Electronic Supplementary Information (ESI)

Highly sensitive detection of phosphate using well-ordered crystalline cobalt oxide nanoparticles supported by multi-walled carbon nanotubes

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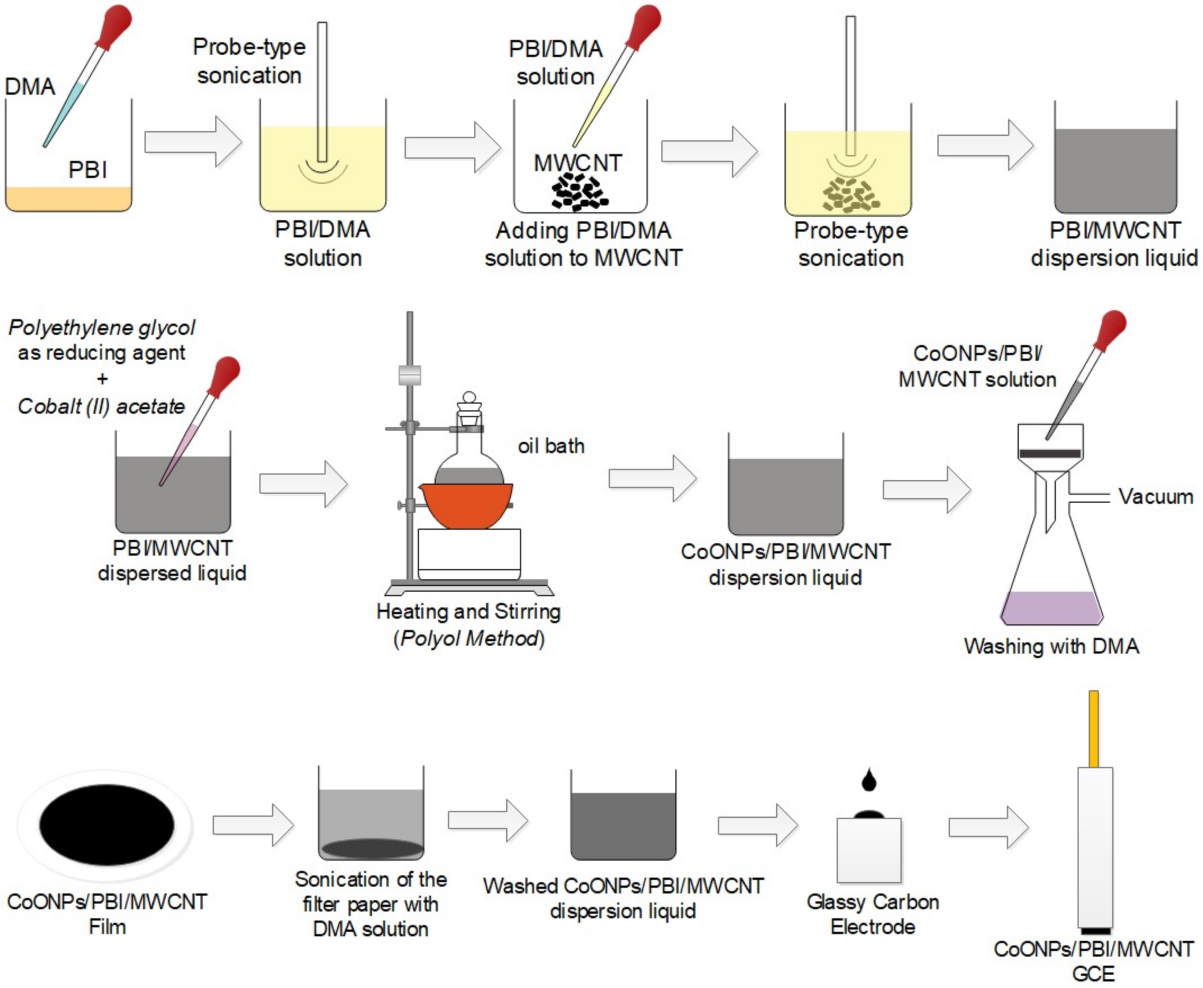

Fig. S1 Scheme of CoONPs/PBI/MWCNE/GCE preparation.

Surface Area of CoONPs/PBI/MWCNTs

1. Specific surface area evaluated from PBI amount

The CoONPs/PBI/MWCNTs catalyst surface area was calculated with assumption polybenzimidazole (PBI) uniformly wrapped MWCNTs. The size of PBI molecule was obtained 1.48 nm × 0.5 nm (Fig. S2). The value of 1.4×10^{-3} g and 2.8×10^{-4} g were calculated as initial weight of PBI/MWCNT and weight of PBI (ca. 20% weight loss) at around 550 °C from the thermal gravimetric analysis (TGA) result, respectively. Considering the molecular weight for one molecular unit of PBI (310 g mol^{-1}), the occupied area of one molecular unit of PBI (7.5×10^{-19} m^2) and Avogadro's number (6.023×10^{23} mol^{-1}), the value of 0.5 m^2 per mol was obtained. The catalyst surface area by initial weight of PBI/MWCNT was evaluated of 3×10^3 cm^2 mg^{-1} for one layer of PBI. Since PBI existed in few layers from TEM images, the range of 1–3 × 10^3 cm^2 mg^{-1} was determined for the surface area of CoONPs/PBI/MWCNTs catalysts.

2. Electrochemically active surface area evaluated from double-layer capacitance

The electrochemically active surface area (ECSA) of a catalyst sample can be calculated with a cyclic voltammetry (CV) method. We calculated the double-layer capacitance (C_{dl}) of CoONPs/PBI/MWCNTs on glassy carbon electrode based on the scan rate dependence of cyclic voltammetry measurements. By plotting the difference in current density between anodic and cathodic sweeps at a fixed potential (-0.7 V vs Ag|AgCl|sat.KCl) against the scan rate, a linear trend is observed. The fitting slope is twice of the double-layer capacitance (C_{dl}), which is linearly proportional to the ECSA, according to the following formula:

$$ECSA = \frac{C_{dl}}{C_s}$$

where C_s is the specific capacitance. As seen from Fig. S3, for CoONPs/PBI/MWCNTs on glassy carbon electrode, C_{dl} = 3.75 mF cm^{-2}. Assumed the capacitive behavior (C_s) of the well-ordered graphite structure from our previously reported value of 2–5 μF cm^{-2} with small defect, the ECSA of 750–1800 cm^2 was obtained.[1]

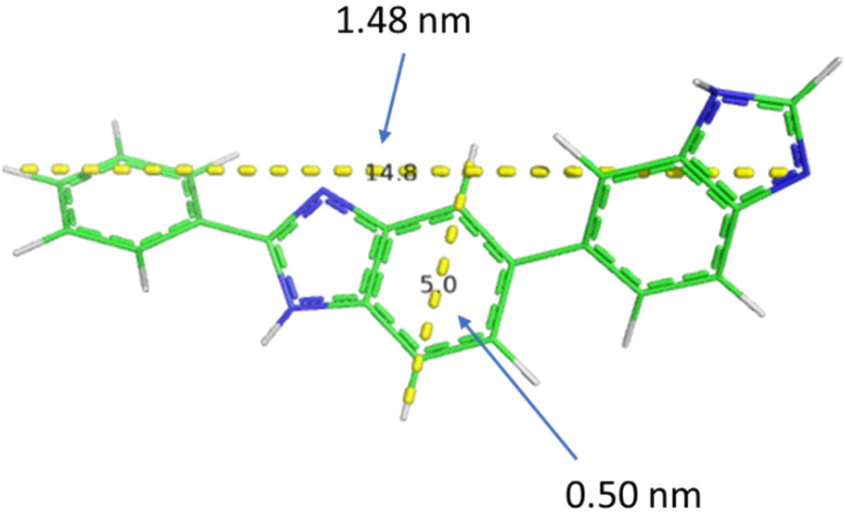

Fig. S2 Molecular size of one molecular unit of PBI (polybenzimidazole) measured using PyMOL.

