 10 g of 2 wt% NaOH solution. Then, the kraft lignin solution was mixed with the PVA solution with 1:1, w/w until clear, dark brown liquid was obtained. The liquid was cast onto a plastic Petri dish with 9 cm in diameter and dried at 35 ºC in an incubator with humidity of 25-50% for about 30 h. After drying, the film was peeled off from the Petri dish and attached to a glass slide using adhesive tape for laser writing.

A CO_2 laser (30 W, 10.6 μm, Universal Laser Systems VLS3.50 Laser Cutter/Engraver) was used for DLW. The process was conducted under ambient conditions, with 1000 pulses per

inch, 10% speed, varying z-axis distance from the focal plane (0.0, 1.0, 2.0, and 3.0 mm), and varying power (20%, 30%, and 40% of the upper limit of laser power setting). An area of 3.0×0.5 cm^2 on the lignin-based film was subjected to laser writing. LIG samples were denoted as LxPy with 2 mm z-axis defocus distance unless stated otherwise, where x stands for the initial mass loading of lignin in a film (i.e., 0.5, 1.0, or 1.5 g) and y for laser power level (i.e., 20%, 30%, or 40%).

2.2. Fabrication of strain sensors

A strain sensor was fabricated by transferring LIG onto Dragon Skin™ (Dragon Skin™ 10 FAST Silicones), an elastomeric substrate. First, Dragon Skin™ was prepared by mixing two prepolymers (Part A: Part B = 1:1, w/w) and then coated to LIG embedded onto the lignin film by a spin coater (Model WS-650MZ-23NPPB) with a spin speed of 3000 rpm and an accelerated speed of 500 rpm/sec. After spinning coating, Dragon Skin™ was cured in a convection oven at 35 ºC for 30 min. The Dragon Skin™-coated film was then immersed in DI water for about 10 min to facilitate the detachment of LIG from the lignin film. The LIG/Dragon Skin™ composite was then dried at 35 ºC in a convection oven for 20 min, cut into a dimension of 3.8×0.85 cm^2, and used for the sensor fabrication. The composite was further attached with two copper wires on both ends by conductive epoxy adhesive followed by air drying. Fig. 1 illustrates the sensor fabrication from lignin derived LIG.

2.3. Characterization

LIG embedded onto a film was used for characterization, unless stated otherwise. Raman spectra were acquired on inVia™ confocal Raman microscope at a wavelength of 633 nm. Sheet resistance (Rs) was measured using Pro-4 Four Point Resistivity Systems (Lucas Labs, Gilroy, CA). Morphology of LIG samples was examined using a scanning electron microscope (SEM,

FEI Quanta 600 FEG) equipped with a Bruker Quantax 200 Silicon Drift Detector and operated at a 15 kV and 100 pA. High resolution transmission electron microscopy (HRTEM) images were acquired on a JEOL-2100FFEI Tecnai G2 F30 300 kV microscope, and LIG power was sonicated in ethanol for 10 min and imaged. X-ray diffraction (XRD) scanning was conducted for LIG power at 0.02º step size with a scanning rate of 12 s/0.02º using Bruker SMART CCD system.

2.4. Sensing evaluation

Signal patterns for sensing were acquired on an LCR meter (HIOKI IM3523 LCT meter) operated at a DC voltage of 0.1 V. For strain sensing, the sensor was stretched at a varying strain with a rate of 0.2 mm/min by LCR for testing. To detect vibration, a Permanent Magnet Shaker LDS (B&K V203) was used to vibrate the sensor at a frequency of 0-135 Hz or an input voltage of 0-2 V. The invoked amplitudes were proportional to the input voltage. At each level of frequency or input voltage, the strain was kept being vibrated for 10 s. Small-scale human motion detections were also performed, including speaking, eyeball movement, heartbeat (pulse), and breath. The sensor was attached onto a tester's throat, wrist, belly using a biocompatible adhesive gel for signal collecting.

3. Results and Discussions

3.1. Characterization of lignin derived LIG

Raman spectra reveal that all the LIG samples had three dominant peaks including D, G, and 2D peaks (Fig. S1). Specifically, a D peak at ~1360 cm^{-1} reflects defects and bending of sp^2 carbon bonds; a G peak at ~1580 cm^{-1} arises from the first order band of all sp^2 hybridized bonds; and a 2D peak at ~2670 cm^{-1} originates from the second order zone boundary phonons.[35] High I_G/I_D and I_{2D}/I_G ratios indicate high degree of graphitization and quality graphene,

