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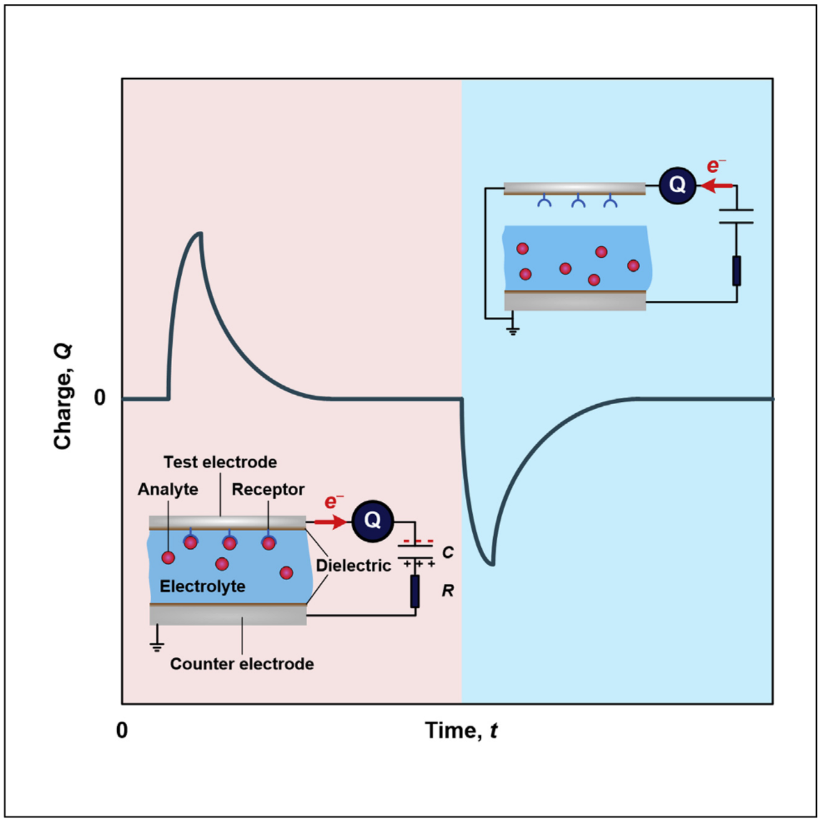
Chemical sensing by interfacial voltage



In this work, Wang et al. describe an approach to chemical sensing by interfacial voltage. The sensors de-integrate adsorption and detection, enabling flexible choice of electrodes and rapid prototyping of receptor-analyte pairs. Several species of ions and organic molecules are detected using electrodes of various metals and receptors of various molecular weights.

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Highlights

An approach to chemical sensing by interfacial voltage is developed

The design de-integrates adsorption and detection

No microfabrication is required for device use

Wearable chemical sensing is demonstrated, and biological tissues are tested

Wang et al., Cell Reports Physical Science 3, 101119
November 16, 2022 © 2022 The Author(s).
https://doi.org/10.1016/j.xcrp.2022.101119

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Physical Science

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Chemical sensing by interfacial voltage

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SUMMARY

Developing methods for chemical sensing is of importance in broad applications, including food safety, healthcare, and ecology. The work herein describes an approach to chemical sensing by interfacial voltage. A test electrode is coated with a dielectric and a receptor. When the test electrode contacts an electrolyte, the receptor adsorbs an analyte from the electrolyte. The adsorption generates an interfacial voltage, a measurement of which reports the concentration of the analyte. This design de-integrates two aspects of sensing: adsorption and detection. Consequently, the test electrode can be made of any electronic conductor. This flexibility enables sensors to be fabricated without microelectronic facilities. Several species of ions and organic molecules are detected, and a wearable chemical sensor worn on a fingertip is demonstrated. Needle-shaped electrodes are developed to test soft biological tissues. Chemical sensing by interfacial voltage holds promise for the development of ubiquitous sensing technology.

