*Supporting Information for*

# Maintenance-free antifouling polymeric membrane potentiometric sensors based on self-polishing coatings

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**Reagents and chemicals.**

N,N,N',N'-Tetracyclohexyl-3-oxapentanediamide (ETH 129), sodium tetrakis [3,5-bis-(trifluoromethyl)phenyl] borate (NaTFPB), high molecular weight poly(vinyl chloride) (PVC), 2-nitrophenyl octyl ether (*o*-NPOE), propidium iodide (PI), and PDDA (MW = 100000-200000 $g \cdot mol^{-1}$, 20 wt % aqueous solution), ordered macroporous carbon (OMC), acrylic acid (AC), triisopropylsilyl methacrylate (TIPSMA), styrene (St), methyl methacrylate (MMA), *n*-butyl acrylate (BA) and butyl methacrylate (BMA), $NaHCO_3$, ammonia water solution (25 % m/m), Triton X-100, sodium dodecyl sulfate (SDS) and potassium persulfate (KPS) were obtained from Sigma-Aldrich. The SYTO 9 green-fluorescent nucleic acid stain was received from Invitrogen (Eugene, OR).The artificial Seawater was obtained from Solarbio. All the other reagents were of analytical grade and purchased from Shanghai Chemical Reagent Co., Ltd. (China). *Chlorella sp.*, *Dunaliella sp.*, and their respective culture mediums were provided by Freshwater Algae Culture Collection at the Institute of Hydrobiology. All chemicals were used without further purification. Deionized water (18.2 MΩ cm specific resistance) was obtained with a Pall Cascada laboratory water system.

**Characterization of SPCs**

The micelle size of SPCs was tested by dynamic light scattering (DLS) (Zeta sizer Nano ZS, Malvern Instruments, UK) at 25 ◦C after SPCs were diluted with ethanol. The chemical compositions of the resulted SPCs were characterized by using an

attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectroscopy (Nicolet iS10, Thermo Scientific, USA) with the attenuated total reflection mode, and the infrared spectra were recorded range from 4000 to 400 $cm^{-1}$ with a resolution of 4 $cm^{-1}$. The thermal properties of SPCs were evaluated with thermogravimetry (TG) and differential scanning calorimetry (DSC) (model: STA 449F3, NETZSCH-Geratebau GmbH).

**Characterization of the surface coating.**

The surface morphologies of the obtained $Ca^{2+}$-ISEs were observed by using a scanning electron microscope (SEM, S-4800, Hitachi). Elemental analysis was performed by using an energy-dispersive X-ray microanalyzer (EDX, EX-350, HORIBA). Additionally, the surface hydrophilicity was evaluated through water contact angle measurements with the sessile drop method recorded by an optical instrument (ADS300, Data Physics, Germany), in which the static contact angles were measured three times on random regions for the individual sample and the mean values were regarded as the corresponding apparent contact angles.

**Electromotive force measurements.**

The electromotive force (EMF) values were measured by an electrochemical workstation (CHI 760D, Shanghai Chenhua Apparatus Corporation, China) at room temperature with an Ag/AgCl (3 M KCl) electrode as the reference electrode in the galvanic cell: Ag/AgCl/3 M KCl/sample solution/ISM/OMC/GCE. Prior to the potentiometric measurements, the membrane electrodes were conditioned in $10^{-3}$ M

$CaCl_2$ solution overnight. Selectivity coefficient measurements were carried out by using the separated solution method,[1] and the electrodes were conditioned in $10^{-3}$ M NaCl solution overnight before measurements. The ion activity coefficients were calculated by the modified Debye-Hückel equation,[2] and The EMF values for inorganic ions were corrected for the liquid-junction potentials by using the Henderson equation.[3]

