Lanthanide-based Receptors Functionalized Electrode for Real-time Phosphate Detection

Xiyu Sun[1], Zinan Yu[2], Jason D.Azoulay[3], Valerie C. Pierre[2], Tse Nga (Tina) Ng[1]
[1]Electrical and Computer Engineering, University of California, San Diego, [2]Department of Chemistry, University of Minnesota, & [3]School of Materials Science and Engineering ,Georgia Institute of Technology

INTRODUCTION

Phosphorus (P), a crucial nutrient for organism development in the ecosystem, poses a significant environmental challenge due to the excessive discharge of phosphates into water, leading to widespread algae proliferation and degradation of water quality.

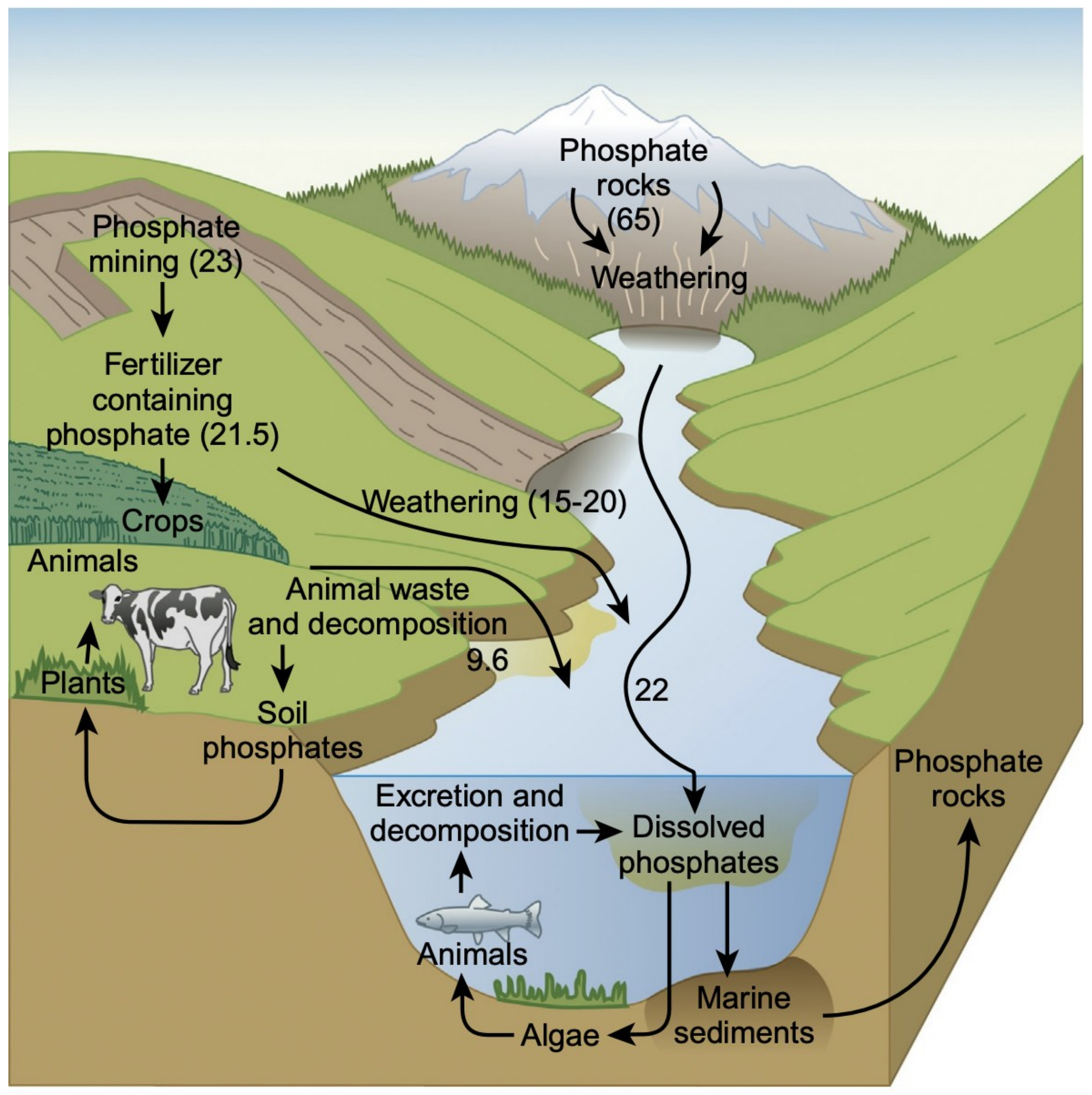

Fig. 1 Summary of global phosphorus cycle.[1]

