Electronic Supplementary Information

Photoelectric current as a highly sensitive readout for potentiometric sensors

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S1. Experimental section

Reagents and materials

The calcium ionophore II (ETH 129), 2-nitrophenyloctyl ether (*o*-NPOE), sodium tetrakis [3,5bis (trifluoromethyl)phenyl] borate (NaTFPB), high molecular weight poly (vinyl chloride) (PVC), poly (sodium 4-styrenesulfonate) and 3,4-ethylenedioxythiophene (EDOT, 97%) were purchased from Sigma-Aldrich. Graphene oxide nanoplatelets (GO) was provided by Nanjing XFNANO Materials Tech Co., Ltd. Zinc chloride (ZnCl₂) and selenium metal powder (Se) were obtained from Macklin Biochemical Co., Ltd. *N*,*N*-dimethylformamide (DMF), polyvinyl pyrrolidone (PVP), anhydrous purified sodium sulfite (Na₂SO₃), calcium chloride (CaCl₂), sodium chloride (NaCl), and ethanol were provided from Sinopharm Chemical Reagent Co., Ltd. Tetrahydrofuran (THF) was freshly distilled prior to use. All other chemicals were of analytical grade and the aqueous solutions were prepared with freshly deionized water (18.2 M Ω cm specific resistance) obtained with a Pall Cascada laboratory water system.

Apparatus

The ZnSe/r-GO composite was characterized by transmission electron microscopy (TEM, JEM-2100 transmission electron microscope) with an EDS analytical system. The crystallographic structure was characterized with a Rigaku SmartLab III diffractometer (XRD) using Cu Ka radiation (1 ¼ 1.5406°A) and Raman spectra were collected on a Laser Raman spectrometer (DXR Raman Microscope, Thermo, United States).

Membrane preparation

The ion-selective membranes containing 0.46 wt% ETH 129, 0.48 wt% NaTFPB, 66.04 wt% *o*-NPOE, and 33.02 wt% PVC were prepared as described before.¹ PEDOT/PSS films were synthesized on the electrodes (GC, a diameter of 3 mm) by applying a current of 0.014 mA for 714 s in aqueous solution containing 0.01 M EDOT and 0.1 M NaPSS.² Then, 80 μ L of the membrane cocktail was drop-cast on the GC/PEDOT-PSS and left to dry overnight at room temperature. The solid-contact Ca²⁺-ISEs were conditioned in 10⁻³ M CaCl₂ overnight.

Synthesis of ZnSe/r-GO

The ZnSe/r-GO composite was prepared by a facile hydrothermal process. Typically, a certain amount of GO was dissolved in 18 mL of deionized water by sonication. Then 618.6 mg of ZnCl₂ was added into the above solution by ultrasonication. Finally, 18 mL of the freshly prepared

sodium selenosulfate (Na₂SeSO₃, prepared by refluxing 0.05 M Se powder with 0.125 M Na₂SO₃ at ca. 80°C for 3 h), 2 g of urea and 0.4 g of polyvinyl pyrrolidone (PVP) were added into the mixture solution of GO and ZnCl₂. After stirring for 30 min, the mixture was poured into a 50 mL Teflon-lined autoclave and allowed to react at 180°C for 12 h. Followed by natural cooling to room temperature and the obtained precipitate was washed by ethanol and distilled water for three times. The composites with the additions of 10, 20, 30, 40, and 50 mg of GO, denoted as ZnG-1, 2, 3, 4, and 5, respectively. For comparison, the pristine ZnSe material was prepared by the same process without GO.

Fabrication of the Modified Electrodes

Before modification, the gold electrode (GE, a diameter of 5 mm) was polished with 0.3, 0.05 μ m alumina slurries sequentially and washed ultrasonically with deionized water and ethanol. A ZnSe/r-GO suspension (2 mg mL⁻¹) was prepared by dispersing ZnSe/r-GO in *N*,*N*-dimethylformamide (DMF) with ultrasonic agitation for 5 min. Then 30 μ L of as-prepared suspension was dropped onto the gold electrode surface and dried at room temperature. 0.5 wt % nafion was dropped onto the electrode surface in order to improve the stability.

