SUPPORTING INFORMATION FOR

A potentiometric resolved photoelectrochemical system based on CdS nanowires and $SnNb_2O_6$ nanosheets: A case application for dual biomarkers analysis

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Section 1: Experimental

Chemicals. Myo standards, anti-Myo, cTnI standards and anti-cTnI were purchased from Shanghai Linc-Bio Science Co., Ltd (Shanghai, China). Cadmium nitrate [$Cd(NO_3)_2 \cdot 4H_2O$], thiourea, ethylenediamine, tin (Ⅱ) chloride dihydtate ($SnCl_2 \cdot 2H_2O$) and niobium pentaoxide (Nb_2O_5) were bought from Aladdin Industrial Co., Ltd (Shanghai, China). Chloroauric acid ($HAuCl_4 \cdot 3H_2O$), chitosan (CS) and glutaraldehyde (GA) were obtained from Shanghai Reagent Company (Shanghai, China). Human serum albumin, human immunoglobulin and bovine serum albumin (BSA) were obtained from Shanghai Solarbio Bioscience & Technology Co., Ltd (Seebio Biotechnology). Ultrapure water was from Aike Water Treatment Solution Provider (18.2 MΩ·cm, China).

Apparatus. PEC measurements were performed on a homemade PEC system, containing a 500 W Xe lamp as the irradiation source and a RST5200 electrochemical workstation (Zhengzhou Shiruisi Technology Co., Ltd., China) for bias voltage adjustment and photocurrent response collection. 0.1 M phosphate buffer solution (PBS, pH 7.4) containing 0.01 M H_2O_2 were used for the PEC tests. Cyclic voltammograms (CVs) were also conducted on the RST5200 electrochemical workstation in 0.1 M KCl solution containing 5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) as the electrolyte. In all the PEC and electrochemical experiments, the three electrode system consisted of a modified ITO electrode with two adjacent areas as working electrode, a platinum wire as auxiliary electrode and a saturated Ag/AgCl electrode as reference electrode was used. The size and morphology of the nanomaterials were observed by the scanning electron microscope (SEM, S-4800, Hitachi, Tokyo, Japan) and transmission electron microscope (TEM, Tecnai G^2 F20 TEM, FEI Co., Hillsboro, Oregan, USA).

Synthesis of CdS NWs and $SnNb_2O_6$ NSs. The CdS NWs were prepared according to the literature.[1] Firstly, 2.37 g thiourea and 3.21 g $Cd(NO_3)_2 \cdot 4H_2O$ were dissolved in 50 mL ethylenediamine under stirring. Then, the mixture was transferred to a Teflon-lined autoclave and allowed for reaction at 180 °C for 72 h. After the successive

centrifugation and washing by ethanol and water in turn for three times, the CdS NWs can be eventually obtained by drying in a vacuum oven at 60 °C.

The $SnNb_2O_6$ NSs were synthesized as follows.[2] Firstly, 0.5 g Nb_2O_5 and 2.24 g KOH were added into 40 mL ultrapure water under stirring for 10 min. Then, the suspension was transferred into a 50 mL Teflon-lined autoclave followed by heating at 180 °C for 48 h. After adjusting the pH of the resulted solution to 7.0 with 2.0 M HCl aqueous solution, the $Nb_2O_5 \cdot nH_2O$ was formed. Subsequently, 0.42 g $SnCl_2 \cdot 2H_2O$ was added into the solution and the pH values were adjusted to 2.0 with 2.0 M HCl solution under stirring. After that, the above solution was transferred into a 100 mL Teflon-lined autoclave and kept at 200 °C for 48 h. Finally, the yellow products were centrifuged, washed by water and ethanol for three times and further dried at 60 °C in a vacuum oven.