160 respectively. Laser power showed different effects on the films with different lignin loading. For
161 L0.5, the higher laser power better induced graphene (Fig. S1a). For L1.0, 30% laser power
162 appeared to be sufficient for inducing higher quality LIG with the I_G/I_D and I_{2D}/I_G of 2.7 and 0.77
163 (Fig. S1d&e), respectively, indicating the formation of few-layer graphene with higher quality
164 compared to the counterparts derived from other precursors (e.g., PI, polyetherimide, wood,
165 cellulose paper) and even lignin reported in prior studies.[25-29] Further increasing lignin loading in
166 the film (L1.5) did not necessarily improve LIG quality regardless of laser power applied (Fig.
167 S1c). In general, high laser power can lead to sufficient carbonization and further
168 graphitization.[26, 29] However, laser power, if too high, can cause detrimental effects on LIG
169 quality due to severe photothermal irradiation. It should be noted that PVA in the lignin-based
170 composite film would be decomposed and released as gaseous products (H_2O, CO_2, etc.) during
171 laser scribing rather than contribute to LIG synthesis. The Raman results show that the threshold
172 of laser power for inducing porous graphene would also be related to lignin loading in a
173 substrate. In the case of L1.5, laser parameter would need to be further optimized due to higher
174 lignin loading. In consistence with Raman analysis, the LIG resulting from L1.0 films exhibited
175 at least 2-fold lower Rs than that from the other two films and synthetic polymers-/biomass-
176 based precursors previously reported (Table S1), with the lowest Rs (4.5 Ω/sq) being observed
177 with 30% power level (P30) (Fig. S1f). In addition to optimal laser power, defocused lasing
178 appeared to favor LIG formation compared to focused lasing. Fig. S2 depicts the effects of laser
179 scribing as a function of z-axis defocus when 30% power level was applied. With the z-axis
180 defocus distance increased from 0 (on the focal plane) to 2 mm, the I_G/I_D and I_{2D}/I_G ratios reached
181 the highest values for L1.0 (Fig.S2e). Further increase in the defocus distance to 3 mm led to
182 comprised LIG quality regardless of lignin loading in the films.

The LIG resulting from L1.0P30 was further examined for ultrastructure given its impressive Raman spectrum and low Rs. The HRTEM images showed fringe-like pattens of LIG with *d*-spacing of 0.355 nm between two neighboring (002) planes in graphitic carbon (Fig. 2d). This evidence further supported the presence of graphene and suggested few-layer graphene domain randomly oriented in the LIG. The XRD pattern showed characteristic peaks centering at $2\theta=25.9°$ (assigned to (002) reflection) and $2\theta=42.9°$ (assigned to (100) reflection) (Fig. 2b), with an interlayer spacing of 0.344 nm, indicating that L1.0P30 was well graphitized with high crystallinity. Overall, well-identified graphene domains in L1.0P30 proved successful transformation of lignin into graphene.

3.2. Characterization of LIG/Dragon Skin™ composites

L1.0P30 was selected for the fabrication of strain sensors by transferring the LIG to Dragon Skin™. LIG transfer was assisted by spinning coating followed by water lifting. Specially, after immersing the whole piece of Dragon Skin™ spin-coated film in water for about 10 min, the uncarbonized lignin film was automatically detached from LIG. No residual LIG was found in either the detached lignin film or water, while the transferred LIG showed well retained hierarchical microstructure onto Dragon Skin™ as discussed below. The LIG before and after the transfer was characterized and compared. The SEM images show that rigid and clear lines were formed orderly along with traces of CO_2 laser on the surface of pre-transferred LIG (Fig. 3a &S3a&e). At higher magnification, LIG showed foam-like microstructure as typically observed with LIG synthesis from other precursors (Fig. 3d &S3). The porous structure resulted from rapid release of gaseous molecules (CO_2, H_2O, etc.) as byproducts generated from laser-assisted oxidation and decomposition of lignin film. Water lifting enabled facile transfer of LIG without noticeable loss of LIG. The cross-sectional SEM images also suggested complete transfer of LIG

layer onto Dragon Skin™ with similar thickness (115μm) before and after transfer (Fig. 3c&f) and the total thickness of the LIG/Dragon Skin™ composite of ~150μm. Moreover, this finding suggested sufficient infiltration and curing of Dragon Skin™ into interconnected network of LIG. Overall, water lifting method can overcome common issues associated with LIG transfer onto an elastomeric substrate, such as carbon loss and disruption of microstructure. As a result, LIG/Dragon Skin™ can well preserve intrinsic functional properties of LIG and exhibit excellent sensing capability as discussed below.

3.3. Sensing strains and vibrations

The fabricated strain sensors were evaluated for sensitivity in response to two external stimuli, i.e., strains and vibrations. Like many LIG-based strain sensors, the working mechanism of the proposed strain sensor is proposed to be resistance change caused by increasing gap distance while applying strains. Strikingly, the strain sensor demonstrated ultrasensitivity compared to those based on PI-derived LIG and many other materials (Table S2). For example, the gauge factors of strain sensors based on pristine PI-derived LIG reached only up to 160, about 17% of the maximum value given by the proposed strain sensor.[12, 15, 36] The R_0 of the strain sensor was around 300 Ω, which made it suitable for low power applications. Fig. 4a depicts that the sensor experienced three stages throughout the stretching and the photo in Fig. 4b shows how the sensor was stretched vertically. Its gauge factor was initially about 100 when the strain was below 4%. The sensor also showed good sensitivity even when a strain was applied as low as 0.1% (Fig. S4a). The gauge factor became 160 when the strain was increased from 4% to 9%. When the sensor was stretched further from 9% to 14%, the sensor exhibited a superb gauge factor of ~960. Notably, the signals at three stages had good linearity, i.e., $R^2 > 99$ for Stages 1&2 and $R^2 > 98$ for Stage 3. The sensor was also tested for reversibility in a stretch-release

cycle for hysteresis test. It showed a low degree of hysteresis (<7%) at 9% strain, suggesting good reversibility (Fig. S4b). Compared to strain sensor based on conventional piezoresistive materials such as CNT and nanowires, the LIG-based strain sensors showed much lower hysteresis degree (Table S2).

