Supporting Information

Direct Electrochemical Sensing of Phosphate in Aqueous Solutions Based on Phase Transition of Calcium Phosphate

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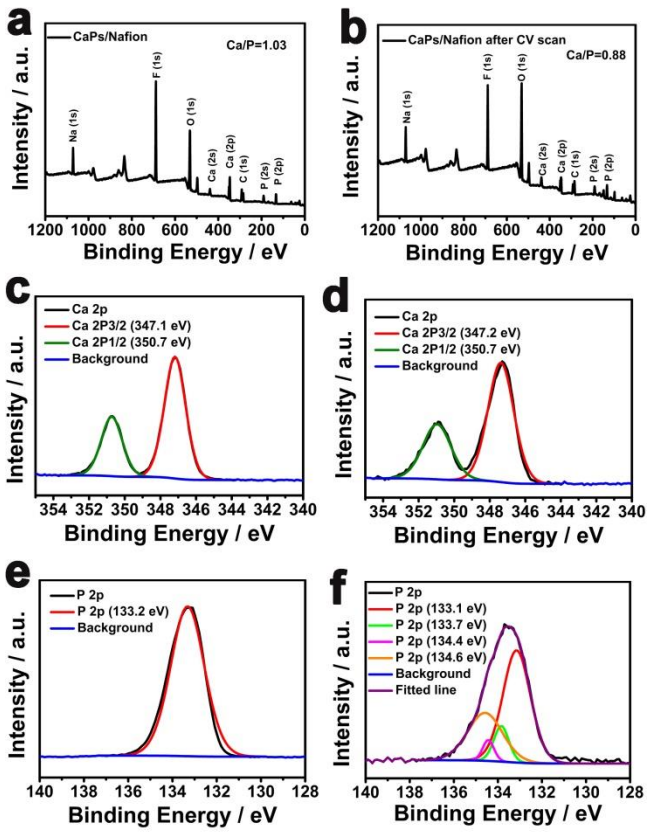

Figure S1. Full-survey X-ray photoelectron spectroscopy (XPS), high-resolution XPS Ca2p spectra, and high-resolution XPS P2p spectra of CaPs/Nafion before (a), (c) and (e) and after (b), (d) and (f) the electrochemical scans in 10 μM phosphate solution with 10 μM Ca^{2+} for 40 times, respectively. According to the literature,[1,2] the P2p (f) can be deconvoluted to the composition of ACP and OCP (133.1 eV) (55.97%), HAP (133.7 eV) (9.66%), PO_4^{3-} (134.1eV) (4.26%) and HPO_4^{2-} (134.6eV) (30.11%), which are also in accordance with the forms of CaPs in the pH value.[3]

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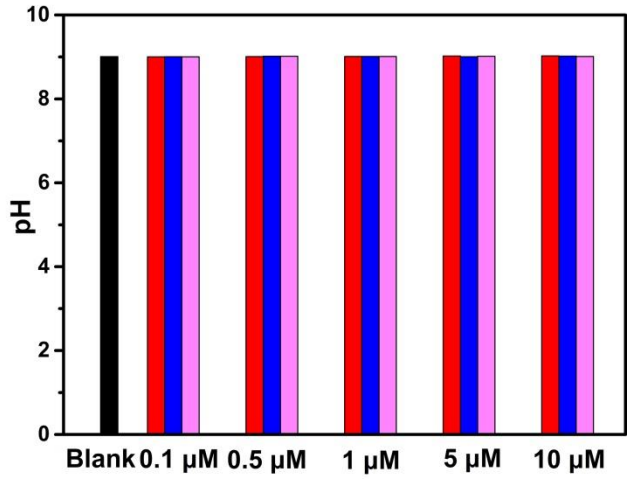

Figure S2. The influence on pH stability of 1.0 mM $Ca(OH)_2$ solution (black) with the addition of 0.1 μM to 10 μM phosphate including $H_2PO_4^-$ (red), HPO_4^{2-} (blue), PO_4^{3-} (pink).

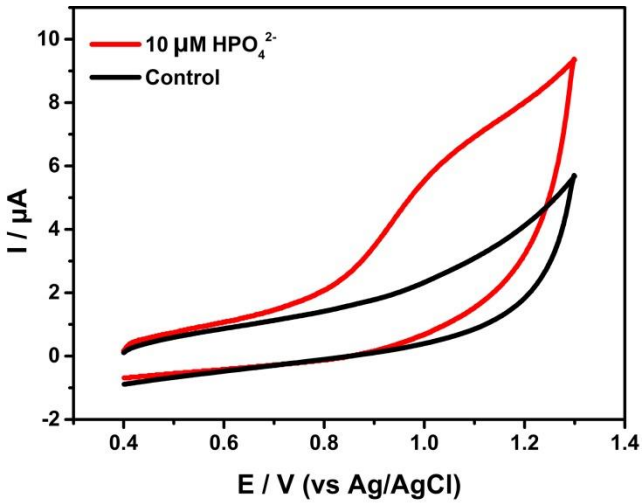

Figure S3. CV curves of CaPs/Nafion in 1.0 mM $Ca(OH)_2$ solution with and without the presence of 10 μM HPO_4^{2-}.

