Supporting Information

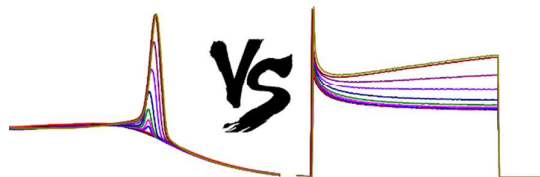## Photoelectrochemical Stripping Analysis

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ABSTRACT

The electrochemical stripping analysis (ECSA) is a promising method for metal ions detection. However, the low sensitivity and poor reproducibility limits its practical applications. The combination with other powerful detection techniques to address these concerns is highly desirable. Herein, the anodic stripping method and photoelectrochemical (PEC) technique are integrated into a new detection platform of PEC stripping analysis (PECSA) with bismuth vanadate ($BiVO_4$) as both optoelectronic material and electrochemical enrichment candidate. The new PECSA strategy presents high sensitivity and excellent reproducibility, in addition, inherited from the ECSA, this strategy also offers new selectivity dimensions through the potential-dependent response, and thus implements reproducible, sensitive, and selective detection of silver ion (Ag^+) in real biological and environmental samples. The success of PECAS strategy

shed light on the rational combination of various analysis techniques for versatile applications.

Experimental Section

Materials. FTO coated glass (FTO-P003) were purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd. Potassium iodide (KI), nitric acid (HNO₃), bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), pbenzoquinone, vanadyl acetylacetonate (VO(acac)₂), dimethyl sulfoxide (DMSO), ethanol, acetone, silver nitrate (AgNO3), copper nitrate hydrate (Cu(NO₃)₂), cadmium nitrate tetrahydrate (Cd(NO₃)₂·4H₂O), chromic nitrate (Cr(NO₃)₃·9H₂O), lead nitrate (Pb(NO₃)₂), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), cobalt nitrate hydrate (Co(NO₃)₂·6H₂O), magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O), nickel nitrate hydrate (Ni(NO₃)₃·9H₂O), potassium nitrate (KNO₃), cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O), acetate (HAc), sodium acetate anhydrous (NaAc) were purchased from Macklin Inc., Shanghai, China. All aqueous solutions were used as received and prepared using deionized water (DI) with a resistivity of 18.2 MΩ cm. The fetal bovine serum was purchased from Procell Life Science and Technology Co. Ltd. The lake water was taken from the Yingtao river, Shanghai, China.

Synthesis of BiVO₄ electrodes. The BiOI film was first electrodeposited on FTO glass with potential of -0.1 V in an electrolyte composed with 0.04 M Bi(NO₃)₃, 0.4 M KI, and 0.23 M p-benzoquinone solutions at room temperature

for 5 min. Then, the obtained BiOI/FTO electrode was rinsed with 0.2 mL of DMSO containing 0.2 M VO(acac)$_2$, and followed annealing in a muffle furnace at 450 ºC for 2 h. After cooling to room temperature, the electrodes were soaked in 1 M NaOH solution for 30 min with gentle stirring to remove the excess V$_2$O$_5$ on the BiVO$_4$. Finally, the pure BiVO$_4$ electrode was rinsed with deionized water and dried in ambient air.

Synthesis of Bi film electrodes. The Bi film electrodes were prepared by electrochemical deposition method at a potential of -0.3 V for 5 min in a supporting electrolyte of 20 μM Bi(NO$_3$)$_3$·5H$_2$O with vigorously stirring.

Material Characterizations. The morphologies of BiVO$_4$ and Ag/Bi/BiVO$_4$ were determined by scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM, JEOL JEM 2100). The crystalline structure of the samples was analyzed by X-ray diffraction (XRD, Bruker D8 Discover diffractometer, using Cu Kα radiation, λ = 1.540598 Å). Photoelectron Spectroscopy (XPS) data were collected by an Axis Ultra instrument (Kratos Analytical) under ultrahigh vacuum (<10^{-8} torr) and using a monochromatic Al Kα X-ray source. Binding energies were referenced to the C 1s binding energy of 285.0 eV.

