

Highly Stretchable and Robust Electrochemical Sensor Based on 3D Graphene Oxide–CNT Composite for Detecting Ammonium in Sweat

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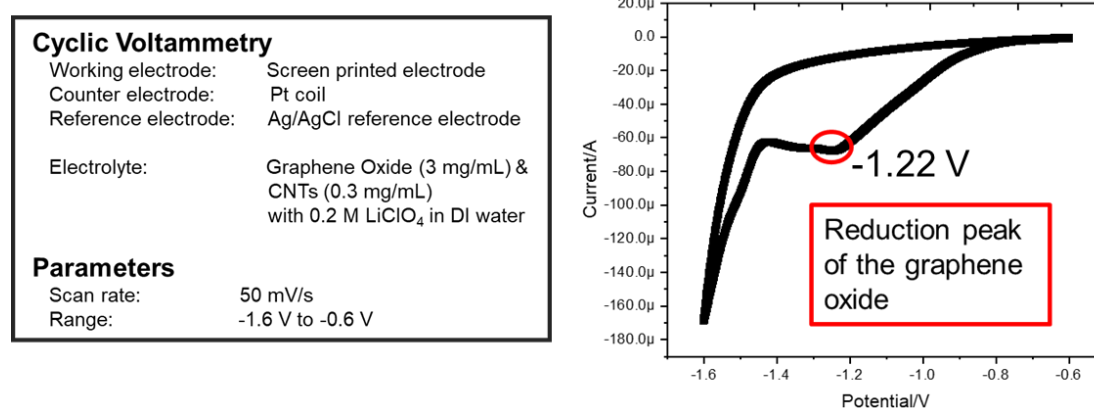


Figure S1. Cyclic voltammetry (CV) for determining the reduction voltage peak of Graphene oxide (GO) solution (3 mg/mL) containing 0.2 M LiClO₄.

(a)

Electrodeposition

Working electrode: Screen printed electrode
Counter electrode: Pt coil
Reference electrode: Ag/AgCl reference electrode
Electrolyte: Graphene Oxide (3 mg/mL) & CNTs (0.3 mg/mL) with 0.2 M LiClO₄

Parameters

Constant voltage: -1.22 V
Deposition time: 300 s

Reduction

Electrode: Screen printed electrode
Electrolyte: 1 g vitamin C in 100 mL DI water

Parameters

Temperature: 40 °C
Soak time: 2 h

(b)

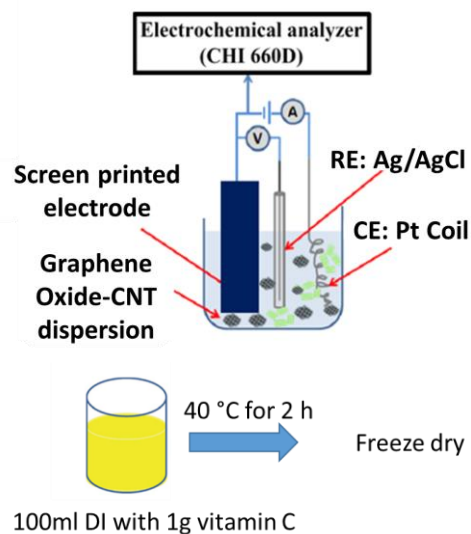


Figure S2. Detailed modification process of the Graphene-CNT layer: (a) Key parameters; (b) Setup.

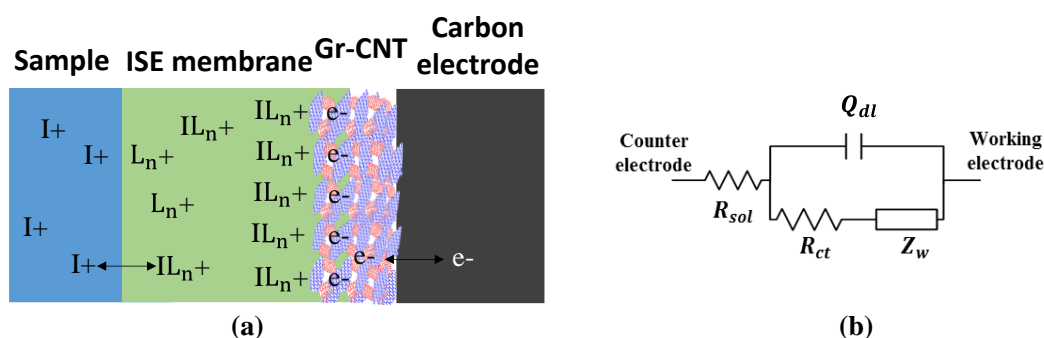


Figure S3. (a) Schematic diagram of the layer structure and interfaces in the sensing process, (b) equivalent circuit model (ECM).

Table S1 Key parameters in ECM for EIS measurement.