With the strain range below 9%, the two responding stages can be explained by the fact that with larger strains being applied, the crack between graphene flakes would keep expanding and change into a new junction consisting of reduced conductive paths, leading to the increased gauge factor. The evolution of the crack structure in LIG at different strains applied is also shown in Fig. 4d-g. Within the strain range of 9%-14%, the gauge factor was remarkably increased due to the more enlarged cracks causing more irregular signals. However, when the crack was too large, the electrical connection between responding stages would be broken, with the maximum strain being applied at 14%. The stability of signal was tested by applying different strains (i.e., 2%, 4%, 6%, 9%) (Fig. 4b). For each applied strain, the device kept being stretched for 50 s. It was found that the signals of relative resistance change ($\Delta R/R_0$) were stable and repeatable at a given strain. Compared to start-of-art strain sensors especially based on LIG (Table S2), the proposed strain sensor exhibited significantly improved gauge factor (as high as 960) and markedly lower detection limits (as low as 0.1%) for small-scale strain detections (Fig. S4a). Considering excellent sensing linearity, it would be interesting to test and compare with other device configurations like sandwiched structures for ultrasensitivity.[18, 19] The sensor was further evaluated for stability over 10,000 stretch-release cycles at 4% strain. There were no significant signal fluctuations being observed after 10,000 cycles (Fig. 4c). The sensor's resistance only increased from around 300 to 450 Ω along with ~10% increase in the gauge factor. The findings demonstrated the strain's superb stability of conductive network and

reliability for repeated uses, which was shown to be superior to most start-of-art strain sensors fabricated from PI-derived LIG and CNT (Table S2).

In addition to strain sensing, the sensor was also shown to be ultrasensitive to vibration, another form of tiny deformation. The resistance change of the strain sensor was continuously monitored throughout the vibration. Fig. 5a&b shows resistance in response to a frequency ranging from 5 to 135 Hz with an increment of 5 Hz when the input voltage was kept at 2V. $\Delta R/R_0$ first increased along with the increasing frequency until reaching the highest value at 85 Hz. When the frequency was increased further, $\Delta R/R_0$ drastically dropped to 35% at 100 Hz and then increased. The spike in $\Delta R/R_0$ at 85 Hz suggested that this frequency could be at or near resonant frequency/natural frequency of the sensor. As a result, the sensor can vibrate with a larger amplitude than that at non-resonant frequencies. Larger vibration amplitude can lead to larger cracks and subsequently more significant signal changes. The electrical resistance of sensor was further measured against amplitudes range controlled by input voltages from 0.2-3V when applying a frequency of 85 Hz (Fig. 5c). An excellent linear correlation between $\Delta R/R_0$ and input voltage was observed ($R^2 > 99$) (Fig. 5d). These results indicate that lignin derived LIG has exceptional piezoresistive property that can also be explored for sound-related applications.

3.4. Sensors for detecting speaking

The sensor was used as a speaking detector given the frequency of human speaking ranging from 50 to 300 Hz. Fig. 6&S5 depicts representative strain's performance on detecting human speaking by sensing throat muscle movements and vibrations (Fig. S5a). Swallow, one of typical muscle movements, was also detected, showing distinguishing patterns (Fig. 6a). When one was asked to speak two example words "today" and "beautiful" as well as the whole sentence "Today is beautiful" 4-5 times, the signature peaks corresponding to two individual

words were well identified in the whole sentence (Fig. 6b-d). More intriguingly, when the speaking testing was extended to a longer sentence "Laser-induced graphene from lignin-based precursor has many good properties." three times, the signature pattens of individual words were clearly detected, with good repeatability (Fig. S5b-m&S7a). These findings suggested that the sensor can distinguish tiny deformations caused by speaking, with reliable and repeatable performance. The sensing mechanism for speaking is a combined effect of strains and vibrations. On one hand, the muscle movements of throat during speaking are unique and repeatable, which can be captured as a strain stimulus by the sensor. On the other hand, sound generated during speaking causes vibrations to the sensor. The sensor's exceptional sensitivity to strains, vibrations, or combined suggests its great potential to be used as a sophisticated speaking detector. One example would be to aid people with disability in speaking by coupling artificial intelligence.

3.5. Sensor for small-scale human motion detection

The sensor's performance in detecting human motions, including eyeball movement, heartbeat (pulse), breath, and seismocardiography (SCG), was depicted in Fig. 7. The sensor showed excellent and stable responses. For eyeball movement, the sensor was horizontally attached at the lower part of one's eyes for eye blink, fast eye blinks, looking up, looking down, looking left, and looking right in order, each three times except fast eye blinks. Fig. 7a shows that the strain sensor can provide instant and clear feedback with the unique, stable, and repeatable resistance change patterns for different eye movements. Muscle movements controlling an eyeball to different directions were at tiny scales. Compared to reported eyeball movement sensors.[37, 38] the proposed strain sensor offers a simpler way to monitor real-time eye movement detection for human health monitoring and virtual reality system.[38, 39] Furthermore,

298 the strain sensor was attached to one's chest for breath detection, including belly breath (deep
299 breath) and chest breath (normal breath) (Fig. 7b). As breath disorder is usually related to
300 pulmonary diseases (asthma, COVID-19, etc.), the strain sensor's ability to distinguish breath
301 patterns would be highly useful for respiratory system monitoring.

