Superhydrophobic, Oleophobic, Self-Cleaning Flexible Wearable Temperature Sensing Device

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We use a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/carbon nanotube (CNT) composite as the temperature sensing layer, and the device exhibited a high sensitivity of \(-2.46\%/{ }^\circ C\). A sandpaper-molded PDMS with fluorinated surface modification protection layer is used as the superhydrophobic, oleophobic, self-cleaning protective encapsulation layer. This device exhibits a self-cleaning function when it makes contact with liquids such as water, tea, coffee, and milk. In addition, the surface can also repel liquids with low surface tension (such as oil), exhibiting good oleophobicity. Resistance to ultrasonication in an organic solvent for 120 min and a 400-cycle tape peel test reveal durability of this device. The device functions under similar conditions after 1000 bending cycles with a bending radius of 0.875 mm. In this work, we demonstrate a simple and low-cost technique to fabricate durable and wearable temperature sensing devices.

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In the modern age of technological advancement and industrialization, real-time monitoring, collection and analysis of data is crucial. Among them, body temperature is an important indicator to measure a person’s health status, and the change of body temperature depends on the metabolic and pathological state of the human body, so the data collection, analysis and interpretation of body temperature are more important. Therefore, real-time temperature monitoring can help doctors in judging the patient’s condition and in predicting potential complications, thereby enabling them to make appropriate judgments and prescribe suitable treatments for patients.

In recent years, many studies have investigated the fabrication of conductive materials on flexible substrates. Studies have developed three main types of flexible temperature sensors: pyroelectric detectors,8–11 resistive temperature detectors,12–15 and thermistors.16–20 The human body temperature range is 34 °C–42 °C; small changes in temperature over a small range are critical, and therefore, the use of negative temperature coefficient (NTC) thermistors with a fast response and high sensitivity has obvious advantages.21–23 A thermistor is a type of semiconductor in which more charge carriers become available as the temperature increases, resulting in a decrease in resistance. In other words, the resistance is inversely proportional to temperature, making NTC thermistors useful as temperature sensors.

Many temperature-sensitive conductive composites have been developed, including metal nanoparticles/nanowires,25,26 graphene,27–29 reduced graphene oxide (rGO),30,31 carbon nanotubes (CNTs),32,33 and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS).34–36 Honda et al.37 printed CNT, PEDOT: PSS and a PEDOT:PSS/CNT combination ink on Kapton. Cycling tests at \(\sim 22 \text{ }^\circ C\) to \(\sim 50 \text{ }^\circ C\) showed good repeatability, and the PEDOT:PSS/CNT showed higher sensitivity (\(\sim 0.6\%/{ }^\circ C\)) than that of both CNT and PEDOT:PSS. The interface produced by mixing PEDOT:PSS and CNT might make electron hopping the dominant electron conduction mechanism, resulting in the increased sensitivity of electrical conductivity to temperature. Kuzubasoglou et al.38 used an inkjet printing technique to print a CNT/PEDOT:PSS composite ink on textile substrates as temperature sensors. This sensor has a temperature sensitivity of \(-0.31 \pm 0.03 \%/{ }^\circ C\) from room temperature to 50 °C, and the resistance change is only 0.3% after a 1000-cycle bending test; these results demonstrate the good stability of the sensor. Ozioko et al.38 drop-cast a PEDOT:PSS/CNT composite ink on a polystyrene sulfonate (PVS) substrate as a temperature sensor and encapsulated it with polydimethylsiloxane (PDMS) to make it immune to environmental influences such as humidity. It exhibits fast response (\(\sim 4.8\) s) and recovery (\(\sim 2.5\) s) times over a temperature range of 20 °C–80 °C and a sensitivity of \(\sim 0.64\%/{ }^\circ C\). Factors such as environmental humidity and temperature will affect the service life and conduction characteristics of the sensor, especially with PEDOT:PSS as the conductive substrate of the temperature sensor. The resistance of PEDOT:PSS is easily affected by the humidity of the environment because the hygroscopicity of PSS negatively impacts the conductivity.39 Wang et al.40 developed a temperature sensor with PEDOT:PSS and systematically investigated the effect of humidity on its sensitivity.

