Supporting Information

Photoelectrochemical thrombin biosensor based on perylene-3,4,9,10-tetracarboxylic acid and Au co-functionalized ZnO nanorods with signal-off quenching effect of $Ag@Ag_2S$

Reagents and apparatus

Thrombin (TB), bovine serum albumin (BSA), L-Cysteine (L-Cys) and lysozyme were all purchased from Sigma-Aldrich. TB binding aptamers were purchased from Sangon Biotech Co., Ltd. Indiumtin-oxide (ITO) glass was purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd. Zinc acetate ($C_4H_6O_4Zn{\cdot}2H_2O$), Diethanolamine ($C_4H_{11}NO_2$), Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), Hexamethylenetetramine ($C_6H_{12}N_4$), Gold chloride trihydrate ($HAuCl_4{\cdot}3H_2O$), 6-Mercapto-1-hexanol (MCH), and Tris(2-carboxyethyl)phosphine hydrochloride (TCEP·HCl) were purchased from Aladdin Reagents Co., Ltd. Ultrapure water (18.2 MΩ) was used for all solution preparation. All other reagents are of analytical grade and used without further purification. The sequences of the oligonucleotides are as follows:

Apt1: 5′- NH_2 -$(CH_2)_6$-GGT TGG TGT GGT TGG-3′

Apt2: 5′-SH - $(CH_2)_6$ - AGT CCGTGG TAG GGC AGG TTG GGG TGA CT -3′

All electrochemical measurements were carried out on a CHI760E electrochemical workstation (Shanghai Chenhua Instruments Co., Ltd., China). A conventional three-

electrode system was used for all electrochemical measurements, consisting of a platinum plate electrode as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, the proposed electrode as the working electrode. Photoreduction of Pt was powered by 200 W Xenon lamp (Beijing Zhongjiao Co., Ltd., Beijing, China). Scanning electron microscopy (SEM) images were obtained by Hitachi S4800 (Hitachi Limited, Japan). Transmission electron microscopy (TEM) images were collected by Talos F240 (ThermoFisher Limited, America). An energy dispersive spectrometer (EDS) accompanied with TEM was also employed for analysis of the elements of the as-prepared composites. The crystal structure identification was determined by X-ray diffraction (XRD) using a Bruker D8 diffractometer with Cu Kα radiation (Bruker, German).

Preparation of ZnO NRs

The preparation of ZnO NRs was divided into three main steps. (1) The first step was the preparation of ZnO seed sol solution: 1.051 g diethanolamine was added dropwise into 50 mL 0.2 M zinc acetate solution with ethanol absolute as the solvent. After stirred thoroughly, it was sealed and heated in 60 ℃ water bath for 30 minutes then aged for 24 hours. (2) The second step was the ZnO crystals' grown on ITO: The ITO was ultrasonically cleaned with water, ethanol absolute, isopropyl alcohol in sequence. The dried ITO was dipped into the ZnO sol solution and dried in 120℃ for 10 minutes. The dipping and drying was repeated for another two times then the sample was annealed in 500℃ muffle furnace for 1 hour. (3) The third step was the growth of ZnO nanorods:

The ITO was leaned against on the inside wall of Teflon-lined autoclave with the conductive side down and heated in 90℃ for 5 hours. In the hydrothermal reaction the aqueous solution containing 0.05 M zinc nitrate and 0.05 M hexamethylenetetramine. Make sure the first two steps are carried out water free strictly.

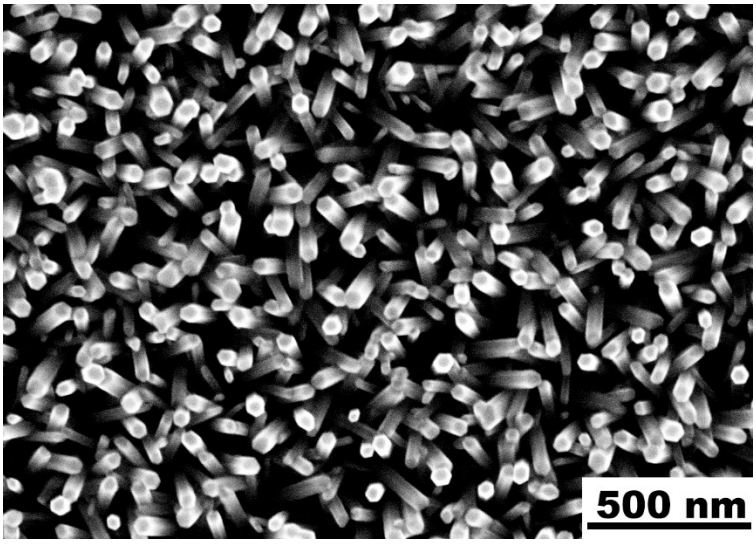

Fig.S1 SEM images of ZnO/PTCA.

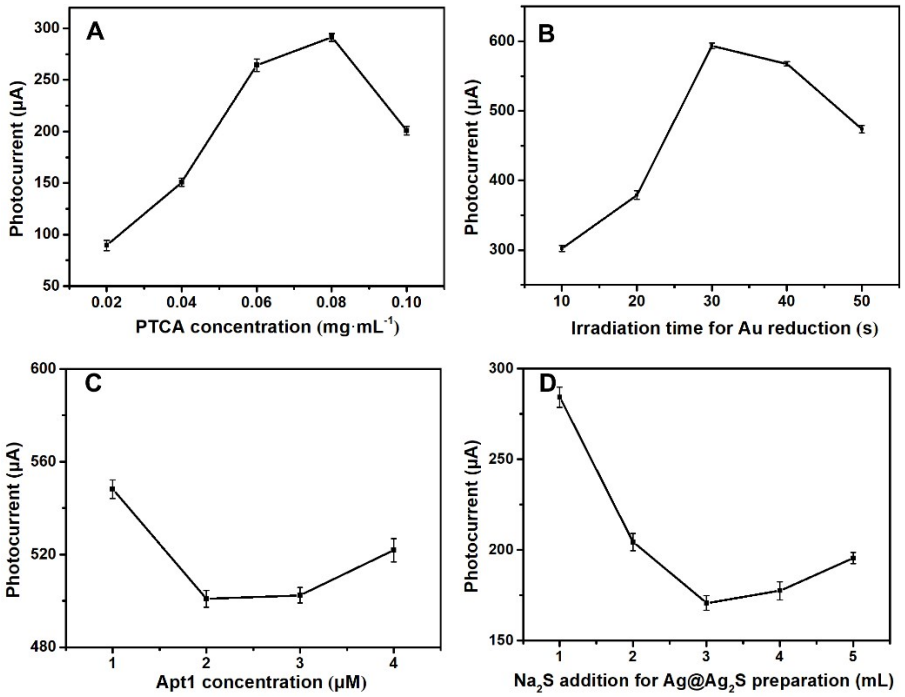

Fig. S2 Condition optimization of (A) PTCA concentration; (B) irradiation time for Au reduction; (C) Apt1 concentration; (D) Na_2S addition for $Ag@Ag_2S$ preparation.