302 SCG is a non-invasive technique used for cardiovascular disease diagnostics by
303 measuring vibrations around chest caused by one's heartbeats. The strain sensor was also
304 evaluated for its performance in SCG signal recording. Fig. 7c depicts the signal patterns to body
305 microvibrations during one cycle of holding breath including systole phrase and diastole phrase.
306 The corresponding region of signal for two phrases as well as their related heart activity are
307 shown in the inset of Fig. 7c. Specially, mitral valve closure (MC), aortic valve opening (AO),
308 and rapid blood ejection (RE) form systole phrase, as well as aortic valve closure (AC), mitral
309 valve opening (MO), and rapid blood filling (RF) from diastole phrase are annotated. The SCG
310 acquired from different positions around the chest including its low part was distinguishing given
311 different structure of human body (Fig. 7c&S6). The signals showed good repeatability across all
312 the testing cycles based on an error band analysis (Fig. S7b). Although the relationship between
313 SCG and electrocardiogram (ECG) is not well understood, recent advances, including more
314 accessible sensors and better algorithms enhanced by machine learning, have demonstrated the
315 potential of SCG in monitoring the health of patient with heart disease.[40] The proposed strain
316 sensor, which can be facilely fabricated from lignin derived LIG at low cost, can serve the
317 purpose for easy and rapid SCG detection.

318 Pulse wave detection is another key parameter in human health monitoring. As shown in
319 Fig. 7d, the sensor can distinguish the deformations caused by percussion wave (P), tidal wave

(T), and diastolic wave (D), which are important indicators to one's cardiovascular health monitoring.[41]

4. Conclusions

Lignin-derived strain sensor had excellent performance in detection of small deformations caused by strains and vibrations. It exhibited a large working range for sensing up to 14% strain, with gauge factor as high as 960 and low hysteresis. A good linear relationship between the relative resistance changes and strains was observed. It was also sensitive to vibrations in response to change in frequency and amplitudes. Moreover, the strain sensor can capture tiny deformations based on human speaking, eyeball movements, breath, seismocardiography, and pulses. In all the tests, the strain sensor showed excellent stability and repeatability and was able to generate distinguishing signal patterns of deformations caused by various external stimuli. This work indicated that LIG induced from lignin can be used as an excellent piezoresistive material to fabricate wearable, high-performance, ultrasensitive strain sensors for detection of strain-/vibration-induced deformations toward applications such as healthcare monitoring and sound sensing.

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Figure captions

Fig. 1. Schematic diagram of strain sensor fabrication from lignin derived LIG.

Fig. 2. Characteristics of LIG (L1.0P30). (a) Raman spectrum. (b) XRD spectra of LIG and pristine film (L.0). (c, d) TEM images: scale bars of 20 and 5 nm, respectively.

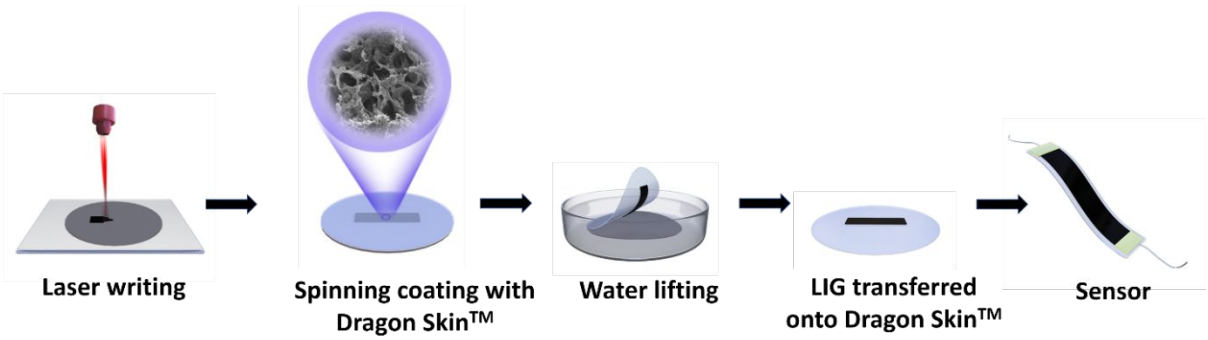
Fig. 3. SEM images of L1.0P30 before and after transfer. (a, d) Top view before transfer: scale bars of 100 and 20 μm, respectively. (b, e) Top view after transfer: scale bars of 100 and 20 μm, respectively. (c, f) Cross-sectional views before and after transfer, respectively: scale bar of 100 μm.

Fig. 4. Strain sensor's sensitivity to strain. (a) $\Delta R/R_0$ in response to up to 14% strain, with the inset demonstrating the signal change at a stain up to 1%. (b) $\Delta R/R_0$ over the course of testing at different strain levels, with the inset showing the photo of strain sensor stretching. (c) Sensing stability at 4% strain over 10,000 cycles, with the inset showing the first and last 10 cycles (left and right). (d-g) SEM images of evolution of microgap with an increase in strain: scale bar of 100 μm.

Fig. 5. Strain sensor's sensitivity to vibration. (a) $\Delta R/R_0$ at different vibration frequencies (5-135 Hz) when the input voltage for vibration was applied at 2 V. (b) Averaged $\Delta R/R_0$ at different frequencies (5-135 Hz). (c) $\Delta R/R_0$ at different input voltages (0.2-3 V) for vibration when a vibration frequency was applied at 85 Hz. (d) Linear correlation between $\Delta R/R_0$ and input voltages. The photo in (a) shows the testing setup in which the sensor was attached to a permanent magnetic electrodynamic shaker where input voltages were provided.

Fig. 6. Strain sensor working as a speaking detector. (a) $\Delta R/R_0$ of detecting swallow. (b-d) $\Delta R/R_0$ of detecting speaking "beautiful," "today," and "today is beautiful", respectively. The photo in (a) shows the sensor's placement for detecting swallowing and speaking.