Experimental Protocols

All measurements were carried out at room temperature using a CHI 660E electrochemical workstation (Shanghai Chenhua Apparatus Corporation, Shanghai, China). Potentiometric measurements were carried out in 10⁻² M NaCl background electrolyte using a conventional twoelectrode system. PEC measurements were carried out in 10⁻² M NaCl solution using a conventional three-electrode system, in which ZnSe/r-GO/GE, Ag/AgCl (3.0 M KCl) and a platinum wire was used as working, reference and auxiliary electrodes, respectively. A white LED (10 W, 10.0 lm/W) light was switched on and off every 10 s.

Determination of Real Samples

Seawater samples were collected from Bohai and Yellow Seas. The standard addition method was used for determination of Ca^{2+} ion in seawater samples. 30 mL of the original seawater samples were successively spiked with 2.0 M fresh $CaCl_2$ solution to obtain samples containing different concentrations of calcium and the corresponding photocurrent values were recorded. Inductively coupled plasma atomic emission spectrometry (ICP-OES, Perkin Eimer optima 7000 DV) was utilized as reference method to detect Ca^{2+} in seawater. For the calcium detection using

ICP-OES, seawater samples were acidified to pH 2.0 with HNO₃ and stored at 4°C before analysis.

Theoretical model

Based on the assumption of no photocurrent losses, Petermann et al.³ derived an expression for the photocurrent (I_{pc}) taking into account the absorption coefficient ($\alpha(\lambda)$), the minority carrier diffusion length (L_{min}), the incident photon flux (ϕ) and h_0 :

$$I_{pc} = e\phi\{1 - \exp[-\alpha(\lambda)h_0(E_{we} - E_{fb})^{\frac{1}{2}}]/(1 + \alpha(\lambda)L_{\min})\}$$
(1)

where *e* is the elementary charge, E_{we} is the potential of the working electrode, E_{fb} is the flat band potential of ZnSe/r-GO composite, h_0 is constant which dependents on the charge carrier concentration in the material.

The potential response of the ISE conforms to the Nernst equation:

$$E = E^0 + \frac{RT}{zF} \log \alpha_x \qquad (2)$$

where E^0 is the standard electrode potential, T is the temperature, R is the gas constant, F is the Faraday constant, z is the number of electron transfer in the electrode reaction and $\alpha(x)$ is the activity of the analyte ion.

In this work, the ISE is used as a reference electrode, thus potential can be varied with respect to the ion activities of the tested solution. When applying a fixed potential (E_{ap}) , the potential of the working electrode can be written as:

$$E_{we} = E_{ap} + E^0 + \frac{RT}{zF} \log \alpha_x$$
(3)

Therefore, the relationship between the photocurrent magnitude and the working electrode potential can be expressed by the following formula:

$$I_{pc} = k - k' A^{[B+k''\log\alpha_x]^{\frac{1}{2}}}$$
(4)

where k is $e\phi$, k' is $e\phi / [1 + \alpha(\lambda)L_{min}]$, k'' is RT / zF, A is $e^{-\alpha(\lambda)h\theta}$, B is $E_{ap} + E^{\theta} - E_{fb}$. Under the experimental conditions, k, k', k'', A and B can be constant.

S2. Results and discussions

Characterizations of materials

In order to achieve highly sensitive PEC detection, a composite of ZnSe/r-GO was prepared. The morphologies of the synthesized composites were characterized by transmission electron microscopy (TEM) images. As shown in **Fig. S1A**, the veil-like r-GO sheet exhibits the typical wrinkles on the surface, which provide an excellent three-dimensional structure for ZnSe deposition. The TEM image of ZnSe particles shows that the morphology is spherical and the average diameter is 500 nm (**Fig. S1B**). The morphology of the ZnSe/r-GO composite can be clearly observed in **Fig. 1A** and the particles of ZnSe were wrapped on the surfaces of r-GO sheets. Graphene sheets act as a bridge between ZnSe particles, which may help provide a pathway for photogenic electrons and thus improve catalytic performance.⁴ Since the negatively charged GO interacts with the positively charged metal ions to deposit ZnSe on the sheet while inhibiting the growth and aggregation of the ZnSe particles, ^{5,6} the size of pure ZnSe particles is larger than that of ZnSe/r-GO composite. The energy-dispersive spectroscopy (EDS) spectrum (**Fig. S1C**) shows that the ZnSe/r-GO composite contains only C, Zn and Se, further revealing that ZnSe is adhered to the surface of r-GO.



