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A novel label-free photoelectrochemical immunosensor based on NCQDs and Bi_2S_3 co-sensitized hierarchical mesoporous SnO_2 microflowers for detection of NT-proBNP

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1. Materials

Bovineserum albumin (BSA) was obtained from Sigma-Aldrich (Beijing, China). Thioglycolic acid (TGA) was obtained from Tianjin Kermel Chemical Reagent Co. 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) were obtained from Aladdin Reagent Database Inc. (Shanghai, China). Ultrapure water (Milli-Q, Millipore) used in all experiments was deionized to 18.25 MΩ·cm. ITO glass (resistivity 10Ω/sq) was obtained from Zhuhai Kaivo Electronic Components Co., Ltd. China. The other materials were analytical pure without further purification.

2. Apparatus

A three-electrode system was used, with a platinum wire as a counter-electrode, saturated calomel electrode as a reference electrode and modified ITO electrode (2.5×0.8 cm^2) as the working electrode. Before preparation of PEC sensor, ITO substrates were cleaned by immersion for 30 min at 50ºC in a series of ultrasonically agitated solvents (acetone, H_2O, ethanol, H_2O) and dried under a nitrogen stream. Scanning electron microscope (SEM) images and energy dispersive spectrometry (EDS) were tested by a field emission SEM (Zeiss, Germany). Transmission electron microscopy (TEM) images were captured under a JEOL JEM-1400 transmission electron microscope (120 kV). HR-TEM images were obtained using a JEOL JEM-2100F (Tokyo, Japan). X-ray diffraction (XRD) patterns were collected on a D8 advance X-ray diffractometer (Bruker AXS, Germany). UV-vis spectra were obtained

on a Shimadzu UV-3101PC spectrometer (Japan). Electrochemical impedance spectroscopy (EIS) analysis was performed on an Zahner electrochemical workstation (Germany) with a three-electrode system in a 5.0 mmol/L $[Fe(CN)_6]^{3-/4-}$ solution containing 0.10 mol/L KCl. Fourier transform infrared (FTIR) spectrum was obtained on Shimadzu VERTEX 70 spectrometer.

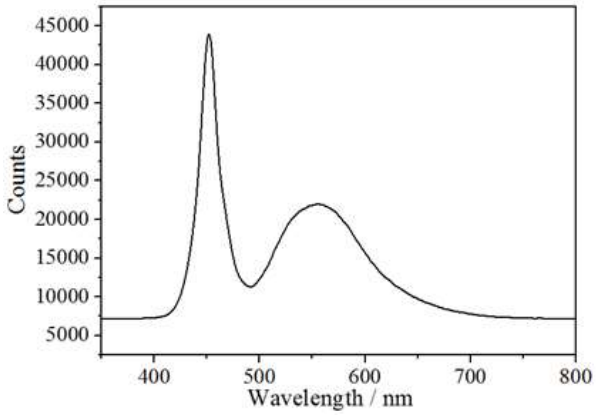

Fig. S1. Wavelength range of the LED light resource.

3. The TEM image and XRD pattern of pure Bi_2S_3

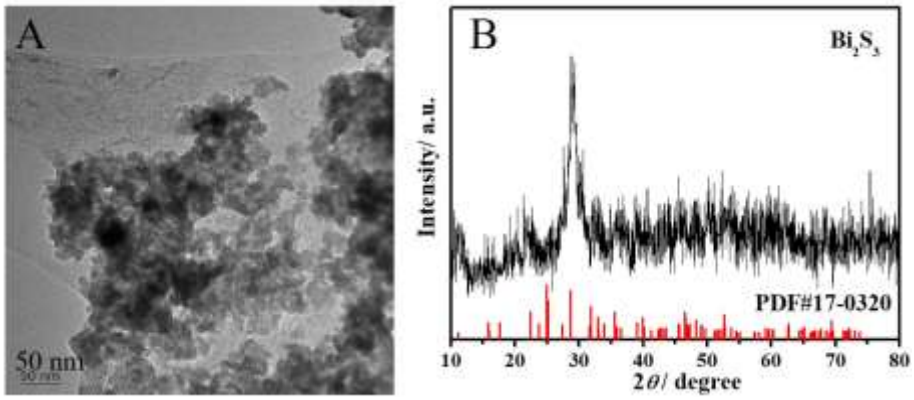

Fig. S2. The TEM image (A) and XRD pattern (B) of pure Bi_2S_3.

4. Time-based photocurrent response curves of ITO/Bi_2S_3, ITO/SnO_2/Bi_2S_3, ITO/NCQDs/Bi_2S_3.

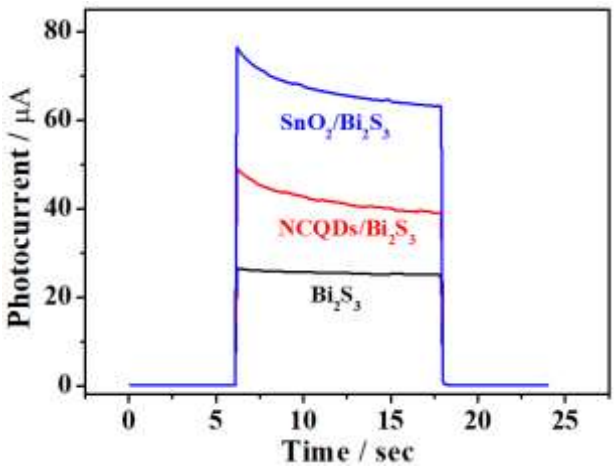

Fig. S3. Time-based photocurrent response curves of ITO/Bi_2S_3, ITO/SnO_2/Bi_2S_3, ITO/NCQDs/Bi_2S_3. The applied potential was 0 V.