- Current methods of quantifying P in water rely on traditional analytical methods, including colorimetric analyses or laboratory-based spectrophotometric, fluorescent, and chromatographic methods, limited by multiple procedure requirement and hazardous waste.
- The measurement of inorganic phosphate (Pi), specifically HPO_4^{2-} and $H_2PO_4^-$, in water remains a significant challenge, particularly when detecting concentrations at or below 10 μg L^{-1}.

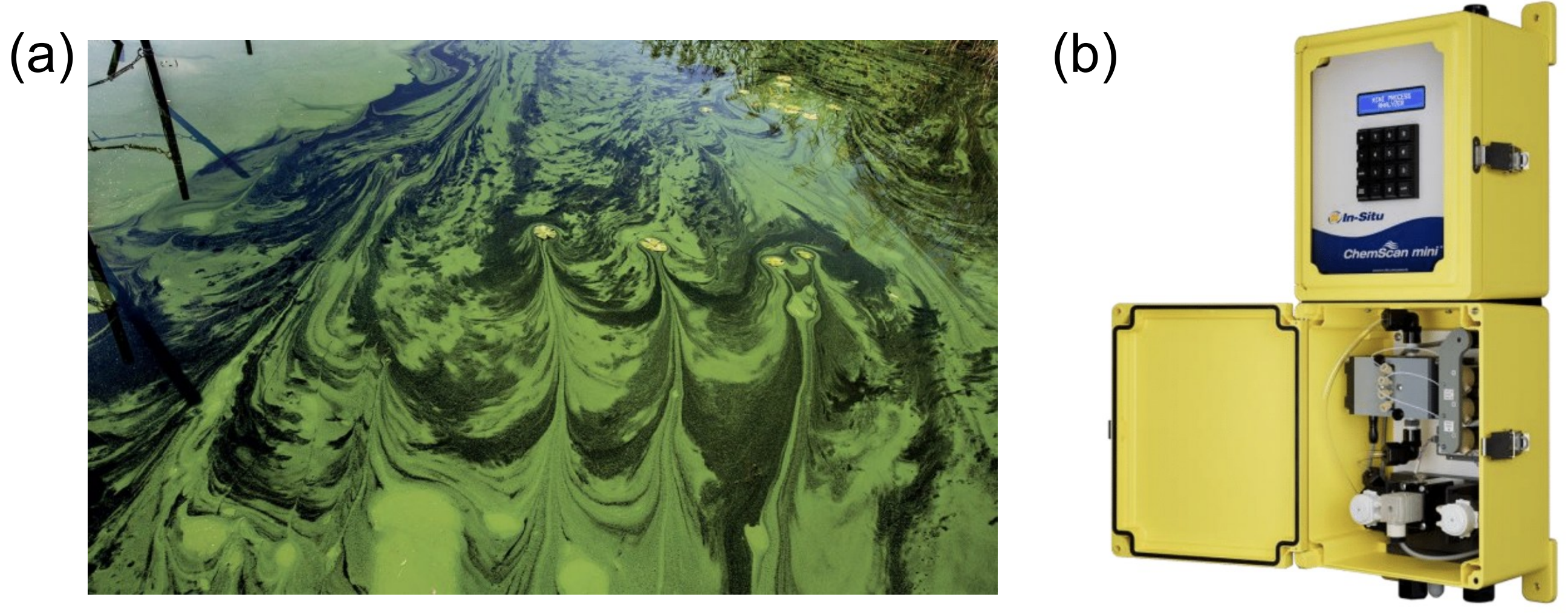

Fig. 2 (a) Algal bloom caused by phosphorus from agricultural runoff. [2] (b) Online colorimetric water analyzer. https://in-situ.com/en/chemscan-mini-analyzer

Phosphate Sensing Requirements:

- **In situ, cost effective, and real time monitoring**
- **Aqueous stability**
- **Sensitive to small changes in concentration (10 ppb)**

METHODS

- The primary challenge in developing phosphate sensors lies in the inability to effectively bind and isolate phosphate from aqueous environments and in the difficulty of transducing this binding event into a detectable sensor signal.
- These difficulties arise from the high hydration energies of phosphate ions (–465 kJ mol^{-1} for $H_2PO_4^-$ vs –340 kJ mol^{-1} for Cl^-), cross-interference with other common nutrients (e.g., nitrate, NO_3^-), and structural ambiguity depending on pH, where phosphate exists as $H_3PO_4/H_2PO_4^-$ in acidic environments and as $H_2PO_4^-/PO_4^{3-}$ in more alkaline conditions. [3]
- Integrating a strong metal−anion interaction into the binding site of the receptor can overcome the high hydration free energy of the phosphate anion, thereby attaining higher affinity in water.
- Lanthanide-based receptors own high affinity for Pi in water (sub-ppm), high selectivity over common competing anions such as Cl^-,NO_3^-, and HCO_3^-, and rapid binding kinetics. [4]

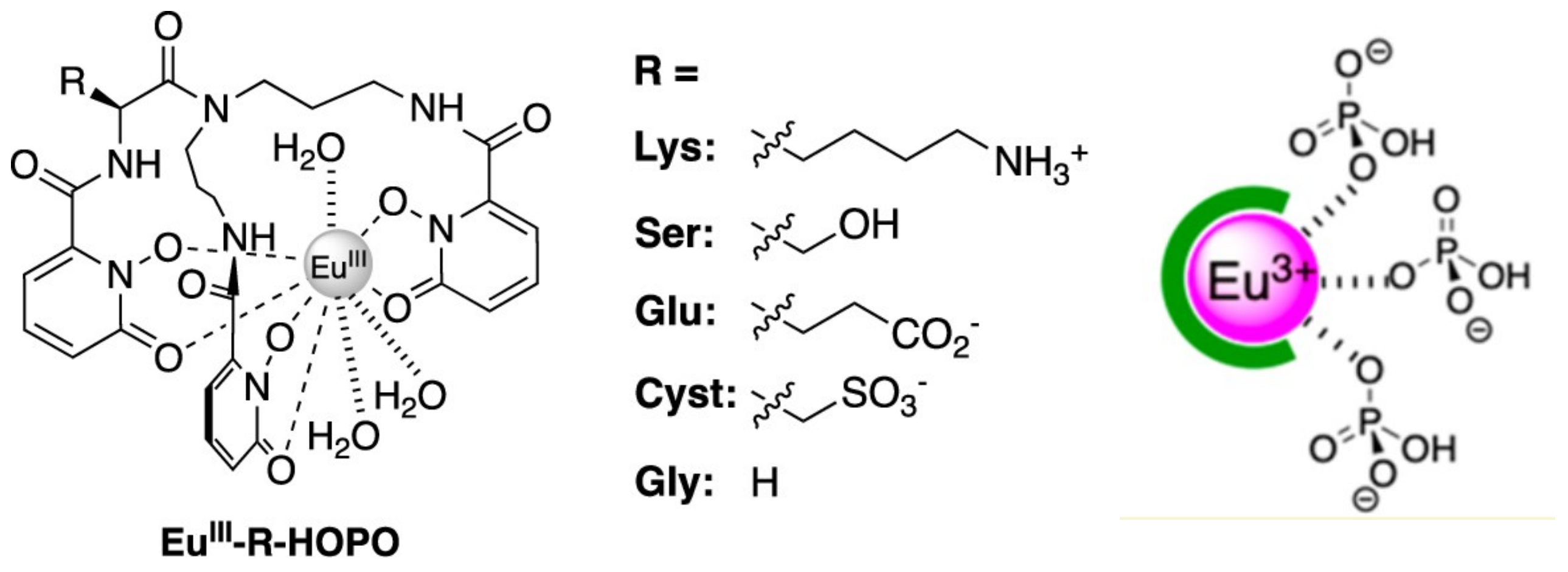

Fig. 3 Chemical structures and schematic representation of Eu^{III} complexes bearing charged and hydrogen-bonding substituents. [4]

By functionalized the electrode with lanthanide-based receptors, we can use a three-electrode electrochemical system to investigate the current signal change and the electrostatic effect of Pi binding, which provides a direct electronic handle to regulate the sensor, along with future opportunities for high sensitivity phosphate sensing.