ECSA for Ag$^+$ detection on BiVO$_4$ and Bi film electrodes. Measurements were carried out with BiVO$_4$ or Bi film as working electrode in NaAc-HAc buffer (0.2 M, pH = 6.0). The BiVO$_4$ or Bi film electrode was immersed in buffer solution containing a known amount of silver ion at a potential of −0.3 V

for 300 s for enrichment of analyte. The stirring was then stopped and after 30 s

the differential pulse voltammogram (DPV) was recorded over the 0.0 to 0.5 V

range (with scan rate of 200 mV s^{-1}, pulse amplitude of 50 mV, and pulse time

of 4 ms).

PECSA for Ag^{+} detection on BiVO$_4$. Both electrochemical enrichment and

photoelectrochemical detection of Ag^{+} were conducted with the BiVO$_4$ as

photoelectrode in NaAc-HAc buffer solution (0.2 M, pH = 6.0). The electrochemical

enrichment parameters of time and potentials were optimized. Subsequently, the PEC

detection of Ag^{+} was evaluated under chopped light irradiation at a fixed stripping

potential of 0.27 V. The photocurrent was measured under irradiation from a 300 W

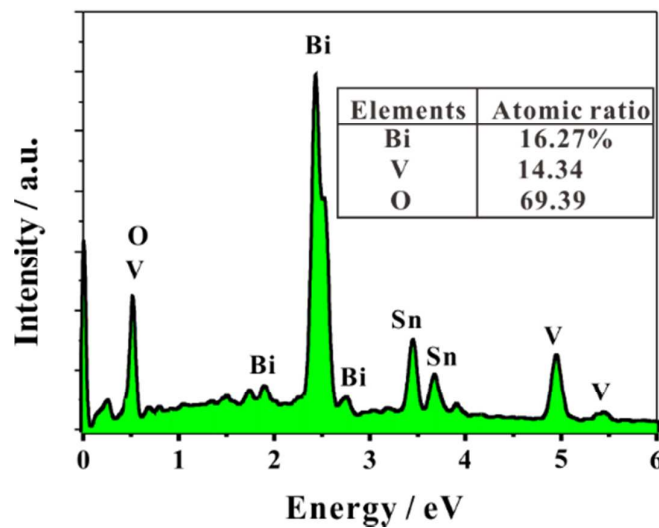Xe lamp (PLS-SXE300, PE300BF) with 420 nm cut-off filter.

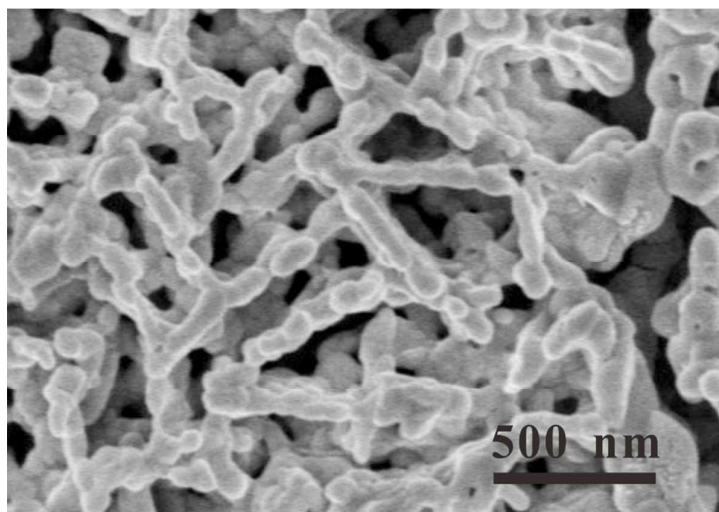| Elements	Atomic ratio
Bi	16.27%
V	14.34
O	69.39

Figure S1. EDS of BiVO$_4$.