Fabrication of the PEC biosensor. Prior to construct the biosensor, the ITO electrode was cleaned by isopropyl alcohol including 2.0 M KOH solution. The cleaned ITO electrode was modified with Au NPs by an electrodeposition method, in which the bare ITO electrode was dipped into 0.05% $HAuCl_4$ solution and the deposition voltage was set as 0.9 V for 150 s. Then, 20 μL CdS NWs (1.0 mg/mL) and 20 μL $SnNb_2O_6$ NSs (2.0 mg/mL) dispersed in 0.1 mg/mL CS solution were separately casted on the two adjacent areas (each with 0.25 cm^2 surface area) of the Au/ITO electrode to gain CdS NWs/$SnNb_2O_6$ NSs modified Au/ITO electrode. After drying at 60 °C, 20 μL GA were pipetted onto the two adjacent areas of the modified electrode at room temperature for 1 h to link with the amino-group of the CS on the interface of the electrode. The same volume of anti-Myo and anti-cTnI at 20 μL were subsequently incubated with the electrode at 4 °C for 12 h .The anti-Myo and anti-cTnI were immobilized on the electrode by the reaction between the amino-group of the protein and the aldehyde of the GA. Finally, the resulted electrode were blocked with 20 μL BSA at 37 °C for 1 h. For Myo and cTnI detection, the same volume (20 μL) of Myo and cTnI with different concentrations were separately dropped on two adjacent areas of the electrode at 37 °C for 1 h.

Section 2: Optimization of experimental conditions.

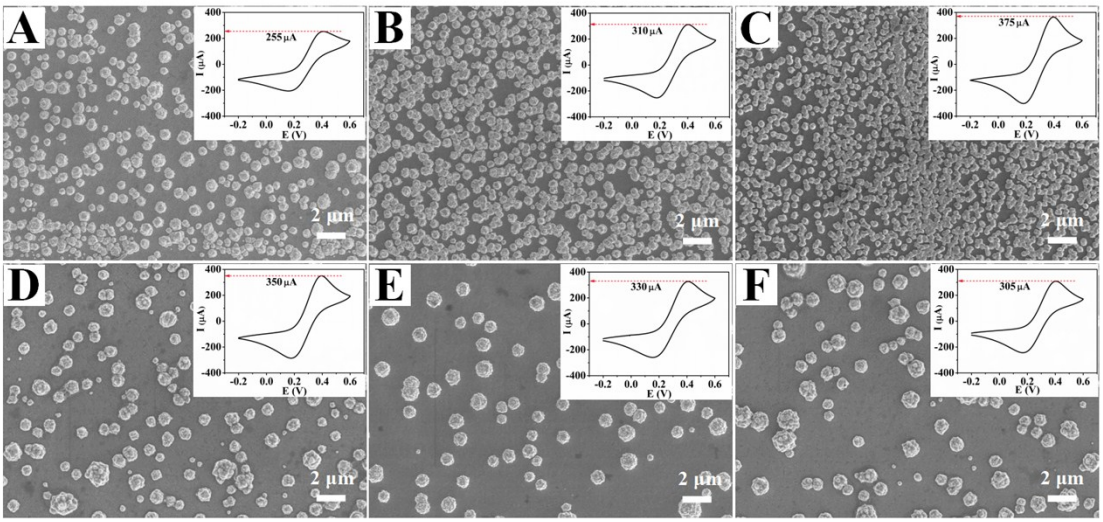

Figure S1. SEM images of the Au NPs at deposition voltage of (A) 0.7 V, (B) 0.8 V, (C) 0.9 V, (D) 1.0 V, (E) 1.1 V and (F) 1.2 V on the ITO electrode. Inset: The corresponding CV responses of the Au NPs/ITO at different deposition voltages.

To improve the PEC performance of the electrode, the Au NPs with high conductivity and large surface area were modified on the ITO electrode by an electrodeposition method. The deposition voltages ranged from 0.7 V to 1.2 V were investigated. As shown in Figure S1, a compact Au NPs layer was formed on the ITO electrode at a deposition voltage of 0.9 V. The CV curve of the Au NPs/ITO at a deposition voltage of 0.9 V also exhibits the highest peak current response. Therefore, the deposition voltage of 0.9 V was chosen for the preparation of Au NPs/ITO.