INTRODUCTION

Ubiquitous sensing is under development to enable the Internet of everything and everyone.[1–7] Detection of substances in a complex background is vital for food safety, healthcare, and ecology. Compared with thermal and mechanical sensing, chemical sensing faces a particular challenge: the world has numerous chemical species.[8–11] Established methods of chemical sensing include atomic absorption spectroscopy,[12] inductively coupled plasma mass spectroscopy,[13] electrochemistry,[14] and fluorescence.[15] New methods of chemical sensing are also being developed, such as hydrogel interferometry,[16,17] flexible nano-electronic nose,[18] and wearable osmotic-capillary patch.[19]

Here, we describe an approach to chemical sensing by interfacial voltage (Figure 1A). The approach measures the concentration of an analyte in an electrolyte. A test electrode is coated with a dielectric and a receptor. When the test electrode contacts the electrolyte, the receptor adsorbs the analyte, which generates an interfacial voltage. A measurement of the interfacial voltage reports the concentration of the analyte in the electrolyte. The interfacial voltage results from the physisorption of the analyte so that no electrochemical reaction takes place—that is, no electrons cross the interface. For electrochemically active electrodes, a dielectric passivates the electrode, retards electrochemical reaction, and stabilizes the sensor. The dielectric can also function as a substrate to anchor receptors. As noted below, thin dielectric layers have been used in electrolyte-insulator-semiconductor devices.[20]

RESULTS AND DISCUSSION

Working principle

We measure the interfacial voltage as follows (Figure 1A). A counter electrode is grounded and immersed in an electrolyte containing an analyte. A test electrode

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https://doi.org/10.1016/j.xcrp.2022.101119

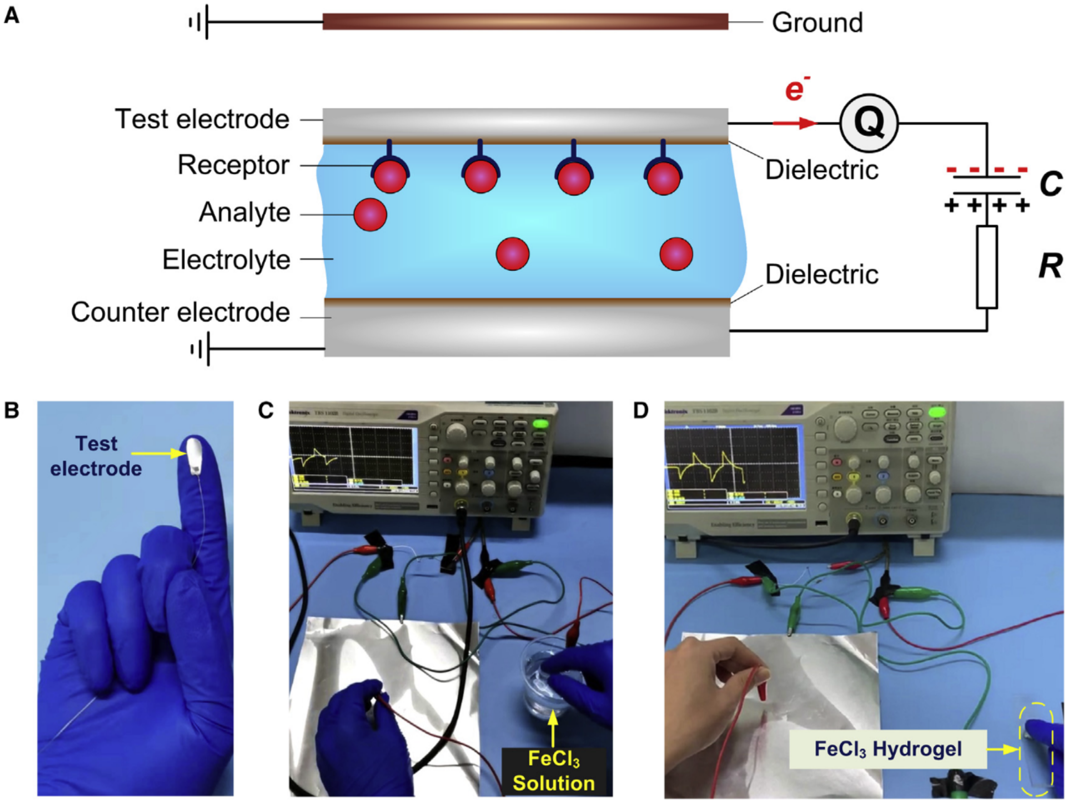

Figure 1. Chemical sensing by interfacial voltage

(A) A schematic of the two aspects of chemical sensing: an interface that adsorbs an analyte, and an electrical circuit that measures interfacial voltage.

