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Enhanced Electrochemical and Physical Properties of Ag/AgCl Planar Reference Electrodesin Potentiometric Sensors by Graphite Oxide Layer

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Abstract: The most common reference electrode (RE) which is used in electrochemical measurements is the Ag/AgCl electrode. In this study, we present a novel solid-state Ag/AgCl planar electrode that was coated with a thin layer of Graphite Oxide (GO) as a protective layer. The Ag/AgCl planar electrode was fabricated by using the photolithography and lift-off method combined with the $Ag[NH_3]_2Cl$ complex. The GO was produced by Hummer's method and was deposited on top of the Ag/AgCl layer by drop-casting method. The layers of the fabricated reference electrode were characterized by micro Raman spectroscopy, Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX). The responding time of the planar electrode was short and the signal was more stable in comparison to the plainAg/AgCl electrode. The Open Circuit Potential (OCP) measurement with the fabricated electrode as the RE and the platinum electrode as the working electrode in electrolyte solutions which had various pH values was performed with a linear response in pH ranges from pH 5 to pH 8 and the linear correlation coefficient ($R^2 = 0.9899$). Moreover, the coating of the GO layers also enhanced the durability of the modified electrode. The results showed that the modified Ag/AgCl electrode with a thin layer GO as the protective layer could be used as plana REs for the potentiometric sensors.

Key words: Graphite oxide, potentiometric sensor, Ag/AgCl reference electrode.

1. Introduction

Nowadays, one of the most common topics which attract lots of attention of researchers is development of the electrochemical sensors that are fabricated by using the micro-fabrication techniques [1]. It is due to the advantages of the fabrication techniques such as easy process to make, effective cost and portability. In an electrochemical measuring system, a reference electrode plays an important role. There are many types of reference electrodes such as hydrogen, calomel, double junction, liquid junction or silver/silver chloride reference electrodes. The most popular material which is used to fabricate the RE is Ag/AgCl, thanks to its good properties for the electrochemical measurements. However, the restrictions of the convention Ag/AgCl electrodes are normally in macro scale and it cannot be applied in the micro-electrochemical sensors [2]. Therefore, many scientists have aimed to minimize the size or integrate the RE with other electrodes on the same platform for the biomedical or environmental purposes [2-7].

Normally, the Ag/AgCl electrode is produced by coating a thin layer of AgCl on top of asilver wire. After that, it will be dipped into a saturate KCl solution as an electrolyte liquid. In order to fabricate the micro-scaled Ag/AgCl electrode, there are numerous methods such as electrochemical coating, screen printing or thin film deposition… For example, an Ag/AgCl thin film was fabricated by Suzuki and his colleagues by Ref. [8] using sputtering and electrochemical method. At first, a thin layer of silver (300 nm) was sputtered then a layer of AgCl was grown on top of that by using chrono-potentiometric technique with a constant current of 20 μA [8].

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Another example is Kim et al. [9], they deposited a silver layer (1,000 nm) on a glass surface by using sputtering technique. Then, the Ag layer was chlorinated by a drop of $FeCl_3$ 50 mM [9]. The same concept with Kim's is Huang et al. [10], they chlorinated the silver layer by using the electrochemical technique. The AgCl layer was formed by using constant voltage of 1.0 V with the chloride solution 0.1 M HCl [10]. After the publication of Huang, lots of research on electrochemical methods has been performed with different chloride solutions (HCl, KCl, NaCl,…) or different currents or voltages to grow the AgCl layer on top the Ag platform [5, 7, 11, 12]. Some other studies preferred screen-printing technique due to its simplicity procedure. A quasi-reference electrode could be fabricated by printing all the components of the electrode step by step. For instant, on a polyester foil, Zielińska et al. [13] printed an ion-selective chloride electrode which contained silver contact, carbon and an insulating layer. Between each printing step, the ink layer was treated with different conditions like UV irradiation or heating to enhance the adhesion of each layer. Moreover, some studies proved that screen-printing techniques could combine with the electrochemical technique or it could be done with various type of ink (gel or paste) [14-16]. However, one of the disadvantages of this technique is the thickness of the printed layer. It is usually from several hundred micrometers to some millimeters. In addition, with this technique, many components are required for the paste formula, which results in less purity of the printed electrode. One common problem of the bare Ag/AgCl electrodes is the self-degradation of electrode in solutions during electrochemical measurements. Hence, a protection layer is needed to coat on top of the Ag/AgCl electrode in order to increase the durability of the RE. There are many types of the protection layer such as polymeric electrode [17, 18], nafion [9, 19], metallic layer [20] or agarose gel [14, 21].

