Plasmon enhanced photocurrent monitoring of the

interaction between porphyrin covalently bonded graphene

oxide and adenosine nucleotides

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Experiments

Materials

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4-formylbenzoic acid methyl ester, 4-picoline, pyrrole, propionic acid, thionyl chloride,
chloroauric acid (HAuCl₄), sodium citrate, potassium hydroxide (KOH), anhydrous sodium sulfate (Na₂SO₄), tetrahydrofuran (THF), diethyl ether, and pyridine were purchased from Sinopharm Chemical Reagent Co., Ltd. Disodium hydrogen phosphate, sodium dihydrogen phosphate and triethanolamine (TEOA) were purchased from Shanghai Ling Feng Chemical Reagent Co., Ltd. adenosine (A), adenosine monophosphate (AMP), adenosine diphosphate (ADP), adenosine

15 triphosphate (ATP) were purchased from BIO Basic Inc., and succinimide, methyl viologen dichloride (MV/MV²⁺), N, N-dimethylformamide and iodomethane were from Aladdin Reagent Database Inc.. All reagents were used as received without further purification.

Synthesis of target compound

The procedure is illustrated in Scheme S1. Firstly, 3.42 g 4-formylbenzoic acid methyl ester, 6.0 20 mL 4-pyridinecarboxaldehyde and 5.0 mL pyrrole were added into 250 mL propionic acid. The reaction mixture was stirred at 140 °C under condensation for 3 h. After the reaction was completed, propionic acid was removed via distillation under reduced pressure. The remaining solid was taken up in dichloromethane and purified three times by flash chromatography using silica gel as absorbent and mixing solvents of dichloromethane/methanol (100/1, 50/1, 20/1, V/V,

25 respectively) as eluent. The solvent was removed under reduced pressure and purple solid of compound 1 with a yield of 2.3%.

Afterward, 290 mg compound 1 was mixed with 30 mL 10% KOH aqueous solution and 100 mL THF/Ethanol (1:1), and the mixture was stirred for 7.5 h with condensation under 60 °C. After finishing the reaction, the solvent was removed under reduced pressure to yield compound 2. Then

- 30 102 mg compound 2 was again dissolved in 10 mL dry pyridine, and 5 mL thionyl chloride was slowly added into the solution (ca. 1 min) to start the reaction under continuous stirring at 50 °C in a dark and moisture-free environment for 30 min to obtain compound 3. N-hydroxysuccinimide (400 mg) was then added and the reaction was monitored by thin layer chromatography (TLC). The reaction was completed after 3 h, and the residual pyridine was removed under reduced
- 35 pressure. The crude material was dissolved in chloroform and washed with saturated sodium hydrogen carbonate aqueous solution for multiple times. The organic layer was collected and dried using anhydrous Na₂SO₄. The solvent was then evaporated under reduced pressure and the solid was collected and recrystallized in mixed solvent of chloroform/petroleum ether to yield compound 4 (91.2 mg). Finally, compound 4 (50 mg) was dissolved in dimethyl formamide (10
- 40 mL) and mixed with methyl iodide (20 mL), the mixture was stirred at 40°C for 5 h. After the reaction was completed, the solution was distilled under reduced pressure and compound 5 was

gained. Graphene oxide (15 mg) and compound 5 (10 mg) was mixed in PBS 8.0 (10 mL), and the mixture was stirred at room temperature for 3 h, and then compound 6 was obtained.



Scheme S1 Synthesis of porphyrin covalently bonded graphene oxide (Por-GO)

Synthesis of Por-GO composite

In order to enhance the photosensitive properties of porphyrin, we applied GO for its potential role in efficient electron separation and transfer, Por-GO composites have been used and studied so far,¹ where the combination was mostly noncovalent bonding through π - π conjugation, electrostatic attraction or covalent bonding between amino-porphyrin and carboxyl acid at the edge of GO sheets²⁻⁶. Though enhanced properties have been obtained through these routes, however, increasing the grafting density of porphyrin on GO sheets through covalent bonding may show a higher sensitivity performance as that would allow more stable connection points on GO