Fig. 7. Strain sensor for human motion monitoring. (a) Signal patterns of monitoring eyeball movements. (b) Signal pattern of monitoring belly and chest breath. (c) Signal pattern of seismocardiography. (d) Signal pattern of pulses. The photos show the sensor's placement at different positions for testing. The inset in (c) annotates mitral valve closure (MC), aortic valve opening (AO), and rapid blood ejection (RE) form systole phrase, as well as aortic valve closure (AC), mitral valve opening (MO), and rapid blood filling (RF) from diastole phrase. The inset in (d) shows the signal changes caused by percussion wave (P), tidal wave (T), and diastolic wave (D).



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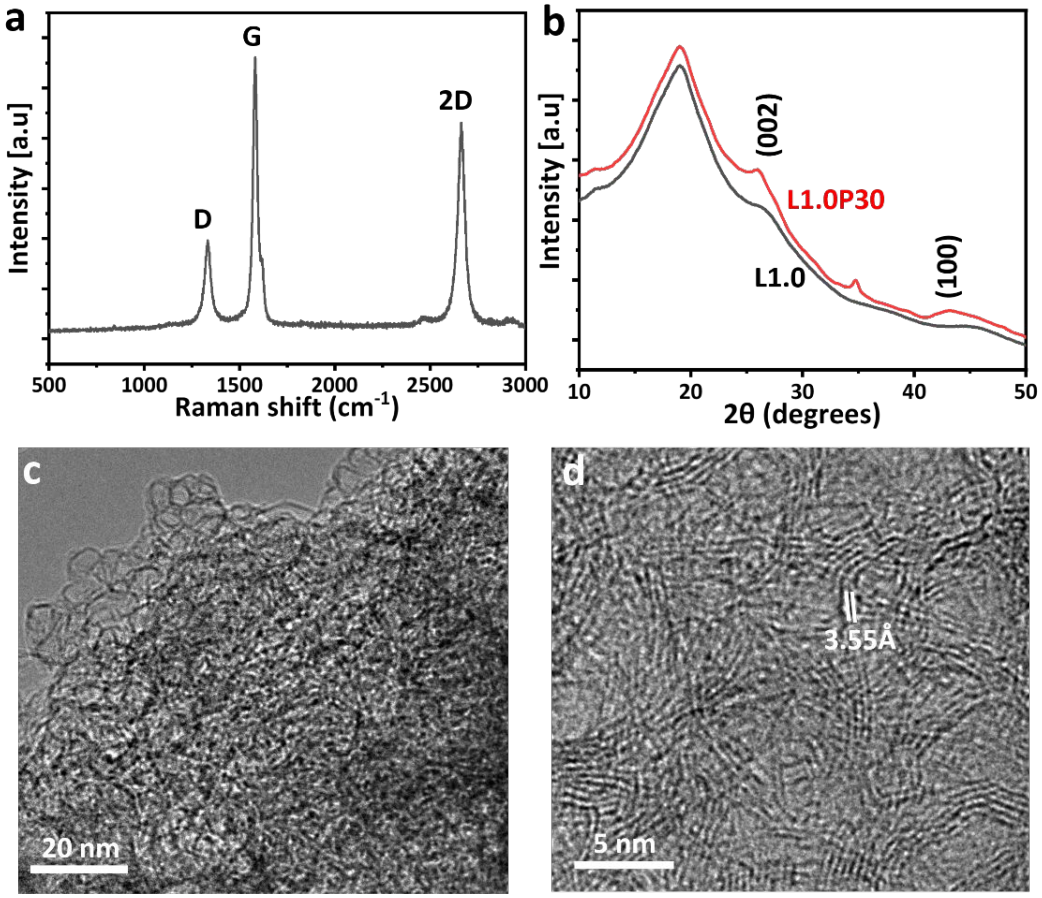

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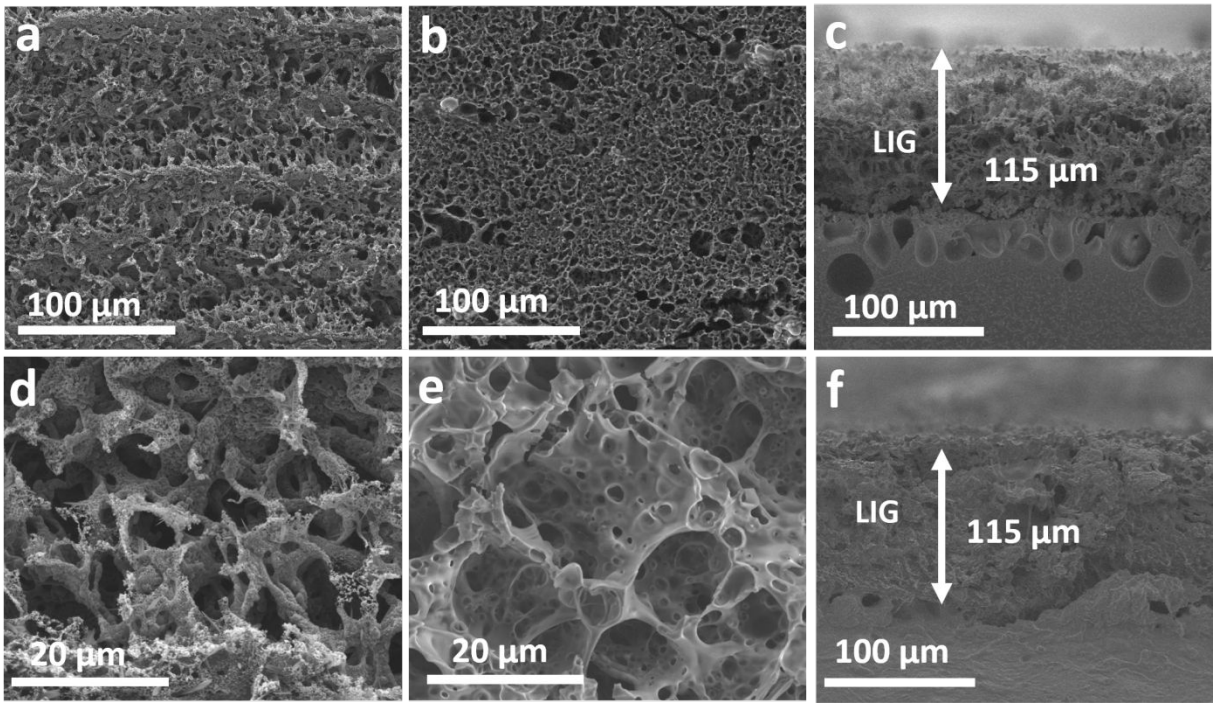

