Supporting Information

A paper-based photoelectrochemical sensing platform based on in situ grown ZnO/$ZnIn_2S_4$ heterojunctions onto paper fibers for sensitively detecting AFP

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Content

Preparation of Au nanoparticle modified paper working electrode (Au-PWE)

The Au/paper substrate of μPAD was obtained by growing Au NPs layer on the cellulose fibers. Herein, 80 mL of ultrapure water was put into a round-bottom flask and heated it to 90 ℃, and 0.8 ml of 1% $HAuCl_4$ solution was dripped to the prepared solution and then heated to 96 ℃ for 1 min. Next, 2.8 ml of 1% trisodium citrate was added and stirred for 20 min. Finally, the above solution was stirred and cooled to receive a gold seed solution. After that, 80 μL of hydroxylamine hydrochloride and gold seed solution (volume ratio 1:1) was dropped on the surface of Au/paper substrate each time and dried at air. After repeated dripping five times, it was thoroughly washed with ultrapure water and dried at 60 ℃. The Au-PWE was prepared successfully.

Modification process of the working electrode

Firstly, chitosan solution (0.1 wt.%, 20 μL) was dropped on the surface of photoelectrode and left to dry at 4 °C for 24 h, followed by washing with 0.01 M NaOH and ultrapure water. After that, glutaraldehyde solution (5 wt.%, 25 μL) was spread onto the photoelectrode, keeping for 35 min and washed thoroughly with ultrapure water. The antibody solution (100 μg/mL, 30 μL) was dropped onto the activated photoelectrode. After being incubated at room temperature for 24 h, the activated photoelectrode was washed with PBS. After that, 25 μL of 0.2% bovine serum albumin (BSA) solution dissolved by PBS (0.1 mol L^{-1}, pH 6.6) was added on the antibody modified photoelectrode for 1 h at 4 °C to block non-specific binding sites. Finally, 30 μL antigen of AFP with different concentration were added onto the photoelectrode and incubated at 4 °C for 40 min, followed by washing thoroughly with PBS. Then, the signals of photocurrent were measured on the CHI 660C electrochemical working station in PBS solution (0.1 mol L^{-1}, pH 6.6) dissolved 0.1 M ascorbic acid. During the PEC signal measurement procedure, a PLS-SXE 300 xenon lamp (500 W) was utilized as the irradiation source, which was switched on and off every 10 s and the applied potential was 0.4 V.

Table S1 Comparison of other PEC-based AFP biosensors

Materials	Detection range ($ng\ mL^{-1}$)	LOD ($ng\ mL^{-1}$)	Ref.
β-In_2S_3@carbon dots	0.5-50	0.0379	[1]
graded oxygen-doped CdS	0.2-100	0.0784	[2]
MoS_2/Au/GaN	1.0-150	0.3	[3]
RGO/dimethyldioctadecylammonium/ZnO	0.05-100	0.05	[4]
ZnO/$ZnIn_2S_4$	0.1-100	0.03	This work

Table S2 Comparison of methods for the detection of AFP

Analytical method	Detection range ($ng\ mL^{-1}$)	LOD ($ng\ mL^{-1}$)	Ref.
Fluorescence immunoassay	1-80	0.45	[5]
Electrochemical immunoassay	0.5-50	0.1	[6]
Chemiluminescent immunosensor	5-70	2.5	[7]
PEC immunosensor	0.1-150	0.1	[8]
PEC immunosensor	0.1-100	0.03	This work