Therefore, it is worth noting that, in addition to the successful use of electronic products in general environments, the challenge to be used in wet conditions (such as for marine divers or in human sweat) is the other general consideration. For this reason electronic products must have additional functions such as hydrophobicity, oleophobicity, and self-cleaning properties, which will protect the product from wetting and have better stability. Recently, much effort has been devoted to fabricate superhydrophobic wearable sensors. Wang et al.41 developed a wearable strain sensor with excellent mechanical robustness and liquid impalement resistance by combining fluorinated PDMS with multi-walled carbon nanotubes (MWCNTs). Sahoo et al.42 fabricated a waterproof flexible strain sensor by spraying CNT solution using oxygen plasma-treated wrinkled PDMS substrates. Liu et al.43 fabricated highly stretchable, superhydrophobic, and wearable strain sensors using laser texturing with an inexpensive CO2 laser engraver. Although superhydrophobic surfaces have been widely used in sensors, sensors with both superhydrophobicity, oleophobicity, and self-cleaning are still in demand.
To make a wearable temperature sensor practical in daily life and harsh environments, we developed a superhydrophobic, oleophobic, self-cleaning surface to encapsulate temperature sensors. The encapsulated surfaces have good resistance to organic solvents and good mechanical durability. Moreover, the wearable device can exhibit a good self-cleaning effect when it comes into contact with liquids such as water, tea, coffee, and milk. The sensitivity of the temperature sensor was not affected by the encapsulation; it remained high, being sensitivity of $-2.46$ %/°C. This should lead to a wider range of practical industrial applications in the future.

**Materials and Methods**

**Materials.**—PDMS precursors and curing agents (Sylgard 184, Dow Corning Corp, USA) are used for fabricating substrates and protective encapsulation layers. Silver nanowires (AgNWs; STAREK Scientific Co., Taipei, Taiwan) with lengths of $10–20\ \mu$m and diameters of $25–35\ \text{nm}$ were dispersed in isopropanol (IPA) and used as sensor electrodes. PEDOT:PSS (1.3 wt% in water) (Sigma Aldrich, USA) and single-walled CNT ink (Sigma Aldrich, USA) were mixed in a predetermined weight ratio for fabricating a temperature sensing layer. Silicon carbide sandpaper (4000 grit, PACE Technologies, AZ, USA) was used as a template for making superhydrophobic surfaces. 1H,1H,2H,2H-perfluoroctyltrichlorosilane (PFDTDS, 96%, Alfa Aesar, UK) and dodecane (95%, Tedla, OH, USA) were used without further purification to modify the surface of the protective layer.

**Fabrication of flexible substrates.**—The PDMS precursor and curing agent were mixed and stirred in 10:1 ratio for 15 min and then kept in a vacuum chamber for 10 min to remove air bubbles. Next, the liquid PDMS precursor mixture was spin-coated on the glass substrate at 100 rpm for 60 s; the PDMS film thickness was $0.45\ \text{mm}$. Finally, the PDMS was cured using an oven at 80 °C for 2 h.

**Fabrication of temperature sensing solutions.**—A previous study of the sensitivities of PEDOT:PSS, CNT, and PEDOT:PSS/CNT ink showed that the mixture of PEDOT:PSS and CNT can significantly improve the sensitivity. Therefore, we study the relationship between different weight ratios of PEDOT:PSS/CNT ink and the sensitivity of the temperature sensor. The mixtures were stirred at 800 rpm for one week to keep the solution from becoming viscous. Subsequently, the solution was used to produce the temperature sensing layer.

**Fabrication of temperature sensor.**—PDMS is a hydrophobic material, and its surface needs to be modified before the PEDOT:PSS/CNT ink can be deposited on it. We treated PDMS surface with oxygen plasma for 1 min to make it hydrophilic for the subsequent deposition of the sensing film. Next, AgNWs were sprayed through a shadow mask to serve as the electrodes of the temperature sensors. Finally, 10 $\mu$l of PEDOT:PSS/CNT ink solution was drop-cast on the substrate, and the drop-cast area was defined by a soft mask and heated at 40 °C with a hot plate. The temperature was increased in steps of 5 °C and held for 5 min at each step until it reached 70 °C. Subsequently, the sample was kept for 30 min until the sensing layer was cured. Figure 1 shows the fabrication process. Figure 2a shows the temperature sensor element.