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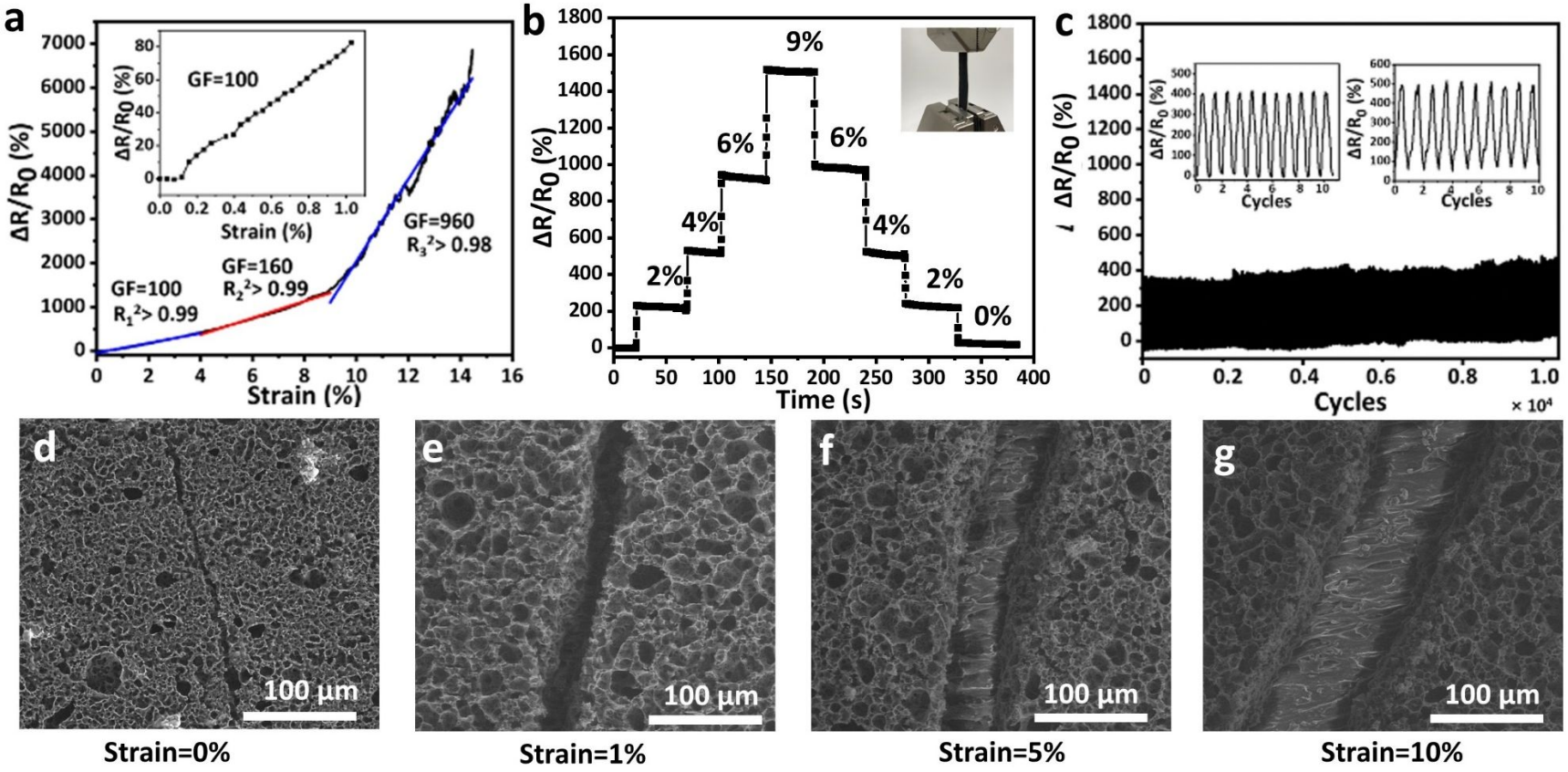