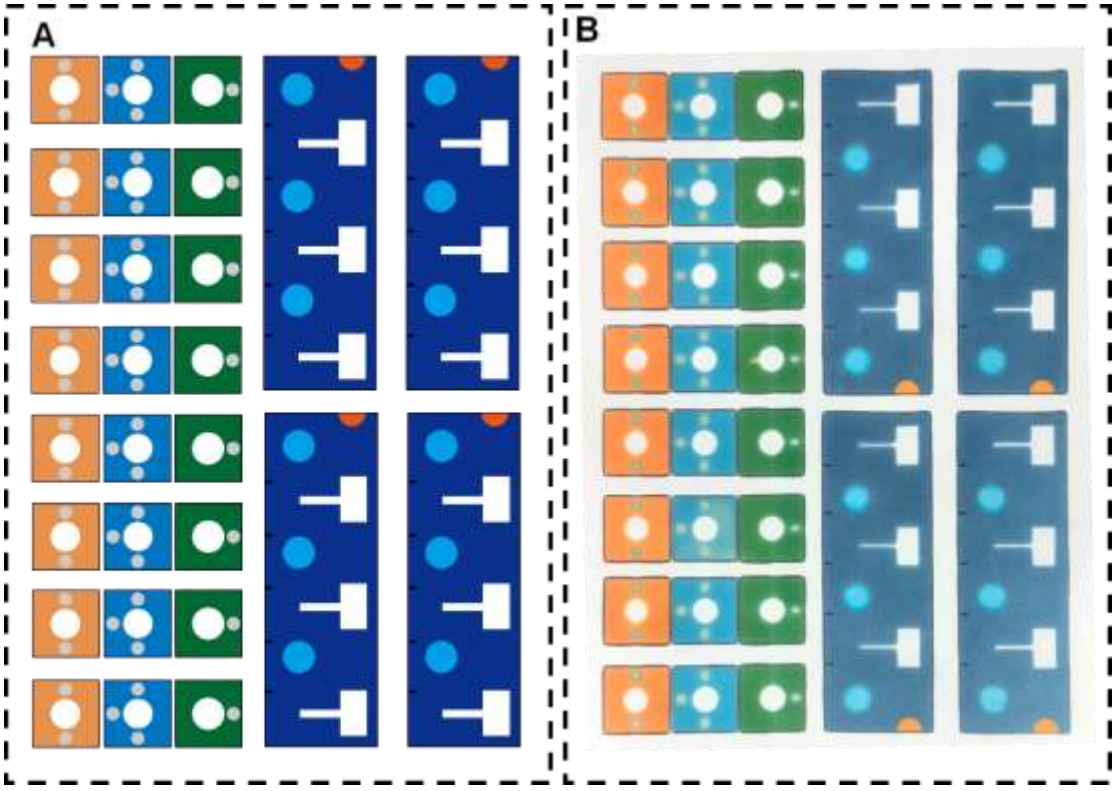

Figure S1. Wax-patterns of the μPAD on a paper sheet (A4). (A): before baking; (B): after baking.