5. Simulation parameters of the equivalent circuit components

Table S1. Simulation parameters of the equivalent circuit components

Electrode	R_s (Ω)	R_{et} (Ω)	C_{dl} (F)	Z_w
ITO	59.15	14.18	3.177×10^{-6}	0.008131
ITO/SnO_2	62.77	19.36	4.523×10^{-6}	0.006400
ITO/SnO_2/NCQDs	61.93	21.71	3.733×10^{-6}	0.009014
ITO/SnO_2/NCQDs/Bi_2S_3	61.13	23.42	6.274×10^{-6}	0.009339
ITO/SnO_2/NCQDs/Bi_2S_3/TGA	62.57	31.79	4.538×10^{-6}	0.007043
ITO/SnO_2/NCQDs/Bi_2S_3/TGA/(EDC/NHS)	59.86	36.86	5.191×10^{-6}	0.007704
ITO/SnO_2/NCQDs/Bi_2S_3/TGA/(EDC/NHS)/Anti-NT-proBNP	60.52	49.91	6.045×10^{-6}	0.007258
ITO/SnO_2/NCQDs/Bi_2S_3/TGA/(EDC/NHS)/Anti-NT-proBNP/BSA	60.28	121.1	8.401×10^{-6}	0.004621
ITO/SnO_2/NCQDs/Bi_2S_3/TGA/(EDC/NHS)/Anti-NT-proBNP/BSA/NT-proBNP	58.29	123.6	6.486×10^{-6}	0.003928

6. Selectivity of experimental conditions

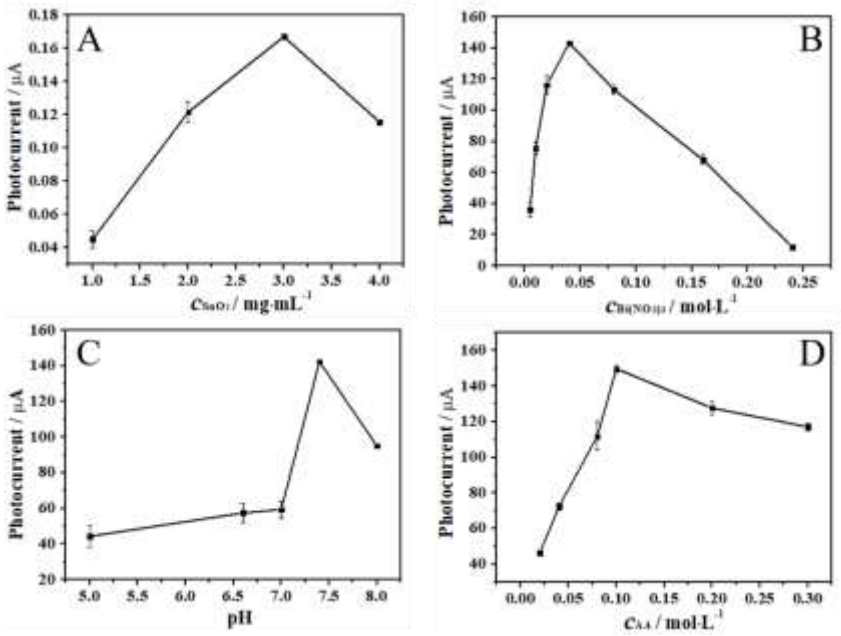

Fig. S4. Optimization of experimental conditions: (A) SnO_2 concentration, (B) $Bi(NO_3)_3$ concentration, (C) pH value, (D) AA concentration, the applied potential was 0 V.

7. Comparison of various methods for NT-proBNP detection

Table S2. Comparison of various methods for NT-proBNP detection

Method	Linear range	Detection limit	Reference
Cyclic Voltammetry	0.02-100 ng·mL^{-1}	6 pg·mL^{-1}	1
microfluidic immunoassay	0.005-1.67 ng·mL^{-1}	0.003 pg·mL^{-1}	2
enzyme-multiplied immunoassay	0.001-10 ng·mL^{-1}	1 pg·mL^{-1}	3
SERS	0.01-100 pg·mL^{-1}	0.75 fg·mL^{-1}	4
Electrochemiluminescence	0.0005-100 ng·mL^{-1}	0.28 pg·mL^{-1}	5
Photoelectrochemical immunoassay	0.0008 - 45 ng·mL^{-1}	0.32 pg·mL^{-1}	6

This work	0.01-50 ng·mL^{-1}	3.7 pg·mL^{-1}	This work

8. Application of the fabricated PEC sensor in human serum

Table S3. Determination of NT-proBNP added in human serum with the fabricated PEC sensor

Human serum sample (ng·mL^{-1})	The addition content (ng·mL^{-1})	The detection content (ng·mL^{-1})	Average value (ng·mL^{-1})	RSD (%)	Recovery (%)
1.05	0.80	1.88, 1.79, 1.82, 1.83, 1.90	1.84	2.46	98.8
	1.00	2.09, 1.98, 2.02, 2.14, 2.10	2.07	3.13	102
	1.20	2.28, 2.23, 2.19, 2.30, 2.08	2.22	3.94	97.5

Reference

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