Synergistic Electrocatalysis in Ag_2S@MoS_2 Nanocomposite Enables Ultrasensitive Label-Free Immunosensing of Prostate Specific Antigen

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1.Experimental Section

1.1. Reagents and Solutions.

Prostate Specific Antigen (PSA), anti-PSA, alpha fetoprotein (AFP) and carcinoembryonic antigen (CEA) were purchased from Shanghai Linc-Bio Science Co., LTD. Bovine serum albumin (BSA), glucose and ascorbic acid (AA) were purchased from Shanghai Macklin Biochemical Co., Ltd. A commercial ELISA kit for PSA detection was purchased from Sigma-Aldrich (St. Louis, MO, USA). All other chemicals were of analytical reagents grade and used without further purification. Phosphate buffered solution (PBS, 0.1 mol/L, pH 7.4) containing 0.1 mol/L KCl was used as electrolyte for all electrochemistry measurement. Ultra-pure water (18.25 MΩ cm, 25 °C) was used for the whole experiment.

1.2. Equipment.

All electrochemical measurements were performed on a CHI 760D electrochemical workstation (Shanghai CH Instruments Co., China). Electrochemical impedance spectroscopy (EIS) was obtained from the impedance measurement unit (IM6e, ZAHNER elektrik, Germany). Scanning electron microscope (SEM) was recorded by JSM-6700F microscope (Japan). Transmission electron microscopy (TEM) was recorded from a JEOL-2100F TEM (Japan). X-ray photoelectron spectroscopy (XPS) was obtained from Thermo ESCALAB 250XI XPS (American). X-Ray Diffraction (XRD) was recorded from (XRD Foucs D8 Brooke AXS Co. Ltd., Germany). A conventional three-electrode system was used for all electrochemical measurements: a glassy carbon electrode (GCE, 3 mm in diameter) as the working

electrode, an Ag/AgCl electrode as the reference electrode, and a platinum wire electrode as the counter electrode.

1.3 Preparation of Ag_2S NP

Ag_2S was synthesized following literature procedures.[1] Silver nitrate (0.34 g) was dissolved in deionized water (80 mL) with magnetic stirring for 20 min at room temperature. Sodium thiosulfate (0.45 g) was subsequently added to the solution with stirring for 4 h. The resulting colloidal suspension was centrifuged at 8,000 r/min, washed sequentially with deionized water and ethanol, and vacuum-dried at 60°C to obtain Ag_2S.

1.4 Preparation of MoS_2 NS

MoS_2 nanosheets were prepared according to literature methods with modifications.[2] Sodium molybdate crystals (0.5 g) were dissolved in deionized water (80 mL) under magnetic stirring (20 min), followed by addition of L-cysteine (0.8 g) and continued stirring for 1 h. Then, the solution was transferred to a Teflon-lined autoclave and hydrothermally treated at 180°C (24 h). After cooling to room temperature, the resulting suspension was centrifuged (8000 rpm) and washed sequentially with deionized water and ethanol, then vacuum-dried at 60°C to obtain MoS_2.