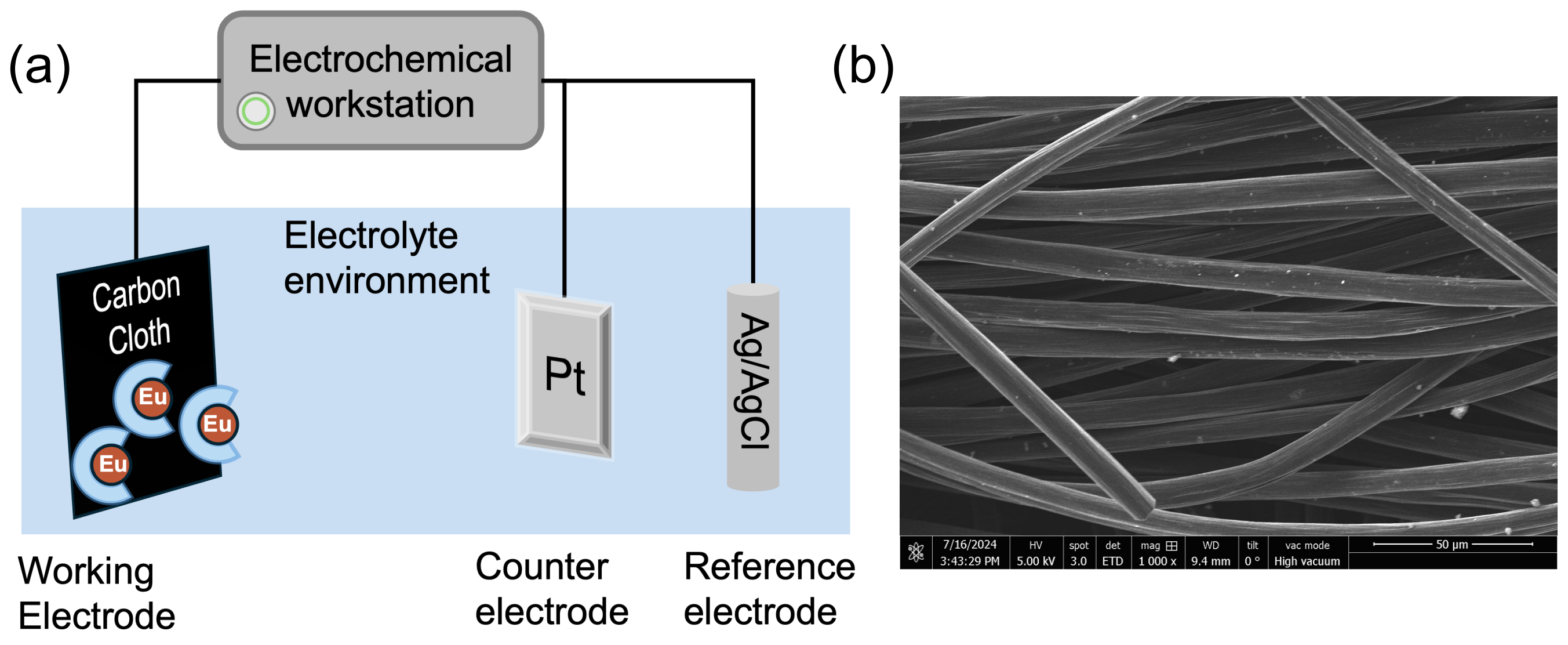

Fig.4 (a) Schematic diagram of three-electrode electrochemical system. (b) SEM image of the Eu^{III}-receptor functionalized carbon cloth electrode.