In this study, graphite oxide produced by using Hummer's method was used as a protection layer for the specific fabricated Ag/AgCl electrode. Finally, the thin layer of graphite oxide was deposited on top of the Ag/AgCl layer to enhance its physical and electrochemical properties of the Ag/AgCl planar electrode.

2. Experiments

2.1 Materials

The fabricated Ag/AgCl electrode was fabricated by using sputtering and drop-casting a complex of $Ag(NH_3)_2Cl$ solution reported in our other article [22].

Graphite powder 99%, sulfuric acid (H_2SO_4) 98%, hydrochloric acid (HCl) 37%, hydrogen peroxide (H_2O_2) 30%, potassium permanganate ($KMnO_4$) 97% were purchased from Sigma-Aldrich, Germany. Deionized (DI) water was supplied by a DI

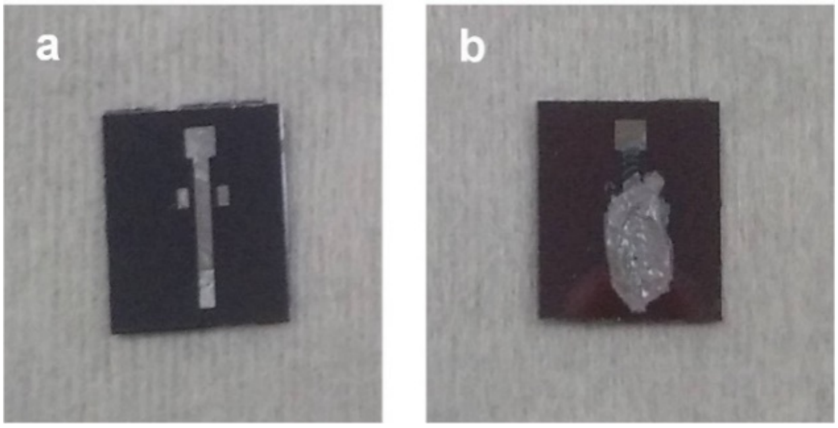

Fig. 1 The photos of the Ag electrode before (a) and after (b) being coated with the AgCl layer.

Fig. 2 The photo of the Ag/AgCl electrode after being put on the GO protective layer.

system (Purelab Ultra, Elga Co., UK), the resistance of the outlet water was 18.2 MOhms. The pH buffer solutions from Hanna Instruments Vietnam were used as electrolyte in the electrochemical measurements.

2.2 Process of Producing Graphite Oxide (GO) by Using Hummer's Method

In a 100 mL flask, 1.5 g of graphite powder was added into 35 mL of concentrated H_2SO_4 and stirred with 150 r.p.m in 15 minutes. The flask was put in an ice bath to prevent the heat of the reaction. After that, 5 g of $KMnO_4$ was slowly added into the flask. The whole solution was stirred with 250 r.p.m in 2 hours at 40 °C. Then, 60 mL of DI water was poured in the flask and solution was continuously stirred for 15 more minutes. All the solution was transfered into a new 500 mL beaker and added in 100 mL of DI water, 15 mL H_2O_2. The solution was kept stirring for further 30 minutes. At this stage, the color of the solution changed from dark brown to yellow. Next, the solution was washed with 50 ml DI water and 40 mL HCl 37% and the solution was continuously stirred for next 2 hours. For the next step, 350 mL of DI water was added into the solution and the solution was stirred for the next 1 hour. After that, the solution was let settle down for 1 day in order to separate the liquid and solid phase inside the beaker. Finally, the liquid inside the beaker was dismissed. The yellow-brownish gel which stayed at the bottom of the beaker was the graphite oxide solution.

2.3 Fabrication of Graphite Oxide and Ag/AgCl/GO Electrode

The GO solution was diluted with DI water (1:100) then shaked well and drop-casted on the surface of the fabricated Ag/AgCl electrode. After that, the Ag/AgCl/GO electrode was dried at 100 °C within 30 minutes (Fig. 2).