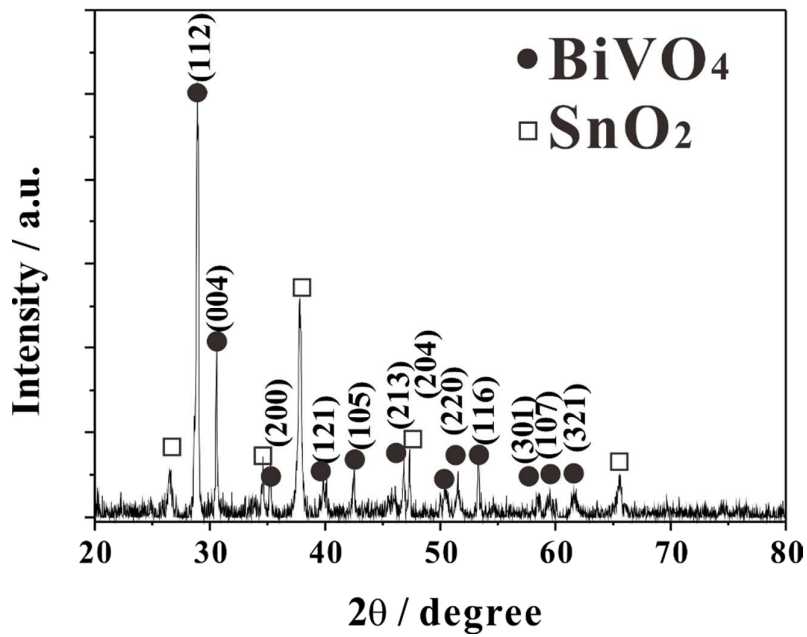**Figure S2**. SEM image of $BiVO_4$ after electrochemical enrichment.

Figure S3. XRD pattern of $BiVO_4$ electrode after electrochemical enrichment.
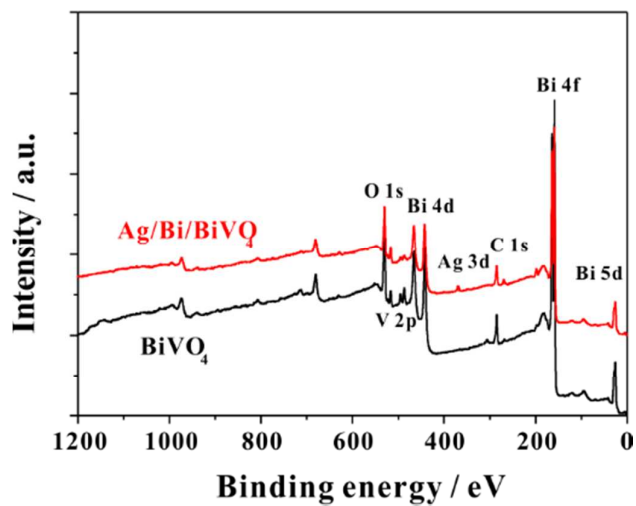
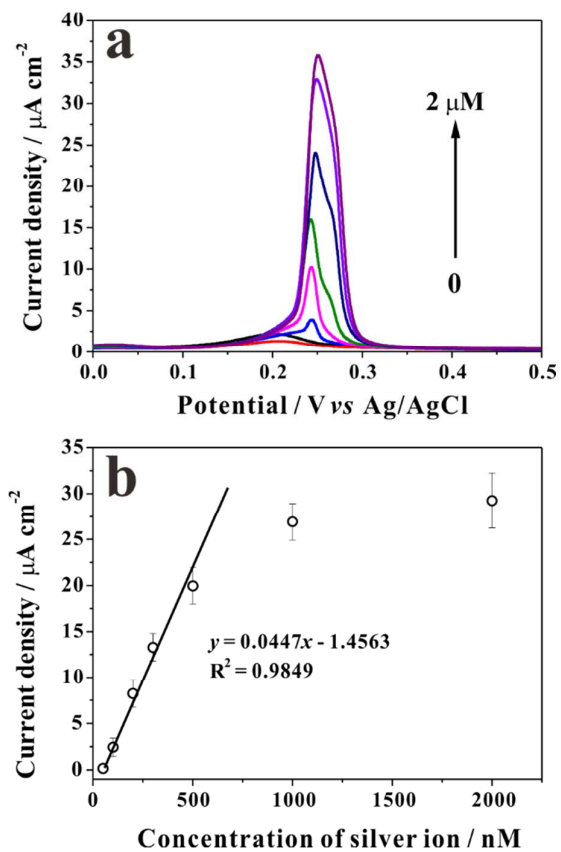**Figure S4**. XPS survey spectra of $BiVO_4$ and $Ag/Bi/BiVO_4$.