	$R_{sol}(\Omega)$	$R_{ct}(\Omega)$	$Z_w (\Omega \cdot s^{-1/2})$	$Q_{dl}(S \cdot s^n)$	n
SPC/ NH_4^+ ISM	5860	1.47×10^7	3.5×10^7	1.59×10^{-10}	0.802
SPC/Graphene-CNT/ NH_4^+ ISM	5240	5.8×10^6	2.2×10^7	3×10^{-10}	0.867

R_{sol}: **Solution resistance**, which is unaffected by the target ion

R_{ct}: **Charge transfer resistance**, which is influenced by the energy potential with the complex ion transfer, and it affects the electrostatic and steric energy barrier with the ion passing

Z_w: **Warburg impedance**, which stands for the impedance at low frequencies and it governs the delay arising from the diffusion of redox species to the electrode

Q_{dl}: **Nonideal electrochemical double layer capacitance**, which describes the quantity of charge formed in the electrical double layer

n: index, which reflects the perfection of Q_{dl}

Electrochemical Mechanism for the Selective Detection of NH_4^+ Cations

An ion-selective electrode (ISE) based sensor is an electrochemical sensor that converts the activity of the selected ions in a sample solution to a potential output. NH_4^+ ISE contains a thin membrane which achieve the selective binding of a target ion NH_4^+ when ions are transported from the high concentration end to the low concentration end. The ISE usually consists of the following components: (1) Ionophore, (2) common matrix polymer (e.g. PVC), (3) plasticizer (e.g. NOPE, DOS, DOA, etc.) and (4) ionic site (e.g. ETH 500, KTFPB, etc.)

The samples analyzed by ISE contain a number of ions. To obtain a film to selectively absorb and combine with the target ions NH_4^+ , the NH_4^+ -selective membrane is doped with NH_4^+ ionophores which combine with the target ions NH_4^+ to form reversible complexes. The NH_4^+ ionophores act as the sensing part of the sensor and determine the selectivity of NH_4^+ ISE. In theory, ionophores need to be lipophilic to the plasticized polymer matrix and must strongly but reversibly bind with the target ions.

An ISE exhibits selectivity because the chosen ionophore has a much larger free energy of complexation with the specific target ion than the other ions [1], as shown in Figure S4. With the specific molecular structure of the ionophore, the target ion NH_4^+ can “size-fit” the complex and combines with the chosen ionophore perfectly. On the contrary, the wall-like ionophores prevent the formation of both a wrapping complex of the crown ether with a small ion and complex with a large ion.

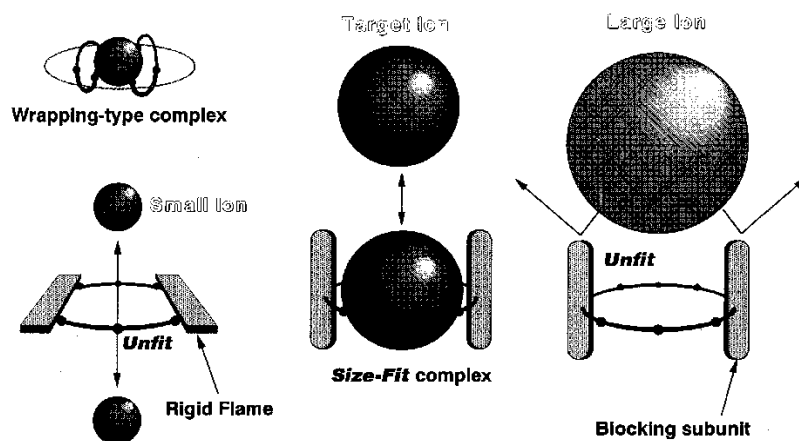


Figure S4. Mechanism of ion selectivity based on the specific molecular structure of ionophore [1]

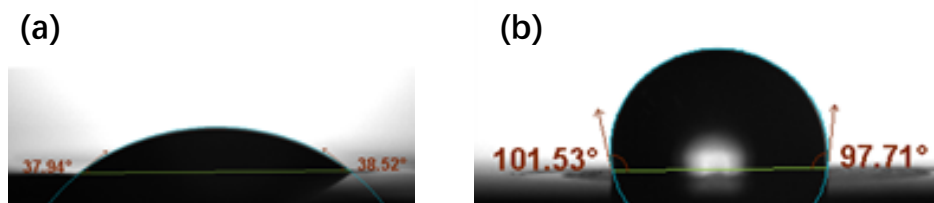


Figure S5. Contact angle test results of (a) screen-printed bare carbon and (b) Graphene-CNT modified surface.

References:

1. Suzuki, K.; Siswanta, D.; Otsuka, T.; Amano, T.; Ikeda, T.; Hisamoto, H.; Yoshihara, R.; Ohba, S. Design and Synthesis of a More Highly Selective Ammonium Ionophore Than Nonactin and Its Application as an Ion-Sensing Component for an Ion-Selective Electrode. *Anal. Chem.* **2000**, 72, 2200–2205. <https://doi.org/10.1021/ac9911241>.