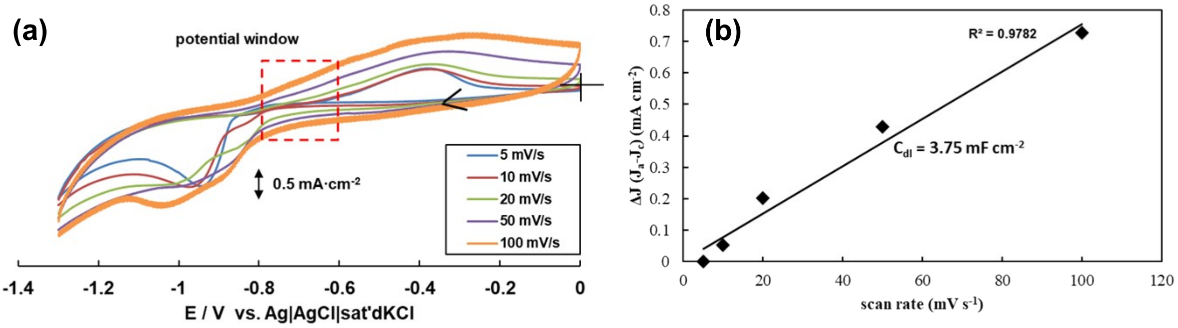

Fig. S3 (a) CV curves of CoONPs/PBI/MWCNT/GCE in 0.1 M PBS (pH 7) at different scan rate (5–100 mV s^{-1}) where potential window of non-Faradaic region from around -0.8 to -0.6 V was selected to determine C_{dl} (electrochemical double layer capacitance) and (b) Linear fitting of the current densities at -0.7 V versus scan rates for the previous CV measurements.

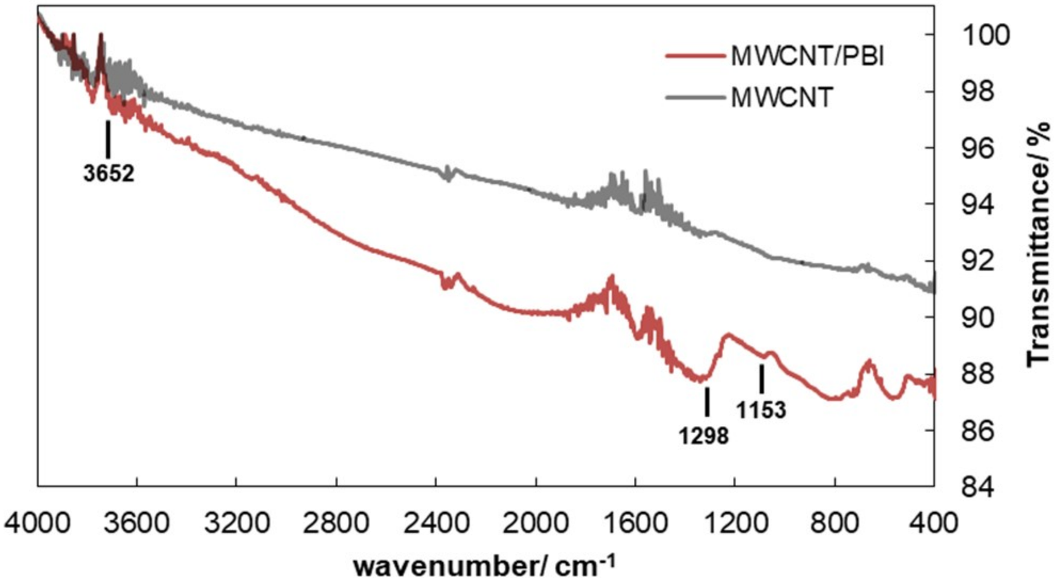

Fig. S4 FTIR spectra of MWCNT (gray solid line) and PBI/MWCNT (red solid line).

Table S1 FTIR spectra and functional groups for PBI/MWCNT.

wavenumber/cm^{-1}	Bond	Functional group
3652	N–H stretch	amines
1298	C–N stretch	aromatic amines
1153	C–N breathing mode	imidazole ring

Fig. S5a shows TGA results for pristine MWCNT, PBI powder and PBI/MWCNT composite. The first weight loss for PBI powder starts at 42 °C and ends at 180 °C with a weight loss of about 20%. This degradation stage corresponds to the evaporation and elimination of volatile products. The second weight loss for PBI happened at around 500 °C. The PBI/MWCNT also exhibits small weight loss which contributed to the evaporation of volatile products at around 50 °C and ends at 170 °C before undergone the second weight loss at around 550 °C. Meanwhile, the TG curve of pristine MWCNT consists of only one weight loss stage at around 550 °C. The PBI coating amount can be calculated to be about 7.4 wt% from the weight difference between MWCNT and PBI/MWCNT (Fig. S5b).