Table S1. Solubility of calcium salts with various anoins.

Compond	Formula	Ksp with Ca^{2+}	References
Octacalcium phosphate (OCP)	$Ca_8(HPO_4)_2(PO_4)_4{\cdot}5H_2O$	2.5×10^{-99}	4
Amorphous calcium phosphate (ACP)	$Ca_xH_y(PO_4)_z{\cdot}\ nH_2O$, n) 3-4.5; 15-20% H_2O	2.8×10^{-29}	4
Hydroxyapatite (HAP)	$Ca_{10}(PO_4)_6(OH)_2$	5.5×10^{-118}	4
Calcium Carbonate	$CaCO_3$	2.8×10^{-9}	5
Calcium Sulfate	$CaSO_4$	4.93×10^{-5}	5

Table S2. Comparison of different electrochemical methods for phosphate detection.

Platform	Linear range	Limit of detection	Supporting electrolyte	References
cobalt phosphate coated cobalt electrode	0.01 to 100 mM	No show	0.1 M NaCl	6
Ni(OH)2/NiO(OH)	No given	0.3 μM	0.1 M NaOH	7
molybdenum phosphide (MoP)	0.1 to 20 mM	0.03 mM	0.1 M tris-HCl buffer	8
surfactant-modified zeolite carbon-paste electrode	15.8 to 1.00×10^3 μM	12.8 μM	pH 4-12, 0.1 to 4 mM $NaNO_3$	9
screen-printed electrode modified with carbon black nanoparticles	0.5 to 100 μM	0.1 μM	0.2 M sulfuric acid	10
CaPs/Nafion	0.1 to 10 μM	0.053 μM	1.0 mM $Ca(OH)_2$	This work

References

(1) Chusuei, C. C.; Goodman, D. W. Calcium Phosphate Phase Identification Using XPS and Time-of-Flight Cluster SIMS. Anal. Chem. 1999, 71, 149-153.

(2) Hanawa, T.; Ota, M. Characterization of surface film formed on titanium in electrolyte using XPS, Applied Surface Science 1992, 55, 269-276.

(3) Lynn, A. K.; Bonfield, W. A Novel Method for the Simul-taneous, Titrant-free Control of pH and Calcium Phosphate Mass Yield. Acc. Chem. Res. 2005, 38, 202-207.

(4) Speight, J. G. Lange's Handbook of Chemistry, 16th ed.; McGrawHill, Inc.: New York, NY, 2005, p. 1.333

(5) Wang, L.J.; Nancollas, G.H. Calcium Orthophosphates: Crystallization and Dissolution. Chem. Rev. 2008, 108, 4628−4669.

(6) Xu, K.B.; Kitazumi, Y.K.; Kano, K.J.; Shirai, O. Phosphate ion sensor using a cobalt phosphate coated cobalt electrode. Electrochim. Acta 2018, 282, 242e246

(7) Cheng, W.L.; Sue, J.W.; Chen, W.C.; Chang, J.L.; Zen, J.M. Activated Nickel Platform for Electrochemical Sensing of Phosphate. Anal. Chem. 2010, 82, 1157–1161.

(8) Zhang, J.X., Bian, Y.X., Liu, D., Zhu, Z.W., Shao, Y.H., Li, M.X. Detection of Phosphate in Human Blood Based on a Catalytic Hydrogen Wave at a Molybdenum Phosphide Modified Electrode. Anal. Chem. https://doi.org/10.1021/acs.analchem.9b03862

(9) Ejhieh, A.N.; Masoudipour, N. Application of a New Potentiometric Method for Determination of Phosphate based on a Surfactant Modified Zeolite Carbon-paste Electrode (SMZ-CPE), Anal. Chim. Acta 2010, 658, 68–74.

(10) Talarico, D.; Arduini, F.; Amine, A.; Moscone, D.; Palleschi,G. Screen-printed Electrode Modified with Carbon Black Nanoparticles for Phosphate Detection by Measuring the Electroactive Phosphomolybdate Complex, Talanta 2015, 141, 267–272.