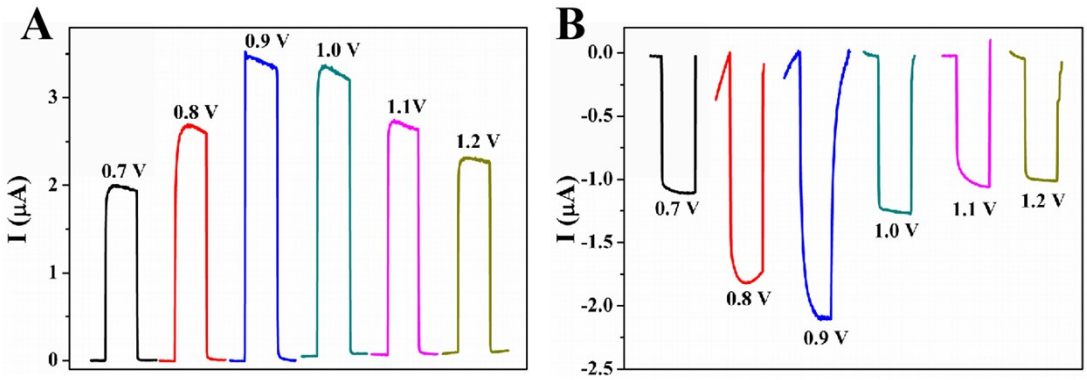

Figure S2. PEC performance on the CdS NWs/$SnNb_2O_6$ NSs/Au/ITO at different deposition voltages in PBS (0.1 M, pH 7.4) containing 0.01 M H_2O_2.

To further evaluate the effect of the deposition voltages on the PEC performance, the PEC behaviors of CdS NWs/$SnNb_2O_6$ NSs/Au/ITO prepared at different deposition voltages were determined. As shown in Figure S2, the anodic photocurrent and cathodic photocurrent enhanced with the increasing of deposition voltage up to 0.9 V, due to the formation of the uniform Au film at the high deposition voltage. However, the PEC intensity fallen when the deposition voltage further increased to 1.2 V. Consequently, the optimal deposition voltage for the immobilization of Au NPs on ITO was set as 0.9 V.

