

## Supporting information

Trace-Level chronopotentiometric detection in the presence of a high electrolyte background using thin-layer ion-selective polymeric membranes

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## Experimental section

**Reagents.** *N,N,N',N'*-tetrabutyl-3,6-dioxaoctanedi (thioamide) (copper ionophore, ETH 1062), tetradodecylammonium tetrakis-(4-chlorophenyl)borate (ETH 500), poly(vinyl chloride) (PVC), 2-nitrophenyl octyl ether (*o*-NPOE), and NaCl ( $\geq 99.999\%$ ) were obtained from Sigma-Aldrich. Methyl methacrylate and 2-ethylhexyl acrylate copolymer was synthesized according to the literature.<sup>1,2</sup> Graphene oxide (GO) (99.5% pure) was purchased from Nanjing JCNANO Technology Co., Ltd.. All other reagents with analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water (18.2 M $\Omega$  cm specific resistance) from a Pall Cascada system was used to prepare all solutions.

**Apparatus and Measurements.** Field emission scanning electron microscope (SEM) images were obtained by an S-4800 instrument (Hitachi, Ltd., Japan). The contact angle measurements were carried out by an optical instrument (ADS300, Data Physics, Germany). Mass spectrometry measurements were carried out by using an ion trap mass spectrometer (LCQ Fleet, Thermo Fisher, USA) in positive ion mode. All chronopotentiometric measurements were performed with an electrochemical workstation (CHI 660E, Shanghai Chenhua, China) with a conventional three-electrode system, which is comprised of a working electrode (PGR@Pt/Cu<sup>2+</sup>-ISE), a reference electrode (Ag/AgCl, 3 M KCl) and an auxiliary electrode (platinum wire). Moreover, a macro-command that executes a series of commands in a specified order was applied to control the switch between the galvanostatic and potentiostatic modes of the instrument.

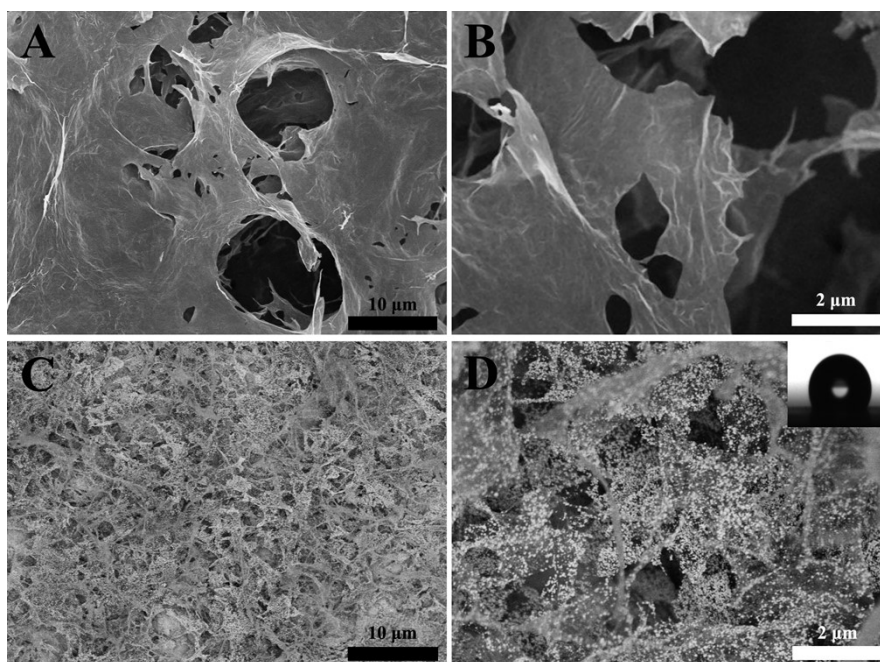
**Preparation of the PGR@Pt/Au electrode.** Since the electrodeposition method is more controllable and easier to form a smooth surface, an electrodeposited PGR@Pt nanocomposite is used for construction of the thin-membrane-based solid-contact ISEs. The cyclic voltammetry technique was applied for preparation of the PGR@Pt SC layer in a potential range from -1.5 V to 0.0 V at a scan rate of 100 mV s<sup>-1</sup> for 60 cycles. An aqueous dispersion containing 3.0 mg/mL graphene oxide, 2.5 mM hexachloroplatinic acid hexahydrate and 0.1 M lithium perchlorate (LiClO<sub>4</sub>) was used as the precursor solution. During the electrodeposition process, the gold (Au) electrode, saturated calomel electrode and platinum sheet electrode acted as working electrode, reference electrode and counter electrode, respectively. The resultant PGR@Pt nanocomposite was further reduced in 1.0 M LiClO<sub>4</sub> at a potential of -1.2 V to increase the conductivity of PGR@Pt.<sup>3</sup> The obtained PGR@Pt nanocomposite with porous structures was freeze-dried, and the PGR@Pt nanocomposite modified Au electrodes were ready for use.