- 10 than non-covalent bonding, Herein, we introduced succinimide to facilitate the esterification between carboxyl acid group on porphyrin and hydroxyl group on GO sheets as indicated in scheme 1. And by forming pyridine iodide as the final step of synthesizing 5-[4-(succinimide-N-oxycarbonyl)phenyl]-10,15,20-tris(N-methylpyridinium-4-yl) porphyrin tri-iodide (Por 5), further enhanced hydrophilicity could be obtained to ensure high dispersity of
- 15 Por-GO (compound 6 shown in scheme 1) composites in aqueous system. ¹HNMR was used to confirm the structure of Por 5 using d-DMSO as solvent. The absorption peak at 1824 cm⁻¹ and double peak appeared at 1215 cm⁻¹were attributed to the carbonyl and carbon-oxygen single bond vibration between carboxyl acid and hydroxyl groups which proved the formation of covalent bonding between GO and porphyrin by FTIR spectrum.⁷ Raman spectrum was also used
- 20 to further support the structure of GO-porphyrin composites (Figure S1). Due to the conjugation of sp2-hybridized carbon in the 2-D lattice of GO sheets, G-band peak at 1580 cm⁻¹ appeared in both grafted and unmodified GO. However after the grafting of porphyrin, the ratio between D'-band at 1345 cm⁻¹ and G-band was significantly increased, which could be attributed to the interruption of the conjugated structure of GO induced by perpendicularly grafted porphyrin molecules.⁷ G'-band
- 25 peaks around 3000 cm⁻¹ which were related to the two phonon double resonance Raman process were not significantly affected by the grafting of porphyrin molecules. Through FTIR and Raman spectrum, Por-GO test system was founded and the covalent combination was certified to be available.

Preparation of gold nanoparticles (GNP)

- 30 GNP were synthesized according to previous reported literature.⁸ Briefly, 50 mL of 254 μM HAuCl₄ aqueous solution was brought to a rolling boil with vigorous stirring. 400 μL of sodium citrate aqueous solution (388 mM) was rapidly added to the vortex of the solution, and a color change from yellow to red occurred. 15 min of boiling in the vortex was continued and stopped afterwards. And then, the vortex was kept stirring for an additional 15 min. After the solution
- 35 reached room temperature, it was filtered by a 0.8 µm gelman membrane filter. The obtained solution of colloidal particles was characterized by an absorption maximum at 520 nm using an Ocean optical USB 2000+ UV-vis spectrometer (Figure S2). Scanning Electron Microscope (SEM, Hitachi, SP2600) shows the diameter of particles was around 28nm with a narrow distribution (Figure S3).

40 Preparation of Por-GO-GNP-MV functionalized electrode

Before modification, ITO electrodes were cut into a plate of $0.6 \text{ cm} \times 3 \text{ cm}$, which were then cleaned by swabbing and sonification with detergent/deionized water, rinsing in DI water, and finally rinsing in acetone and methanol.

A typical procedure of preparing Por-GO-GNP-MV functionalized ITO electrode is described as

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Supporting Information

follows: aqueous solutions of porphyrin-GO composite (5 mL, 0.07 wt.%), AuNPs (Gold nanoparticle solution) (3 mL, 2.6 mM), MV^{2+} (2 mL, 10 mM) and 200 µL 5 % Nafion were mixed together until the solution became homogeneous. Then, 35 µL of the mixed solution was dropped onto pre-cleaned ITO electrode at an area of 0.6 cm×0.6 cm, which was dried under room temperature to form a uniform coating on the electrode surface.

During the preparations of the control electrodes, we eliminated Por-GO composite, MV, and GNP respectively from the mixture modification solution, while added the same volume of water to keep the same concentration of each component.

Photocurrent measurement on the functionalized electrode

- 10 All electrochemical experiments were performed on a CHI 1232a electrochemical workstation (Shanghai Chenhua Co. Ltd., China), together with a Xenon lamp light source (LE-SP-LS-XE 500, Shenzhen Leo-photoelectric Co., Ltd. China). The surface of functionalized ITO electrode in the cell was irradiated from a Xenon lamp, through a home-made light chopper with the shutter chopping frequency controlled manually. The functionalized electrode surface was oriented facing
- 15 the incident light (front irradiation) with a distance of 20 cm between the lamp and the electrode. Photocurrent response of the functionalized ITO electrode as a working electrode was measured using amperometric I-t curve measurements with an Ag/AgCl reference electrode and a Pt wire counter electrode, in 0.2 M sodium phosphate buffer (pH 8.0) with 50 μ M TEOA in the solution, where light was controlled on and off in a certain frequency with the light chopper. The
- 20 photocurrent action spectrum was obtained in the same way except that the light source was equipped with light filters of different wavelength centered at 365 nm, 405 nm, 420 nm, 435 nm, 486 nm, 509 nm, 531 nm, 545 nm, 589 nm and the power were set at 500 W.

UV-Vis absorption measurement

UV/Vis absorption spectra were obtained with an Ocean Optics USB2000 + (190-1700 nm)

25 UV/Vis miniature fiber-optic spectrometer using a high-performance 2048-element linear CCD-array detector, light source (DT-mini-2).



Figure S1. Raman spectrum of GO (black curve) and Por-GO composites (red curve).



Figure S2. Absorption spectrum of Por-GO-GNP-MV composite in water used for functionalization on ITO electrode.





Figure S3. SEM image of gold nanoparticles used for functionalization on ITO electrode.



Figure S4. TEOA effect on the photocurrent response (PBS 8.0, 0.2M. TEOA, 50 µM).

5 **References**

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