Section 3: Anodic and cathodic linear potential scans

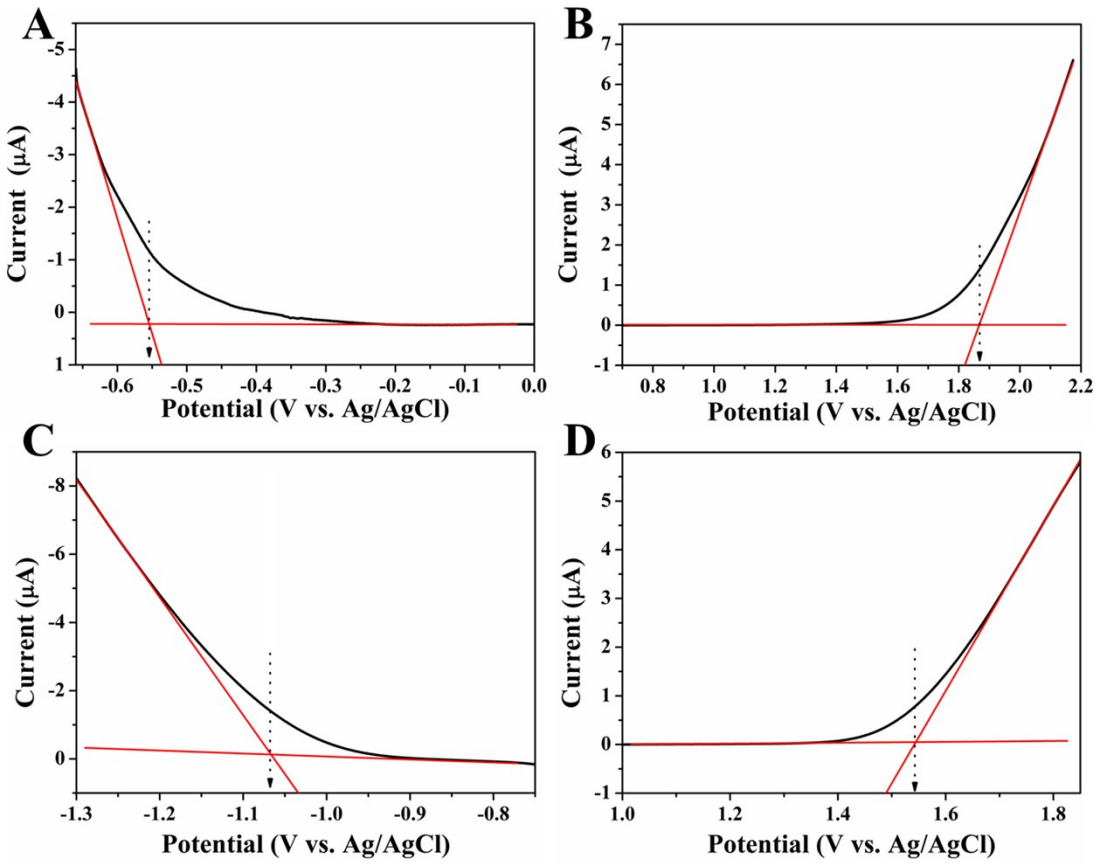

Figure S3. Linear sweep voltammetry for characterizations on CB and VB edge of CdS NWs (A, B) and $SnNb_2O_6$ NSs (C, D) at the scan rate of 5 mV/s in 0.1 M PBS (pH = 7.4). The modified ITO was used as the working electrode.

Section 4: PEC response of photocathode in different electrolyte solutions

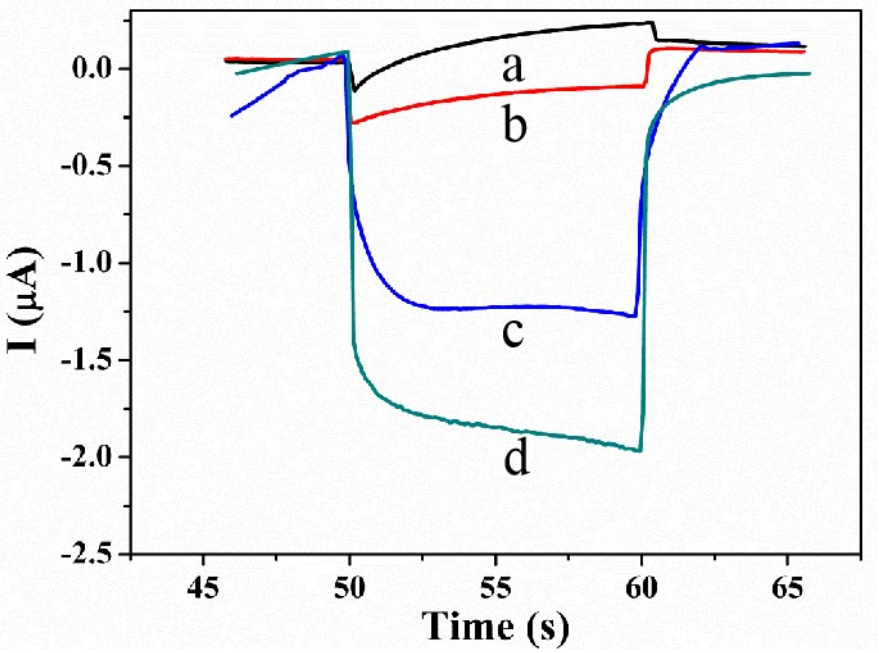

Figure S4. Photocurrent signals of the $SnNb_2O_6$ NSs/Au NPs/ITO electrode in the electrolyte solution without dissolved O_2 (a), the electrolyte solution containing dissolved O_2 (b), the electrolyte solution containing H_2O_2 but without dissolved O_2 (c), the electrolyte solution containing H_2O_2 and dissolved O_2 (d). To remove the the dissolved O_2, the electrolyte solution was pumped into nitrogen for 30 min.

