Electronic Supplementary Information (ESI)

WS₂ nanosheets sensitized CdS quantum dots heterostructure for photoelectrochemical immunoassay of alpha-fetoprotein coupled with enzyme-mediated biocatalytic precipitation

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Experimental section

Apparatus

Scanning electron micrograph (SEM) was characterized using S-4800 field emission scanning electron microscopy (Hitachi, Japan). Transmission electron micrographs (TEM) were performed by a Tecnai 12 microscope (Philips, Netherlands). UV–vis absorption spectra were obtained by a UV-2501PC fluorescence spectrometer (Shimadzu Co. Kyoto, Japan). X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250Xi spectrometer (Thermo Fisher, USA) with an Al $K\alpha$ radiation source. Dynamic light scattering (DLS) spectrum was obtained via Nano-ZS90 light scattering instrument (Malvern, Britain). Raman spectra were performed by a DXRxi Micro Raman imaging spectrometer (Thermo Fisher, USA). Photoelectrochemical measurements were

performed via a home-built PEC system with white light as an accessory excitation source. Intensity-modulated photovoltage spectroscopy (IMVS) measurements were detected on a Zahner intensity modulated photospectrometer (Zahner, German) with a white light as the excitation source. Incident-photon-to-current conversion efficiency (IPCE) data were measured in the wavelength range from 300 to 800 nm (Newport 94063, Stratford, CT, USA). Current-voltage (I-V) experiments were recorded by a CHI 660E electrochemical workstation (CH Instruments Inc., USA). Electrochemical impedance spectroscopy (EIS) was tested using a PGSTAT30/FRA2 system (Autolab, The Netherlands). All experiments were carried out at room temperature using a conventional three-electrode system: a modified ITO electrode (4 mm in diameter) as the working, a platinum electrode as the auxiliary, and an Ag/AgCl as the reference electrodes.

Preparation of CdS QDs

CdS QDs was synthesized as follows.[S1] 250 μL of TGA was dropped into 100 mL three-necked flask containing 50 mL of $CdCl_2$ solution (0.01 M), and was subsequently stirred and purged nitrogen for 30 min. The pH of the above solution could be adjusted with 1.0 M NaOH up to about 11 during this interval. After the injection of 5.0 mL of Na_2S solution (0.1 M), the resulting mixture was refluxed for 4 h at 110 °C under nitrogen atmosphere. Finally, the obtained QDs were diluted by ultrapure water, treated by centrifugal precipitation to remove the impurities with the aid of isopropanol, and redissolved by the equivalent amount of deionized water.