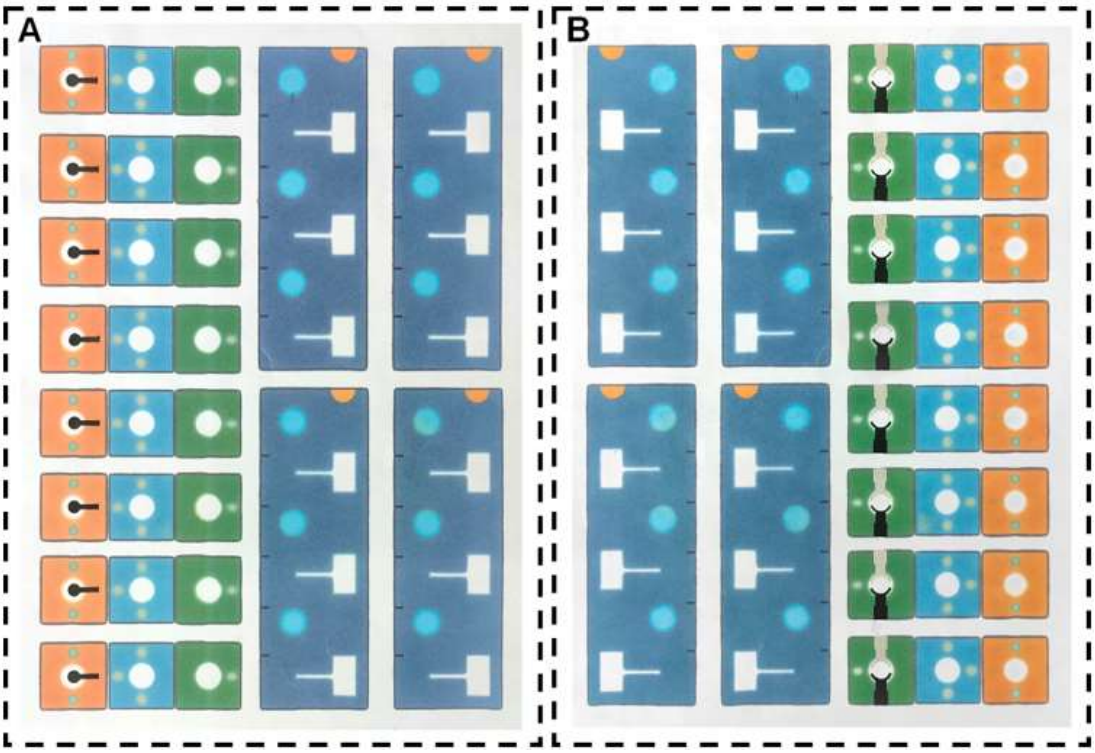

Figure S2. Printing of electrode of the μPAD on a paper sheet (A4). (A): The side of the A4 paper that is printed with carbon electrode; (B): The reverse side of Figure S2A.

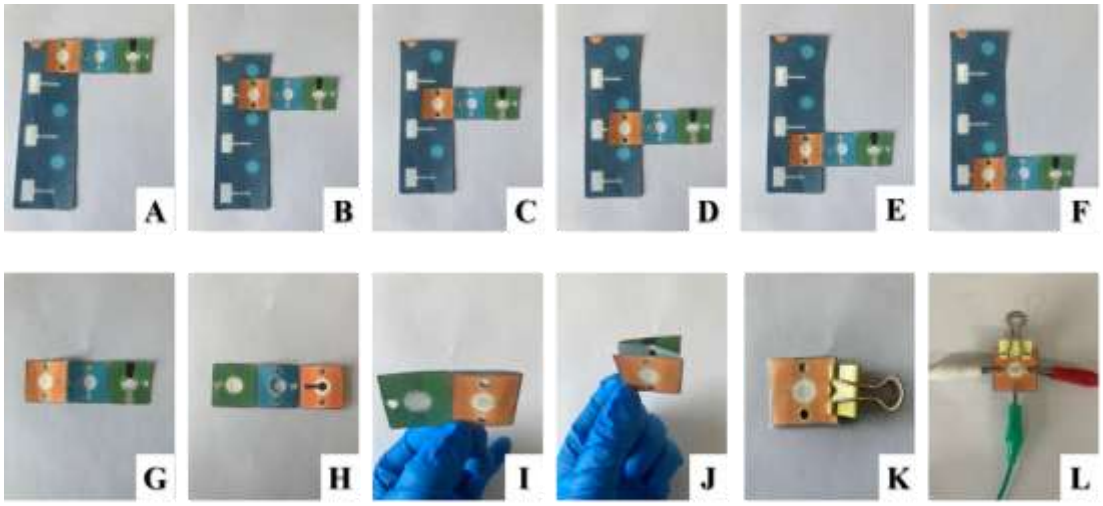

Figure S3. The physical picture of modification and detection of μPAD. (A), (C), and (E): The μPAD during the process of electrode modification; (B), (D), and (F): The washing process of the detection tab; (G) and (H): Unfolded μPAD; (I) and (J): The folding process of the μPAD; (K) and (L): The μPAD fold state during the process of PEC.