2.4 Characterization of the Ag/AgCl/GO

2.4.1 Characterization

The surface morphology was observed with Field Emission Scanning Electron Microscopy—FE-SEM (SU8000, Hitachi, Japan). The composition of Ag/AgCl/GOthin film was detected by Energy Dispersive X-ray Spectroscopy (EDS), Micro Raman spectroscopy with Lab RAM 300 (Jobin Yvon, France).

2.4.2 Potential Measurements

The electrochemical properties of the fabricated Ag/AgCl/GO electrode were characterized by using Autolab PGSTST, 302N, Metrohm, the Netherlands. The Open Circuit Potential (OCP) in the pH buffer solutions was performed with the fabricated Ag/AgCl/GO electrode as the reference electrode. A thin film Pt (0.5 mm in width and 1.5 mm in length) was used as a working electrode.

3. Results and Discussion

3.1 Characterization of GO and Ag/AgCl/GO

The GO layer was formed neatly on top of the Ag/AgCl surface. As shown in Fig. 3, it is clearly shown that the surface morphology of the fabricated Ag/AgCl/GO electrode is formed by multi-layers which lied on top of each other. The thickness of the GO multi-layer was approximately 300 ± 20 nm. On the other hand, the physical stability of the modified electrodes was tested. A quick test was carried out by immersing the modified electrode in DI water and pH 7 buffer solution for 24 hours. After one day, the surface of the modified Ag/AgCl/GO electrode was remained stable and was not damaged whereas the Ag/AgCl electrode was stripped off from the platform just in less than 1 hour. It was proved that the GO layer enhanced the physical property (durability) of the fabricated Ag/AgCl electrode.

Chemical analysis of the Ag/AgCl layers fabricated on the Si/SiO_2 substrates was performed by using Energy Dispersive X-Ray Spectroscopy (EDX) with normal scan and mapping modes. The EDX results (Fig. 4) showed the peaks of the elements presented in the electrode, which are well-matched with the literature EDS results [17]. The elements such as Ag, Cl, C and O were detected in the electrode. From this result, it can be said that a GO layer was formed on the surface of the Ag/AgCl thin film and the Ag/AgCl electrodes were produced with high purity.

Moreover, the change in the structure and the effect of interaction between each layer and element could also be obtained by using the Raman spectra (Fig. 5). The two identical peaks of the graphitic material (D and G bands) were found in Ag/AgCl/GO around 1,350 cm^{-1} and 1,590 cm^{-1}, respectively [23].

3.2 Electrochemical Properties

3.2.1 The Stability of the Fabricated Ag/AgCl/GO Electrode

One of the important factors of the electrochemical sensor performance is the long-term stability. The potential and the responding time of the fabricated electrode were observed in 5 days using a 3 M KCl solution (Fig. 6).

The potential of the fabricated electrode varied by approximately 0.05 mV. It proved that the potential of the electrode remained quite stable over the test period (5 days). Moreover, the potential signal became stable within 20 s after the electrode had been immersed into the solutions during each of the measurements. The results indicated that the fabricated Ag/AgCl/GO electrode had an excellent responding time and it could be stable for long time (5 days). It is clearly shown that the fabricated electrode can be used as a