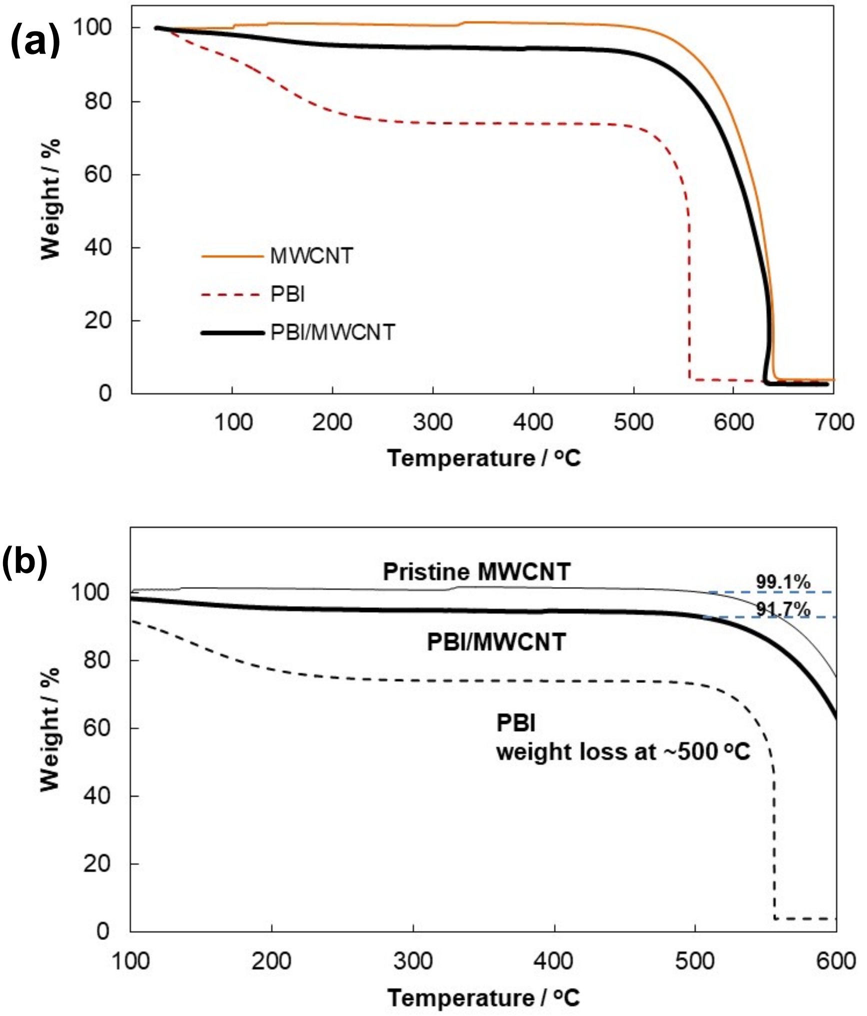

Fig. S5 (a) TGA curves of the MWCNT (solid thin line), PBI (dotted line), and the PBI/MWCNT (solid bold line) and (b) the weight difference calculation between pristine MWCNT and PBI/MWCNT.

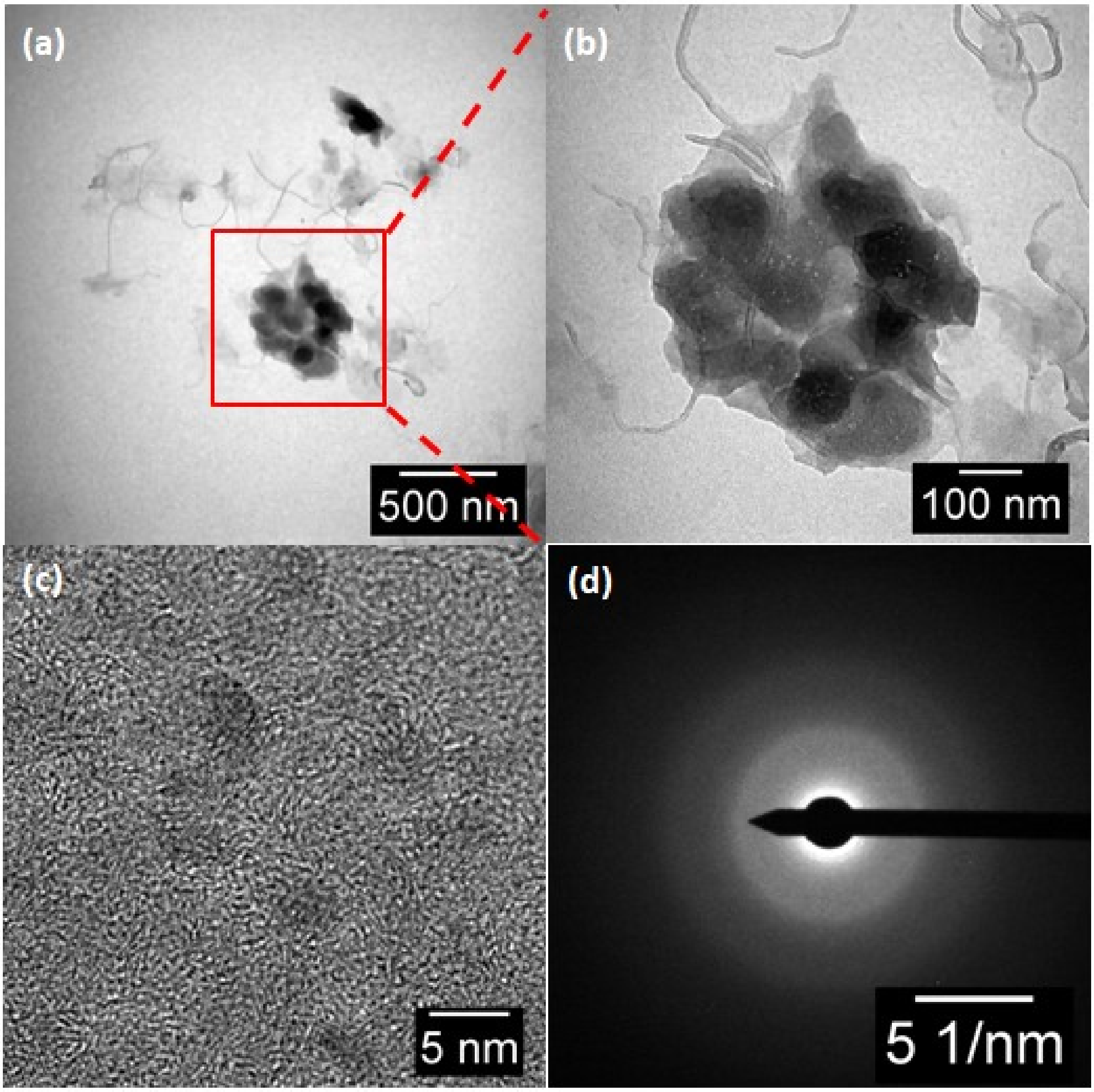

Fig. S6 (a) TEM plane views of CoONPs/MWCNT; (b) zoomed-in of TEM plane view of CoONPs/MWCNT; (c) clusters of CoONPs and (d) SAED pattern of CoONPs/MWCNT.

The diffraction simulation result of Co_3O_4 nanocrystal shown on Fig. S7. White circles represent general spots while pink circles represent extinct spots from screw or glide planes. Screw axes are symmetry axes that imply rotation and an additional translation while glide planes are mirror planes that imply reflection and an additional translation. The (220) plane of hexagonal Co_3O_4 nanocrystals is believed exists in this study as the diffraction simulation result coordinates with FFT image result and the calculation of average lattice spacing of cobalt nanoparticles.

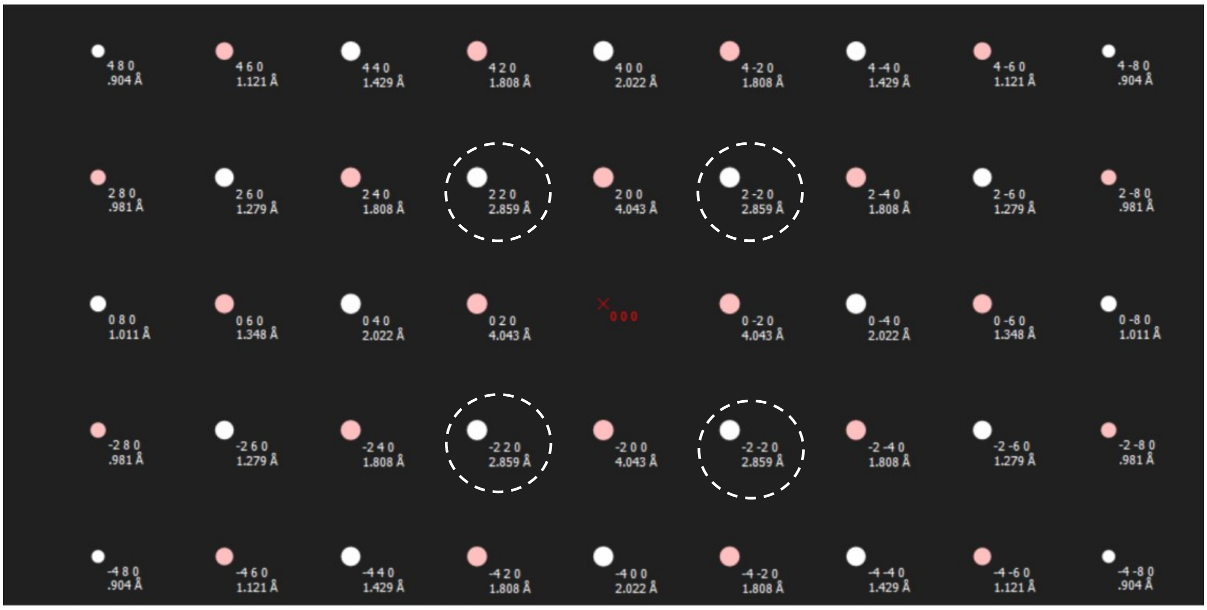

Fig. S7 Diffraction simulation of Co_3O_4 nanocrystal.

