Electronic Supplementary Information

Synergistic bio-recognition/spatial-confinement for effective capture and sensitive photoelectrochemical detection of MCF-7 cells

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Experimental Section

Materials. All reagents are of analytical grade and used as received without any further purification. The fluorine doped tin oxide (FTO) glass was supplied by Zhuhai Kaivo Optoelectronic Technology Co., Ltd. Cupric citrate (2.5 H_2O), trisodium citrate, sodium hydroxide, zinc acetate dihydrate, potassium hydroxide, methanol, sodium chloride, potassium chloride, disodium hydrogen phosphate, potassium dihydrogen phosphate and bovine serum albumin (BSA) were supplied by Macklin Inc, Shanghai, China. MUC1 aptamer (5'-HS-$(CH2)_6$-GCA GTT GAT CCT TTG GAT ACC CTG G-3') was obtained from Sangon Biotech, Shanghai, China. The MCF-7, Hela and A549 cells were supplied by the Institute of Biochemistry and Cell Biology of Chinese Academy of Science (Shanghai, China). All aqueous solutions were prepared using ultrapure deionized water with a resistivity of 18.2 MΩ cm.

Electrodeposition of Cu_2O nanocubes. The Cu_2O nanocubes were electrodeposited in a typical three-electrode system with FTO glass as working electrode, Ag/AgCl as reference electrode, and Pt sheet as counter electrode. 60 mM sodium citrate was used as the supporting electrolyte, which helps avoiding migration phenomena. The pH value of electrolyte of copper citrate was tuned to 12 and the electrodeposition potential was set at –0.50 V vs Ag/AgCl.

Preparation of core/shell Cu_2O@ZnO nanocubes. The ZnO sol-gel solution was prepared as previously reported methode.[1] Briefly, 10 mM zinc acetate and 15 mM KOH were mixed in methanol solution, and actively stirred at 60 °C for 2 h. Then, the FTO glass with electrodeposited Cu_2O nanocubes were dipped into the ZnO sol for 5 min to form a uniform layer, then, the ZnO sol was converted into ZnO film in an annealing process at 350°C for 1 h in N_2 atmosphere.

Preparation of PEC aptasensors. Sputtering method was used to deposit Au NPs on the core/shell Cu_2O@ZnO nanocubes with ion sputtering instrument of HTCY JS-1600 under sputtering current of 6 mA. Then the aptamer (5'-HS-$(CH_2)_6$-GCA GTT GAT CCT TTG GAT ACC CTG G-3') was linked to the Au NPs through Au-S bonds. The DNA aptamer targeting mucin 1 (MUC1) was selected to bind the MUC1 cancer marker with high affinity and selectivity, and the MUC1 is a cell-surface associated glycoprotein, which is aberrantly expressed with greater than 90% of human breast carcinomas and it has been a target of interest for many years with the aim of detecting human breast carcinoma MCF-7 cells.[2]

Material Characterizations. The morphologies of electrodes were characterized by scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM, JEOL JEM 2100). The crystalline structure of the electrodes was analyzed by X-ray diffraction (XRD) (Bruker D8 Discover diffractometer, using Cu Kα radiation (1.540598 Å)). The chemical compositions and status were analyzed by X-ray Photoelectron Spectroscopy (XPS) with an Axis Ultra instrument (Kratos Analytical) under ultrahigh vacuum ($<10^{-8}$ torr) and by using a monochromatic Al Kα X-ray source. The diffuse reflectance UV-vis adsorption spectra were recorded on a spectrophotometer (Shimadzu, UV 3600) with fine $BaSO_4$ powder as reference. The status of cancer cells was observed by optical microscope (Olympus, U-TV0.63XC).

PEC Sensing Performance. The PEC characterization was evaluated using a three-electrode configuration with the aptasensor, Ag/AgCl, and Pt foil as working, reference, and counter electrode, respectively. The supporting electrolyte used was 0.01 M PBS (pH = 7.4) solution. The transient photocurrent response was evaluated under chopped light irradiation (light on/off cycles: 60 s) at a fixed electrode potential of 0 V *vs* Ag/AgCl. The photocurrent was measured under an illumination through a 300W Xe lamp (PLS-SXE300) with calibrated intensity of 100 $mWcm^{-2}$ (AM 1.5G).