(B) A small piece of aluminum foil is glued to the surface of a rubber glove as a test electrode.

(C and D) A hand wears the glove, and the finger moves to make the test electrode switch (C) between the ground and an aqueous solution and (D) between the ground and a hydrogel.

is coated with a dielectric and a receptor and is connected in series to a charge amplifier, a capacitor of capacitance C, a resistor of resistance R, and the counter electrode. The test electrode is cleaned and grounded before use. When the test electrode contacts the electrolyte, the interfacial voltage U develops. The electrode/dielectric/electrolyte interfaces act as a power source of voltage U, charging the capacitor. The charge on the capacitor changes with time t as $Q(t) = Q_{eq}[1 - \exp(-t/RC)]$, where Q_{eq} is the charge on the capacitor in equilibrium. The charge amplifier records Q_{eq}, which gives the interfacial voltage by $U = Q_{eq}/C$.

Our approach can be compared with well-established electrochemical sensors.[14] Electrochemical sensors include ion-selective electrodes[21] and electrolyte-insulator-semiconductor (EIS) devices.[20,22] An EIS device without an electrochemical reaction detects the adsorption of an analyte by applying a gate voltage and measuring the voltage-current curve between the source and drain. An EIS device integrates the two aspects of chemical sensing: adsorption and detection. By contrast, our approach de-integrates them so that the test electrode can be made of any electronic conductor to meet various requirements (softness, stretchability, transparency, biocompatibility, biodegradability, etc.). The construction of the sensor requires no microelectronic fabrication. The ease of fabrication enables rapid prototype of receptor-analyte pairs. Furthermore, the de-integration of adsorption and detection broadens the scope of chemical sensing for emerging applications, such as wearable and biodegradable devices. As a demonstration, we glue a small piece of aluminum foil as a test electrode to the surface of a rubber glove (Figure 1B). A hand wears the glove, and a finger moves between the ground and an electrolyte. Two types of electrolytes are tested: an aqueous solution and a hydrogel, both of which contain an analyte, 10^{-5} M of $FeCl_3$. When the test electrode contacts the solution or the hydrogel, an interfacial voltage develops, which charges a capacitor. The outputs of the charge amplifier are displayed by the oscilloscope (Figures 1C and 1D). The interfacial voltage is sensitive to analyte but insensitive to deformation of the finger (Videos S1 and S2).

We next study the physics and chemistry of chemical sensing by interfacial voltage. We design the external circuit as follows. The capacitance C of the capacitor should be small compared with the capacitance of the electrode/dielectric/electrolyte interfaces so that the capacitor negligibly affects the interfacial voltage. The thickness of the dielectric is taken to be comparable to, or smaller than, the Debye length at the interface so that the capacitance of the electrode/dielectric/electrolyte interfaces is comparable to that of an electrode/electrolyte interface. A representative value of the interfacial capacitance per unit area is 0.1 F/m^2.[23] For an interface of area of 1 cm^2, the interfacial capacitance is 10 μF. The capacitor should also be chosen such that Q_{eq} is within the detection range, which is 10^{-14}–10^{-7} C for the charge amplifier used in this work. Take a representative value of the interfacial voltage, $U = 0.1$ V. For the equilibrium charge on the capacitor, $Q_{eq} = CU$, to stay within the detection range of the charge amplifier, the capacitance needs to be in the range $C = 10^{-13}$–10^{-6} F.

