Skin-Like Transparent Sensor Sheet for Remote Healthcare Using Electroencephalography and Photoplethysmography

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The growing demand for efficient home healthcare applications for brain disorder diagnostics and treatment has inspired the development of wearable devices for monitoring brain activity. However, flexible probe systems that have improved biocompatibility for wearable devices are largely affected by noise due to contact interface issues. In this study, a stretchable (≤1500% strain) and transparent (over 85% transmittance) biocompatible electrode that steadily adheres to skin is developed to fabricate an imperceptible sheet-type device that wirelessly records electroencephalogram (EEGs). The multifunctional characteristic of the electrode results from the double-network structure in an elastomer/conductive additive blend on a metal-nanowire-based track, which contributed to EEG monitoring with ultralow noise (≈0.14 μV noise floor) and sleep-stage classification. Furthermore, the optical transparency enabled camera-based photoplethysmography to detect pulse waves and blood oxygen saturation without interfering with the light path, which is a crucial factor in realizing a remote healthcare system.

1. Introduction

Brain diseases such as dementia and depression are significant problems for individuals living in advanced societies.[1] Precise monitoring of brain activity will further our understanding of these diseases and will help us to overcome them.[2–5] However, the action potentials of cerebral nerve activities are the smallest in the human body and are markedly affected by noise.[6–9] Conventional, brain activity is monitored in medical institutions using large medical devices, such as magnetic resonance imaging devices, magnetoencephalograms, and electroencephalograms (EEGs), which must be operated in environments with extremely low external noise.[8] Their large size and specialist nature mean that trained personnel must selectively use these devices. In addition, monitoring using large medical devices induces different brain activity to that in the daily steady state. If brain activity could be monitored easily at home, like body temperature, blood pressure, and weight, then the signs of severe diseases could be recognized before their onset. Therefore, the development of small, high-accuracy EEG systems with minimal presence and discomfort is strongly desired.

Wireless EEG systems have attracted attention for the elucidation, diagnosis, and treatment of certain disorders[2–8] and typically feature soft probes as key electronic components considering the low elasticity of skin.[10–12] Soft probes reduce invasiveness and hinder inflammation to skin during long-term use.[2,4,12–15] Facilitating monitoring from surfaces of the human body,[2,9,12–18] Conventional medical devices used for EEG recording require gel- or paste-based wet electrodes[19] to be attached to the head of the patient. During long-term use, these electrodes are prone to cause skin irritation due to water accumulation, and the initial low electrode/skin contact impedance increases as the electrode dries.[20,21] On the other hand, wearable headset-type systems with partially pressured dry electrodes have reduced electrode/skin contact impedance and eliminate exogenous noise for wireless EEG acquisition.[6,22,23] Although such systems benefit from a reduced attachment time, their size needs to precisely match the size of the head of the individual, and the applied attachment pressure (typically around 13.8 kPa) may induce skin irritation.[6,22,23] These drawbacks, as well as those associated with long-term use, need to be mitigated.

In this study, an imperceptible EEG system was developed using a stretchable and transparent skin-like sensor sheet that is worn on the forehead (Figure 1a,b). The EEG system wirelessly monitors brain waves without physical or visual discomfort, with a measurement accuracy similar to that of medical equipment. This is achieved due to the high conductivity, high stretchability, high transparency, and ultralow noise of the...
sensor sheet, which are realized through the advanced fusion of organic and inorganic materials. The organic material, which consists of an extremely stretchable elastomer and a conductive polymer that form a biocompatible composite with a nano- to micrometer-sized phase-separated structure, acts as a dry adhesive and shows moderate adhesion strength (≈24 Pa) to skin while the EEG system is worn. Two types of biocompatible elastomers, acrylate and polypropylene oxide/polysiloxane (PPO/PSi), were utilized owing to their advantageous properties such as excellent elongation, transparency, and moderate adhesion strength. The conductive polymer was poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS). The double network structure in the adhesive electrode is crucial for maximizing the optical and mechanical properties of the elastomers and the electrical properties of PEDOT/PSS (Figure 1c). The inorganic material, which comprises Ag/Au core–shell nanowires (AgNW/Au) that are invisible to the naked eye, was further developed to improve the cyclic strain resistance compared with that reported previously. There have been several reports on dry-type flexible adhesive electrodes, including transparent ones,[4,9,12–14,24–27] however, no electrodes that can precisely monitor brain waves, which have the smallest action potentials in the human body, have been reported thus far (Table S1, Supporting Information).