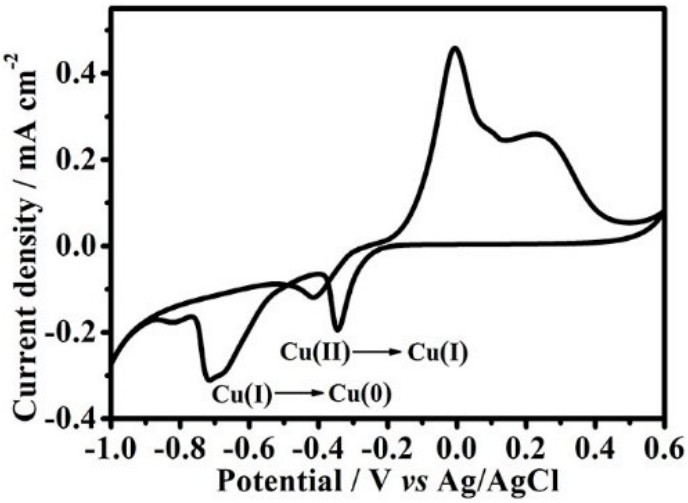

Fig. S1 Cyclic voltammogram of FTO electrode in 1 mM copper citrate solution at a potential scan rate of 5 mV s^{-1}.

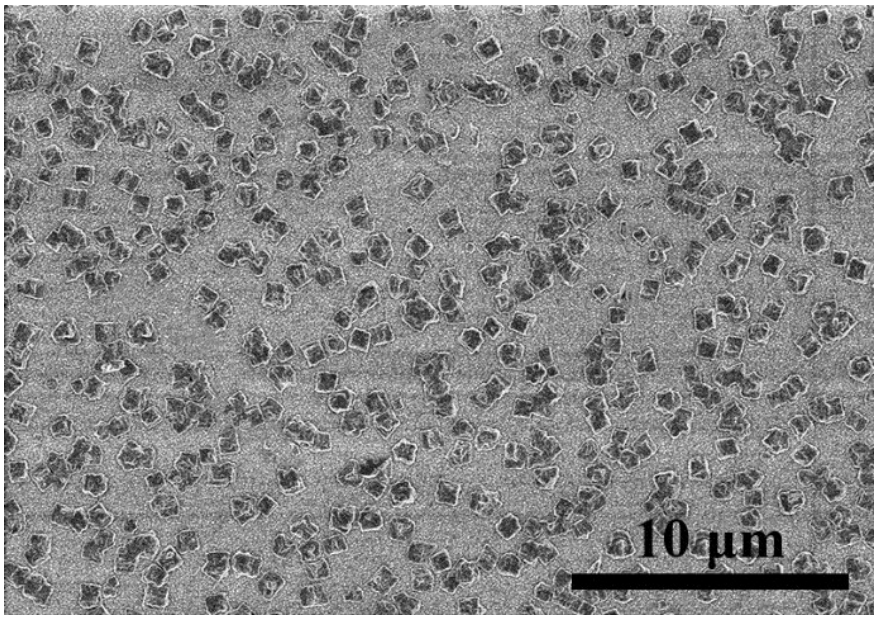

Fig. S2 SEM image of Cu_2O@ZnO in large scale.

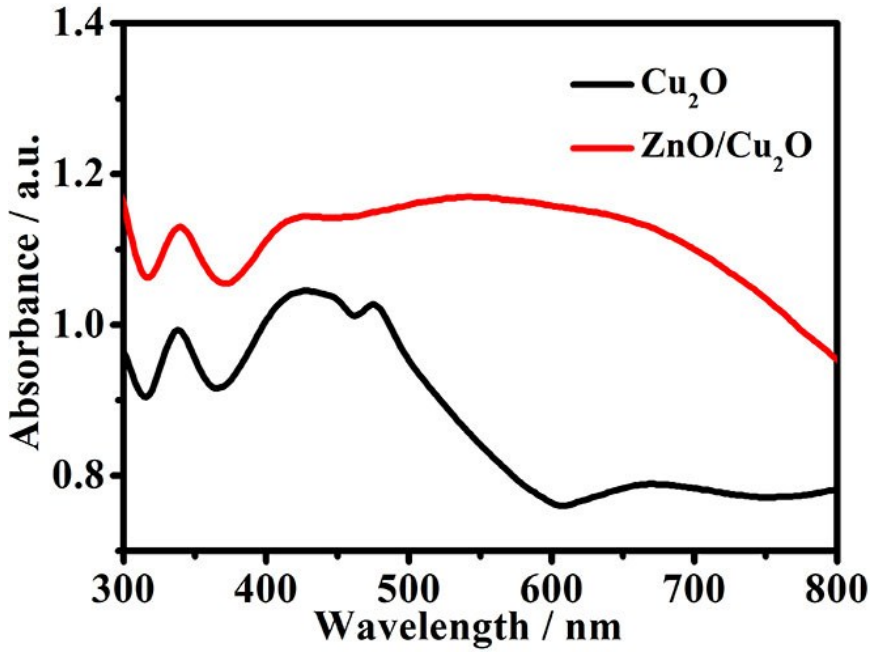

Fig. S3 UV−visible diffuse reflectance spectra (DRS) of Cu_2O and Cu_2O@ZnO.