**Evaluation of the antimicrobial properties.**

The antifouling properties of the proposed self-polishing antifouling coating-modified $Ca^{2+}$-ISE were evaluated by using confocal laser scanning microscopy (CLSM, Fluo View FV 184 1000, Olympus, Japan) analysis after the direct contact with bacterial suspension. Firstly, *pseudomonas aeruginosa* was cultured in Luria-Bertani (LB) medium at 37 °C overnight. Secondly, 1 mL of bacterial suspension was added to 9 mL of sterile LB culture medium and cultured at 37 °C for 2 h. And then, bacterial cells were collected by centrifugation and washed 5 times with a sterile 0.9% NaCl solution to remove LB medium. Lastly, the resulting bacterial cells were re-suspended in a 0.9% sterile NaCl solution (pH = 8) to obtain a $10^8$ or $10^9$ CFU • $mL^{-1}$ bacterial suspension. The proposed self-polishing SPC-coated $Ca^{2+}$-ISEs were placed in the bacterial suspension at a concentration of $10^8$ CFU • $mL^{-1}$ at room temperature for 2 h. After that, the fouled membranes were gently rinsed with 0.9% NaCl solution to remove the unattached bacterial cells. All apparatus used in this study were autoclaved prior to the biological experiments, and the operations were carried out in a biosafety cabinet. After an exposure of 2 h, the attached bacterial cells on the ISE

membranes were stained for 30 min in the dark at room temperature by SYTO 9 (3.34 μM) for live cells and PI (20 μM) for dead cells, respectively. The stained bacteria cells were observed by CLSM to distinguish the live and dead bacterial cells. And then the bacterial attachment and inactivation were evaluated by analyzing the obtained CLSM images via the ImageJ Pro software (National Institutes of Health).

**General application test**

The selected materials include fiberglass reinforced plastic (FRP), 201 stainless steel (201SS), polytetrafluoroethylene (PTFE), polystyrene (PS), aluminum alloy (Al alloy) and polyurethane (PU) were evenly coated with the proposed SPC. After being dried completely at room temperature, the adhesion properties of the coating on the selected material surfaces were determined by the classical scratching method. The adhesion grade was calculated by the American Iron and Steel Institute standard (ASTM). In order to explore the antifouling performance of the proposed SPC on other substrates, the SPC-coated PVC, PS, PU, PTFE, 201SS and control group were soaked in $1 \times 10^5$ /L of the *Chlorella sp.* suspension for 3 months.

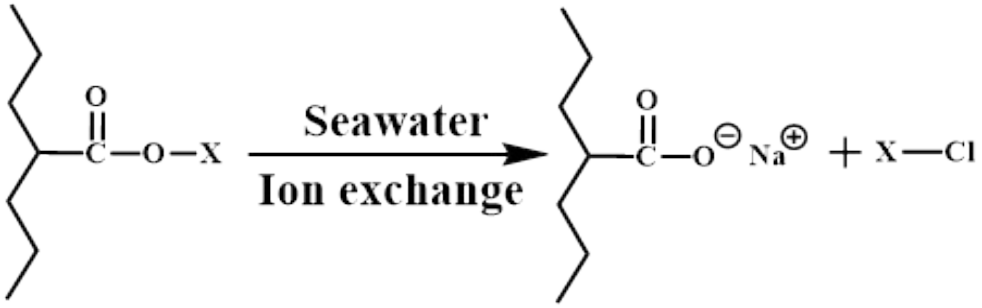


**Fig. S1**. Self-polishing principle of SPCs.

**Table S1**. Response slopes of the control and SPC-coated $Ca^{2+}$-ISEs to $Ca^{2+}$ in the concentration range of $10^{-4}$ to $10^{-1}$ M.

| Coating | Paint dosage / µL | Response slope / mV·dec$^{-1}$ |
|---|---|---|
| Control $Ca^{2+}$-ISE | 0 | 27.61 ± 0.03 |
| SPC-coated $Ca^{2+}$-ISE | 10 | 27.25 ± 0.81 |
| SPC-coated $Ca^{2+}$-ISE | 15 | 23.17 ± 0.77 |
| SPC-coated $Ca^{2+}$-ISE | 20 | 15.93 ± 0.12 |