Figure S5. (a) ECSA performance for Ag^+ detection on Bi film electrode and (b) corresponding current density *vs* Ag^+ concentration calibration curve.
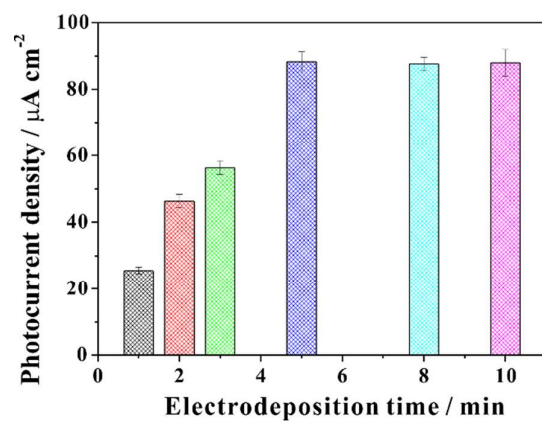
Figure S6. Optimization of the amounts of $BiVO_4$ for PECSA detection of Ag^+ (400 nM).
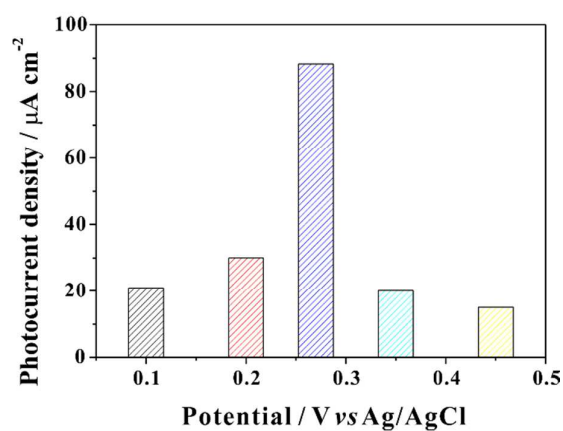

Figure S7. PECSA performances of Ag^+ (400 nM) on $BiVO_4$ with different applied potentials.
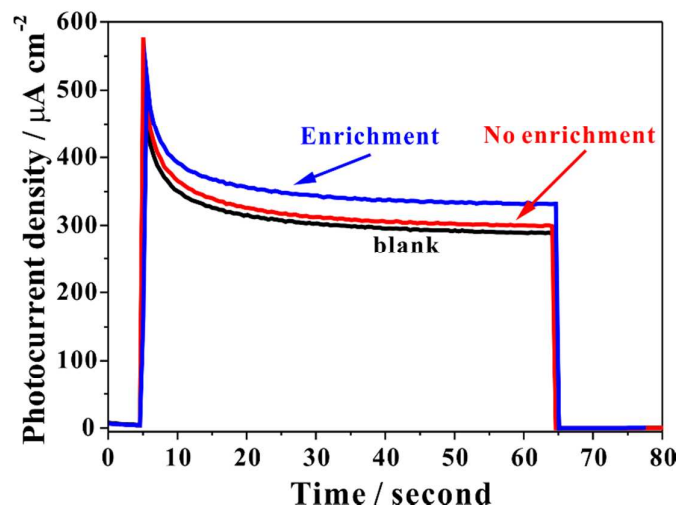