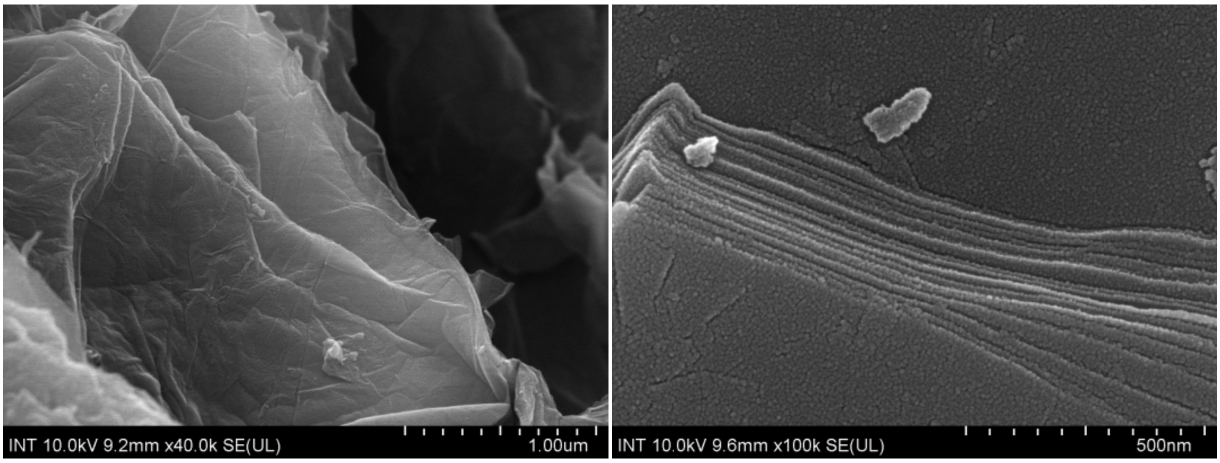

Fig. 3 The surface morphology of the electrode as observed using FE-SEM.