Table S2 Chemical analysis of the EDX spectrum for CoNPs/PBI/MWCNT.

Element	**Weight %**	**Atomic %**	**Uncert. %**	**Correction**	**k-Factor**
C (K)	52.47	84.62	0.74	0.28	3.601
Co (K)	4.07	1.34	0.12	0.99	1.492
Si (K)	1.48	1.02	0.06	0.92	1.000
Cl (K)	0.88	0.48	0.05	0.95	1.063
Cu (K)	41.07	12.52	0.40	0.99	1.663

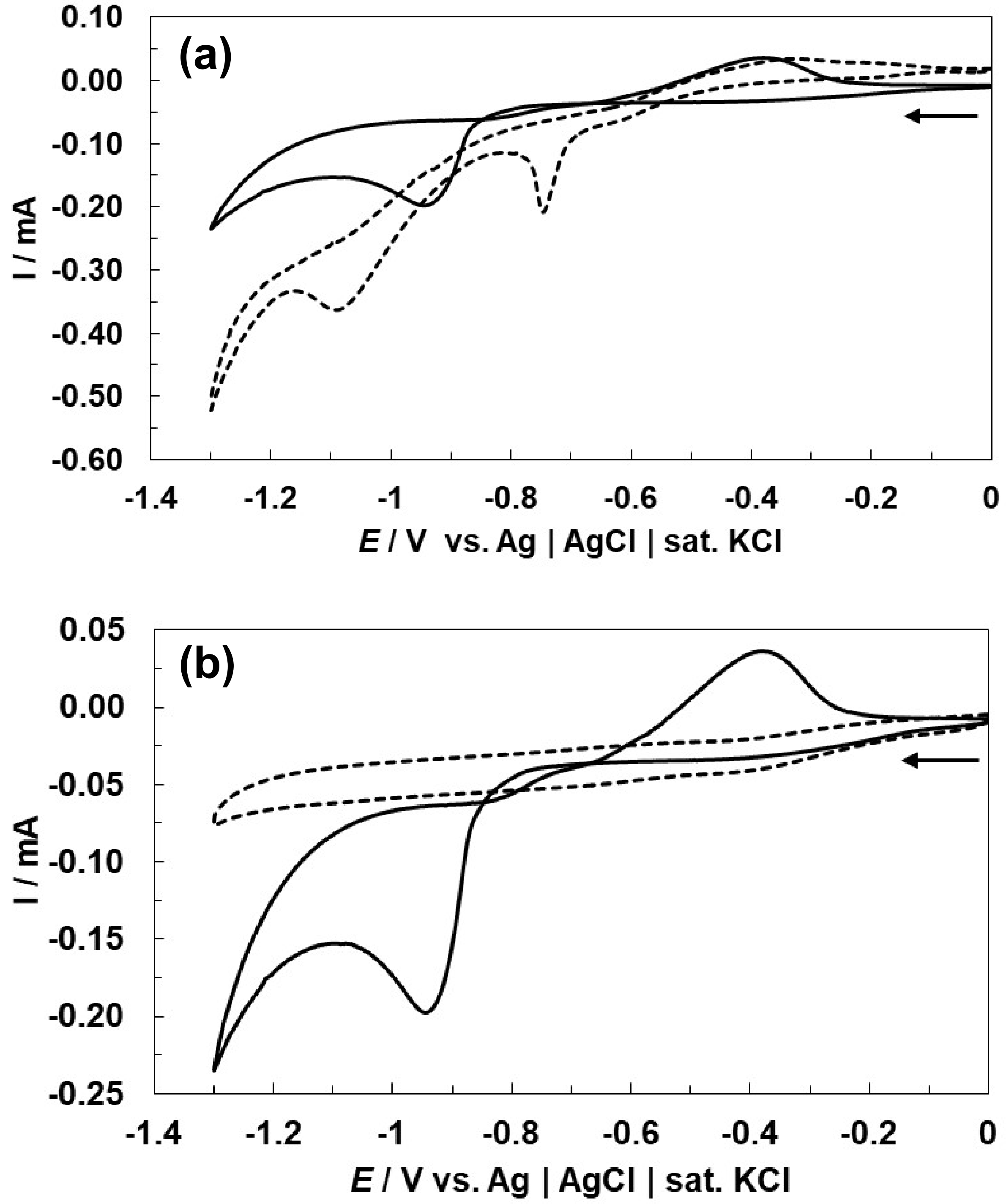

Fig. S8 Actual current vs. potential of CV curves recorded at 5 mV s^{-1} for (a) the bulk Co wire electrode (broken line) and CoONPs/PBI/MWCNTs/GCE (solid line) in 0.1 M PBS with pH 7 and (b) CoONPs/PBI/MWCNTs/GCE in 0.1 M Na_2SO_4 (broken line) and 0.1 M PBS with pH 7 (solid line). Electrode surface area: apparently 0.283 cm^2.