Fig. S1 TEM images of the as-prepared (A) r-GO and (B) ZnSe. (C) EDX elemental microanalysis of the ZnSe/r-GO composite (ZnG-3). (D) Magnifications of the XRD patterns for r-GO, ZnSe, and the ZnG-1, ZnG-2, ZnG-3, ZnG-4 and ZnG-5 composites. Raman shifts of (E) r-GO and of (F) the ZnG-1, ZnG-2, ZnG-3, ZnG-4, and ZnG-5 composites.

The X-ray diffraction (XRD) patterns of the ZnSe/r-GO composites were characterized (**Fig. 1B**). For the pristine ZnSe material, several major diffraction peaks at 27.224°, 45.195°, 53.568°, 65.858°, and 72.632° are indexed to the (111), (220), (311), (400), and (331) (crystal planes) crystalline ZnSe with the zinc blende structure (JCPDS no 88-2345). As shown in Fig. 1B, the positions of the diffraction peaks of ZnG-1, 2, 3, 4, 5 are the same as those of pristine ZnSe. Moreover, the XRD patterns include the characteristic peak (002) of r-GO, indicating that the ZnG-1, 2, 3, 4, and 5 materials were successfully prepared (see the magnification of the XRD patterns in **Fig. S1D**). The observed weak peaks (002) of the ZnSe/r-GO composites are probably due to the relatively small amounts of r-GO in the composites. In addition, the characteristic peak (001) of GO in the ZnG-1, 2, 3, 4, and 5 patterns cannot be observed (**Fig. 1B**), demonstrating the bulk of GO was reduced to r-GO.

In addition, Raman spectroscopy was also used to characterize the synthesized graphene-based materials. **Figs. S1E** and **S1F** show the typical Raman spectra of the r-GO and ZnG-1, 2, 3, 4, 5. It can be seen that the characteristic peaks (D and G bands) of the graphitic material appear at 1339 cm⁻¹ and 1605 cm⁻¹, respectively.⁷ It is recognized that the degree of reduction of GO to graphene is represented as the intensity ratio of D and G band (I_D/I_G). The I_D/I_G ratio is calculated as 1.79 for r-GO and the maximum intensity ratio of D band and G band is 1.52 for ZnG-3, which confirms the well reduction of GO. The increased I_D/I_G ratio of ZnG-3 can be ascribed to the presence of the defects and separation of the graphene layer. However, as the amount of GO continues to increase, I_D/I_G decreases.

Optimization for the PEC measurements



Fig. S2 (A) Effect of the volume of ZnSe/r-GO on the photocurrent response at the ZnSe/r-GO modified gold electrode (GE). (B) Effect of pH of the electrolyte (0.01 M PBS) on the photocurrent response at the ZnSe/r-GO modified GE. Each error bar represents one standard deviation of three measurements.

PEC responses of the ZnSe-3/GE working electrode



Fig. S3 (A) Derived calibration curve with potentials from 0.150 to 0.156 V. (B) Derived calibration curve with potentials from 0.200 to 0.206 V. PEC tests were performed *vs.* Ag/AgCl (3 M KCl).

Potential responses of the Ca²⁺-ISE



Fig. S4 (A) Time traces of the potential responses of the polymeric membrane Ca^{2+} -ISE for detecting various concentrations of Ca^{2+} in 10⁻² M NaCl. (B) Corresponding calibration curve of Ca^{2+} -ISE. Each error bar represents one standard deviation of three measurements.

Potential responses of the ZnSe-3/GE working electrode



Fig. S5 Time traces of the potential responses of the ZnSe-3/GE working electrode for detecting various concentrations of Ca^{2+} in 10⁻² M NaCl. The polymeric membrane Ca^{2+} -ISE was used as the reference electrode.



Fig. S6 Potential responses of the ZnSe-3/GE electrode in the presence of 10⁻² M NaCl containing 10⁻² M Ca²⁺. The Ag/AgCl (3 M KCl) electrode and the Ca²⁺-ISE were used as the reference electrodes, respectively.