The time needed to charge the capacitor is RC. This RC delay time may be compared with the time for the adsorption of the analyte to set up the equilibrium interfacial voltage. The receptor traps the analyte in the electrolyte through physisorption, which is typically fast, in a range between 1 fs and 1 ns.[24,25] Thus, the time needed to reach the equilibrium interfacial voltage U is determined by the diffusion of the analyte over a distance on the scale of the Debye length. Taking representative values of the Debye length $L = 1$ nm and the diffusivity of ions $D = 10^{-9}$ m^2/s, the diffusion time is $t \sim L^2/D = 10^{-9}$ s. The RC delay time should also be chosen to fall within the range of detection time of the charge amplifier, which is 10^{-5}–10 s. Consequently, the response time of the sensor is limited not by adsorption and diffusion of the analyte but by the detection time of the charge amplifier.

Sensing performance

Unless otherwise specified, the capacitance of the capacitor is $C = 1$ μF, the resistance of the resistor is $R = 100$ kΩ, and $RC = 0.1$ s. The counter electrode is gold. As a demonstration, an aluminum foil is used as the test electrode. On the surface of aluminum is a dense and thin layer of native aluminum oxide.[26,27] The oxide is a dielectric, passivates aluminum, retards electrochemical reaction, and stabilizes the sensor. We switch the test electrode between the ground and an aqueous solution of 10^{-5} M $FeCl_3$ multiple times and record the output of the charge amplifier by an oscilloscope (Figure 2A). The output of the sensor is repeatable. Because the capacitor and resistor are chosen such that the charging time of the capacitor is much shorter than the discharging time of the charge amplifier, the output of the charge amplifier rises steeply to a peak and then decays over the discharging time of the charge amplifier. The peak is the equilibrium charge on the capacitor, Q_{eq}. When the test electrode is switched from the electrolyte to the ground, the capacitor discharges, and the charge in the circuit flows in the opposite direction. The

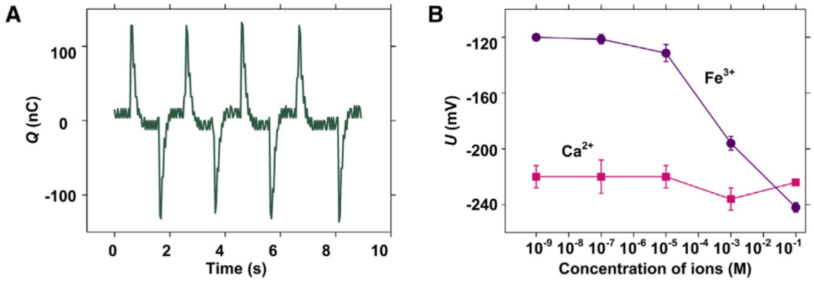

Figure 2. Chemical sensing using aluminum as the test electrode

(A) Outputs of the charge amplifier as the test electrode is repeatedly switched between the ground and an aqueous solution of $FeCl_3$ at a concentration of 10^{-5} M.

(B) The interfacial voltage as a function of concentration of Fe^{3+} and of Ca^{2+}.

Each data point represents the mean and standard deviation of 3–5 measurements.

magnitudes of the positive and negative peaks of charge are similar. The measured interfacial voltage, $U = Q_{eq}/C$, varies with the concentration of Fe^{3+} (Figure 2B).

The sensor can detect the concentration of Fe^{3+} as low as 10^{-9} M. By contrast, the sensor is insensitive to Ca^{2+}. The sensor is durable and its output is stable during the 21 days tested (Figure S1). We have separately used a commercial battery to charge a capacitor to confirm that the measured peak of charge is the equilibrium charge on the capacitor (Figure S2). To further ascertain the above choices of capacitance and resistance, we detect the $FeCl_3$ solution of 10^{-5} M using various values of capacitance (Figure S3) and resistance (Figure S4). The results indicate that the interfacial voltage is similar.

Selective sensing

Sensing by interfacial voltage can be made selective by using different receptors. As an example, we graft poly(acrylic acid) (PAA) chains to the surface of an aluminum foil, which is then used as a test electrode in contact with an aqueous solution of $CaCl_2$ (Figure 3A). The deprotonated carboxyl groups on the PAA chains interact with Ca^{2+}.[28] To ensure that the charge amplifier works within its detection range, in this case, the capacitance of the capacitor is $C = 10$ nF and the resistance of the resistor is $R = 10\ \text{M}\Omega$. Our measurement shows that the chemical sensor using aluminum with PAA chains is sensitive to Ca^{2+} but insensitive to Fe^{3+} (Figures 3B and 3C). By contrast, the chemical sensor using aluminum without PAA chains as the test electrode is sensitive to Fe^{3+} but insensitive to Ca^{2+} (Figure 2B).