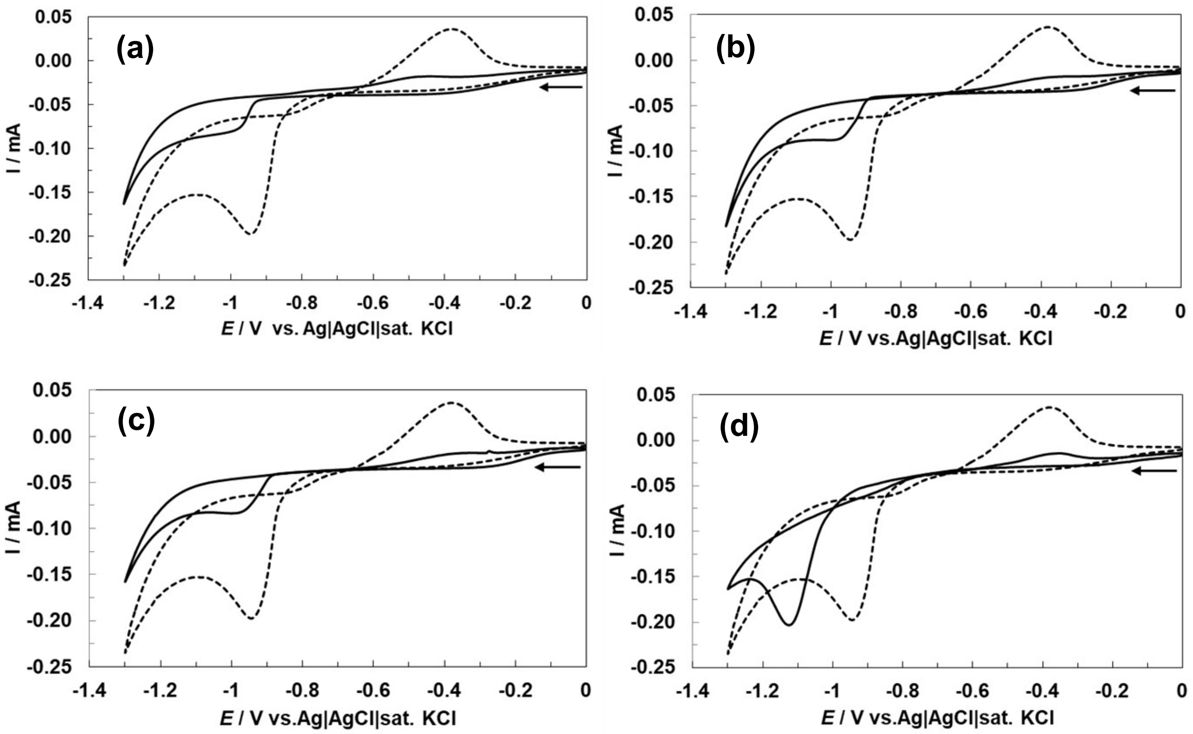

Fig. S9 CV curves recorded at 5 mV s^{-1} for CoONPs/PBI/MWCNT/GCE in 0.1 M PBS (broken line) and mixed solution (solid line) of 0.1 M PBS and another anion: (a) SO_4^{2-}, (b) Cl^-, (c) CH_3COO^- and (d) NO_3^-. Electrode surface area: apparently 0.283 cm^2.

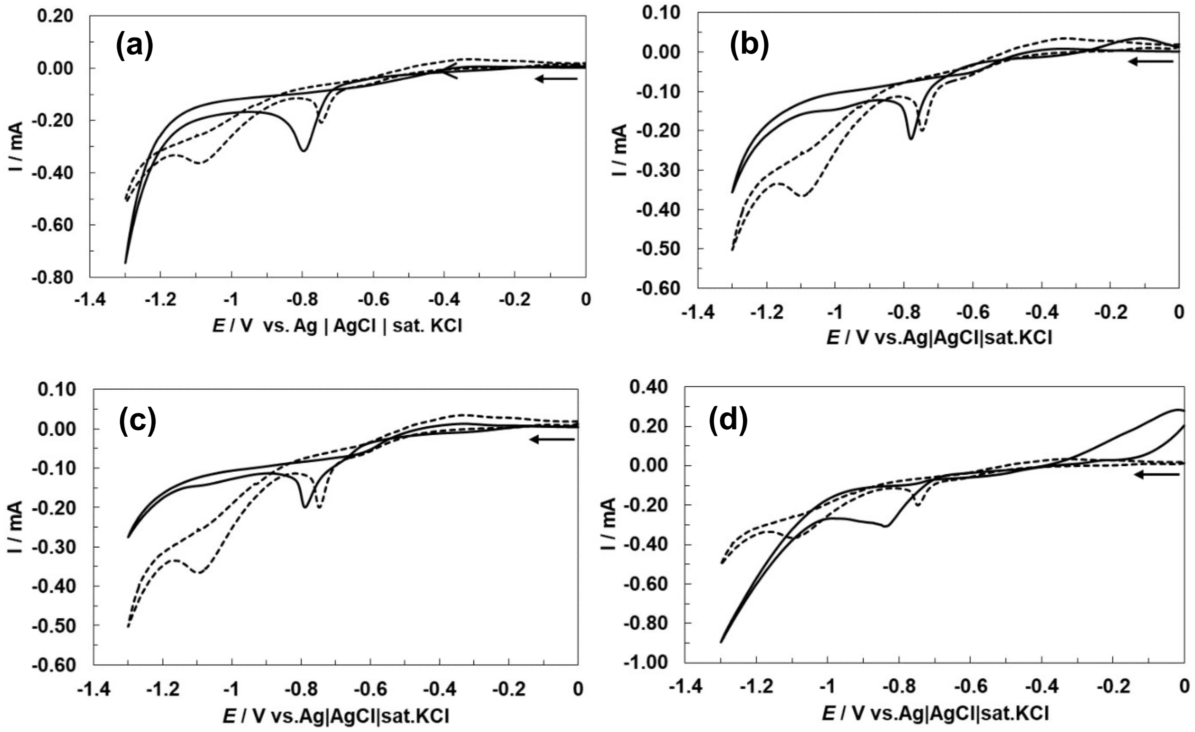

Fig. S10 CV curves recorded at 5 mV s^{-1} for Co wire electrode in 0.1 M PBS (broken line) and mixed solution (solid line) of 0.1 M PBS and another anion: (a) SO_4^{2-}, (b) Cl^-, (c) CH_3COO^- and (d) NO_3^-. Electrode surface area: apparently 0.283 cm^2.

The phosphate species formed in the reaction depend on the range of pH so the investigations of pH effects were also carried out for both electrodes in 0.1 M phosphate ion solution at different pH values. Cobalt precipitate will be formed when the phosphate ion exists inside the solution. For acidic condition, the potentiometric response originates from a mixed potential resulting from slow oxidation of Co and simultaneous reduction of oxygen. At pH is greater than 7, oxygen reduction reaction (ORR) peak was observed rather than redox peaks suggesting the reaction happened was mainly oxygen reduction reaction for CoONPs/PBI/MWCNT (Fig. S11). Cobalt has used as base metal for ORR catalyst in alkaline electrolyte[2-3]. Meanwhile, the second cathodic peak disappeared for Co wire electrode in alkaline condition suggesting the electrode has lost its ability to react with phosphate ion in alkaline condition (Fig. S12).

