

Supporting Information

A Photoelectrochemical Sensor through Quenching of Photoinduced Electrons based on G-quadruplex/Hemin Complex

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1. Materials

Hemin was purchased from Sigma. G-quadruplex DNA (PS2.M:5'-NH₂-AAAAA-GTG GGT AGG GCG GGT TGG-3') was purchased from Sangon Biotechnology Co., Ltd. (Shanghai, China). Before use, this oligonucleotide was dissolved in PBS buffer. The stock solution of hemin (1 mM) was prepared in DMSO, stored in the dark at -20 °C, and diluted to the required concentration with the TH buffer.

2. Instrumentations

UV-vis spectroscopy measurement was carried out on a Jasco V-660 spectrophotometer (Japan). The structure characterization of samples was performed on a diffractometer (ARL X'TRA, American Thermo Elemental Company) employing Cu-K α radiation ($\lambda = 0.15406$ nm), with a scanning rate of 5°/min in the 2 θ angle ranged from 20° to 70°. The morphology and size of N-doped TiO₂ NPs were measured by SEM (FEI Quanta 400F). Photocurrents were carried on CHI660D Electrochemical Workstation (Shanghai, Chen Hua Instrument Company, China) equipped with a 500 W xenon lamp as the excitation source at room temperature. A three-electrode system was employed with Pt sheet as auxiliary electrode, Ag/AgCl electrode as reference electrode and the modified N-doped TiO₂ as the working electrode.

3. Fabrication of PEC sensor

Preparation of N-doped TiO₂ N-doped TiO₂ was synthesized according to a previously published procedure, while urea was used as the N-source. 28.2 g Urea was mixed with 300 mL ethanol. 40 g tetrabutyl titanate was added dropwise to this solution under vigorous stirring. After stirred at room temperature for 2 h, the solution was dried at 80 °C overnight to allow the formation of N-doped TiO₂ particle. The as-prepared N-doped TiO₂ powder was annealed under air at 500 °C for 6 h in a muffle,

and then the sample was cooled down to room temperature naturally.

Construction of the PEC sensor FTO conducting glass substrate was sonicated in acetone, isopropanol, ethanol and water for 30 min, respectively. And then the as-prepared N-doped TiO₂ was added in the mixture solution of anhydrous terpeneol and ethyl celluloses, and the mixture was coating on FTO glass by doctor blade method. The N-doped TiO₂ modified FTO electrode was annealed under air at 450 °C for 4 h to remove the redundant anhydrous terpeneol and ethyl celluloses. The N-doped TiO₂ on the FTO (area = 0.5 x 0.5 cm²) was prepared as the photoactive substrate. Then the electrode was immersed in 1% (v/v) APTES/ethanol, 2.5% (v/v) glutaraldehyde aqueous solution, and G-quadruplex DNA buffer respectively to immobilize the amino-modified DNA.

4. Photocurrent measurements

The photocurrent detection was performed in the TH buffer at room temperature in the presence of hemin. Different concentrations of K⁺ were added into the solution and kept at room temperature for a certain time, allowing the G-quadruplex DNA to bind hemin properly to form the G-quadruplex/hemin complex. I-t curves were recorded under the illumination of Xe lamp with the on/off periods as 30/50 s.

5. Optimum conditions

Fig. S1 shows the investigation about the reaction time of the G-quadruplex/hemin complex. 50 μM K⁺ was selected as an excessive concentration for the saturation state of the G-quadruplex formation. As observed from the presented results, 15 min was the optimum reaction condition for G-quadruplex/hemin complex.