Section 5: Selectivity of the biosensor

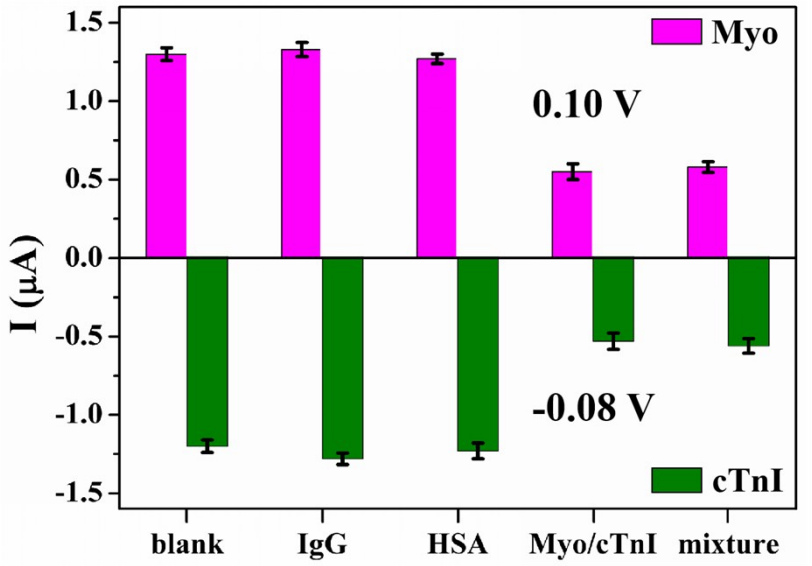

Figure S5. Selectivity of the biosensor for Myo and cTnI detection.

Section 6: Table S1 Analytical results of different methods to detect Myo and cTnI.

Different methods	Detection of Myo			Detection of cTnI		
	Linear ranges (ng/mL)	Detection limits (ng/mL)	References	Linear ranges (ng/mL)	Detection limits (ng/mL)	References
Electrochemistry	1 - 1400	0.67	[3]	0.024 - 240	0.024	[6]
Fluorescence	4.95 - 976.85	3.2	[4]	0.05 - 32	0.032	[7]
Surface plasmon resonance	10 - 5000	10	[5]	0.01 - 1000	0.005	[8]
PEC	0.005 - 50	0.002	This work	0.005 - 50	0.0025	This work

Section 7: Table S2 Analytical results of Myo and cTnI in human serum samples by the proposed method and the reference method.

Serum sample	Myo			cTnI		
	The reference method (ng/mL)	This work (ng/mL)	Relative errors (%)	The reference method (ng/mL)	This work (ng/mL)	Relative errors (%)
1	17.7	17.0	-4.0	0.03	0.028	-6.7
2	8.8	9.2	4.5	0.01	0.0096	-4.0
3	18.5	19.6	5.9	0.02	0.021	5.0
4	12.6	11.7	-7.1	0.04	0.037	-7.5
5	24.5	26.5	8.2	3.04	3.18	4.6
6	11.5	12.4	7.8	0.07	0.075	7.1
7	15.2	14.0	-7.9	0.09	0.085	-5.6

Section 8: Table S3 Recovery test for Myo and cTnI in human serum samples.

Myo					cTnI				
Found (ng/mL)	Added (ng/mL)	Total found (ng/mL)	Recovery (%)	RSD (%, n = 3)	Found (ng/mL)	Added (ng/mL)	Total found (ng/mL)	Recovery (%)	RSD (%, n = 3)
	0.10	8.91	110.0	5.7		0.01	0.02	100.0	5.7
8.8	1.00	9.75	95.0	5.2	0.01	0.10	0.12	110.0	6.8
	10.0	18.5	97.0	6.3		1.00	0.93	92.0	5.5
	0.10	24.6	100.0	4.3		0.10	3.13	90.0	4.9
24.5	1.00	25.4	90.0	5.9	3.04	1.00	4.19	115.0	5.8
	10.0	35.7	112.0	4.6		10.0	13.6	105.6	6.1

Section 9: Reference:

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