2. Results and Discussion

Adhesive electrodes comprising acrylate elastomer (98 wt%) and PEDOT/PSS (2 wt%) were fabricated by a blade-coating method. Laser Raman microscopy revealed that the PEDOT/PSS agglomerated as submicron-size particles (Figure 1d). The adhesive electrode simultaneously maintained moderate adhesion, stretchability with 1500% strain, and visible light transmittance of 86–94% at a wavelength of 550 nm (Figure 1e,f and Figure S1, Supporting Information). If these multifunctionalities are assumed to be derived from a phase-separated structure, the conductivity should be anisotropic. The anisotropy factor, which is equal to the in-plane resistivity divided by the vertical resistivity, was evaluated to be more than 563, indicating highly anisotropic vertical conduction (Figure 1f). These results suggest that the acrylate elastomer formed a network itself, while PEDOT/PSS agglomerated to form a second network structure (Figure 1c). Therefore, the advantages of the elastomer (excellent elongation, transparency, and adhesion) and PEDOT/PSS (excellent conductivity) are both maximized in this adhesive electrode. In particular, the adhesion strength to skin (≤13 kPa) was equal to that of clinical-standard wet electrodes and was the highest among those of dry-type flexible adhesive electrodes (Tables S1 and S2, Supporting Information).
Wireless EEG monitoring with the adhesive electrode was successfully achieved for the α-wave (8–13 Hz) for even a 1.8–13.9 µV peak in the closed-eye state, which was similar to the measurement results obtained with clinical-standard wet electrodes (Figure 2a–c). Minute potential changes from the human skin were monitored using the sheet-type EEG system placed on the forehead by utilizing a previously developed opaque stretchable track \(0.2\ \Omega\ \text{sq}^{-1}\).[15,28] The noise floor level was calculated at 55 ± 0.5 Hz when used for wireless recording with a 125 Hz sampling rate; similar noise floor levels were obtained for adhesive electrodes (0.36 ± 0.20 µV) and clinical-standard wet electrodes (0.44 ± 0.17 µV) (Figure 2c). The noise level of the adhesive electrode under strain was so low that a few microvolts could be measured clearly: at strains of 100% and 1000%, the noise floors were 0.46 and 1.8 µV, respectively (Figure S1, Supporting Information). The adhesive electrode with ultralow noise and biocompatibility was applicable to classification of the sleep stage using an artificial intelligence system supported by PGV Inc. (Figure 2d). The characteristic brain waves, such as α-waves and K-complexes, were clearly monitored in the sleep stage (Figure 2e and Figure S2, Supporting Information).

Noise in EEG measurements is closely related to the electrode/skin contact impedance, and the level of noise reduces as the impedance decreases (Figure S3, Supporting Information). The adhesive electrode with ultralow noise and biocompatibility was applicable to classification of the sleep stage using an artificial intelligence system supported by PGV Inc. (Figure 2d). The characteristic brain waves, such as α-waves and K-complexes, were clearly monitored in the sleep stage (Figure 2e and Figure S2, Supporting Information).

PEDOT/PSS allows an efficient charge transfer system;[15,29–31] therefore, the PEDOT/PSS agglomerates in the adhesive electrodes, which form as a result of phase separation, contribute to reductions in the vertical resistivity of the adhesive electrode, electrode/skin contact impedance, and noise in EEG measurements (Figure S3c,d, Supporting Information). The phenomenon of phase separation is presented in Figure S4 (Supporting Information). The contact impedance was affected by the size and content of the PEDOT/PSS agglomerates. The conductive adhesive containing 2 wt% submicron-size PEDOT/PSS agglomerates (size distribution: 0.1–9.4 µm) showed an average contact impedance of 64 ± 18 kΩ, which is comparable to that of the wet electrodes used in medical applications. In comparison, a conductive adhesive containing 2 wt% micron-size PEDOT/PSS agglomerates (size distribution: 3–212 µm) had a higher maximum contact impedance of 238 kΩ, although the average impedance was 97 kΩ. When the PEDOT/PSS content was increased to 9 wt%, the contact impedance decreased to 19 kΩ with micron-size PEDOT/PSS agglomerates. However, the anisotropy factors of the adhesive electrodes with micron-sized PEDOT/PSS agglomerates (0.39 and 0.95 for the samples with 2 and 9 wt% PEDOT/PSS, respectively) were much smaller than that with 2 wt% submicron-size PEDOT/PSS agglomerates (anisotropy factor of 563), which means that they showed isotropic conduction (Figure 3a). Therefore, the multifunctional properties, such as adhesion and transparency deterioration,
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Figure 3. Electrode/skin contact impedance versus anisotropy factor. a) Acrylate-based adhesive electrode for blade coating. Increment in anisotropy observed using submicron-size agglomerates or Ag/AgCl microparticle addition. b) PPO/PSi-based adhesive electrode for screen printing. Increment in anisotropy observed with Ag/AgCl microparticle or PEG addition. The insets show schematic microstructures of each adhesive electrode.

were lost (Table S2, Supporting Information). Importantly, the high anisotropy of the adhesive electrode with submicron-size PEDOT/PSS agglomerates provides low contact impedance as well as multifunctionality, resulting in low noise and imperceptible measurement.