**Fabrication of thin-layer membrane ISEs.** A total amount of 200 mg of the ISM components including 1.1 wt % ETH 1062, 1.1 wt % ETH 500 and 97.8 wt % MMA-EHA copolymer, were dissolved in 40 mL methylene chloride to prepare a membrane cocktail solution. The thin-ISM-based Cu<sup>2+</sup>-ISEs were fabricated by drop-casting different volumes (40, 80, 120, 160 and 200 μL) of the membrane cocktail on the PGR@Pt/Au electrode. After the PGR@Pt/Au electrode was covered by the thin-layer membrane, the contact angle of the electrode is 105° (Fig. S2). The process of preparing PVC-based thin membrane was similar to that of the MMA-EHA membrane

with the exception of the PVC membrane components (1.0 wt.% ETH 1062, 1.0 wt.% ETH 500, 32.7 wt.% PVC, and 65.4 wt.% *o*-NPOE). After staining the membrane with methylene blue, a CX31-32C02 Olympus microscope (Tokyo, Japan) was used to evaluate the thickness of the membrane. Before measurements, the Cu<sup>2+</sup>-ISEs were conditioned in 0.01 M NaCl for 1 hour.

**Chronopotentiometric measurements.** All the measurements were performed with an electrochemical workstation (CHI 660E, Shanghai Chenhua, China) with a conventional three-electrode system consisting of a working electrode (PGR@Pt/Cu<sup>2+</sup>-ISE), a reference electrode (Ag/AgCl, 3 M KCl) and an auxiliary electrode (platinum wire). A macro-command that executes a series of commands in a specified order was applied to control the switches between the galvanostatic and potentiostatic modes of the instrument. First, a zero-current pulse with a duration of 1 s was applied and the open-circuit potential of the membrane electrode was recorded. Then, a 0.6 μA cathodic current pulse of 1 s was applied for generation of an ion flux in the direction of the membrane. Finally, an open-circuit potential pulse of 60 s was used for regeneration of the membrane.

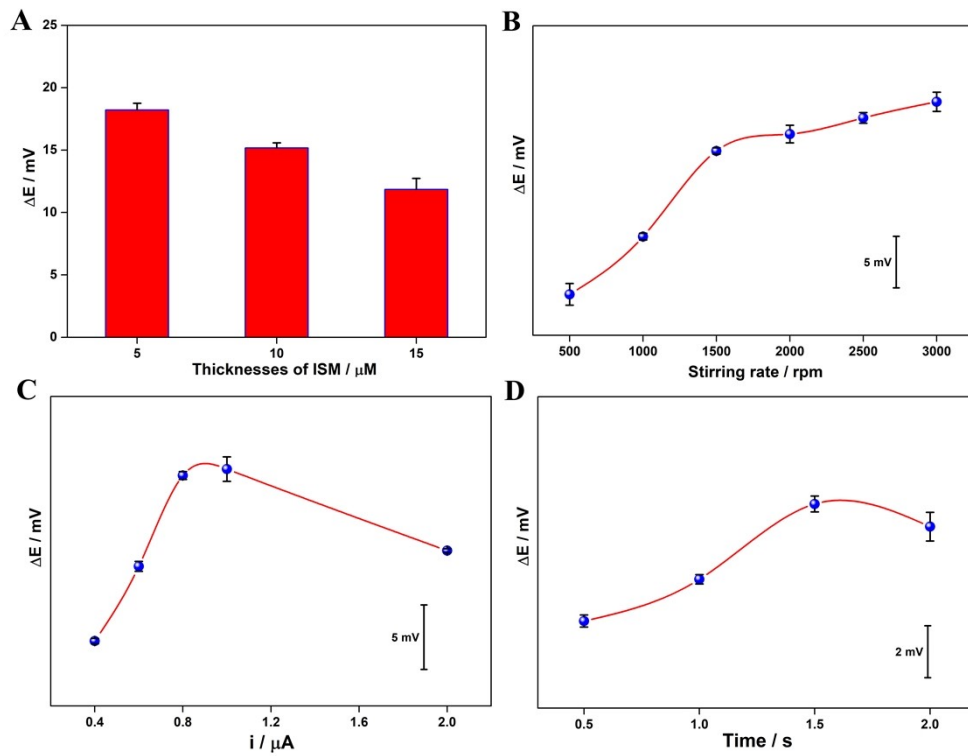
**Seawater analysis.** The recovery test was performed to evaluate the feasibility of the proposed chronopotentiometric solid-contact ISE based on the thin membrane configuration. Before measurements, the seawater samples from the Yellow Sea were filtered through a standard 0.22 μm filter, acidified to pH 2.0 with HNO<sub>3</sub> and diluted 100-fold by 0.5 M NaCl.