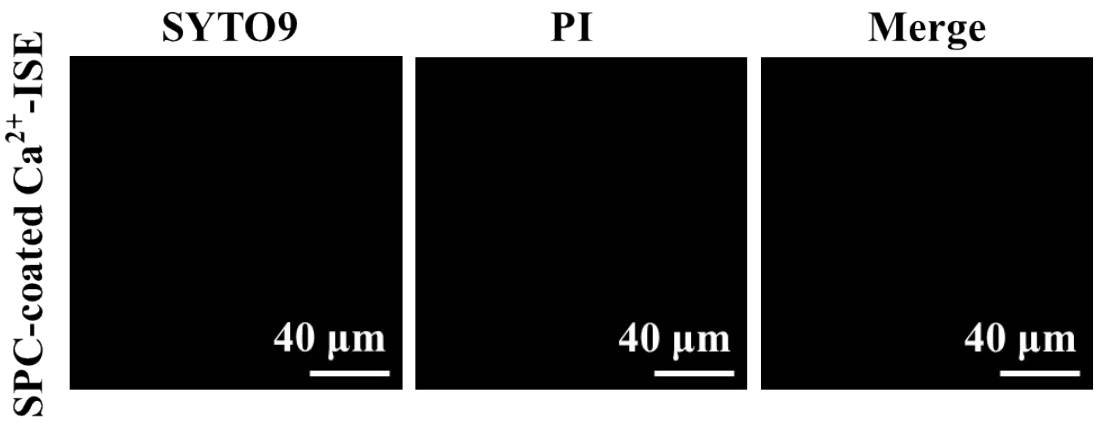


**Fig. S2**. CLSM images of the SPC-coated $Ca^{2+}$-ISE after contact with a bacterial suspension (~$10^8$ CFU·$mL^{-1}$) for 2 h. The electrode was then rinsed with water at a flow rate of 3 mL/s for 1 min.

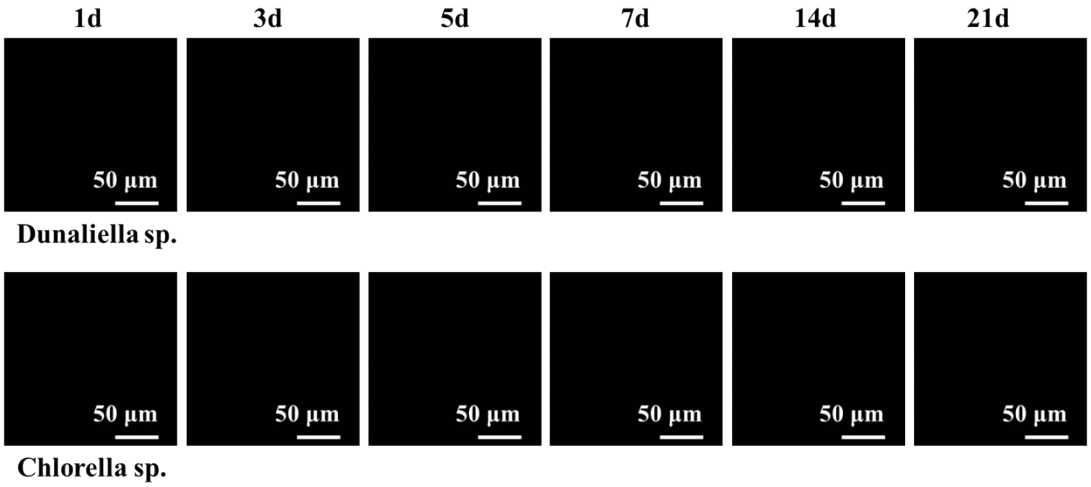


**Fig. S3**. CLSM images of the SPCs-coated $Ca^{2+}$-ISE after contact with *Dunaliella sp.* and *Chlorella sp.* suspension (~$10^5$ CFU·$mL^{-1}$) for different time. The electrode was then rinsed with water at a flow rate of 3 mL/s for 1 min.

