Support information

A sandwich electrochemical immunosensor based on polypyrrole microspheres for the detection of cancer marker CA125

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Section S1 Synthesis of materials

Preparation of PPy nanospheres

PPy nanospheres were synthesized referencing to literature [1]. Simply, 0.1 g $FeCl_2$ and 0.50 mL 30% H_2O_2 were added into 60 mL water containing 1.0 mL pyrrole, and reacted for 12 h. During the process, ppy nanospheres was formed via oxidation polymerization. After the mixture was filtered washed and freeze-dried, the obtained product was PPy nanospheres.

Preparation of PPy-AuNPs

300 mg PPy nanospheres was dispersed in 15 mL H_2O for 1h ultrasonic treatment to obtain PPy suspension,suitable amount of PPy nanospheres suspension was placed into round-bottom flask and added Au NPS (the preparation method was refereed to literature) for 6h stirring and centrifugal separation at12000rpm. The precipitate was collected and dried for 12h at 60℃, thus, PPy-AuNPs microcomposites was obtained.

1 J. Q. Zhao, Z.L. Guo, J..J. Guo, J.C. Wang, and Y.Z. Zhang, RSC Advances, 2016, 6: 31448-31453

Section S2 Characterizations of materials

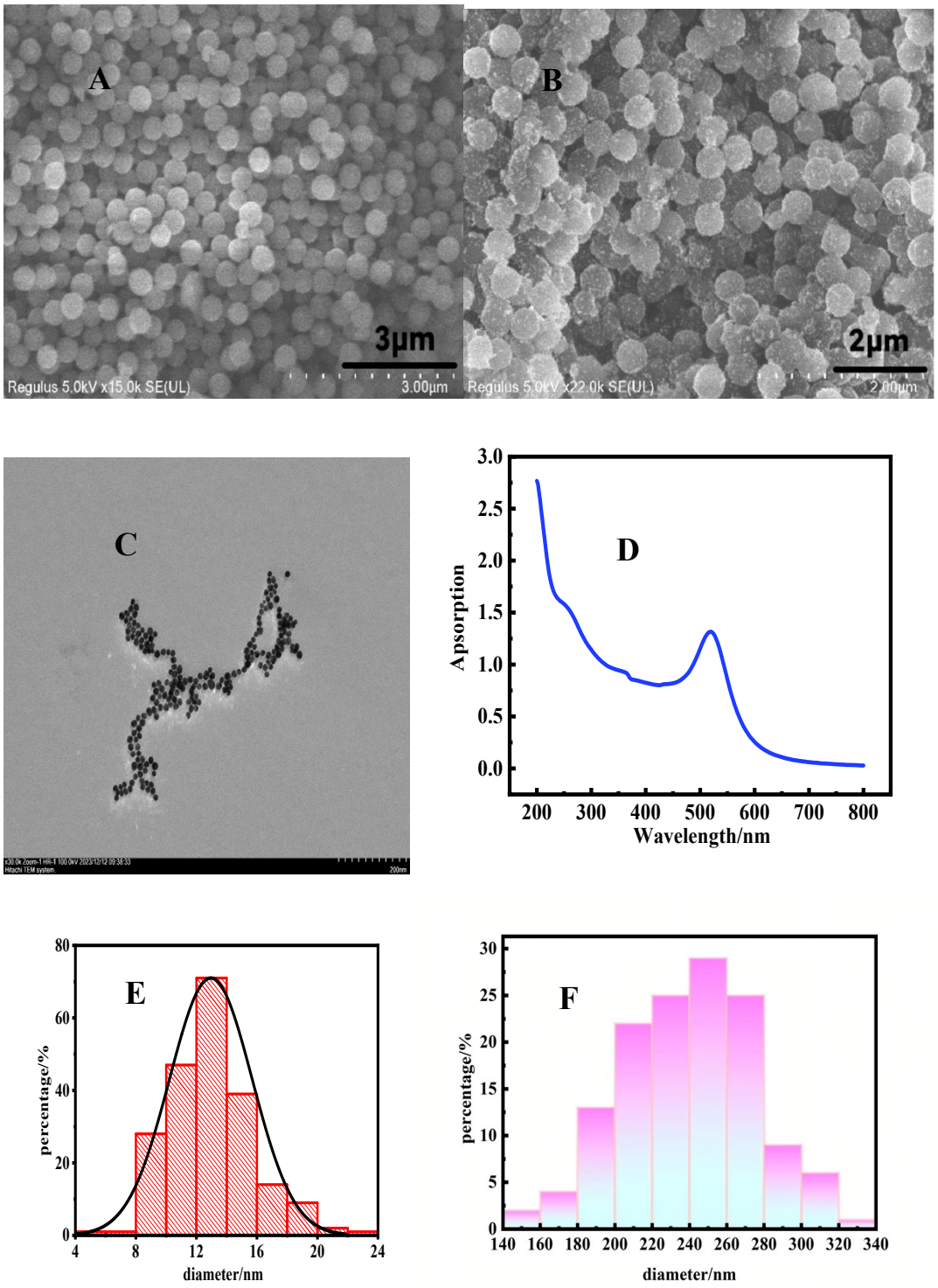


Fig.S1: SEM images of PPy (A) and PPy@Au NPs (B); TEM images of Au NPs(C) ; UV-vis absorption cure of Au NPs (D) and Size distribution of Au NPs(E) and PPy microsphere