Lanthanide-based receptor:

- **High affinity for Pi in water**
- **High selectivity over common competing anions**
- **Rapid binding kinetics**

- To demonstrate a real-time, in-situ monitoring, we employ a portable potentiostat with amperometric measurement to conduct the phosphate sensing experiment.
- Initially, we utilized a 0.1 M NaCl solution at pH = 7 as the baseline solution and gradually increased the concentration of phosphate ions ($H_2PO_4^-/HPO_4^{2-}$ at pH = 7) in the solution. The binding between the receptor and the phosphate occurred rapidly, within a few seconds, as shown in Fig. 5 (a).
- We recorded the changes in the current signal generated during the recognition process and subsequently plotted the phosphate sensitivity plot, as shown in Fig. 5 (b).

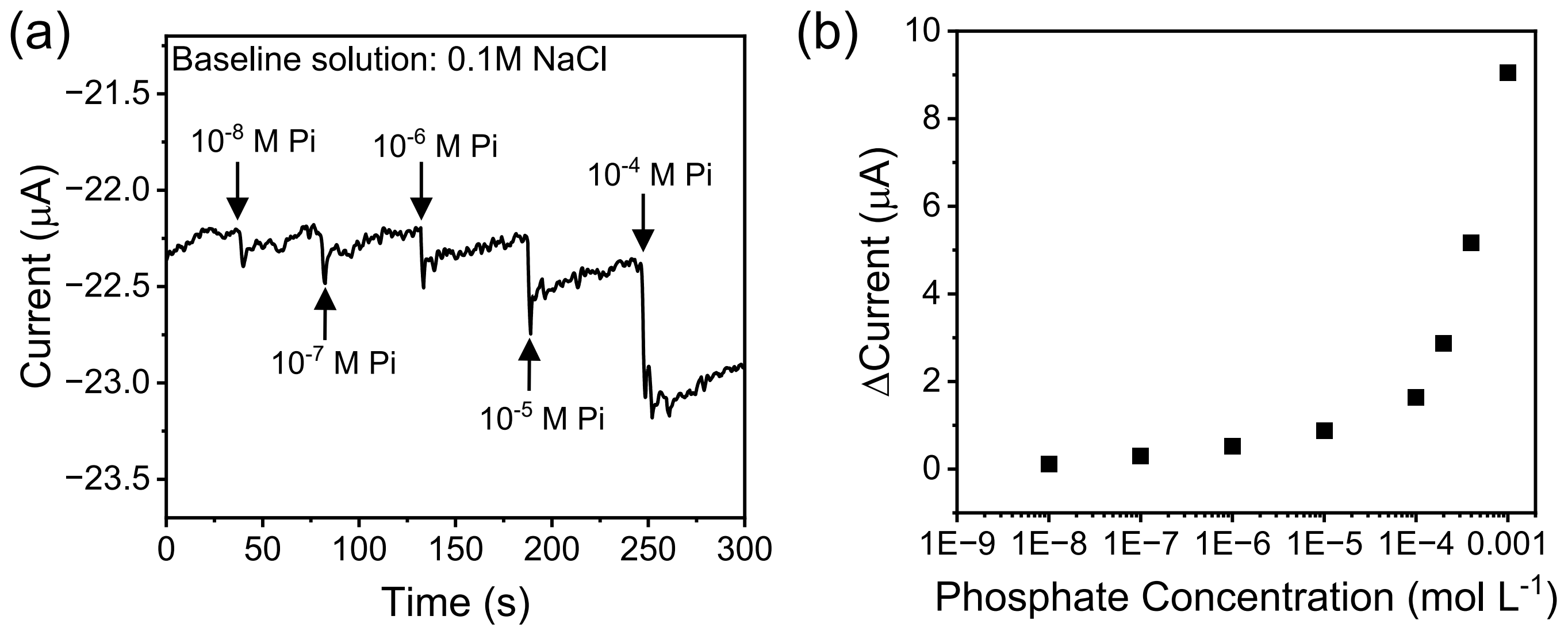

Fig. 5 (a) Current-time test and (b) sensitivity plot of Eu^{III}-receptor with different phosphate concentration.

CONCLUSIONS

- **In this study, we functionalized the electrode with lanthanide-based receptors and utilized a portable potentiostat with amperometric measurement to investigate phosphate sensing within a real-time monitoring platform.**
- **In future work, by integrating this system with an organic electrochemical transistor device, we aim to develop a low-power, miniaturized system capable of enabling in-situ, wireless phosphate sensing platforms.**

REFERENCES

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ACKNOWLEDGEMENT

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