We investigated whether the phase-separated structure could be intentionally induced in the adhesive electrodes with micron-sized PEDOT/PSS agglomerates (Figure 3). First, adhesive electrodes with the PEDOT/PSS and Ag/AgCl microparticles were fabricated by blade-coating and screen-printing methods, with an acrylate and PPO/PSi polymer mixture, respectively, whereby the Ag/AgCl microparticles-induced phase separation. The AgCl surface is important for ion conduction and nontoxicity (Figure S5, Supporting Information).[22,32,33] PEDOT/PSS is trapped and agglomerated on the surface of the Ag/AgCl particles without spreading in-plane, thus building a phase-separated structure that exhibits high conductivity along the thickness direction. The high anisotropy for both blade-coating and screen-printing methods exhibits an improved anisotropy factor of \( \approx 30–147 \), resulting in a low contact impedance of \( \approx 20 \) kΩ. In the absence of PEDOT/PSS, for example, electrodes with 6 wt% Ag/AgCl microparticles in PPO/PSi exhibit a relatively high anisotropy (\( \approx 25 \)) and large contact impedance of 139 kΩ (Figure 3b and Table S2, Supporting Information). This result indicates that the synergistic effect of PEDOT/PSS and microparticles is significant. Second, the phase-separated structure was induced by adding polyethylene glycol (PEG), a nonvolatile solvent with high affinity to PEDOT/PSS and low affinity to elastomer of PPO/PSi for screen-printing methods (Figure S7 and Table S3, Supporting Information). The addition of PEG tended to improve the anisotropic conductivity, stretchability, and contact impedance. However, PEG caused bleeding from the adhesive electrode, thereby deteriorating the electrode/skin contact. Thus, the Ag/AgCl microparticles were concluded to be the most suitable additive to produce adhesive electrodes for use as a probe.

In this study, detailed biocompatibility tests were conducted on the primary materials. Unfortunately, both polymer mixtures used for blade-coated and screen-printed adhesive electrodes were low to moderately positive in cytotoxicity tests conducted as per ISO 10993 using mammalian-cultured cells and could cause inflammatory reactions when implanted in the body or applied to mucosal tissues. Further investigations are needed to verify if improvements can be made toward the development of such implant electronics. For example, polymer mixtures used for blade-coated adhesive electrode showed good signs of nontoxicity when the sample thickness was reduced from 20 to 10 µm. Substances such as residue monomers, byproduct, etc. that demonstrated adverse effect will be necessary to identify and bring them down to safe levels. Notably, the biosafety evaluation items, which are important for wearable bioelectrodes attached to skin, have been cleared. Both polymer mixtures used for blade-coated and screen-printed adhesive electrodes passed skin irritation safety assays, which checked for erythema and edema, and sensitization safety assays, which checked for allergic reactions, according to ISO 10993 using rabbit skin. In addition, no skin irritation was reported by 20 human subjects after 24 h of continuous wearing. This biocompatibility was attributed to not only the molecular design that was unresponsive to skin but also the softness of binder resins that comprised 94–98 vol% of the adhesive electrodes. The polymer mixtures have a higher stretchability (maximum strain: 1126–1537%) and lower stress (modulus: 7 kPa–0.5 MPa under strains) than human skin (maximum strain: 115%, modulus: 2 kPa–21MPa) (Tables S2 and S4, Supporting Information).[10–12] Because all electrode materials including additives were fabricated using biologically friendly materials, no skin irritation was observed during evaluation, as shown in Figure 3 and Tables S1 and S2 (Supporting Information).