The sensitivity depends on the amount of deprotonated carboxyl groups available for interacting with Ca^{2+}. Recall that $pK_a = -\log\left(\frac{[COO^-][H^+]}{[COOH]}\right)$ and $pH = -\log[H^+]$. When $pH > pK_a$, $\frac{[COO^-]}{[COOH]} > 1$, and more carboxyl groups are deprotonated than not. PAA is a weak acid with $pK_a = 4.5$ at room temperature. As pH increases, more carboxyl groups are deprotonated and available to interact with Ca^{2+} so that the interfacial voltage is higher (Figure 3D). Even at the low pH (1.5), Ca^{2+} can still be detected over a wide range of concentration. We then graft PAA chains on aluminum using precursors of various concentrations of the acrylic acid monomer. At low concentrations of the monomer, the PAA chains are short, and the sensitivity is low (Figure 3E). These experiments indicate that chemical sensing by interfacial voltage can selectively detect various analytes via specific surface modifications of the test electrode.

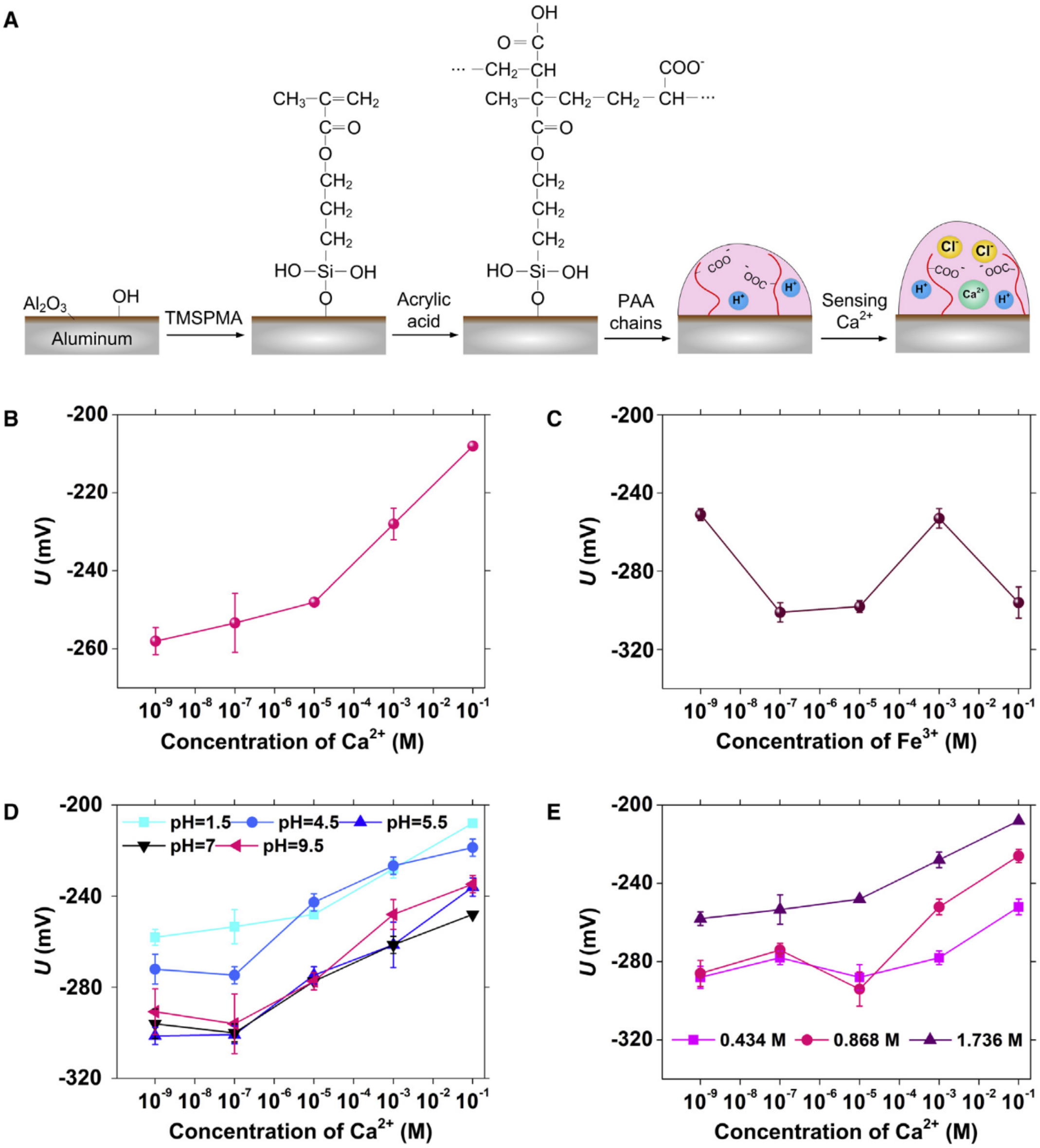

Figure 3. Selective chemical sensing using different receptors

(A) Poly(acrylic acid) (PAA) chains are grafted on the surface of aluminum foil, which is then used as a test electrode.

(B) The interfacial voltage measured when the test electrode with PAA chains contacts $CaCl_2$ solutions of various concentrations.

(C) The interfacial voltage measured when the test electrode with PAA chains contacts $FeCl_3$ solutions of various concentrations.

(D and E) The interfacial voltage between the aluminum with PAA chains and $CaCl_2$ solutions of various concentrations, when the aluminum with PAA chains is prepared with precursors of various (D) pH and (E) concentrations of monomer.

Each data point represents the mean and standard deviation of 3–5 measurements.

Detection of metal ions and organic molecules

We further show that the chemical sensor can detect various metal ions and organic molecules commonly existing in industrial wastewater (Figure 4). In principle, various test electrodes can be used. As examples, we employ copper (Figures 4A and 4B) and gold (Figures 4C and 4D) as the test electrode to measure interfacial voltage of various metal ions. A copper test electrode detects Fe^{3+} of ultralow concentration of 10^{-17} M (Figure 4A). We compare the sensitivity of