Figure S8. PEC response of Ag^+ with or without electrochemical enrichment processes.
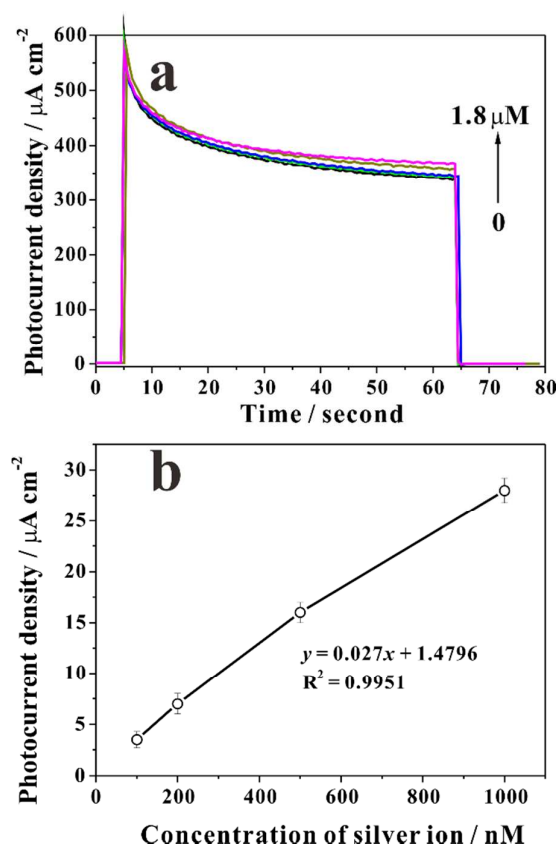
Figure S9. PEC sensing of silver ions of (a) amperometric transient photocurrent density *vs* time plots and (b) photocurrent density–Ag$^+$ concentration calibration curve.
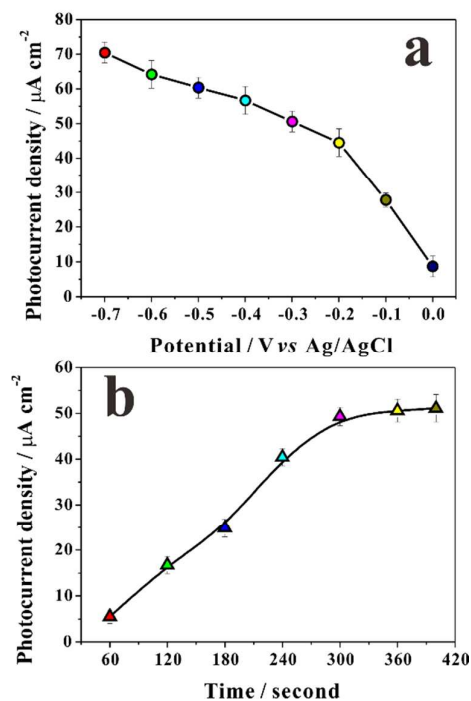

Figure S10. Optimization of electrochemical enrichment parameters of (a) applied
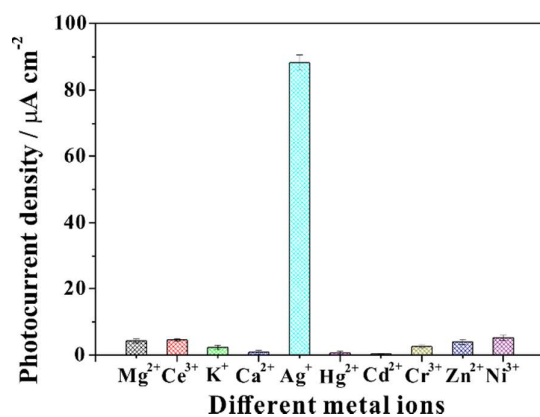
potentials and (b) time.