The paste for blade coating had a low viscosity of 1–10 Pa s, which is unsuitable for continuous manufacturing due to the sedimentation of particles. In contrast, the screen-printing paste had a viscosity of 200–400 Pa, which offers improved process stability. Thus, adhesive electrodes were fabricated using a screen-printable paste consisting of PPO/PSi, PEDOT/PSS, and Ag/AgCl microparticles (Figure S6, Supporting Information). The PEDOT/PSS agglomerate was clearly visible after the paste
was printed using a screen mesh (opening distance: 70 µm) and was approximately of the same size as that of the mesh opening (Figure S8, Supporting Information). With the addition of Ag/AgCl microparticles, the microparticles trapped and adsorbed a PEDOT/PSS agglomerate (Figure 4a,b and Figure S9, Supporting Information). Consequently, the optical transmittance of the sample containing Ag/AgCl particles was slightly increased (Figure 4c); at 4 wt% loading, the adhesive electrode exhibited a transmittance of 87% at 550 nm. It is assumed that a PEDOT/PSS agglomerate shrinks in-plane while being adsorbed on the particle surface, resulting in an expanded area of light transmission in the adhesive electrode. Owing to the high cohesion created by this mass transfer, the anisotropic conduction property was improved, with an anisotropy factor of 29.7, compared with a factor of 73 without Ag/AgCl particles (Figure 3b and Table S2, Supporting Information). As an additional benefit, the electrode/skin contact impedance of the adhesive electrode containing Ag/AgCl particles was comparable to that of clinical-standard wet electrodes (Figure 4d and Table S2, Supporting Information). The observed nonlinear response to the input current was ascribed to polarization of the electrode surface, the extent of which decreased with increasing Ag/AgCl content, decreasing the deviation of the electrode/skin contact impedance. Wireless EEG monitoring was also successfully achieved with an average noise level of 0.27 ± 0.16 µV, which was the highest level among dry-type probes (Figure 4e and Table S1, Supporting Information). Notably, after 24 h of continuous wear, 3 years of storage in the atmosphere, and 1000 cycles at 100% strain, the electrode/skin contact impedance was maintained at a level sufficient for EEG recording, within the allowable input impedance (Figure 4f,g). Furthermore, the adhesion strength to the skin was sufficiently high for attachment and allowed the weight of the wireless module (weight, 12 g; thickness, 6 mm; pressure via sheet sensor to skin, ≈24 Pa) to be sustained with maximum durability of ≤11 kPa.[15,34] Owing to its excellent skin adhesion and stretchability, the screen-printed adhesive electrode did not peel at all during light activities such as walking, climbing up/down stairs, and sleeping. However, the adhesive electrode may peel off when the kinetic energy of the wireless module increases or when the level of sweat or moisture increases; therefore, further improvements may be required in future. (The same tendency was observed for the blade-coated adhesive electrode.) The contact impedance and adhesion strength were comparable to those of wet electrodes and superior to those of novel gentle-attachment systems consisting of surface-modified electrodes with microstructural patterning and electrodes prepared from nonconductive adhesive/conductive pigment composites (Tables S1 and S2, Supporting Information).[4,9,13,14,24,27] Thus, our wireless EEG system enabled successful monitoring even of a 1–3 µV peak with ultralow noise, whereas previous EEG systems using novel electrodes featured high noise levels of 3.5–25 µV (Figures 2c and 4e). The phase separation in the adhesive electrode (Figures 1c,d and 4a) meant that both
moderate adhesion strength and low electrode/skin contact impedance were maintained, which contributed to the reduced noise level and enhanced signal-to-noise ratio during EEG acquisition under stress-free and long-term use.

In order to obtain transparent probes for EEG measurement, transparent track materials were developed. An AgNW/Au-based transparent track was fabricated by electroless Au plating and photonic sintering of a polyurethane (PU) sheet spray-coated with AgNWs. After the plating process, a thin uniform Au shell (4.3 ± 1.5 nm) was present on the surface of the AgNWs (Figure 5a and Figure S12, Supporting Information). Localized deposits at the wire–wire junctions, called the Au nano-bonding effect, apparently contributed to the reduced sheet resistance of the tracks; the average resistance of three samples with a transmittance of ≈85% decreased from 17 to 3 Ω sq.−1 after plating and remained constant for a year under atmospheric conditions. Compared with the pristine AgNWs, which demonstrated almost no adhesion between the nanowires, those subjected to Au nano-bonding featured mechanically strengthened networks and enhanced stretchability.[15] However, the change in track resistance was large under cyclic stretching because Au nano-bonding could exhibit weak binding strength, and the bonds could be broken in the nanowire network (Figure 5c). The electrical stability during cyclic stretching between 0% and 60% strain further increased upon photonic sintering, which resulted in sintered nanowires and strong bonding of the nanowires to the substrate (Figure 5b,c). The adhesion between the AgNW/Au network and the PU substrate was sufficiently strong for the network to withstand mechanical strain. During photonic sintering, the top 10 µm of the PU substrate softened upon heating the AgNWs, whereas the bottom side of the substrate remained at room temperature because of its low thermal conductivity.[15] In fact, both fully and partially embedded AgNWs were observed on the substrate surface, as confirmed by a simple tape test (Figure S13, Supporting Information). Meanwhile, localized fractures occurred under strain and acted as sacrificial positions, whereas the rest of the network remained conductive. Thus, the combination of Au plating and photonic sintering was concluded to result in high mechanical and atmospheric stability, making the corresponding probe well suited for EEG acquisition.