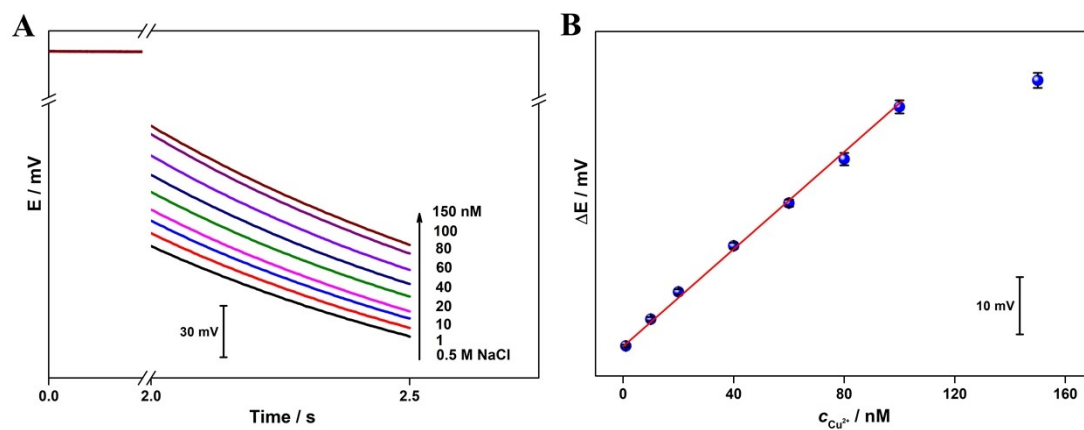
**Fig. S1** SEM images of the (A, B) PGR and (C, D) PGR@Pt nanocomposite with low and high magnifications, respectively. The inset in Fig. S1D shows the contact angle of the PGR@Pt nanocomposite.



**Fig. S2** Contact angle of the thin-layer membrane.

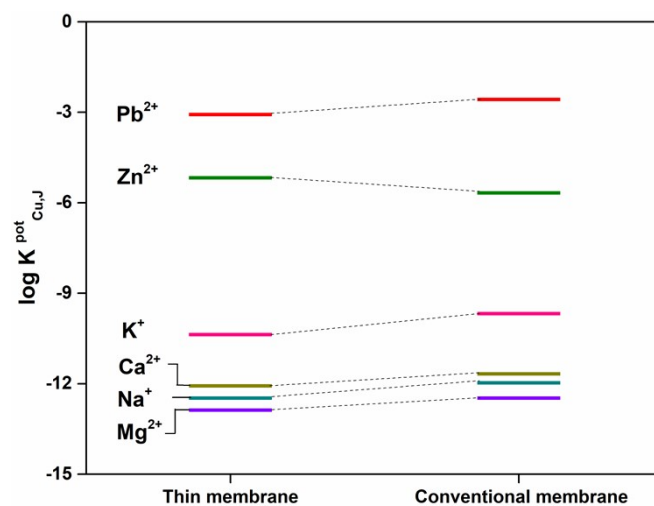


**Fig. S3** Effects of (A) thickness of ISM, (B) stirring rate, (C) current amplitude and (D) current pulse duration on the chronopotentiometric responses of the PVC-based thin membrane ISE to 40 nM  $\text{Cu}^{2+}$  with 0.5 M NaCl background. Error bars represent one standard deviation for three measurements.

