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SUPPORTING INFORMATION

Ultrasensitive photoelectrochemical immunoassay for prostate-specific antigen based on silver nanoparticles-triggered ion-exchange reaction with ZnO/CdS nanorods

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Chemical and Reagent. Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), cadmium chloride ($CdCl_2$), thioacetamide ($CH_3CSNH_2$), silver nitrate ($AgNO_3$), sodium hydroxide (NaOH), trisodium citrate dihydrate ($C_6H_5Na_3O_7$), sodium borohydride ($NaBH_4$), and sodium carbonate (Na_2CO_3) were purchased from Aladdin. Phosphate-buffered saline (PBS, 10 mM, pH 7.0), bovine serum albumin (BSA), and Tween 20 (0.05%, v/v) were obtained from Sinopharm Chem. Re. Co., Ltd. (China, Shanghai). Monoclonal mouse anti-human PSA antibody (as the capture antibody), polyclonal rabbit anti-human PSA antibody (as the detection antibody), and PSA standards were obtained from Sangon Biotech. Co., Ltd (Shanghai, China). The separable high-binding polystyrene 96-well microplates (as the immunoreaction cell) were acquired from Greiner Bio-One (Frickenhausen, Germany). All other reagents were analytical grade and were used without further purification. Tween 20 (0.05%, v/v) and BSA (1.0%, w/v) were added to the PBS solution to prepare washing buffer and blocking buffer, respectively.

Apparatus. The transmission electron microscopy (TEM) images, HAADF-STEM images, and element mappings of ZnO/CdS nanorods were acquired from the FEI Talos F200s. The scanning electron microscopy (SEM) images were characterized by Nova NanoSEM 230. The X-ray diffraction (XRD) patterns were obtained from the RigakuUltima III. The full XPS pattern and the high-resolution XPS spectra were acquired from Thermo Scientific K-Alpha.

Preparation of Silver Nanoparticles (Ag NPs). Ag NPs were synthesized according to the reported literature.[1] Before synthesis, the glass container should be soaked in aqua regia. Then it was washed and dried for further use. Primarily, under vigorous stirring, trisodium citrate (2.0 mL, 1.0 wt%) was added to 50 mL of boiling water containing $AgNO_3$ (1.0 mM). Following that, the mixed solution was continuously stirred vigorously for 30 min, and it was observed that the color of the solution changed from bright yellow to brownish yellow. After cooling to room temperature, the silver colloids were obtained and stored at 4 °C.

Preparation of Ag NPs-Labeled Detection Antibody (Ag NPs-dAb). The Ag NPs-dAb was prepared following our previous literature with minor modification.[2, 3] Before labeling, 0.1 M Na_2CO_3 solution was added to the as-prepared silver colloids until pH reached 9.0-9.5 to prevent the precipitation after adding protein. Afterwards, the detection antibody (300 μL of 0.5 mg mL^{-1}) was added into the above colloidal silver nanoparticles (4.5 mL) and then the resultant suspension was incubated at room temperature for 12 h under the gently shaking condition. Following that, the

precipitate collected by centrifugation (12000 rpm, 15 min) was AgNPs-dAb. Finally, the obtained AgNP-dAb was dispersed into 2.0 mL of PBS (pH 7.0) containing 1.0 wt% BSA and 0.5 wt% Tween 20 and stored at 4 °C for further use.

Preparation of cAb-Coated Immunoreaction Cell. Initially, 10 μg mL^{-1} cAb (50 μL per well) was injected into the immunoreaction cell (the separable high-binding polystyrene 96-well microplate) containing 50 mM sodium carbonate buffer (pH 9.6). Following that, the above-mentioned immunoreaction cell was encapsulated with an adhesive plate sealing film and incubated overnight at 4 °C. Afterwards, the immunoreaction cell was washed with 10 mM PBS containing 0.05% Tween 20 three times. Then the obtained cAb-coated immunoreaction cell was incubated in 300 μL blocking buffer (10 mM PBS containing 1.0 wt% BSA) for 1 h at 37 °C. After washing with washing buffer again, the cAb-coated immunoreaction cell could be used for further testing.

Preparation of ZnO/CdS Nanorod-Modified FTO Electrode. Primarily, the FTO electrode was washed with acetone, ethanol, and water and then dried at 60 °C for further use. Then, a waterproof transparent tape was attached to the conductive layer of the clean FTO electrode, exposing a hole with a diameter of 3 mm. Then, 1 mg mL^{-1} ZnO/CdS nanocomposites suspension (20 μL) was drip-coated into the hole on the FTO surface and dried in an oven at 60 °C.

Enzyme-Linked Immunosorbent Assay (ELISA) for PSA. The serum sample suspension (50 μL per well) was added into the standard polystyrene 96-well plate and incubated for 1 h at 37 °C. After the plate was washed with washing buffer three times, the anti-PSA-HRP conjugate solution (50 μL per well) was added into the above-microplate and reacted at 37 °C for 1h. After washing again, the chromogen solution A (50 μL) and the chromogen solution B (50 μL) were injected into the microplate in turn. Following that, the mixture was reacted for 15 min at 37 °C. Finally, after adding stopping solution (50 μL per well), the enzymatic reaction was stopped and the results were obtained by using 450 nm UV-vis spectroscopy.

References

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