Figure 5. Fabrication and properties of the stretchable and transparent sensor sheet. a) Cross-sectional AgNW/Au image obtained using transmission electron microscopy (TEM). b) Schematic of AgNW/Au after photonic sintering. c) Change in resistance (measured resistance divided by resistance before the test) under mechanical tensile strain for pristine and photonic sintered AgNW/Au. Recovery to 1.4–4.5-fold variation is observed after 100 cycles. d) Schematic of the sensor sheet. e) Time–frequency analysis of an EEG signal recorded at 125 Hz. f) FFT results of two EEG segments for 10 s obtained in open-eye and closed-eye states.
The adhesive electrode with PPO/PSi, PEDOT/PSS, and 4 wt% Ag/AgCl microparticles was screen printed on the AgNW/Au-based transparent tracks (Figure 5d and Figure S14, Supporting Information). The stretchable and transparent sensor sheet successfully achieved wireless EEG monitoring (Figure 3e, f). The sensor achieved an averaged noise level of 0.14–0.41 µV, which was similar to the noise floor levels of the adhesive electrodes using the opaque stretchable track. The contact resistance was less than 100 Ω between the adhesive electrode and transparent track having a sparse metal nanowire network, which was sufficiently low in comparison with the electrode/skin contact impedance and had no effect on the noise during EEG recording. The same trend was confirmed for the blade-coated adhesive electrode as well as the screen-printed one. In addition, for the stretchable and transparent sensor sheet, the electrical impedance remained constant at 1–10⁴ Hz under strain, which indicated no fluctuation in the transferred signals (Figure S15, Supporting Information). The maximum on-forehead strain was ≈10% in the relaxed state and 40% upon muscle contraction. The stretchability of the sensor sheet was sufficient to endure deformation.

The electrically and mechanically distinctive sensor sheet could be used for several additional optical applications, such as remote photoplethysmography (rPPG) and laser Doppler flowmetry (Figure 6 and Figure S16, Supporting Information). rPPG is a noncontact camera-based method of measuring pulse rate and arterial blood oxygen saturation (SpO₂) by capturing pixel intensity changes from the skin by monitoring the change in blood volume. Owing to its high transmittance, the sensor sheet allows light from the rPPG system to easily pass through (Figure 6a). For rPPG evaluation, it is important for the incident and reflected light to remain unobstructed near the skin surface, and the sensor sheet accomplishes this. First, the pulse rate was calculated based on the pulse waves obtained at rest with and without the sensor sheet attached to the skin, which is the target area of rPPG. Figure 6b shows the pixel intensity at a wavelength of 930 nm from the skin using a multispectral camera, which represents the pulse wave. Similar pulse waves and pulse rates were recorded with and without the sensor sheet attached to the skin (Figure 6b). Next, pulse rate and SpO₂ were calculated based on the pulse wave when breath was held for 20 s, while the sensor sheet was attached to the target part of the rPPG. SpO₂ was calculated from the pixel intensities at wavelengths of 730 and 860 nm. The pulse rate and SpO₂ evaluated using an on-forehead sensor sheet were comparable to those measured with a conventional contact-type pulse oximeter (Figure 6c). It was discovered that the decreasing trend in blood oxygen observed in the breath-holding condition was well realized. Based on this evidence, it is possible to simultaneously evaluate rPPG during electrophysiological measurements using a sensor sheet in the near future. Fusing an rPPG system to a skin-like transparent sensor sheet for wireless electrophysiological recording can expand the system functionality toward multimodal remote technology to simultaneously monitor physiological signals such as EEG, electromyogram, SpO₂, pulse and respiratory rate, and blood pressure in the target area, without interfering with human movement.

3. Conclusion

In summary, a rational material design was proposed to develop a skin-like transparent sensor sheet for a skin-adherent low-noise sheet-type wireless EEG system. The sensor sheet was obtained by combining inorganic AgNW/Au tracks with biocompatible adhesive electrodes comprising a small amount of PEDOT/PSS and adhesive elastomer. Importantly, the phase-separated structure of the adhesive electrode provides multi-functional properties: transparency (86–87%), stretchability (2–16 times), adhesion strength (11–13 kPa), recovery after cyclic strain (100–1000 cycles), and anisotropic conductivity. The optical and mechanical properties derived from the characteristics of the adhesive elastomer network, whereas the anisotropic conductivity derived from the micron- to submicron-size PEDOT/PSS agglomerates. The anisotropy factor was 4–376 and 1443 times larger after the addition of Ag/AgCl microparticles and the reduction of agglomerate size, respectively. Thus, the electrode/skin contact impedance is comparable to that of clinical-standard wet electrodes. In addition, the photonic-sintered AgNW/Au network is a promising candidate for imperceptible tracks; it exhibits a high transmittance of 85% and a very low sheet resistance after 100 stretching cycles between 0% and 60% strain. The integrated skin-like transparent sensor sheet, which could be attached to the skin surface without any difficulties, showed an ultralow noise of 0.14 µV, which is lower than that of previously reported dry-type flexible adhesive electrodes. The low noise contributed to sleep-stage determination. In addition, camera-based photoplethysmography can...
be integrated into the sheet sensor to detect pulse waves and SpO₂ during wireless EEG recording, offering the possibility of remote, accurate, and stress-free point-of-care assessment for sleep quality and brain diseases. In future, next-generation digital healthcare can be directed to enable further long-term measurements and reductions in environmental burden by integrating our remote healthcare system with soft electronics such as self-healing materials, printable materials, ultrainfrared transducers, and energy-harvesting devices.[39–48]