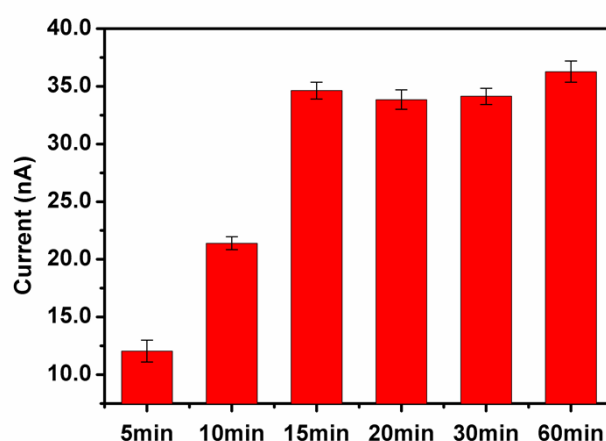


Fig. S1 Effect of the reaction time of the G-quadruplex/hemin complex. Experimental conditions: 10 mM Tris-HNO₃ (pH = 7.4) containing 1 μM hemin and 50 μM K⁺.

6. Photocurrent Responses

The photocurrent intensities of the G-quadruplex/hemin complex were examined at different concentrations of K^+ in the presence of 140 mM Na^+ . The photocurrent intensity gradually reduced as the concentration of K^+ increased.

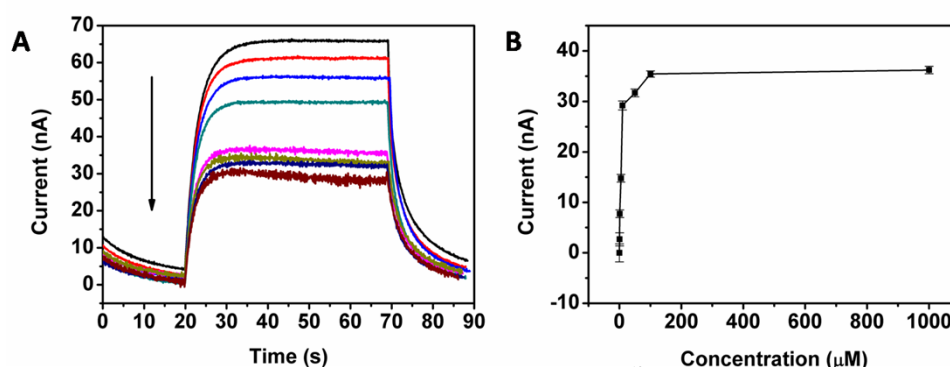


Fig. S2 (A) Photocurrent response of the G-quadruplex/hemin complex upon addition of different concentrations of K^+ in the presence of 140 mM Na^+ . (B) Plot of photocurrent intensity versus K^+ concentration. Experimental conditions: 10 mM Tris- HNO_3 (pH = 7.4) containing 1 μM hemin.

7. The Electron Transfer Mechanism

Fig. S3 showed the mechanism of the electron transfer. The conduction band edge of the N-doped TiO_2 was -0.68 V (vs. NHE) and the value band edge was 2.31 V (vs. NHE). At the same time, the reduction potential of the G-quadruplex/hemin complex was reported around -0.026 V (vs. NHE)¹. In such condition, the photo-generated electrons could transfer to the ferric iron ions of the bound hemin to reduce it to ferrous iron ions.

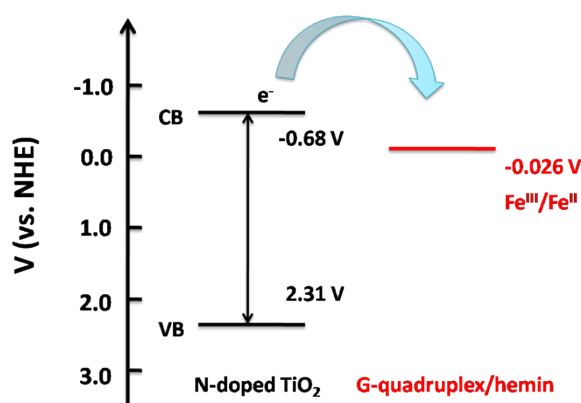


Fig. S3 The mechanism of the electron transfer between the N-doped TiO_2 and G-quadruplex/hemin.

Reference

1. G. Pelossof, R. Tel-Vered, J. Elbaz, I. Willner, *Anal. Chem.*, 2010, **82**, 4396-4402.