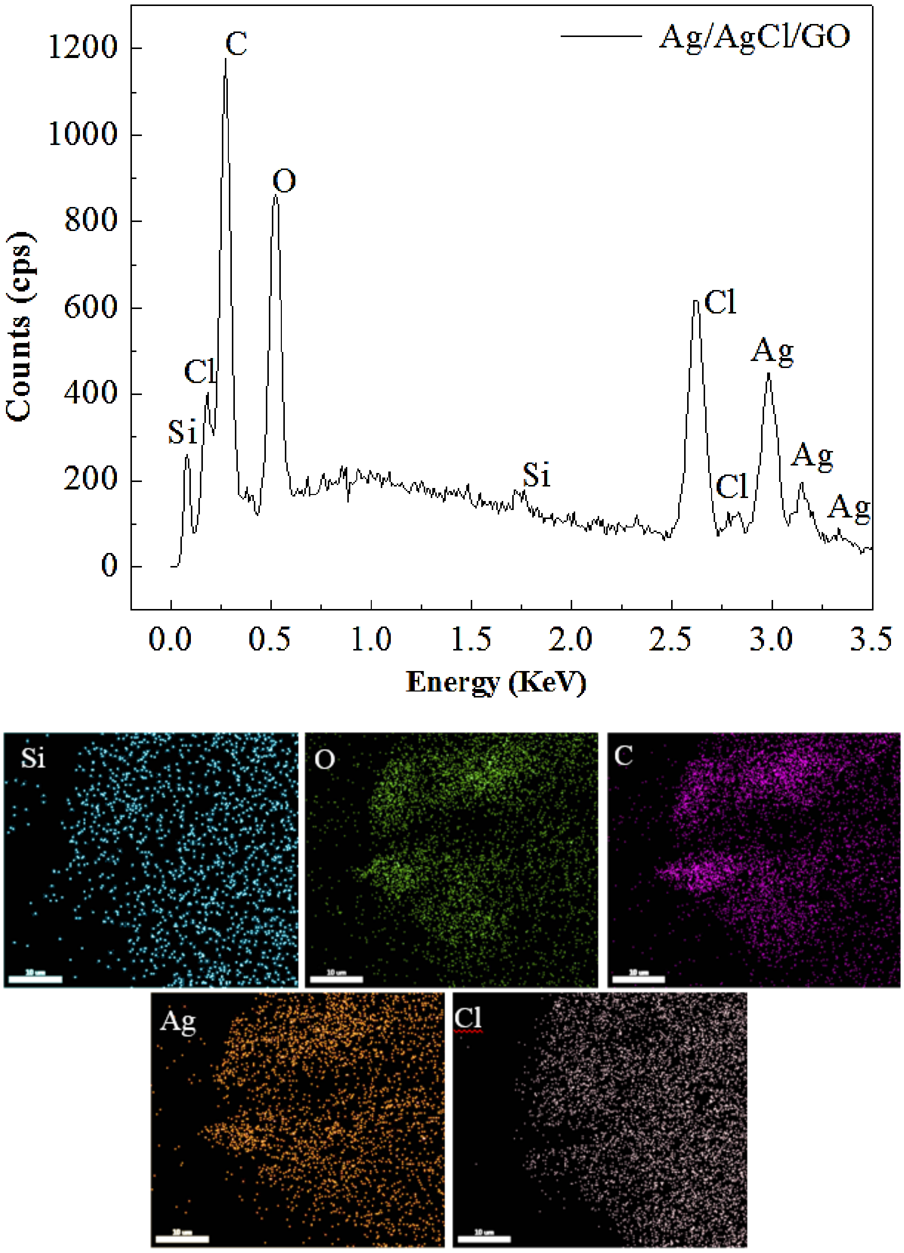

Fig. 4 **The EDS spectrum of the Ag/AgCl layer (top) and EDS mapping of Ag, Cl, C, Si, O.**

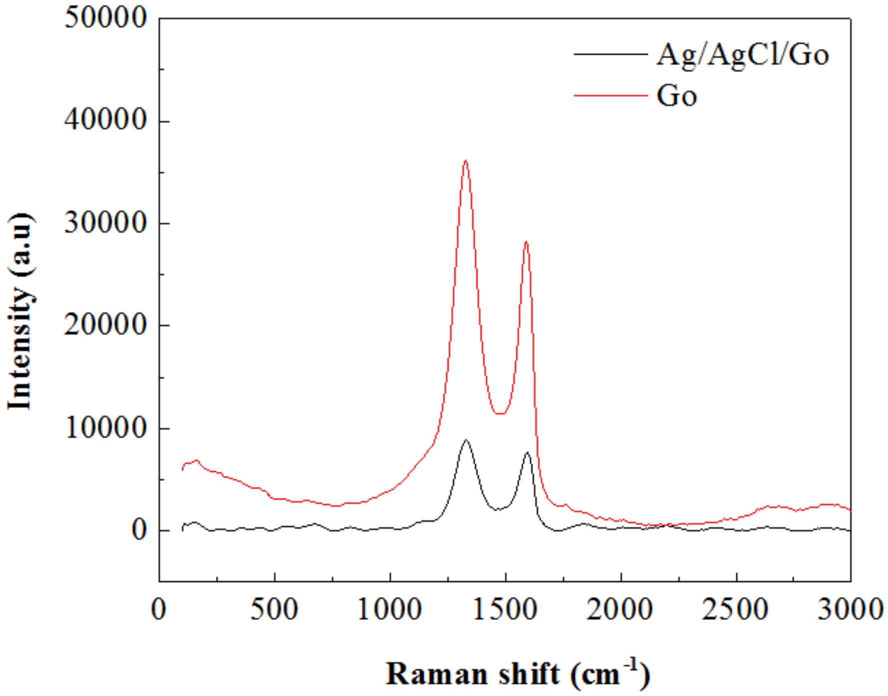

Fig. 5 The Raman spectra of the Ag/AgCl/GO electrode.