4. Experimental Section

Fabrication of AgNW/Au-Based Track: AgNWs (average diameter, 91 nm; average length, 44 μm) were grown using a simple one-pot polyol process and dispersed in ethanol.[49] The AgNW dispersion (10 mL, 0.01 mg mL⁻¹) was sprayed onto a transparent PU substrate (5 × 12 cm, 50 μm thick, MG; Takeda Sangyo Co., Ltd.) with a carrier substrate followed by drying at 100 °C for 2–5 min.[50] A glass plate (SP111, Matsunami Glass Ind., Ltd.) was introduced as a weight to facilitate the adherence of the AgNWs to the PU substrate. Cyanide-free electroless Au plating was performed using reagents provided by JX Nippon Mining & Metals Co. (Tokyo, Japan).[51] The obtained AgNW/Au composite was subjected to room-temperature photonic sintering (PulseForge 3300, Novacentrix, Austin, TX, USA) in air at various light intensities and for different exposure times (Figure S13, Supporting Information). Eight AgNW/Au-based tracks prepared as described above were patterned using a laser ablation (MD-T1000; Keyence Co., Osaka, Japan; Figure S14, Supporting Information). A stretchable Ag paste provided by Cemedine Co., Ltd. was mask printed onto the AgNW/Au film and cured at 80 °C for 30 min to afford a terminal for the sensor sheet and stretching test. The specimen for stretching test was cut into 5 × 2 cm samples without laser ablation.

Fabrication of Ink and Blade-Coated Adhesive Electrode: An adhesive electrode was prepared using water-based dispersions of PEDOT/PSS and acrylate elastomer (BPW; Toyohem Co., Ltd., Japan). An aqueous ink after mixture was coated on a release film (provided from Fujimori Kogyo Co., Ltd., Japan) using an applicator (Tester Sangyo Co., Ltd., Japan). Then, heating was performed at 105 °C for 1 min to fabricate the adhesive electrode (20 μm thickness). The adhesive electrode was laminated on a track with pressure of 2 MPa at 50 °C for 1 min, followed by peeling off the release film. Two kinds of PEDOT/PSS dispersions were used to prepare the aqueous ink. First, the pellets (768618, Merck KgaA, Germany) were stirred with a mixture of distilled water and isopropanol (3:2 ratio) and dispersed spontaneously. Second, an aqueous solution was dispersed homogeneously (739324, Merck KgaA, Germany). Micron-sized PEDOT/PSS agglomerates formed in the adhesive electrode using the spontaneous dispersion method, whereas submicron-sized PEDOT/PSS agglomerates formed in the adhesive electrode using the homogeneous dispersion method.

Ag/AgCl microparticles were added to the spontaneous PEDOT/PSS dispersion before blade coating. The Ag/AgCl microparticles were prepared by treating Ag flakes (327077; Merck KgaA, Germany) with 18 wt% FeCl₃ solution (60 parts by weight with respect to the resulting composition; Fujifilm Wako Pure Chemical Corp.). The prepared Ag/AgCl microparticles were sequentially washed with ethanol and distilled water during filtering (HE-40T; Advantec Co., Ltd., Tokyo, Japan), dried at 110 °C for 10 min, and sieved to a pore size of 53 μm (Sanpo, Tokyo, Japan).