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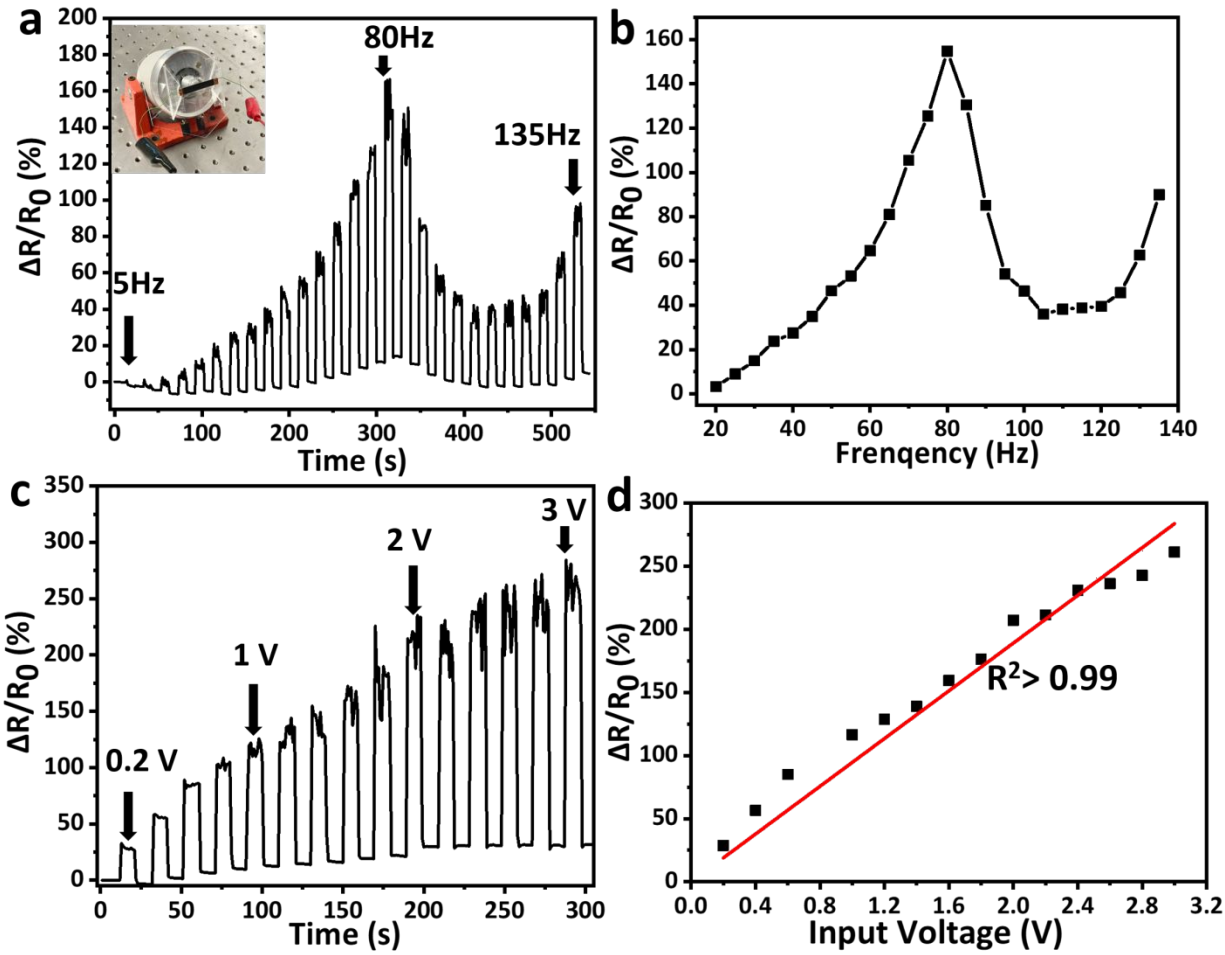

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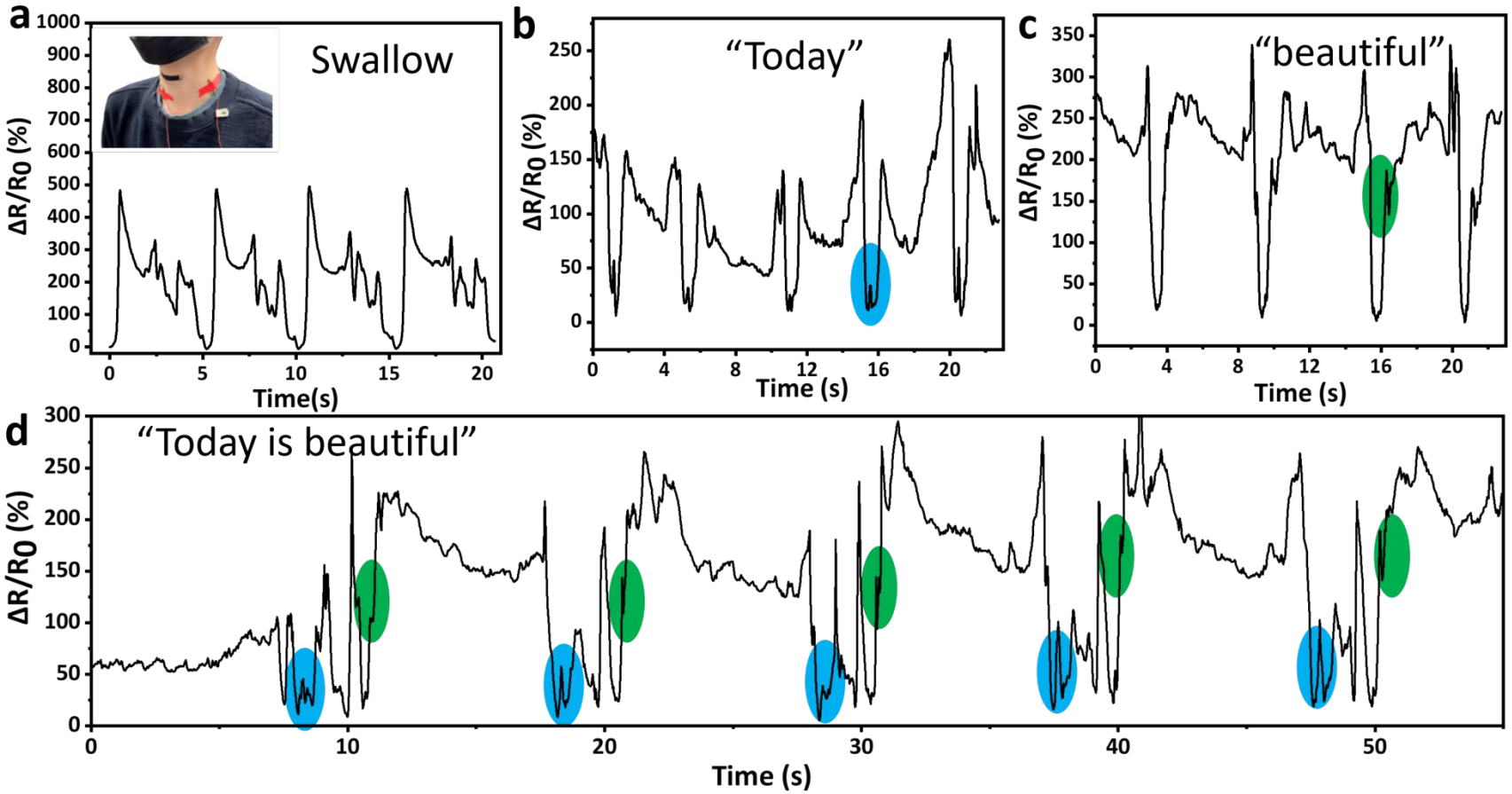