Preparation of WS$_2$ NTs

Exfoliated WS$_2$ NTs were prepared via mixed-solvent strategy according to the previous work.[S2] Briefly, 300 mg of WS$_2$ powder was dispersed into 100 mL ethanol-water solution (the volume fraction of water was 65%), and then sonicated for 16 h. The generated dispersion was centrifuged for 20 min twice at 3000 rpm to remove the unexfoliated bulk WS$_2$. The resulting supernatant was further collected via a vacuum-rotary evaporation procedure at 70 °C. After being dissolved, the aqueous solution of WS$_2$ NTs was obtained and stored at 4 °C for next experiments.
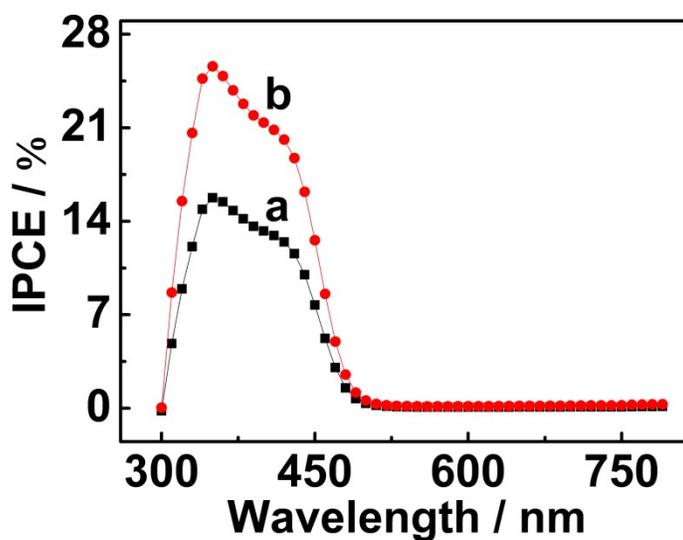
Fig. S1 IPCE spectra of CdS (a), WS$_2$/CdS (b) modified ITO electrodes in 0.1 M Tris-HCl of pH 7.4 containing 0.1 M AA.
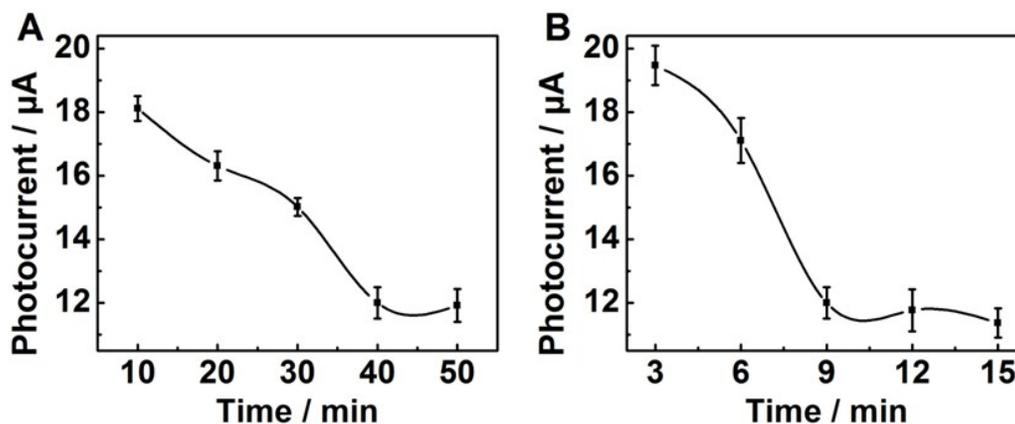
Fig. S2 Effects of (A) incubation time between Ab_1 and AFP, and (B) biocatalytic precipitation time of HRP-Ab_2 on photocurrent responses of prepared immunosensor. The AFP concentration was 5 ng mL^{-1}.

Table S1 Comparison of the analytical performances of vairous immunosensing methods toward target AFP.

Detection methods	Linear range (ng mL^{-1})	Detection limit (ng mL^{-1})	References
Electrochemistry	$1 \times 10^{-5} - 1$	3.7×10^{-6}	S3
Electrochemistry	$5 \times 10^{-3} - 50$	1.6×10^{-3}	S4
Electrochemiluminescence	$1 \times 10^{-4} - 30$	3×10^{-5}	S5
Electrochemiluminescence	$1 \times 10^{-2} - 100$	3.3×10^{-3}	S6
Fluorescence	$9.8 \times 10^{-2} - 15$	9.5×10^{-2}	S7
Fluorescence	$1 - 80$	0.45	S8
Photoelectrochemistry	$5 \times 10^{-2} - 100$	4×10^{-2}	S9
Photoelectrochemistry	$1 \times 10^{-3} - 1000$	3.1×10^{-4}	S10
Photoelectrochemistry	$1 \times 10^{-3} - 20$	4.3×10^{-4}	This work

Table S2 Detection results of clinical serum samples using proposed and reference methods.

Sample	Proposed method (ng mL^{-1})	Reference method (ng mL^{-1})	Relative error (%)
1	11.19	10.58	+5.8
2	3.85	3.67	+4.9
3	1.67	1.72	-2.9
4	0.72	0.67	+7.5

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