Fabrication of Paste and Screen-printed Adhesive Electrode: A thermosetting resin of allyl-terminated polypolyene oxide (100 parts by weight, Mr = 7–29 × 10⁶, Kaneka Corp.) was mixed with 1 wt% PEDOT/PSS ink (550 parts by weight; 768618, Merck KgaA, Germany) prepared by ultrasonication in 2-propanol/ethanol (98:2, w/w), and the alcohols were evaporated at 80 °C under atmospheric pressure. The resulting material was added to a mixture of dimethyl silicone (antifoaming agent; 2.0 parts by weight with respect to the thermosetting resin, KF-96-100cs; Shin-Etsu Chemical Co., Ltd., Japan) and methyl maleate (1.0 part by weight with respect to the thermosetting resin). The obtained mixture was supplemented with a curing catalyst consisting of a solution of the Pt(1,3-divinyltetramethyldisiloxane complex in 2-propanol (1 mL by weight with respect to the thermosetting resin, 3 wt% Pt complex solution; N.E. Chemcat Corp., Japan) and polysiloxane with two (on average) hydroxyil groups per molecule (2.5 parts by weight with respect to the thermosetting resin; Kaneka Corp.). All components were mixed by hand for 5 min with or without the addition of Ag/AgCl (4.5 parts by weight with respect to the resulting composite) or PEG (CAS number: 25322-68-3; 200, 400, and 600; Fujifilm Wako Pure Chemical Co., Japan). The prepared paste was screen printed (mesh, 360 wires/inch) on tracks and cured at 120 °C for 5 min and at 40 °C for 24 h to fabricate the adhesive electrode (20 μm thickness). The screen printer was operated at a clearance of 2 mm, an air pressure of 0.2 MPa, and a squeegee and doctor blade speeds of 30 and 50 mm s⁻¹, respectively.

Observation and Characterization: Micro- and nanometer-scale observations were performed by light microscopy (DM56; Leica Microsystems GmbH, Wetzlar, Germany), field-emission scanning electron microscopy (FE-SEM; SU8020; Hitachi High-Technologies Co., Tokyo, Japan), and scanning transmission electron microscopy (STEM; JEM-ARM200F; Jeol Ltd., Tokyo, Japan). The optical transmittance (parallel transmittance) was measured using a UV-visible–near-IR spectrophotometer (V670, Jasco International Co., Ltd.). The total light transmittance was measured using a UV-visible–near-IR spectrophotometer (V770 and ISN-923; Jasco International Co., Ltd., Tokyo, Japan). Raman analysis was performed at room temperature by laser Raman microscopy (RAMAN touch and RAMAN Viewer, Nanophoton Co., Japan) using a 532-nm laser excitation.

Electrical measurements for the AgNW/Au tracks were performed using a four-probe method involving the use of a surface resistivity meter (Loresta GP T610; Mitsubishi Chemical Analytech Co., Ltd., Kanagawa, Japan) for sheet samples and a digital multimeter (34410A; Keysight Technologies, Santa Rosa, CA, USA) for real-time monitoring. A mechanical testing machine (EZ test; Shimadzu Co., Kyoto, Japan) was used to stretch the electrodes and release them back to their initial positions.

The electrical resistivity of the adhesive electrodes was measured using the four-probe method involving the use of a chemical impedance analyzer (IM3590; Hioki E. E. Corp., Japan). The impedance analyzer was utilized with excitation in the range of 1 V.

The vertical and in-plane resistivities of the acrylate-based adhesive electrodes were measured using the impedance analyzer. A two-electrode parallel plate (effective area of 5 × 5 mm²) composed of a Ni plate and Al foil was used to measure the vertical resistivity. The thickness of the adhesive electrode sandwiched between the parallel plates was 20 μm before stretching. The dimensions of the adhesive electrode for in-plane measurement were 10 mm width, 5 mm length, and 20 μm thickness. The thickness under strains was measured using light microscopy and a micrometer. For the impedance measurements, the average values of more than three samples were calculated using the results at 10 Hz with excitation voltage of 1 V.

The PPO/Psi-based adhesive electrodes were fabricated by mask printing on a glass plate and screen printing on a polyimide film (Kapton 300H; Du Pont-Toray Co., Ltd., Tokyo, Japan). Silver electrodes with a gentle slope at the edge were fabricated on both substrates by mask printing of the silver paste (PA-301CA; Fujikura Kasei Co., Ltd., Tokyo, Japan) and heating at 100 °C for 30 min. The thickness of the silver electrode was 30 μm at the middle and 50 μm at the edge. The resistivity was calculated with the following dimensions of the PPO/PSi-based adhesive electrode: 1 cm (length) × 2.5 cm (width) × 10 μm (thickness) for the in-plane measurement of the screen-printed specimens; 3 cm (length) × 0.3 cm (width) × 40 μm (thickness) for the in-plane measurement of the mask-printed specimens; and 1 cm (diameter) × 20 μm (thickness) for the vertical measurement of the screen-printed specimens. Two printed adhesive electrodes were faced and adhered for the vertical measurements.
To record the impedance in saturated saline (NaCl) solutions (Otsuka Normal Saline; Otsuka Pharmaceutical Factory, Inc., Tokushima, Japan), we employed a chemical impedance analyzer for excitation in the range of 10 mV with the three-electrode method using a Ag/AgCl/saturated KCl reference electrode, Pt coil counter electrode, and 1-cm-window-diameter sample as a working electrode. The electrode/skin contact impedance was measured using a chemical impedance analyzer with excitation at 10 μA using the three-electrode method. The reference electrode (conductive paste with 12.5% NaCl content, used as a wet electrode, TEN20; Weaver and Co., USA) was placed on the forehead near the temple, the counter electrode (conductive paste) was located near the mastoid process, and the working electrode (sample) was placed on the forehead near the brow.[22] Each of the three electrodes had a diameter of 1 cm, and each conductive paste specimen was mounted on an Ag-based disk electrode. The thus-assembled system was also tested by measuring the electrode/skin contact impedance at 0.04 μA and 10 Hz.[28] The skin was wiped with alcohol prior to all impedance measurements. Because of the performance of the instruments, it was difficult to separate the noise without applying a certain voltage amplitude; thus, the measurement was performed on the order of millivolts.