**Fabrication of protective layer.**—For the protective layer, we used sandpaper-molded PDMS as it is simple and economical, can be mass-produced, and has high compatibility when encapsulating the temperature sensing layer. First, silicon carbide sandpaper was ultrasonically treated with ethanol for 15 min, blow-dried with a nitrogen gun, and oven-dried at 70 °C for 20 min. Next, the liquid PDMS precursor mixture was coated on a glass substrate, covered with silicon carbide sandpaper, and kept in a vacuum chamber for 1 h to remove air bubbles to ensure that PDMS could fully penetrate the structure of the sandpaper. After curing, the protective layer was ultrasonically treated with ethanol for 15 min, blow-dried with a nitrogen gun, and dried in an oven at 70 °C for 20 min to ensure cleanliness. It was then treated with oxygen plasma for 1 min to facilitate better grafting of the PFDTDS. We mixed 62.88 $\mu$l of PFDTDS solution with 20 ml of dodecane, resulting in concentration of 8 mM. Finally, the protective layer was immersed in the PFDTDS solution and ultrasonicated for 30 min, following which it was oven-dried at 70 °C for 20 min. Figure 2b shows the protective layer.

**Instruments.**—Field emission scanning electron microscopy (FE-SEM; JSM-7610F, JEOL) was used to inspect the surfaces of electrodes, temperature sensing layers, and protective layers. An ultrasonic cleaner (D150H, TOHAMA) was used to clean the sample and PDMS coating processes. An electric oven (GX700, YSC) was used to dry the samples. Surface modification was performed using a low pressure plasma machine (Harrick, Plasma Cleaner PDC-32G, New York, NY, USA) with 95% argon and 5% oxygen gases, pressure of 0.6 Torr, flow rate of 5 scm, and power of 7 W. Resistance measurements were performed by linear sweep voltammetry (LSV; scan rate: 20 mV s$^{-1}$) using an electrochemical workstation (Autolab PGSTAT204, Metrohm, Utrecht, The Netherlands). A goniometer (100SB, Sindatek) was used to measure the water contact angle (WCA) and oil contact angle (OCA). Deionized water droplets (5 $\mu$l) were used for measuring the static WCA. n-Dodecane (99%, Alfa Aesar, UK) (5 $\mu$l) were used for measuring the static OCA. Sliding angles (SAs) were measured using 15 $\mu$l droplets. Five measurements were taken to obtain the average WCA, OCA, and SA.

**Results and Discussion**

**Sensitivity.**—The temperature sensor measures over the temperature range of $-28^\circ\text{C}$ to $46^\circ\text{C}$ on the hot plate and a thermocouple was used to calibrate the temperature. We tested the composite ratio of PEDOT:PSS and CNT ink to determine the highest temperature sensitivity. Figure 3 shows the normalized resistance change ($R/R_0$, where $R_0$ and $R$ are the initial temperature resistance and resistance at 28 °C to 46 °C, respectively. The sensitivity of each ratio was fitted using a linear first-order curve fitting equation, and the R$^2$ values were all greater than 0.98, indicating high precision. According to Table I, the highest sensitivity ($R/R_0$) of $-2.46\%$/°C was obtained when the weight ratio of PEDOT:PSS and CNT ink was 7. Table II lists a comparison of the sensitivity among achieved in this and previous studies; these results indicate that the sensitivity ($R/R_0$) of $-2.46\%$/°C is very promising. In addition, because a PEDOT:PSS/CNT ink weight ratio of 7 has the highest sensitivity, we used the sensor with this composition to test the effect of the addition of a protective layer on the sensitivity. Figure 4 shows the results. The sensitivity without the protective layer is $-2.46\%$/°C, and after adding the protective layer, it is $-2.48\%$/°C, and the sensitivity value error is only about 0.8%. Obviously, the stability and repeatability of the sensor are good, and it is not affected by adding the protective layer.

**Bending test.**—A wearable temperature sensor must be able to maintain a mechanically and conductively stable structure under long-term use. Therefore, different bending radius and bending cycle tests were performed. Figure 5 shows the normalized change in resistance, where $R_0$ and $R$ are the resistances under flat and bent states, respectively. Figure 5a shows that the resistance change when the bending radius changes from 0.875mm to 30 mm is only at most $-2\%$ compared to that in the flat state. In addition, 1000 cyclic bending tests were performed at the smallest bending radius of 0.875 mm, and very stable performance was observed, as shown in Fig. 5b. These bending tests demonstrate the flexibility and stability of the fabricated temperature sensors. Figure 6 shows a photograph of the developed flexible temperature sensor.
Figure 1. Fabrication process of temperature sensor.