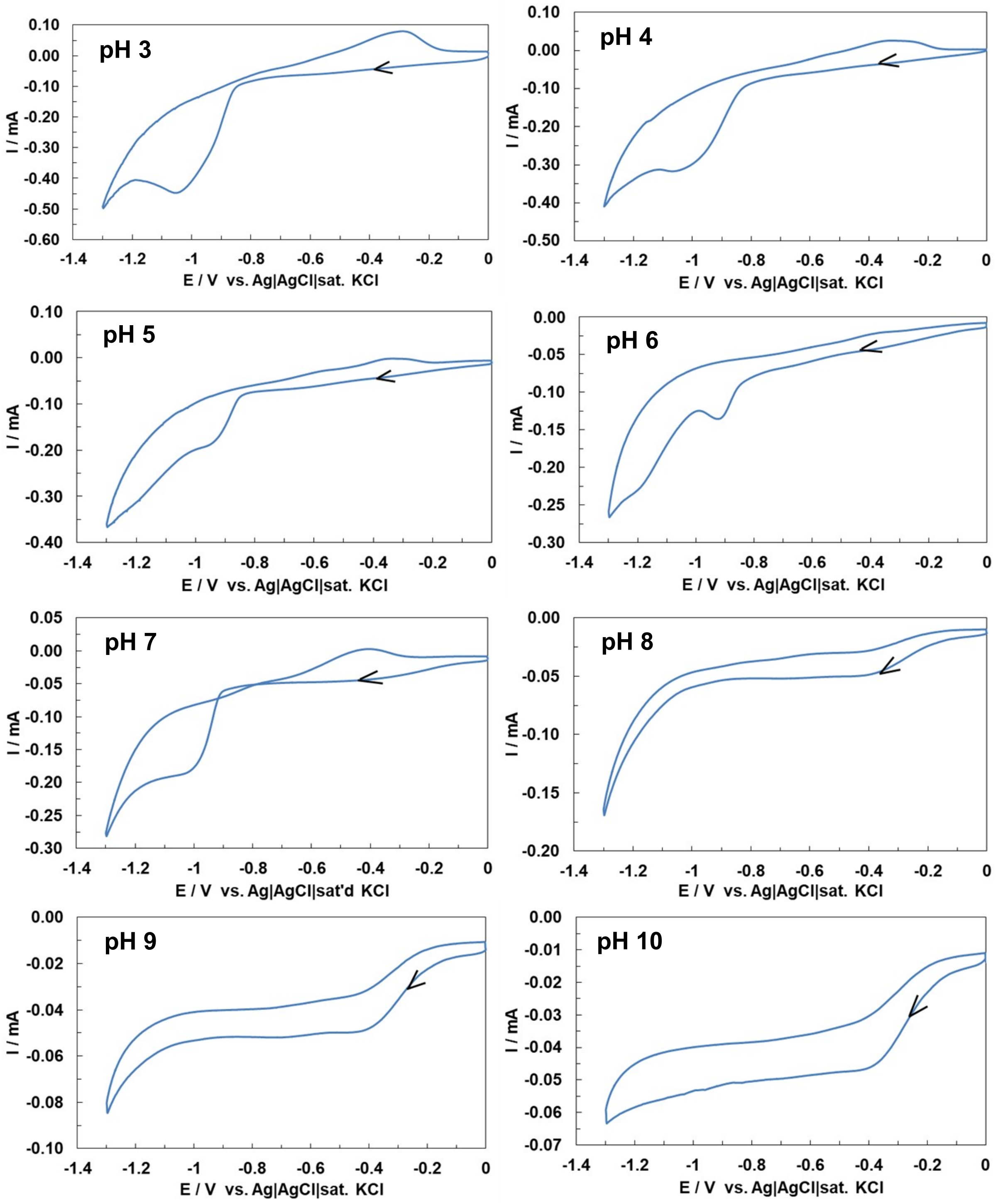

Fig. S11 CV curves recorded at 5 mV s^{-1} for CoONPs/PBI/MWCNT/GCE in 0.1 M phosphate solution at various pH. Electrode surface area: apparently 0.283 cm^2.

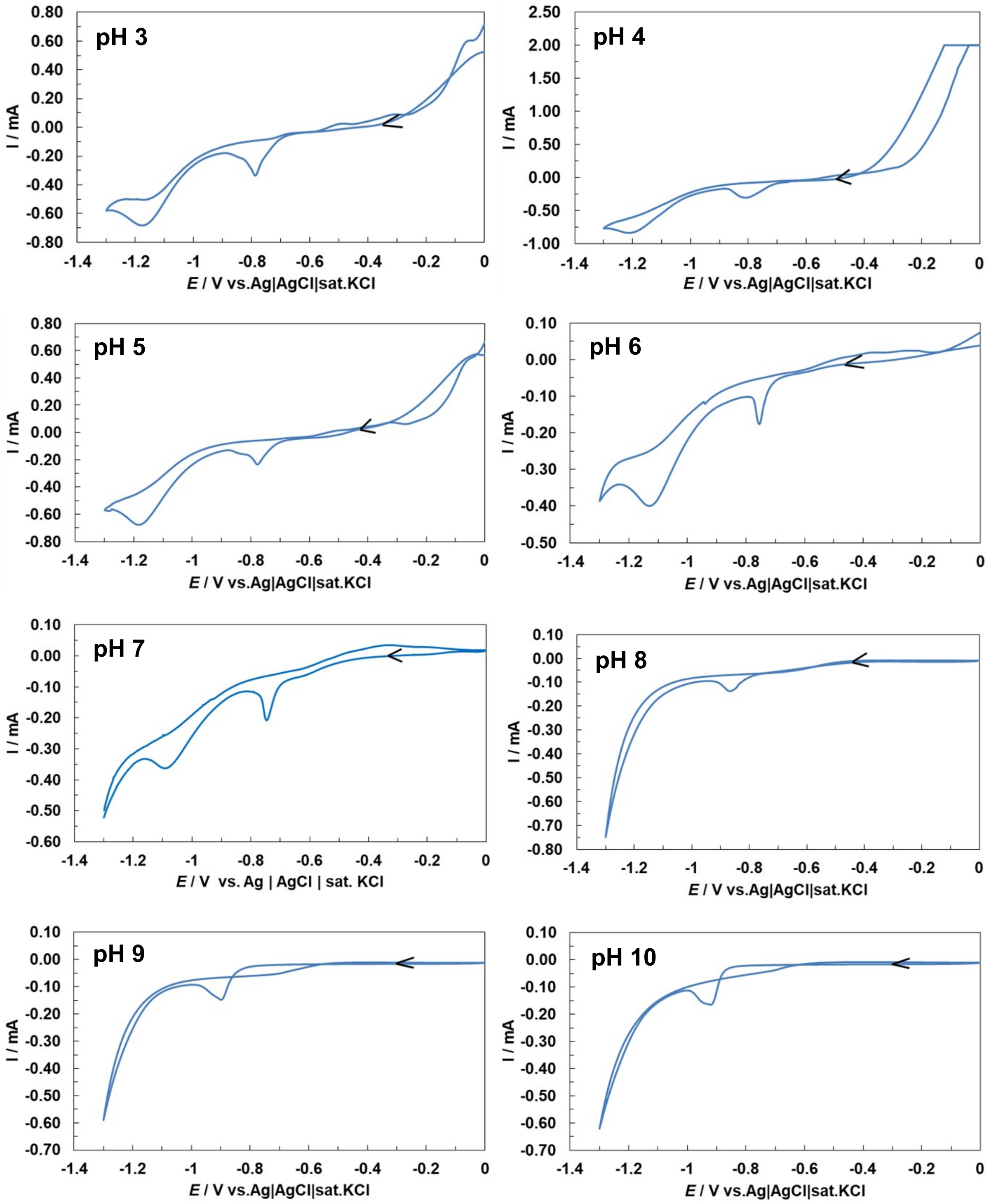

Fig. S12 CV curves recorded at 5 mV s^{-1} for Co wire electrode in 0.1 M phosphate solution at various pH. Electrode surface area: apparently 0.283 cm^2.

