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Supplementary Information

Post-Synthetic Modification-Driven ZIF Reconstruction and Functionalization for Efficient SARS-CoV-2 ECL Detection

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Experimental Procedures

Materials and reagents

Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, AR, 99 %), potassium chloride (KCl), 2-[4-(2-Hydroxyethyl)-1-piperazinyl] ethanesulfonic acid (HEPES), potassium ferricyanide ($K_3[Fe(CN)_6]$), potassium ferrocyanide ($K_4[Fe(CN)_6]$) ,ethanol and methanol were purchased from Aladdin (Shanghai, China). 2-methylimidazole ($C_4H_5N_2$, AR, 99 %) was obtained from Maclin (Shanghai, China). Zinc(II) meso-tetra (4-carboxyphenyl) porphine (ZnTCPP) was purchased from J&K Chemical Ltd. (Shanghai, China). Tetraoctylammonium bromide (TOAB) was commercially available from Alfa Aesar Chemicals Co. Ltd. (Shanghai, China). Ultrapure water obtained from a Millipore water purification system (≥18 MΩ, Milli-Q, Millipore) was used throughout the whole experiment. ECL measurements were conducted in 10 mM pH 7.0 HEPES containing 0.1 M KCl as the electrolyte.

Characterization

The graphic morphologies of the synthesized hybrid materials were obtained by using FEI Quanta250 Field Emission Scanning Electron Microscope (FESEM). Fourier-transformation infrared (FT-IR) spectra were obtained with an IR-Prestige-21 FT-IR spectrometer (Shimadzu Co., Japan). Powder X-ray diffraction patterns (PXRD) were recorded on a Bruker D8-Focus Bragg-Brentano X-ray Powder diffractometer equipped with a Cu sealed tube (λ = 1.54178 Å) at room temperature. X-ray photoelectron spectroscopy (XPS) was performed by K-Alpha X-ray photoelectron spectroscopy (PHI Quantera II ESCA System). Cyclic voltammetries (CV) were measured using a CHI 660D electrochemical workstation (CHI Co., China). ECL measurements were performed on an MPI-E multifunctional electrochemical and chemiluminescent analytical system (Xi'an Remex Analytical Instrument Co., Ltd, China). Electrochemical impedance spectroscopy (EIS) measurements were carried out using an Autolab PGSTAT30 (Eco Chemie) controlled by NOVA 1.10 software. The fluorescence spectra were recorded through a fluorescence spectrophotometer (Edinburgh Analytical Instruments, FLS920). All electrochemical studies were carried out with a conventional three electrode system. A Pt wire electrode and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. Modified glassy carbon electrodes (GCE, 5 mm in diameter) were used as working electrodes.

Synthesis of ZIF-67 and pm-ZIF/P(Zn)

The ZIF-67 were synthesized according to the method described as follows: 8 mmol of 2-MI and 2 mmol $Co(NO_3)_2 \cdot 6H_2O$ were initially dissolved in 10 mL and 20 mL of methanol under sonication treatment at room temperature, respectively. Then

the above two solutions were rapidly mixed and stirred vigorously for 6 hours. The superfine purple powder was collected by centrifugation (8000 rpm, 5 min), washed with ethanol three times, and dried in a vacuum at 60 °C for 24 h.

The pm-ZIF/P(Zn) was synthesized according to the method described as follows: 0.03 mmol $Co(NO_3)_2 \cdot 6H_2O$ and 0.12 mmol of 2-MI were dissolved in 3 mL and 12 mL of methanol, respectively. After ultrasonic treatment at room temperature, they were mixed and stirred for 12 hours. Then a methanol solution containing 0.03 mmol ZnTCPP was added and stirred vigorously together for 12 hours. The ultrafine greenish purple powder was collected by centrifugation (8000 rpm, 5 min), washed three times with ethanol, and then dried under vacuum at 60 °C for 24 h.

Preparation of BSA modified DNA probe (pDNA-2-BSA)

Firstly, 200 μL pDNA-2 (10^{-6} mol L^{-1}) and 100 μL 12.5% glutaraldehyde were incubated at 37 °C for 1 h with shaking. Then, 100 μL 1% BSA was added to the incubated solution and incubated at 37 °C for 2 h with shaking. Finally, the incubated solution was washed three times with ultrapure water through an ultrafiltration tube (MWCO=30KD) to remove unreacted pDNA-2 and glutaraldehyde. The corresponding pDNA-2 for the RdRp gene with BSA modified was named pDNA-2-BSA.

The sequence is DEVD (aspartate glutamate valine aspartate)

Preparation of Electrode

Initially, 1 mg of materials (e.g., ZIF-67, pm-ZIF/P(Zn)) were dispersed in 1mL ultrapure water. Then, 10 μL of the solution was spread on the surface of a glassy carbon electrode (GCE)，which was polished carefully with 0.3 and 0.05 μm of Al_2O_3 powder and sonicated sequentially in ethanol and ultrapure water. In order to enhance the stability of the electrode, after drying at room temperature, 10 μL of TOAB solution, which was prepared by dispersing 10 mmol of TOAB in 1 mL of ethanol under ultrasonication, was spread on the surface of GCE.