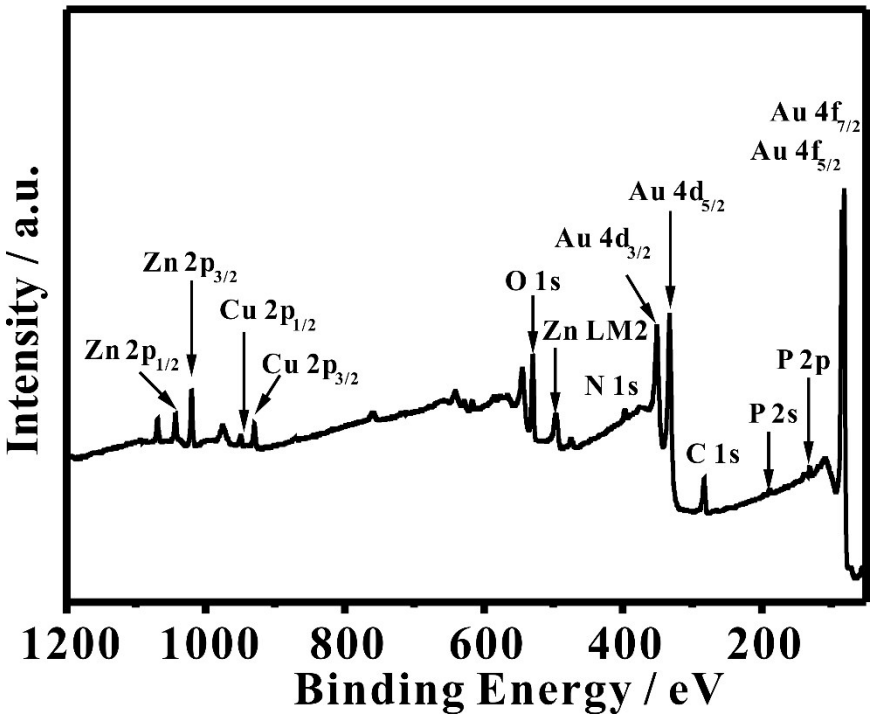

Fig. S4 XPS survey of Cu_2O@ZnO/Au-aptamer.

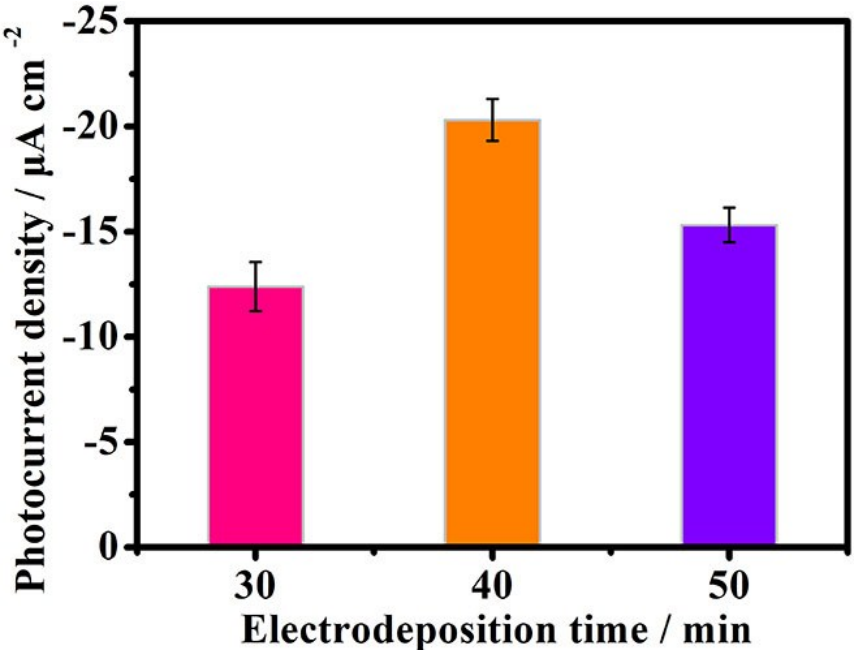

Fig. S5 Optimization of PEC performance of Cu_2O with different electrodeposition time.