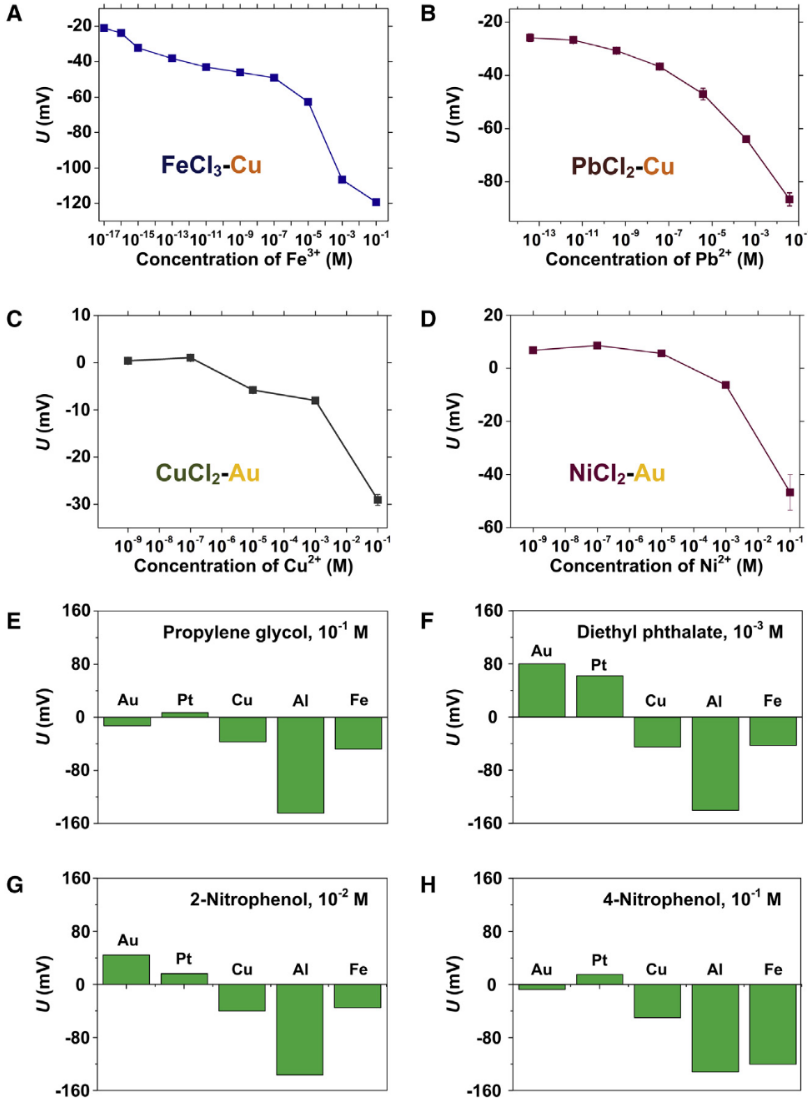

Figure 4. Chemical sensing of various metal ions and organic molecules using various test electrodes

For metal ions, $C = 1$ μF and $R = 100$ kΩ. For organic molecules, $C = 10$ nF and $R = 10$ MΩ.

(A and B) Interfacial voltage as a function of concentration of (A) $FeCl_3$ and of (B) $PbCl_2$ using copper as the test electrode.

(C and D) Interfacial voltage as a function of concentration of (C) $CuCl_2$ and of (D) $NiCl_2$ using gold as the test electrode.

(E–H) Interfacial voltage of organic molecules using various test electrodes: (E) propylene glycol (10^{-1} M), (F) diethyl phthalate (10^{-3} M), (G) 2-Nitrophenol (10^{-2} M), and (H) 4-Nitrophenol (10^{-1} M). Each data point represents the mean and standard deviation of 3–5 measurements.