Section S3 Optimization of experimental conditions

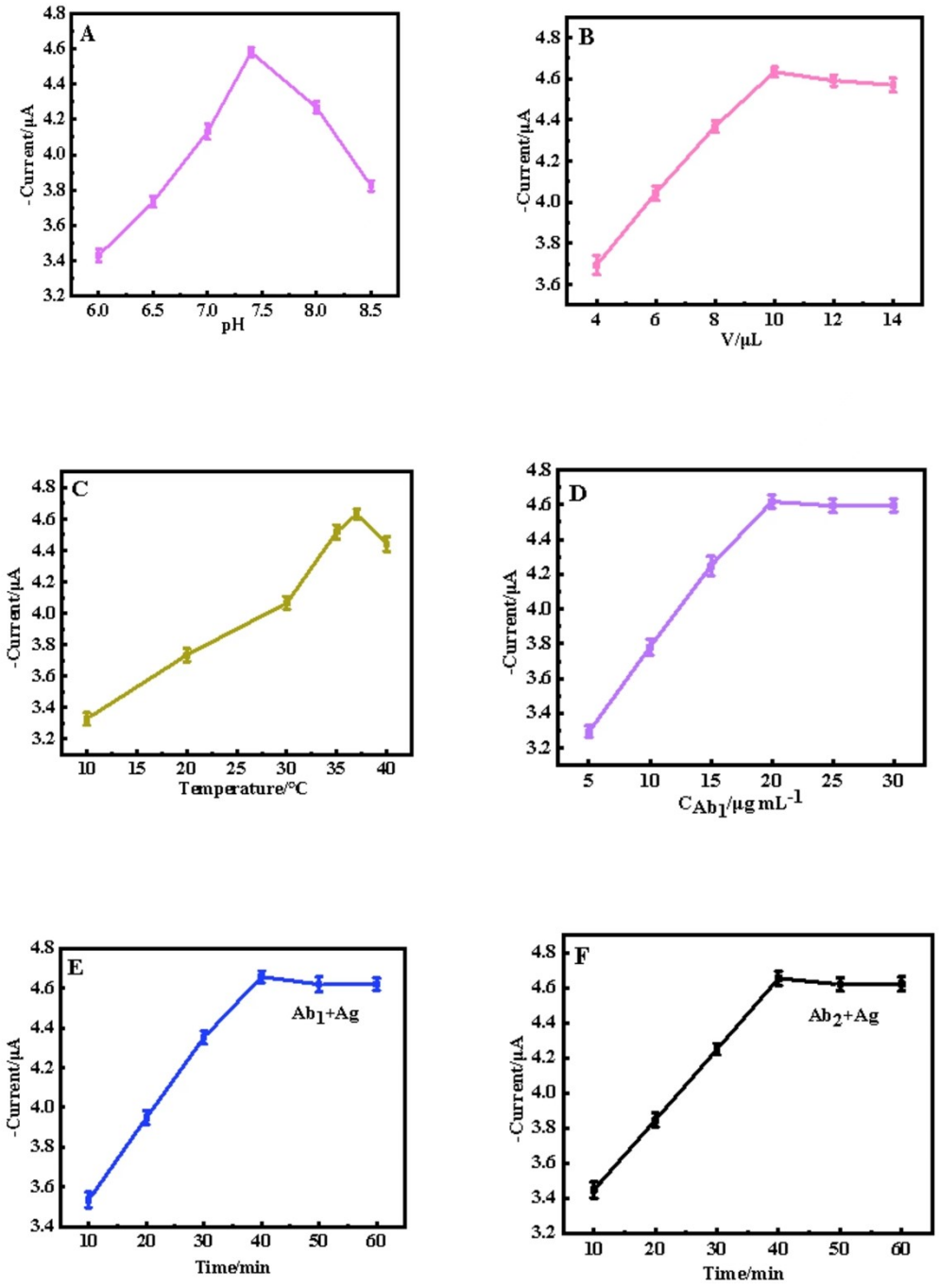
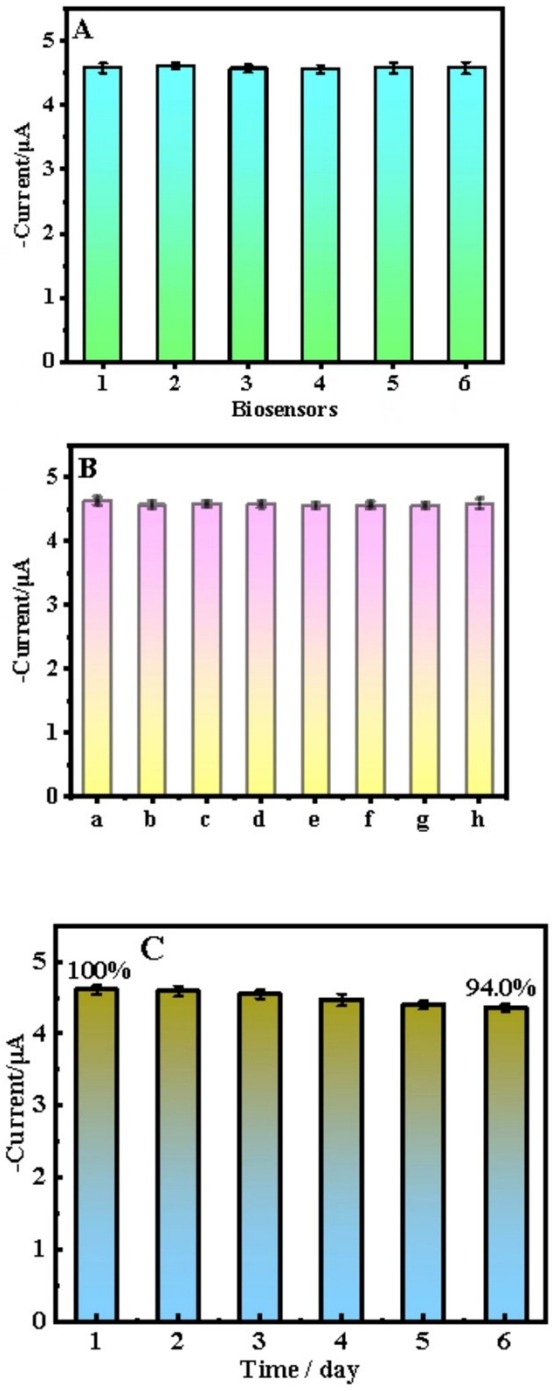