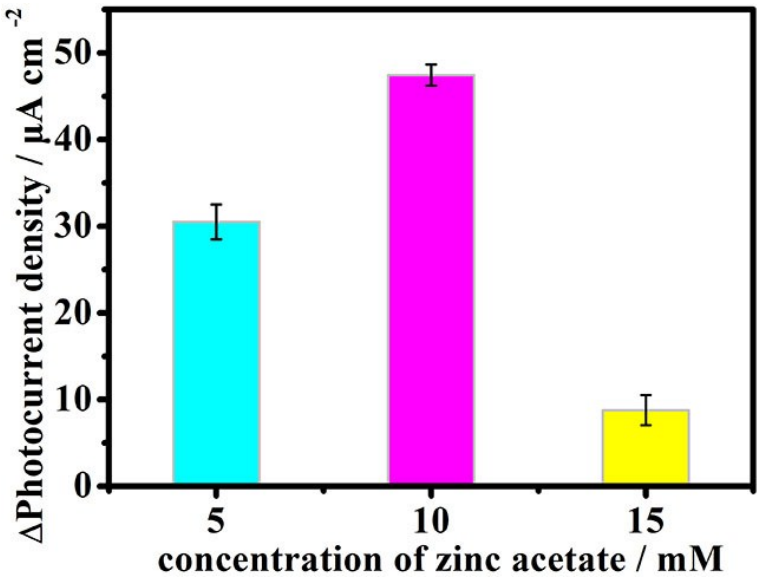

Fig. S6 Optimization of PEC performance of Cu_2O@ZnO with different concentration of zinc acetate.

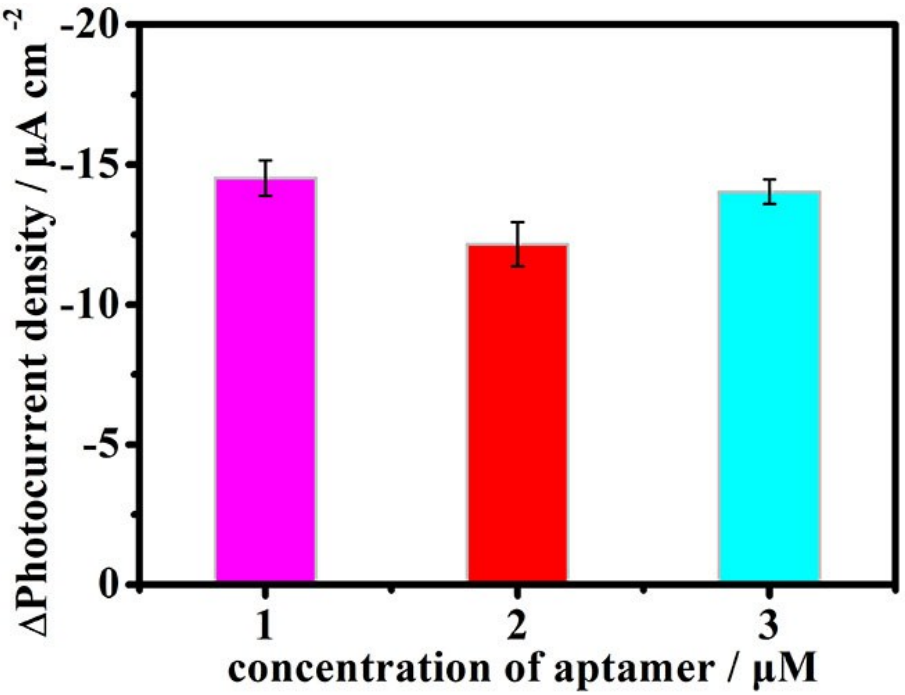

Fig. S7 Optimization of PEC performance of Cu_2O@ZnO/Au-aptamer with different concentrations of aptamer.

Table S1. Comparison of the dynamic range and detection limit of several biosensors for determination of MCF-7 breast cancer cell

Method	Materials	Liner range/ cells·mL^{-1}	Limit of detection/ cells·mL^{-1}	Ref.
Photoelectrochemisrty	**ZnO/Cu_2O**	**8–6 × 10^3**	**2**	**This work**
Electrochemisrty	CdS NPs	1.0 × 10^4–1.0 × 10^7	330	3
Electrochemiluminescence	CQDs@MSNs	500–2 × 10^7	230	4
Photoelectrochemistry	Ag_2S QDs	3.0× 10^2–2.0× 10^3	98	5
Photoelectrochemistry	$NaYF_4$:Yb,Er and CdTe/TiO_2	1.0 × 10^3 –1.0 × 10^5	400	6
Localized surface plasmon resonance	Aptamer-functionalized gold nanorods	1.0 × 10^2 –1.0 × 10^5	100	7
Electrochemistry	AgNPs labeled aptamer	1.0 × 10^2–1.0 × 10^7	25	8
Fluorescence and Electrochemisrty	DNA-AgNCs	10–1.0 × 10^5	3	9

References

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