Figure S11. Anti-interference property with different addition sequence of metal ions.
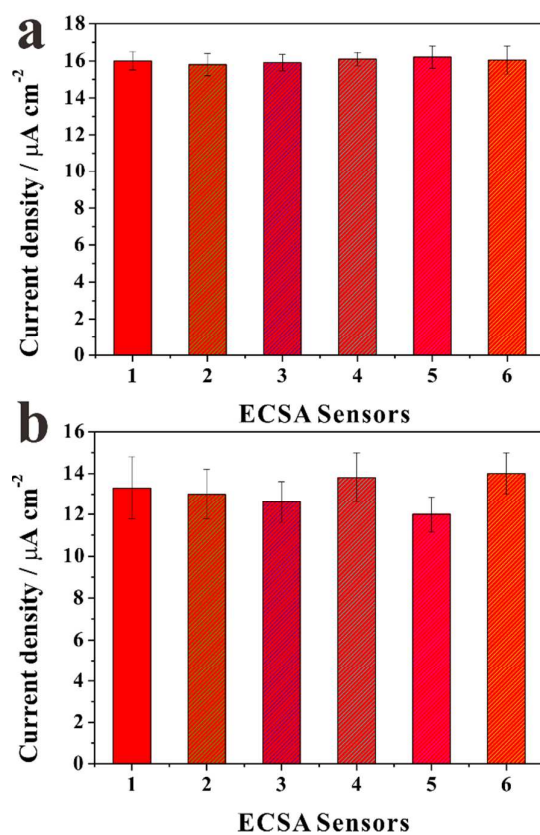

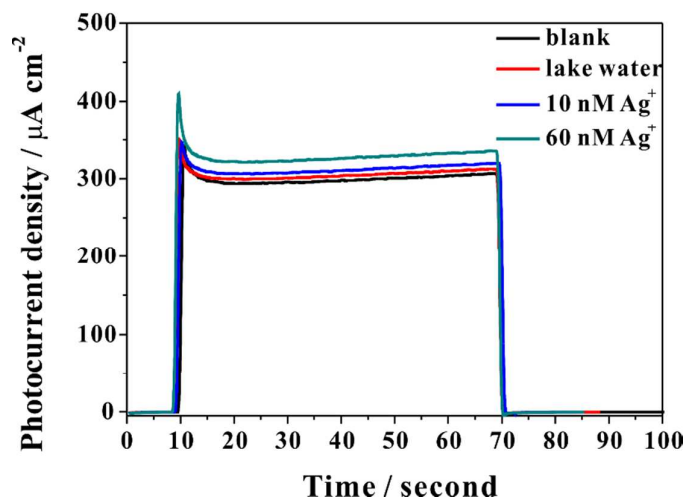**Figure S12**. Reproducibility of ECSA sensors of (a) $BiVO_4$ and (b) Bi film.

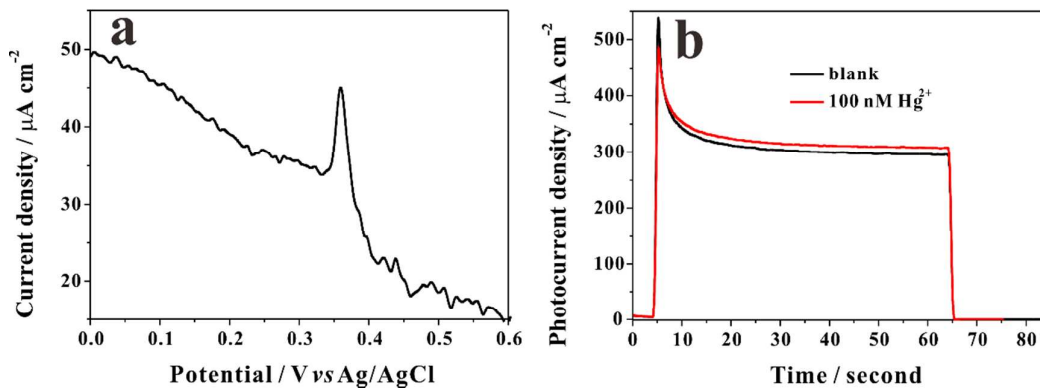**Figure S13**. PECSA response of Ag$^+$ in lark water.