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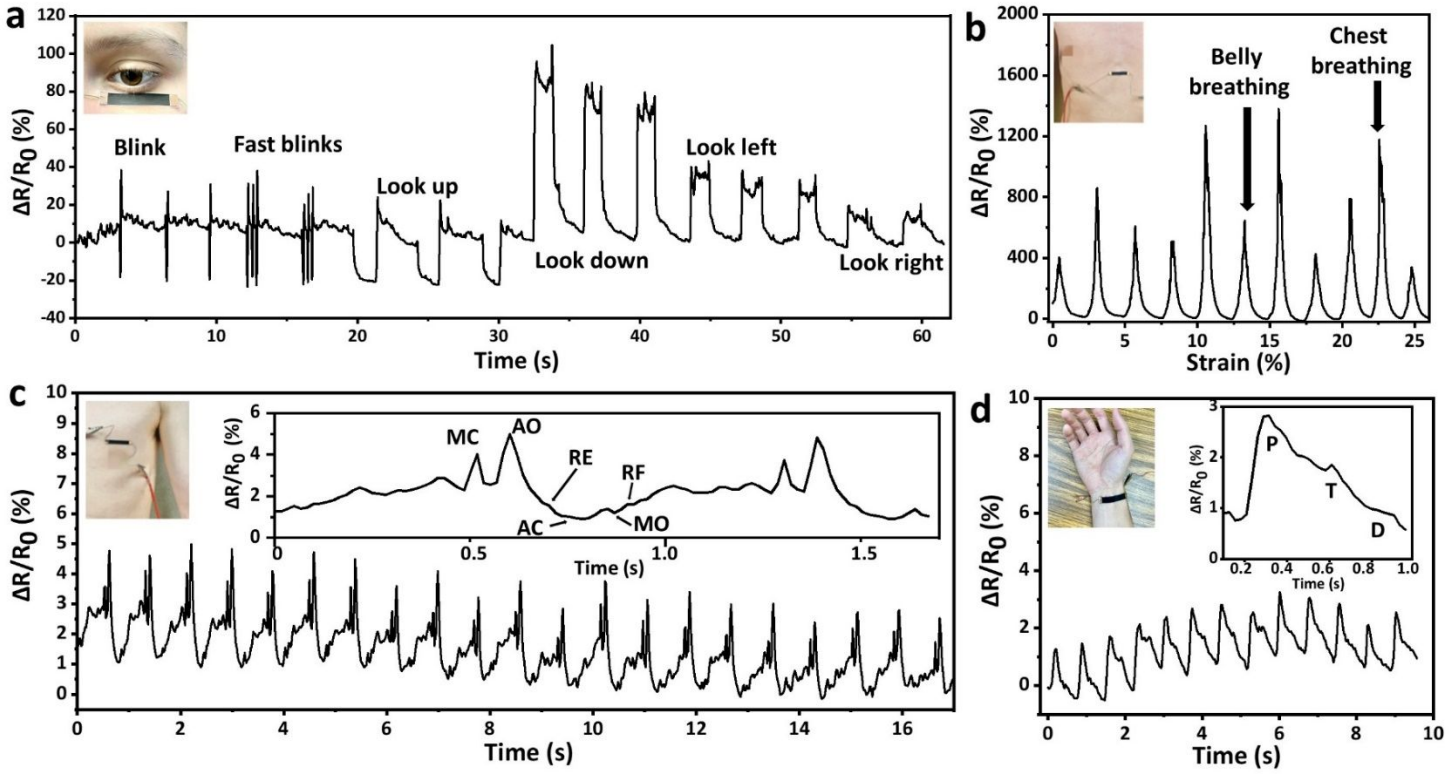

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