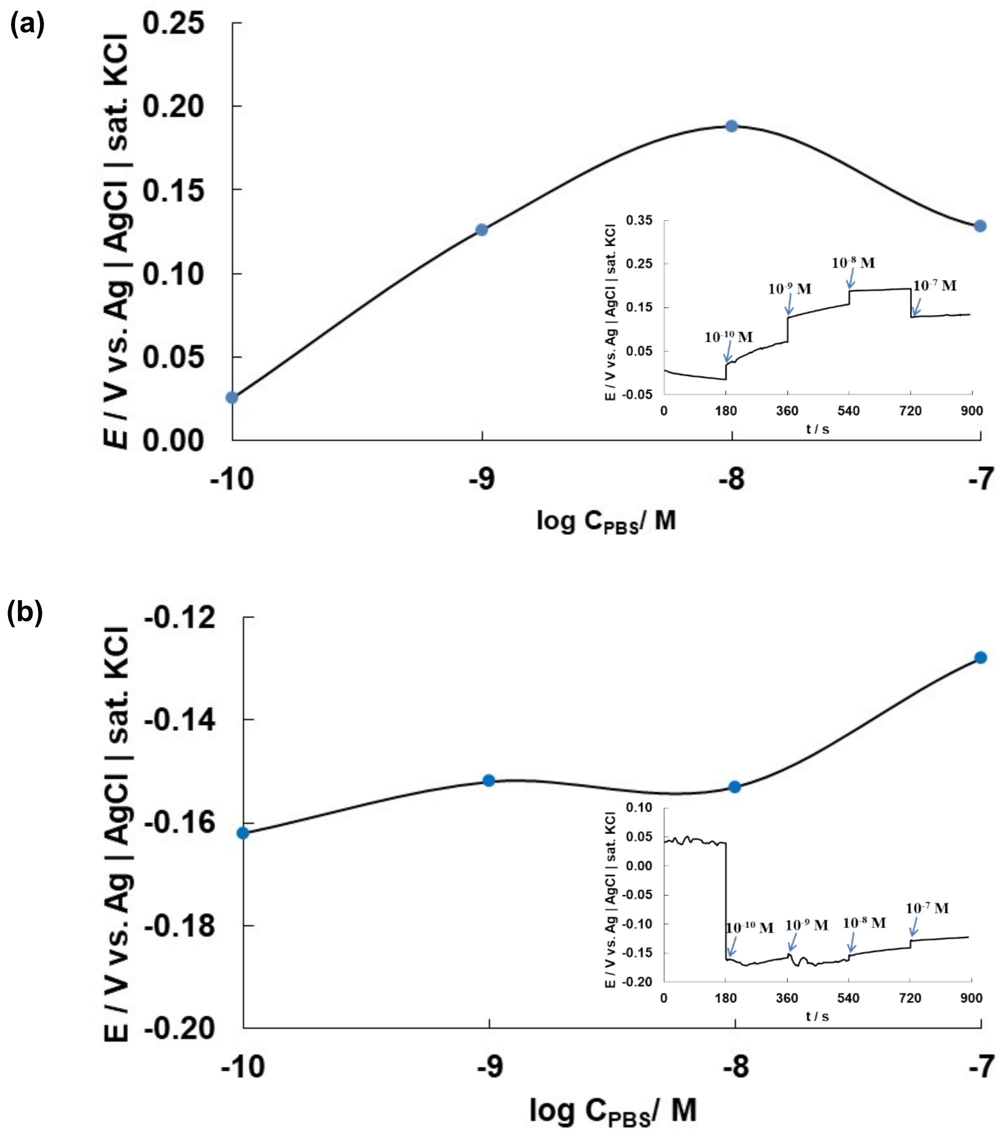

Fig. S13 OCPs (*E*) obtained at MWCNT/GCE in different phosphate concentrations (C_{PBS} = 1.0×10^{-10} to 1.0×10^{-7} M) at pH (a) 4 and (b) 7.

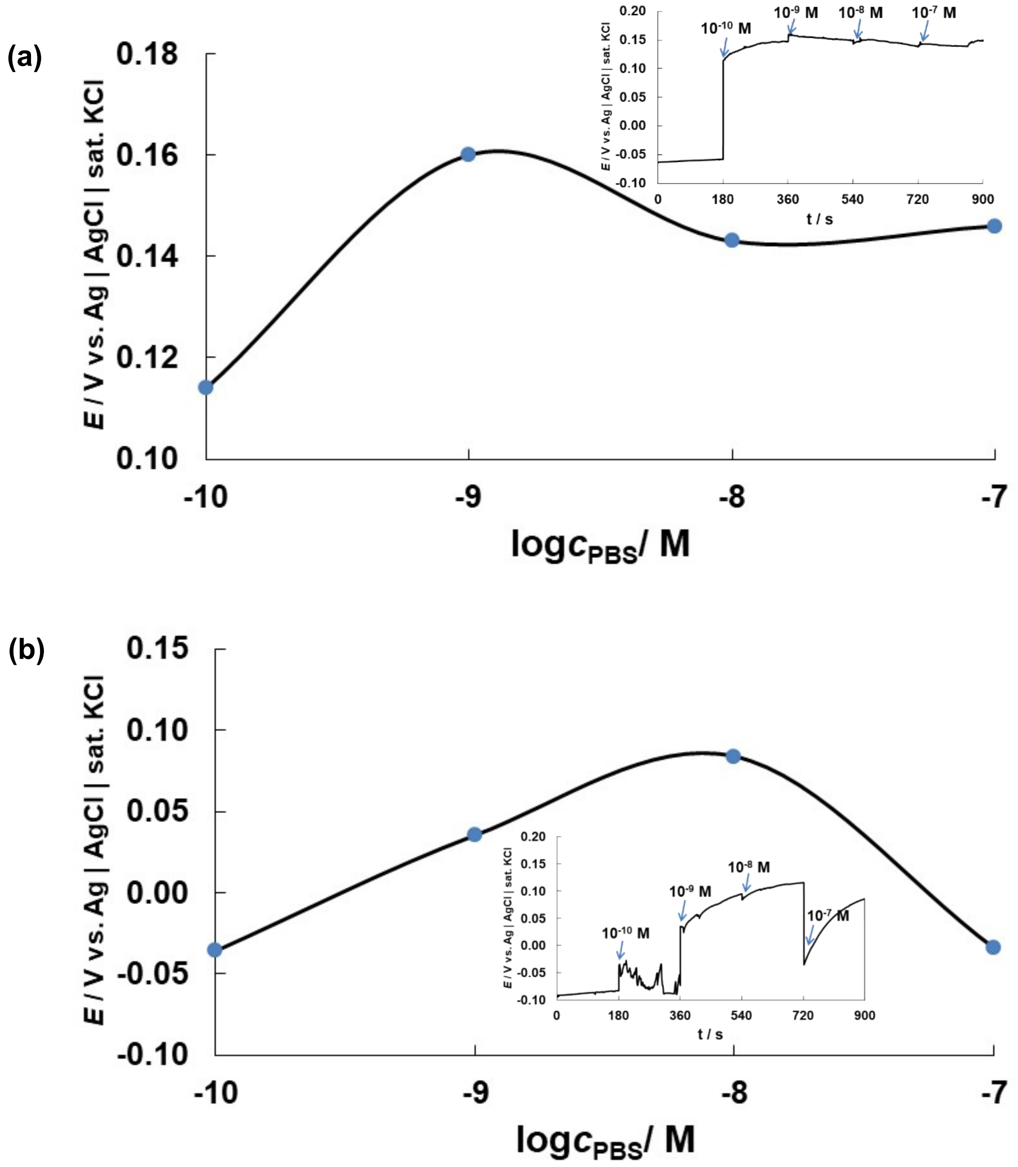

Fig. S14 OCPs (*E*) obtained at CoONPs/MWCNT/GCE in different phosphate concentrations ($C_{PBS} = 1.0 \times 10^{-10}$ to 1.0×10^{-7} M) at pH (a) 4 and (b) 7.