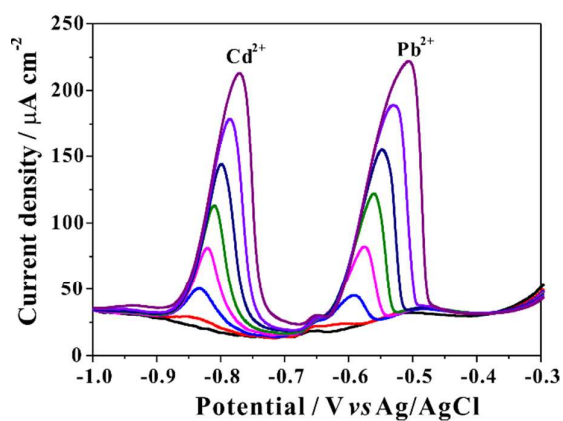**Figure S14**. (a) ECSA and (b) PECSA of Hg^{2+} on BiVO$_4$.

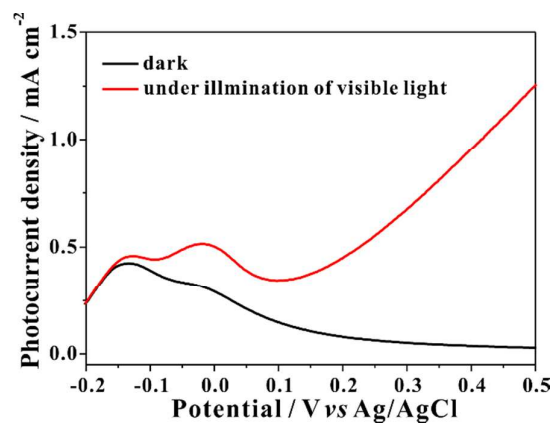**Figure S15**. ECSA of Cd^{2+} and Pb^{2+} on BiVO$_4$.

Figure S16. LSV curves of BiVO$_4$ in dark and under illumination of visible light.

Table S1. Comparison of sensing performances of BiVO$_4$ and Bi film electrodes in ECSA and PECSA model

Sensing Model	Materials	Sensitivity / μA cm^{-2} nM^{-1}	Limit of detection / nM	Linear range / nM
PECSA	BiVO$_4$	0.2068	0.3	1-1200
ECSA	BiVO$_4$	0.0460	10	30-500
ECSA	Bi film	0.0447	20	50-500
PEC	BiVO$_4$	0.0270	40	100-1000

Table S2. Comparison of Ag$^+$ sensing with different methods.

Electrode	Method	Linear range / nM	Limit of detection / nM	References
Carbon nanotubes	ECSA	10-10000	1.8	1
Silver hexacyanoferrate(II)	Amperometric	80-3000000	50	2
Silver thimerosal	Potentiomtery	500-1000000	250	3
Dipyridyl-functionalized silica gel	Potentiometry	500-1×10^8	100	4
AgNPs- graphene quantum dots	Fluorescence	0 -100	3.5	5
Silver nanomaterials	colorimetric	100-7500	56	6
Silicon−Carbon-Dots@Dopamine	Fluorescence	5-50	2.5	7
PVP-Pt	Colorimetric	0.01-10000	0.08	8
Carbon Nanoparticles	Fluorescence	0-400	0.5	9
BiVO$_4$	PEC(ECE)	1-1200	0.3	This work

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