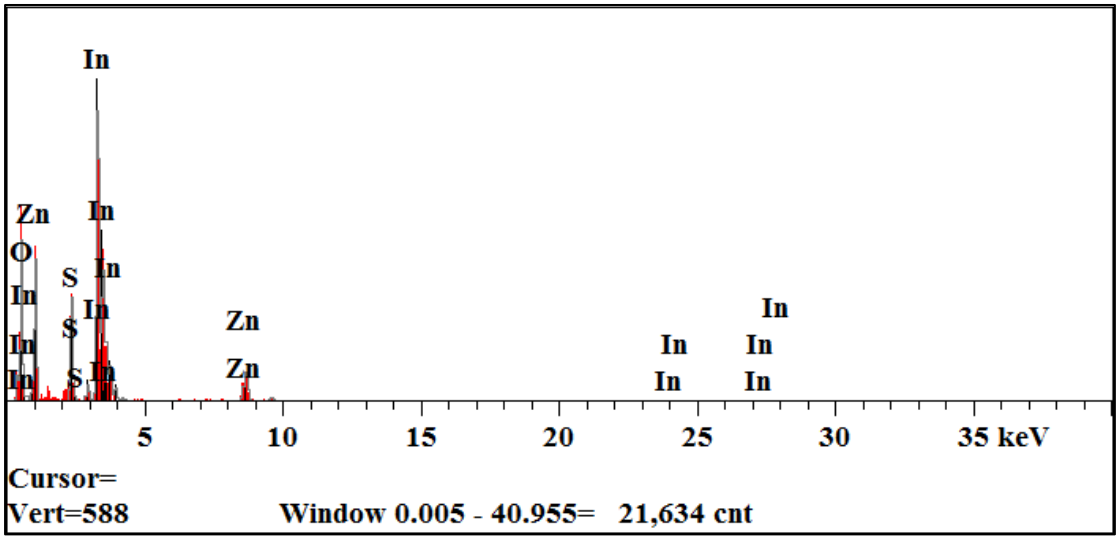

Figure S4. Energy-dispersive spectrum (EDS) spectrum of $ZnO/ZnIn_2S_4$.

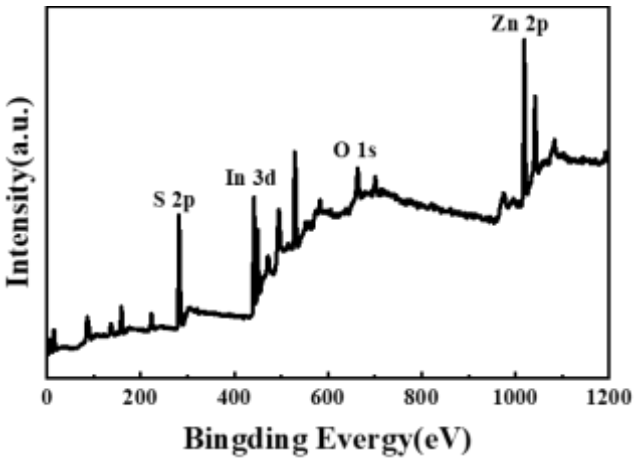

Figure S5. XPS spectra of ZnO/$ZnIn_2S_4$ wide scan.

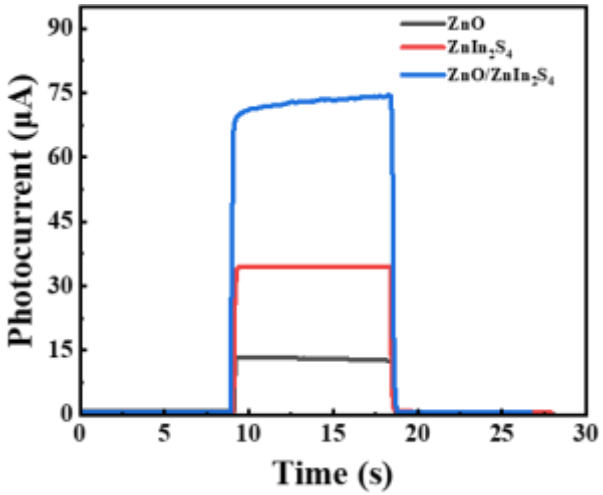

Figure S6. Photocurrent responds of ZnO, $ZnIn_2S_4$ and ZnO/$ZnIn_2S_4$. The PEC measurement was performed in the PBS (0.1 M, pH 6.6) containing 0.1 M AA, and the applied potential was 0.4 V.

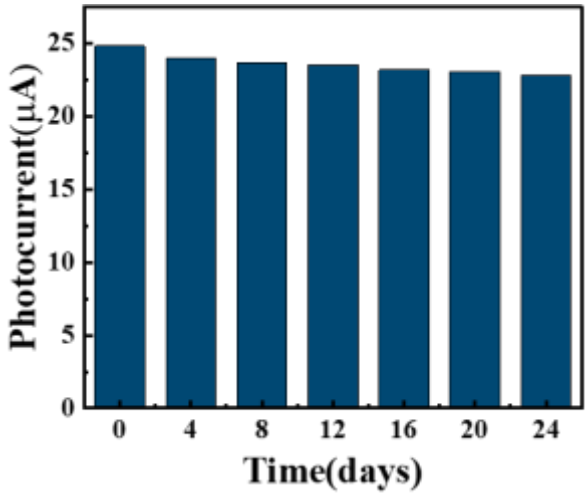

Figure S7. Stability of the proposed μPAD for different periods of storage: 0 days, 4 days, 8 days, 12 days, 16 days, and 24 days (c_{AFP} = 0.1 ng mL^{-1}). The PEC measurement was performed in the PBS (0.1 M, pH 6.6) containing 0.1 M AA, and the applied potential was 0.4 V.

References

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