Fig. S2 Optimization of experimental conditions:e, (A) volume of Ab_1; (B) pH; (C) incubation temperature ; (D) Ab_1 concentration；(E) incubation time between Ab_1 and Ag; (E) Incubation time between immunoprobes and Ag

Section S4 The reproducibility, selectivity andstability



FigS3 (A) The reproducibility of the immunosensor, conditions: 10 U mL^{-1}.

(B)The selectivity of the immunosensor, 10 U mL^{-1} and mixture containing 100U mL^{-1}CA19-9,100 100 U mL^{-1} CA 15-3, 100 μg mL^{-1} BSAa, 100 μg mL^{-1} PSA, 100 μg mL^{-1} HSA.100 μg mL^{-1}ALB

(C) Stability of the immunosensor. Condition: 10 U mL^{-1}

Table S1 Comparison of the different electrochemical methods for CA125 detection

Measure technology	signal	Used materials	Linear range (U mL^{-1})	Detection limit (U mL^{-1})	Ref.
SWV	Toluidine blue	3D rGO-MWCNTs And Suc-CS@MNPs	0.0005–75	6×10^{-6}	3
CHA	H_2O_2	CS-AuNP/MWCNT/GO and AuNP/LOx	0.01–100	0.002	13
DPV	$[Fe(CN)_6]^{3-/4-}$	poly(3-hydroxyphenylacetic acid)	5 – 80	1.45	14
DPV	Fc	3DrGO/MWCNTs and UiO-66	0.01 – 80	0.0089	15
DPV	$[Fe(CN)_6]^{3-/4-}$	CuCo-ONSs@AuNPs	1×10^{-7} - 1×10^{-3}	3.9×10^{-8}	16
EIS Ap	H_2O_2	Magnetic microsphere and HRP	2-100	0.08	17
DPV	Methylene blue	MXene/MIL-101-NH_2 and UiO-66	0.2-1000	0.006	18
DPV	Thi	rGO/AuNPs	0.1-200	0.01	19
DPV	DOX	Au NPs and PPy@AuNPs	$1.\times10^{-3}$ - 100	2.4×10^{-6}	This work

CS- AuNPs- Chitosan-gold nano particles ; MCNT/GO-Multiwall carbon nanotube/graphene oxide ; Fc-Ferrocenecarboxylic acid ; Thi -Thionine ;DOX-Adriamycin

CHA-Chronoamperometry; AP-Amperometry

DPV-Different pulse voltammetry; EIS -Electrochemical impedance spectra

SWV-Square wave voltammetry

HRP-Horseradish peroxidase