Fabrication of the ECL biosensor

First, 5 μL1 mg mL^{-1} pm-ZIF/P(Zn) was placed on the GCE and coated with 10 μL 0.1% chitosan solution to obtain the CS/ pm-ZIF/P(Zn) /GCE after dried at room temperature. Subsequently, 20 μL 12.5% glutaraldehyde was dripped onto the CS/ pm-ZIF/P(Zn) /GCE and incubated at 37 °C for 1 h. After the reaction, the electrodes were washed with ultrapure water, and 20 μL pDNA-1 (10^{-6} mol L^{-1}) was covered onto the modified GCE and incubated at 37 °C for 2 h. Then, 20 μL of 1% peptide solution was dripped onto the surface to block the non-specific binding sites. After being washed thoroughly with ultrapure water, 20 μL of the tDNA was dripped onto the surface of the electrode and incubated at 37 °C for 2 h. Next, after washing thoroughly with ultrapure water, 20 μL pDNA-2-BSA was added to the electrode and incubated at 37 °C for 2 h. Finally, the electrode would generate an ECL signal in the

O_2-saturated aqueous electrolyte solution (HEPES，pH7.0) and give the quantitative criteria for the proposed DNA assay.

Supporting Figures

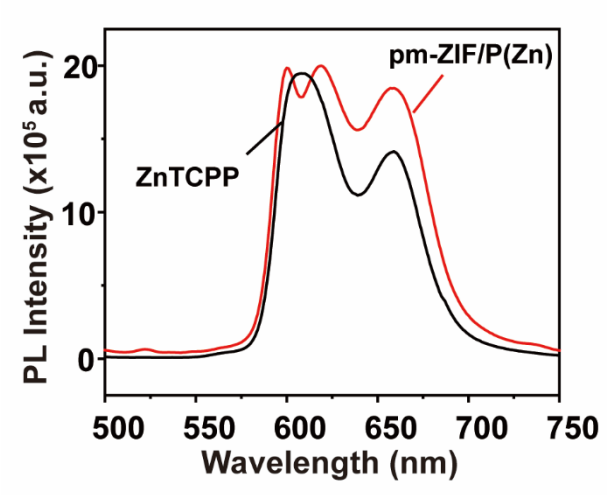

Figure S1. PL emission spectra of ZnTCPP and pm-ZIF/P(Zn)

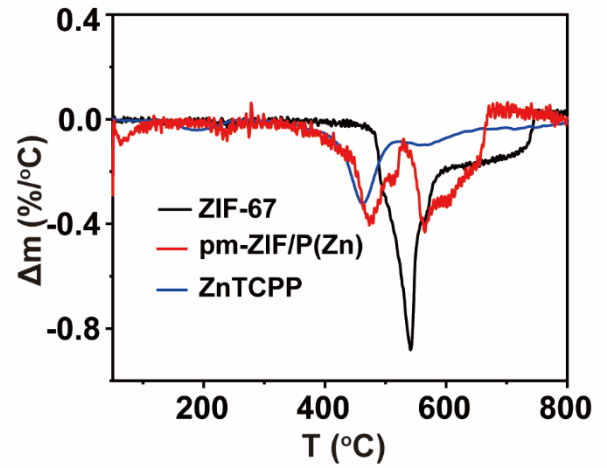

Figure S2. Thermogravimetric differential curve of ZIF-67, ZnTCPP and pm-ZIF/P(Zn)

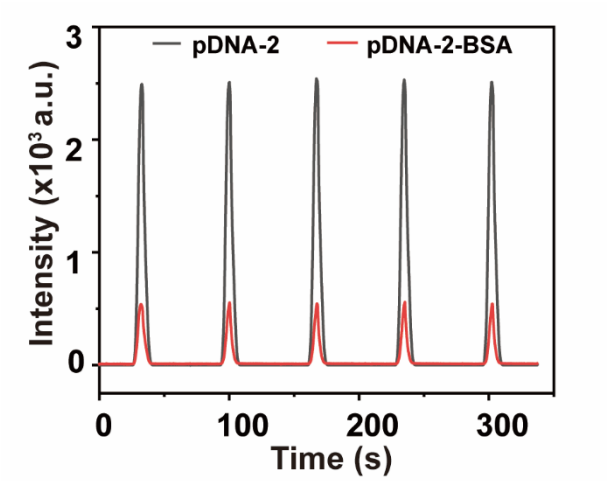

Figure S3. Comparison of ECL intensity between pDNA-2 and PDNA-2-BSA

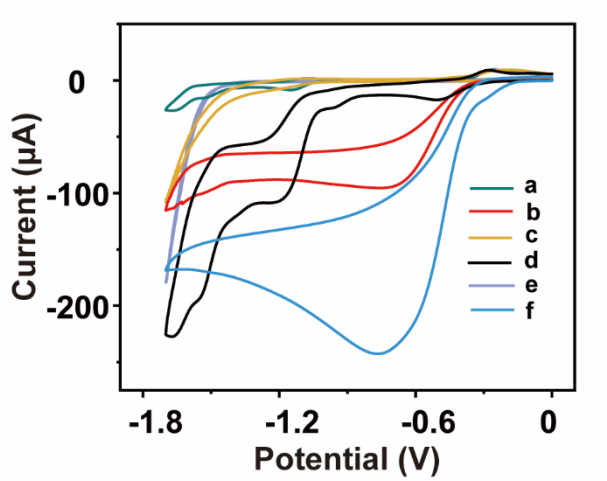

Figure S4. Cyclic voltammograms of ZnTCPP (a), pm-ZIF/P(Zn) (c) and ZIF-67 (e)) in the absence of H_2O_2 and in the presence of 0.05 M H_2O_2 (b, d, f,).