The adhesion strength to skin was evaluated with a specimen glued on the flat surface (1 × 1 cm) of a metal tip that was attached to a tensile testing machine. The pressure applied to the skin before the test was 2–4 N/cm². The specimen was debonded at a speed of 1 mm min⁻¹. The shear strength (N/cm²) to the skin was evaluated using a specimen with an area of 2.5 × 2.5 cm that was fixed on the cramp of the tensile testing machine at a pulling speed of 300 mm/min. The evaluation of the adhesive strength to a stainless-steel plate was conducted in accordance with the test method of JIS standard Z0237.

Biological Measurements: Prior to the biological measurements, the skin was wiped with alcohol-soaked cotton wool. The wireless module used for EEG acquisition featured an eight-channel analog-to-digital converter with an effective noise of 0.3 μVmax. Bluetooth low-energy communication ability, and a 200 mAh lithium-ion battery.[28] The total module size was 3 cm × 9 cm × 6 mm, and the total weight was only 12 g. A sensor sheet with seven electrodes connected to the wireless module was placed on the forehead and sampled at 125 Hz. The stretchable transparent sensor sheet was connected to the wireless module using a custom-made flexible flat cable and an anisotropic conductive film (9703; 3M, USA). Adhesive electrodes were patterned on an entire sensor sheet or conductive paste was manually fabricated on each electrode with a diameter of 1 cm. A reference electrode with the conductive paste or the adhesive electrode was placed near the mastoid process, which was prepared separately from the aforementioned seven electrodes. Alternatively, the adhesive electrode for reference was used to increase the coverage area. A previously developed opaque stretchable sensor sheet was also used to evaluate the adhesive electrode and wet electrode.[28] The wireless electromyogram sensor device was provided by Murata Manufacturing Co., Ltd. The blood velocity was measured through the stretchable transparent sensor sheet using a laser Doppler blood flow meter (ATBF-LN1; Unique Medical Co., Ltd.).

Remote PPG Measurements: The pulse rate and SpO₂ were estimated after extracting a video (20 × 20 pixels, 30 fps) of the target area captured by a multispectral camera (50 mm/F2.8 of Lens, msCAM; Spectral Devices Inc.) using a neutral white light source (Figure S16, Supporting Information). The signals were bandpass filtered at 0.5–3 Hz before the estimation. The pulse rate was determined as the frequency with the maximum amplitude based on the fast Fourier transform (FFT) results, which were analyzed with sequentially shifted signals of 930-nm-wavelength at a fixed interval (128 samples). SpO₂ was estimated from the results of FFT analysis in the fixed interval with sequential shifts of 730-nm-wavelength (R) and 865-nm-wavelength (IR) signals. The R/IR ratio was defined as follows:[31]

$$\frac{R}{IR} = \frac{R_{AC,max}/R_{DC}}{I_{RAC,max}/IR_{DC}}$$  (1)

where $R_{AC,max}$ and $IR_{AC,max}$ are the maximum AC amplitude of the R and IR signals, respectively, and $R_{DC}$ and $IR_{DC}$ are the DC of the R and IR signals, respectively. The pulse rate and SpO₂ were simultaneously measured with a conventional on-forehead contact-type pulse oximeter (Covidien Nellcor PM1000N; Medtronic plc.).

Ethical Approval: Methods of measurement for EEG, impedance, and PPG were approved by the Osaka University Research Ethics Committee and complied with the research guidelines of Osaka University (Approval number: 31–2 and R02-1). The skin irritation tests of 20 human subjects complied with the research guidelines and had approval from the ethics committee of an external evaluation organization.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

T.A. and T.S. designed the work and wrote the manuscript. T.A., S.Y., T.U., T.N., Y.H., N.K., Y.K., J.S., and A.M fabricated and characterized sensors and systems. T.A., S.Y., T.N., H.I., and S.I. processed data obtained under acquisition of biological signals.

Data Availability Statement

Research data are not shared.

Keywords

biocompatible materials, electroencephalography, flexible electronics, photoplethysmography, transparent electrodes, wireless recording system

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