Fe^{3+} of the chemical sensor with that of the luminol test. The luminol test, a chemiluminescence reaction triggered by iron-enhanced oxidation of luminol, has long been used to detect bloodstains with sensitivity of 1 μL blood in 1 L water.[29] As the concentration of Fe^{3+} in blood is ~1 μg/mL,[30,31] its sensitivity of Fe^{3+} is ~10^{-11} M. By contrast, the sensitivity of Fe^{3+} of our sensor is six orders of magnitude higher than that of the luminol test.

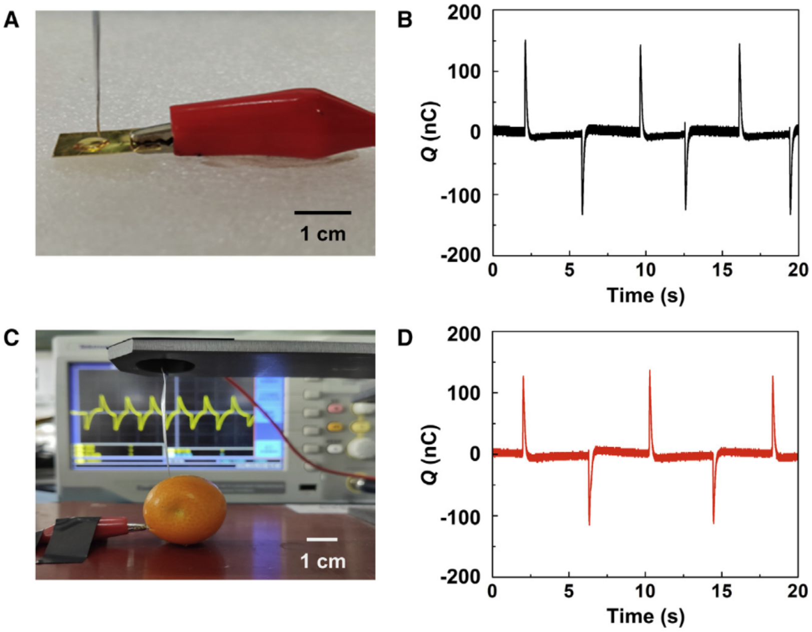

Figure 5. Chemical sensing using a needle test electrode

(A) A droplet of $FeCl_3$ solution (10^{-5} M) is placed on a sheet of grounded gold counter electrode, and the aluminum needle electrode is switched between the droplet and the ground.