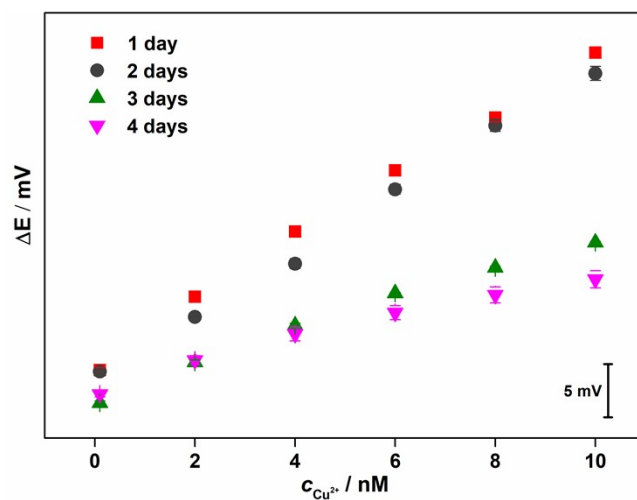


**Fig. S4** (A) Chronopotentiometric responses and (B) corresponding calibration curve of the PVC-based ISE with the thin membrane of  $\sim 5 \mu\text{M}$ . Measurements were performed in 0.5 M NaCl with a stir rate of 1500 rpm, a cathodic pulsed current of 0.8  $\mu\text{A}$  and a duration of 1.5 s. Error bars represent one standard deviations of three measurements.

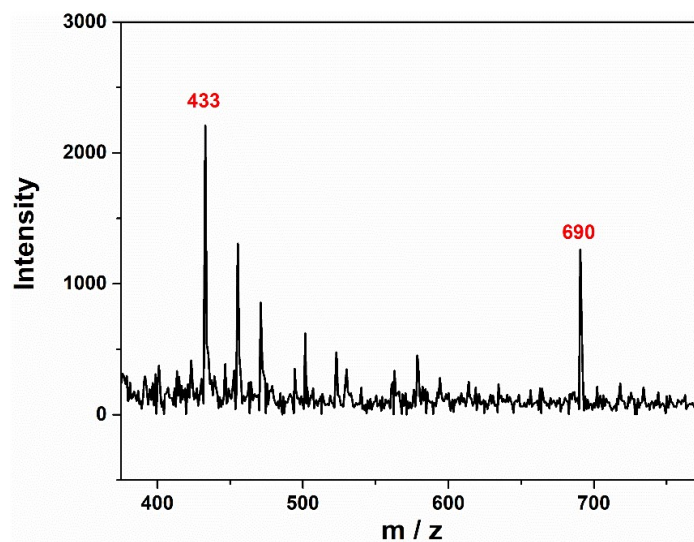




**Fig. S5** Selectivity coefficients ( $\log K_{Cu,J}^{pot}$ ) obtained with the separate solution method for the chronopotentiometric thin-layer membrane  $Cu^{2+}$ -ISE and conventional zero-current thick membrane  $Cu^{2+}$ -ISE, respectively.



**Fig. S6** Long-term stability of the thin-membrane-based  $\text{Cu}^{2+}$ -ISE. The experimental conditions are as given in Fig. 2. When not used, the ISE was conditioned in 0.01 M NaCl.



**Fig. S7** MS spectrum of 1 mL H<sub>2</sub>O after continuous contact of three thin membrane Cu<sup>2+</sup>-ISEs for 3 days. ETH 1062 and ETH 500 are identified at 433 m/z and 691 m/z in the mass spectrum with positive mode, respectively.

Table S1 Determination of copper in diluted seawater samples by the thin-membrane-based chronopotentiometric Cu<sup>2+</sup>-ISE.<sup>a</sup>

Sample	Added (nM)	Found (nM)	Recovery (%)
1	0	1.71 ± 0.06	/
	2	3.67 ± 0.13	98
2	0	1.29 ± 0.33	/
	2	3.15 ± 0.41	93
3	0	5.22 ± 0.57	/
	2	7.34 ± 0.47	106
4	0	2.76 ± 0.06	/
	2	4.89 ± 0.10	107
5	0	3.37 ± 0.29	/
	2	5.37 ± 0.39	100

<sup>a</sup> Average value of three determinations ± standard deviation.

## References

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2. K. Liu, Y. Song, D. Song and R. Liang, *Anal. Chim. Acta*, 2020, **1121**, 50-56.
3. K. Sheng, Y. Sun, C. Li, W. Yuan and G. Shi, *Sci. Rep.*, 2012, **2**, 247.