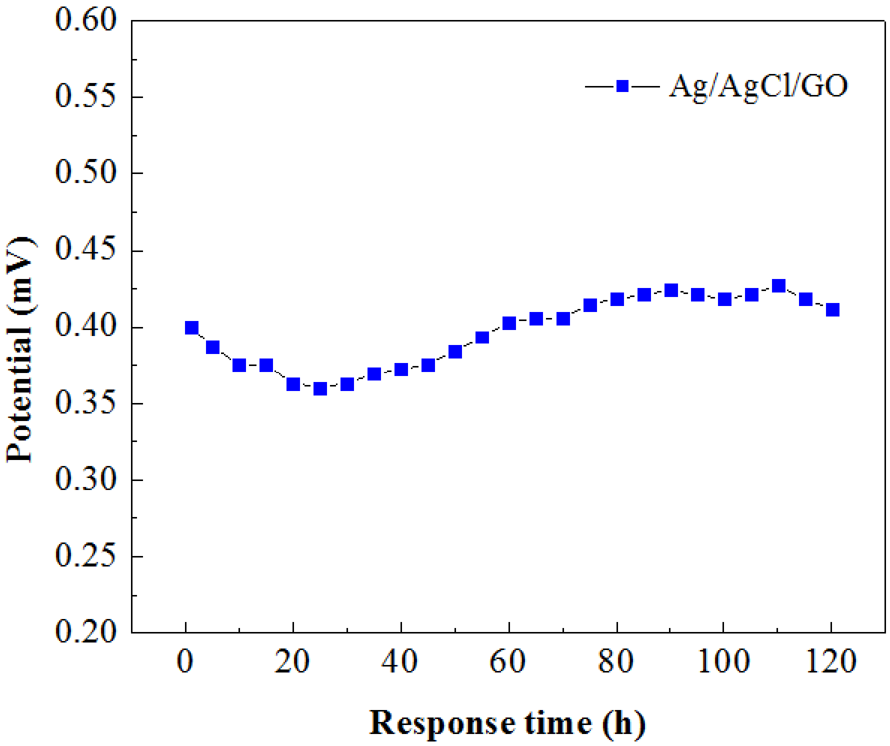

Fig. 6 The responding time and potential of the fabricated electrode were measured in a 3 M KCl solution over 5 days.

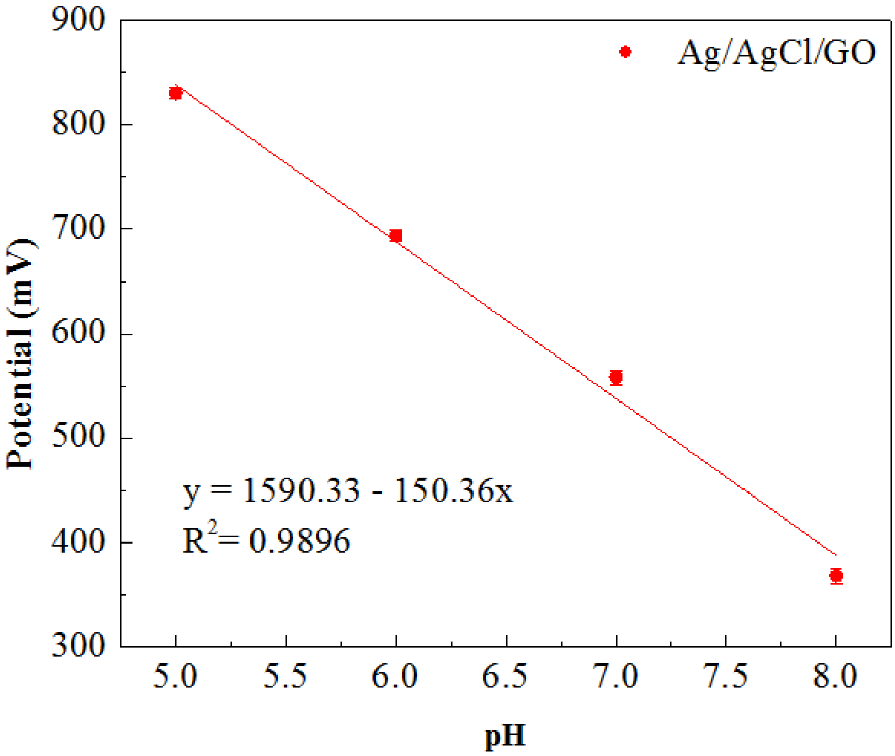

Fig. 7 The potential values of the Pt chips with the Ag/AgCl/GO electrode as the reference electrode.

reference electrode in the potentiometric sensor and provide a good signal.

3.3 Effect of pH on the Fabricated Electrode

The effect of pH on the fabricated electrode was investigated in the solutions with pH varying from 5-8. The fabricated electrode was dipped in the pH solutions. The potentials were measured versus the fabricated Ag/AgCl/GO electrode as the reference electrode and the platinum electrode was used as the working electrode. The potential response was plotted (Fig. 7). The operation was performed for 60 s for every electrolyte solution at temperature of 30 ± 2 °C.

The potential respond of fabricated electrode exhibited a linear response in pH ranges (5-8). The sensitivity was calculated to be -150.36 mV/pH and the linear correlation coefficient was greater than 0.9899.

4. Conclusion

In this article, a thin layer of GO as protective layer was fabricated on top of the surface of the Ag/AgCl electrode by a simple technique. With the presence of the GO layer, the physical (durability) and the electrochemical properties of the fabricated Ag/AgCl electrode were enhanced. With all these results, the fabricated Ag/AgCl/GO electrode showed a good sight that it could be used as a planar reference electrode in potentiometric sensor.

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