2.Results and discussion

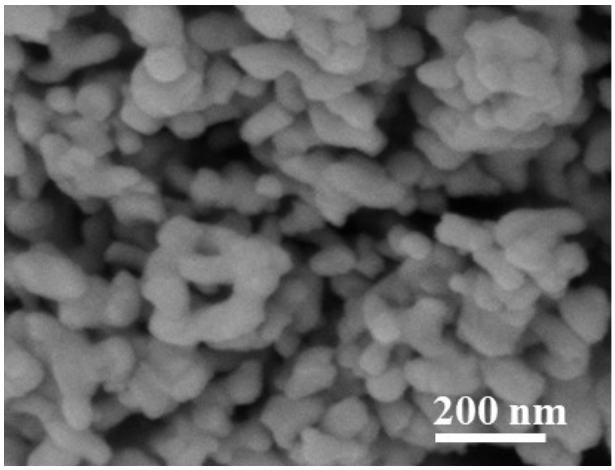

Fig.S1 SEM image of Ag_2S NP

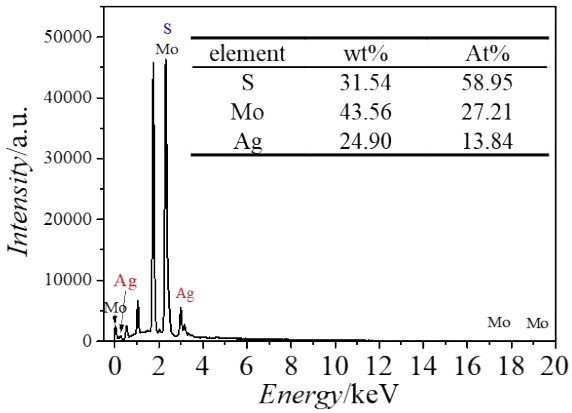

Fig.S2 Energy Dispersive Spectrometer spectrum of $Ag_2S@MoS_2$.

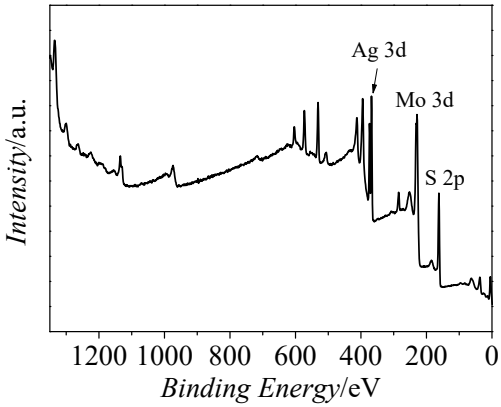

Fig.S3 XPS integral spectrum of $Ag_2S@MoS_2$.

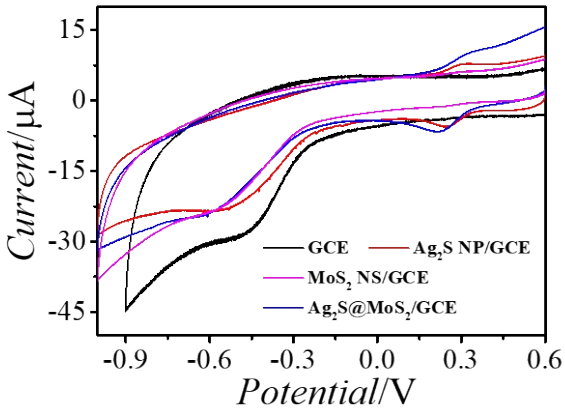

Fig.S4 CV curves of bare GCE, Ag_2S NP/GCE, MoS_2 NS/GCE and Ag_2S@MoS_2/GCE in pH=7.4 PBS.

Table S1 The fitted parameters of the EIS data of Ag_2S NP/GCE, MoS_2 NS/GCE and Ag_2S@MoS_2/GCE.

	R_{ct}/Ω	C_{dl}/F	R_s/Ω
Ag_2S NP	58.4	5.2E-008	4.6
MoS_2 NS	53.2	8.5E-008	4.4
Ag_2S@MoS_2	48.7	3.9E-007	3.9

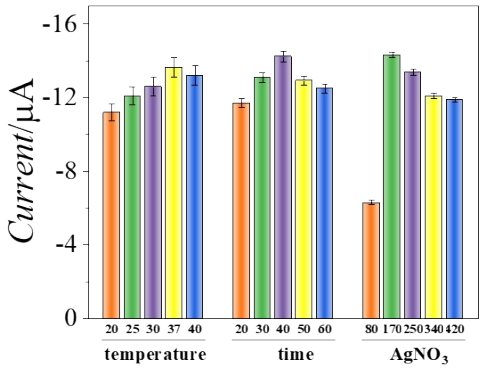

Fig.S5 Effect of incubation temperature, incubation time and the addition of amount $AgNO_3$ on response of the immunosensor.

Fig.S6 Effect of pH and concentration of $Ag_2S@MoS_2$ and $K_3[Fe(CN)_6]$ on response of the immunosensor.

Table S2 Analytical characteristics of different PSA immunosensors.