(B) Measured signal.

(C and D) Measurements when the aluminum needle electrode is inserted into a kumquat. Scale bar: 1 cm. C = 10 nF and R = 10 MΩ.

We have also detected various analytes ($FeCl_3$, $CuCl_2$, $NiCl_2$, $CdCl_2$, and $PbCl_2$) using various test electrodes (Al, Al with PAA chains, Au, Cu, and Fe) (Figures S5–S11). In addition, we demonstrate detections of various organic molecules (Figures 4E–4H).

We make an aluminum test electrode in the shape of a needle by cutting a 0.2-mm-thick aluminum plate into a triangular shape using scissors. We place a droplet of $FeCl_3$ solution on a sheet of gold counter electrode, which is grounded, and switch the needle test electrode between the droplet and the ground (Figure 5A). The counter electrode and test electrode are connected to an external circuit as described before. The signal recorded using the needle aluminum test electrode (Figure 5B) is similar to that using a plate aluminum test electrode (Figure 2A). This observation confirms that the signal is independent of the shape and area of the test electrode. The needle-shaped test electrode enables us to measure biological tissues. As a demonstration, we insert the gold sheet counter electrode into a kumquat, an orange-like fruit with a soft skin (Figure 5C). After the aluminum needle test electrode is inserted into the kumquat, removed, and has made contact to the ground, an electrical signal is recorded (Figure 5D; Video S3).

As shown in Figures 2A, 5B, 5D, and S1–S11, reversibility of the sensor under various ionic conditions is good. For long-term use, the test electrode needs to contact the electrolyte multiple times, and some adsorbed analytes from the electrolyte may stay on the surface of the test electrode, leading to a decrease in the number of receptors available for further detection of the analytes. Consequently, the stability of the sensor depends on the type of the test electrode and electrolyte, as well as on the contacting time between the test electrode and the electrolyte.

Our approach to chemical sensing by interfacial voltage relies on non-faradaic interfaces. The species and concentration of analytes affect not only adsorption but also the Debye length. Consequently, quantitative prediction of sensitivity is difficult.

In summary, we have developed chemical sensors by interfacial voltage. The interfacial voltage can be measured accurately by choosing the external capacitor and resistor. The approach de-integrates two aspects of chemical sensing: adsorption and detection. Consequently, sensors can be fabricated without using microfabrication facilities, and receptor-analyte pairs can be screened at low cost. The de-integration allows the test electrode to be made of any electronic conductor. In principle, the electrodes can be made stretchable, transparent, and biodegradable. A multiplex detector may be designed and trained to simultaneously detect multiple analytes and their concentrations in a confounding background. The approach broadens the scope of chemical sensing for the development of emerging applications such as wearable and implantable devices.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information should be directed to the lead contact, Prof. Zhigang Suo (suo@seas.harvard.edu).

Materials availability

This study did not generate new unique reagents.

Data and code availability

All study data are included in the article and/or supplemental information. Any additional requests for data will be fulfilled by the lead contact upon reasonable request.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.xcrp.2022.101119.

ACKNOWLEDGMENTS

This work was supported by NSF through the Harvard University Materials Research Science and Engineering Center DMR2011754. S.Z. was supported by NSFC (12002259) and Post-doctoral Innovation Talent Program of China (BX20200271). K.J. was supported by NSFC (11872292).

AUTHOR CONTRIBUTIONS

Y.W. and Z.S. conceived the idea. Y.W., S.Z., K.J., and Z.S. designed the study and interpreted the results. Y.W., S.Z., Y.B., and K.J. conducted the experiments. Y.W. drafted the manuscript with input from all other authors. Z.S. and K.J. supervised the study.

DECLARATION OF INTERESTS

The authors declare no competing interest.

Received: June 15, 2022
Revised: August 28, 2022
Accepted: October 4, 2022
Published: October 24, 2022

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