Selectivity, stability and reproducibility of the PEC sensor

In order to evaluate the anti-interference ability of this PEC sensor for Ca^{2+} , photocurrent responses of ZnSe/r-GO/GE electrodes were measured for various ions. The selectivity of the Ca²⁺-selective membrane was determined in our previous research. The logarithms of the selectivity coefficients toward Na⁺, K⁺ and Mg²⁺ were -8.3, -10.1 and -9.3, respectively.¹ As shown in **Fig. S7A**, the photocurrent responses for diverse ions show little change compared with that for the blank solution by using the Ag/AgCl reference electrode. However, when the Ca²⁺-ISE electrode serves as the reference electrode, all the interfering ions display negligible photocurrent responses as compared with Ca²⁺ (**Fig. S7B**). Both results demonstrate that the established PEC sensor shows excellent selectivity for the detection of Ca²⁺.



Fig. S7 (A) Photocurrent responses (I_{pc}) of the PEC sensor using (A) the Ag/AgCl (3 M KCl) as the reference electrode. (B) Photocurrent responses ($I_{pc} - I_0$) of the PEC sensor using the Ca²⁺-ISE as the reference electrode. (C) Time-dependent photocurrent response traces of the PEC sensor with the 10-s on/off irradiation cycles. The background solution was 10⁻² M NaCl. The concentrations of the tested ions were 10⁻² M for Ca²⁺ and K⁺, 0.05 M for Mg²⁺, 0.5 M for Na⁺, and 10⁻⁵ M for Zn²⁺, Mn²⁺, Fe³⁺, Cu²⁺, Pb²⁺, and Cd²⁺, respectively. Each error bar represents one standard deviation of three measurements. The bias voltage was 0.25 V (*vs.* the reference electrode).

The stability of the PEC sensor was also investigated by performing the detection of 10^{-2} M Ca²⁺. As shown in **Fig. S7C**, no obvious change of photocurrent response could be observed with irradiation under 22 on/off irradiation cycles, and the RSD was 1.0%. The result indicates that the PEC sensor has high stability for the detection of Ca²⁺.

Furthermore, the reproducibility of the PEC sensor was examined by performing the detection of 10^{-2} M Ca²⁺ at five different electrodes. The coefficient variation was calculated to be 1.7%, indicating acceptable fabrication reproducibility. Moreover, the reproducibility can be improved by using a ratiometric photoelectrochemical technique.

Simulated photoelectrochemical response

As shown in **Fig. S8**, the theoretical simulation is almost identical to the experimental data, indicating that the results are reasonable. Moreover, as shown in **Table S1**, the parameters including $\phi = 1.28 \times 10^{15}$ cm⁻², $\alpha(\lambda) = 9.92 \times 10^4$ cm⁻¹, $L_{min} = 6.07$ µm, $h_0 = 1.50$ µm, and $E_{fb} = -0.135$ V (*vs.* the Ca²⁺-ISE) are all in the reasonable ranges.



Fig. S8 Simulated PEC responses of the ZnSe/r-GO modified GE electrodes to Ca²⁺.

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Effect of salinity on the response of the ZnSe-3/GE working electrode

Fig. S9 Time-dependent photocurrent response traces of the PEC sensor in the 10^{-2} M Ca²⁺ solutions containing 0.01 and 0.5 M NaCl, respectively. The bias voltage was 0.25 V (*vs.* the Ca²⁺-ISE).

	This work	Values	Material	Reference
φ (cm ⁻²)	1.28×10 ¹⁵	2×10 ¹⁴	ZnSe	8
$\alpha(\lambda)$ (cm ⁻¹)	9.92×10 ⁴	6-8×10 ⁴	ZnSe	9
		4.7×10^{4}	ZnSe	10
L_{min} (µm)	6.07	1.20	ZnSe	11
h_0 (µm)	1.50	0.23	$Cd_{1-x}Zn_xSe$	12

Table S1. Values of the photon flux ϕ , optical absorption coefficient $\alpha(\lambda)$, the minority carrier diffusion length L_{min} and h_0 in material which is dependent on the charge carrier concentration.

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