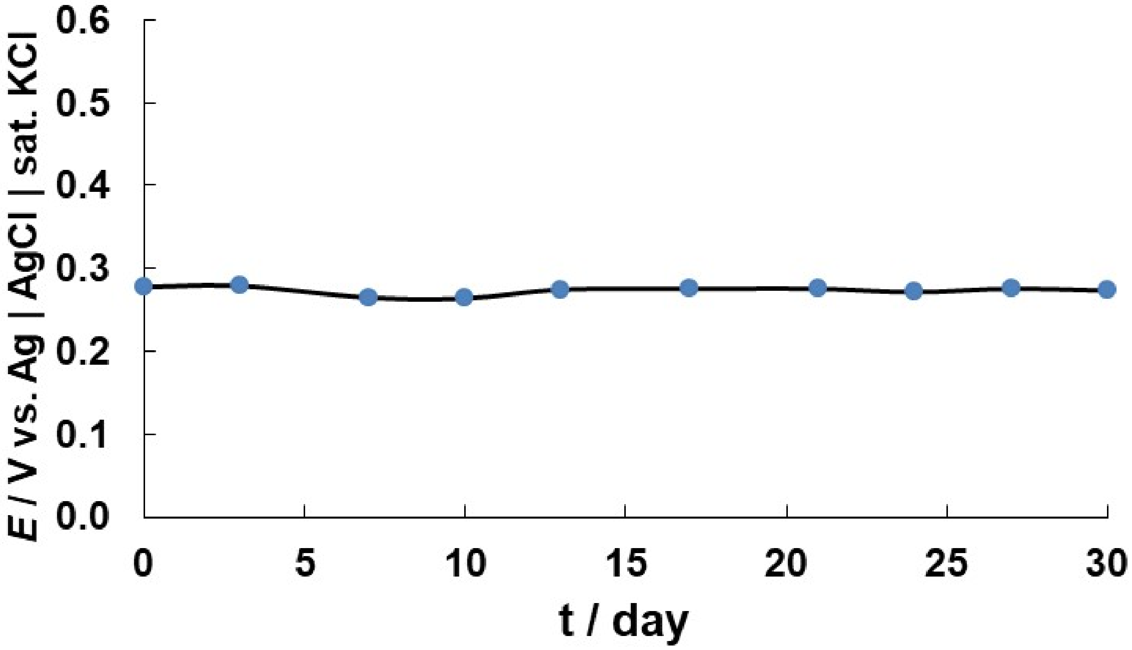

Fig. S15 The OCPs (*E*) stability at CoONPs/PBI/MWCNT/GCE in 10 nM phosphate solution pH 7 recorded for 1 month.

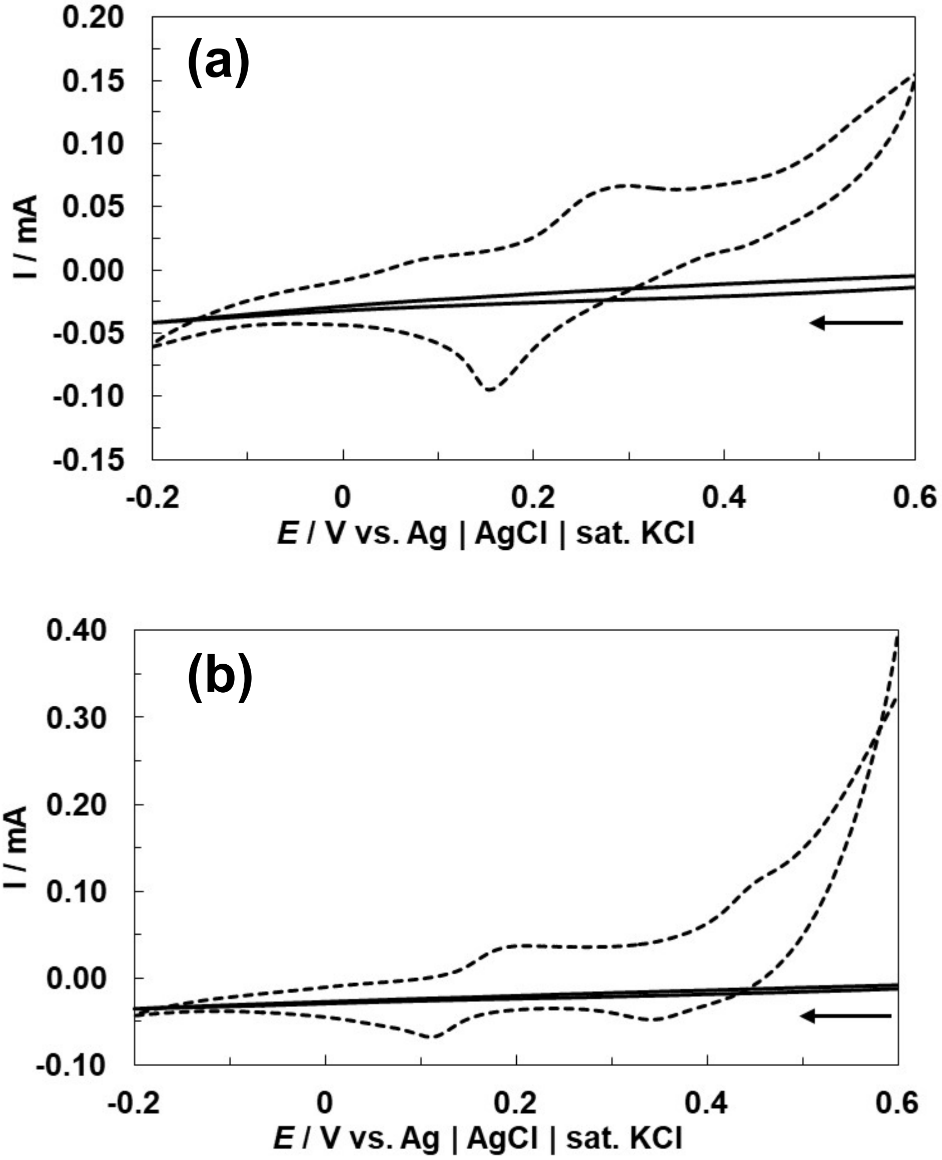

Fig. S16 Actual current vs. potential of CV curves at CoONPs/PBI/MWCNTs/GCE recorded in a mixed solution of 0.1 M NaOH and 0.1 M $HClO_4$ (broken line) and in 0.1 nM PBS (solid line) at (a) pH 4 and (b) pH 7 using a scan rate of 5 mV s^{-1}. Electrode surface area: apparently 0.283 cm^2.

$$\mathbf{H_3PO_4 \xrightleftharpoons[]{\substack{pK_{a1}\\ = 2.15}} H_2PO_4^{-} \xrightleftharpoons[]{\substack{pK_{a2}\\ = 7.20}} HPO_4^{2-} \xrightleftharpoons[]{\substack{pK_{a3}\\ = 12.35}} PO_4^{3-}}$$

Fig. S17 pK_a value changes for different phosphate species.

References

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