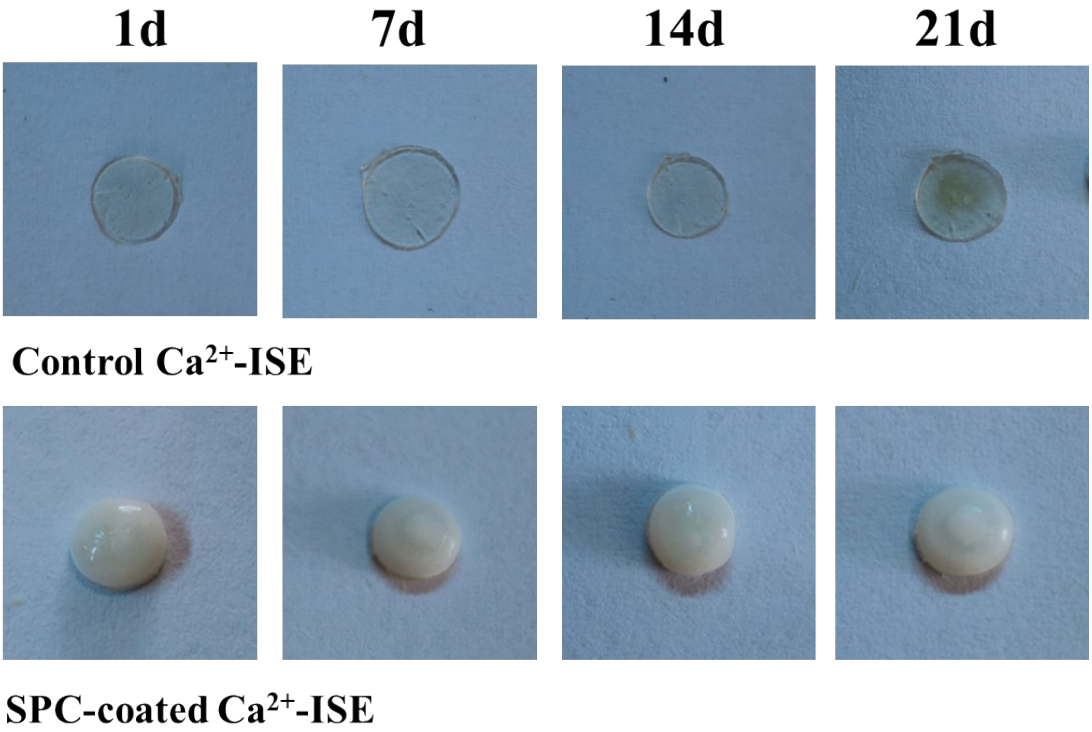


**Fig. S4**. Images of the blank control and and SPC-coated $Ca^{2+}$-ISEs after contact with a *Chlorella sp.* suspension (~$10^5$ CFU•$mL^{-1}$) for 21 days.

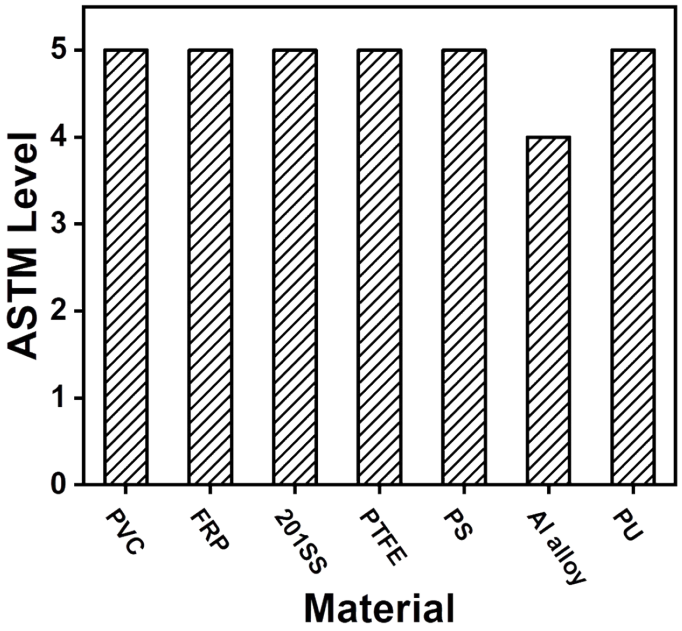


**Fig. S5**. The adhesion class of the coating on the surface of different materials.

**References**:

[1] E. Bakker, J. Electrochem. Soc. 143 (1996) L83-L85.

[2] Meier, P. C. Anal. Chim. Acta 1982, 136, 363−368.

[3] Morf, W. E. The Principles of Ion-Selective Electrodes and of Membrane Transport; Elsevier Science: New York, 1981; Vol. 5, pp 3-92.