Electrode	Linear range (ng/mL)	Detection limit (ng/mL)	References
AuNPs/CHI/SPE	1-18	0.001	3
MOF-235	0.01-1.2	0.003	4
nitrogen-doped graphene	0.05-100	0.017	5
APBA/6-PICA	0.50-100	0.11	6
MWCNTs-Fe_3O_4	0.0025-100	0.00039	7
$Ag_2S@MoS_2$	0.005~50	0.005	This work

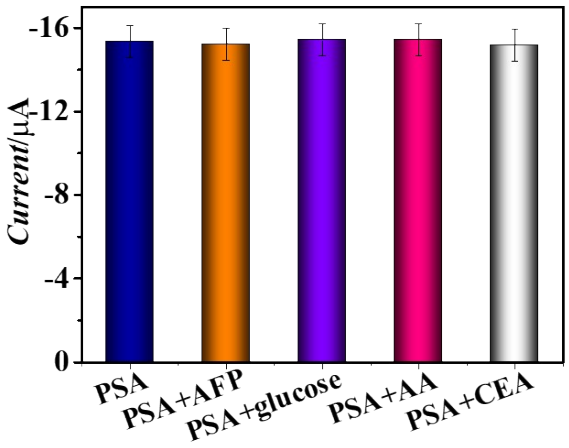

Fig.S7 the selectivity of the developed immunosensor.

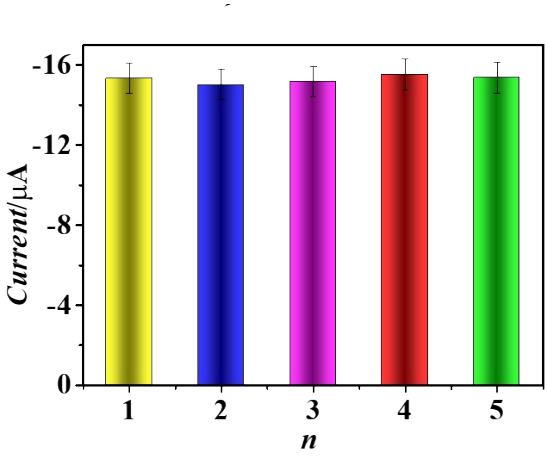

Fig.S8 the reproducibility of the developed immunosensor.

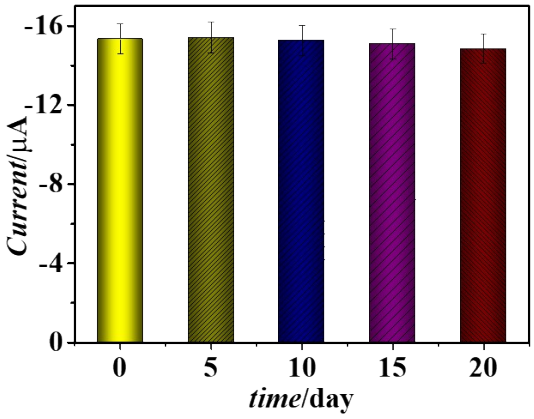

Fig.S9 the stability of the developed immunosensor.

Table S3 The recovery of the prepared immunosensor

	Sample PSA (ng/mL)	PSA addition content (ng/mL)	Fo und PSA(ng/mL)	RSD (%)	Recovery (%)	*t*-value
the prepared	1.31	1.0	2.33, 2.29, 2.42, 2.38, 2.47	2.99	106.8	1.71
mmunosensor		5.0	6.28, 6.39, 6.44, 6.43, 6.44	1.06	101.7	1.60
based on		10.0	11.2, 11.29, 11.54, 11.45,	1.17	100.6	1.68
$Ag_2S@MoS_2$			11.37			
commercial	1.31	1.0	2.39, 2.28, 2.21, 2.27, 2.45	4.20	101.0	1.84
ELISA kit		5.0	6.15, 6.35, 6.28, 6.48, 6.51	2.32	100.9	1.71
		10.0	11.17, 11.22, 11.26, 11.31,	0.69	99.6	1.7
			11.37			

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