Figure 2. (a) Temperature sensor, (b) protective layer, (c) encapsulated temperature sensor, and (d) actual application image.
Superhydrophobic, oleophobic, self-cleaning surface.—In practical applications, wearable sensors are easily affected by the environmental factors such as moisture, sweat, rubbing alcohol, and cleaning agents, resulting in a short lifetime. Therefore, it is very important to have superhydrophobic, oleophobic, and self-cleaning properties, which can make the wearable sensor have a better service lifetime. The superhydrophobic surface must have a high WCA $> 150^\circ$ and low SA $< 10^\circ$. This surface can make it difficult for water droplets to stick to the surface such that the surface is not easily contaminated. This phenomenon is known as the lotus effect.

In this study we measured the static contact angles of water ($\gamma = 72.8$ mN/m) and n-dodecane ($\gamma = 25.4$ mN/m) as shown in Fig. 7.

| Weight ratio of PEDOT:PSS/CNT ink | $\alpha$ (%/°C) |
|----------------------------------|----------------|
| 1                                | −1.12          |
| 3                                | −1.93          |
| 5                                | −2.23          |
| 7                                | −2.46          |
| 9                                | −1.89          |

Organic solvent resistance test.—Ethanol, acetone, and IPA are often used in cleaning products, and 75% ethanol is used for disinfection. During the global COVID-19 epidemic, 75% ethanol has often been used for disinfection and epidemic prevention. Therefore, the wearable device’s tolerance to organic solvents is a must-have ability. In this study, we placed the protective layer in three different organic solvents (75% ethanol, acetone and IPA) and treated it with ultrasound for 30, 60, 90 and 120 min to observe the change in the superhydrophobic properties of the protective layer. Figure 9 shows that before and after ultrasonication treatment, WCA remained $\sim 153^\circ$–$154^\circ$ and SA remained $\sim 3^\circ$–$10^\circ$. The protective layer was proved to continue to maintain good superhydrophobicity and exhibit good mechanical durability after 400 cycle tape peeling tests.

Mechanical durability test.—The evaluation of the mechanical durability has always been an indicator of superhydrophobic surfaces, because problems such as collisions and scratches often occur in real-life applications. In this experimental test, we used a tape peel (3M 3036) to test the mechanical durability of the protective layer. Figure 10 shows WCA and SA as a function of tape peel cycles. After multiple tape stripping cycles, WCA remained $\sim 153^\circ$–$156^\circ$ and SA remained $\sim 3^\circ$–$8^\circ$. The superhydrophobicity (WCA $> 150^\circ$, SA $< 10^\circ$) can be maintained under long-term treatment, thus demonstrating that the wearable device has good resistance to organic solvents.
Figure 5. Normalized resistance change under different (a) bending radius and (b) number of bending cycles.

Figure 6. Photograph of flexible temperature sensor.

Figure 7. Static CA of water and n-dodecane on the protective layer.
Conclusions

A flexible temperature sensor with high sensitivity of −2.46 %/°C is demonstrated under the small change range of human body temperatures. After 1000 cyclic bending tests, the resistance change is stable, showing that the proposed wearable device has good flexibility. In addition, after being encapsulated by the superhydrophobic, oleophobic, and self-cleaning protective layer, the sensitivity was not influenced and remained stable in organic solvent resistance and mechanical durability tests. Resistance to ultrasonication in an organic solvent for 120 min and a 400-cycle tape peel test demonstrate the durability of this device. The device functions similarly after 1000 bending cycles with a bending radius of 0.875 mm. For the wearable temperature sensor, this protective layer can prolong the service life of the device and provide a good practical application experience.

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Figure 8. Photographs of self-cleaning test results on protective layer. (a) water, (b) tea, (c) coffee and (d) milk.

Figure 9. Relationship between WCA and SA with different ultrasonic treatment times under organic solvent tests.

Figure 10. WCA and SA versus number of cycles under cyclic tape peeling test.
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