# Supporting Information

## 3D Semiconducting Polymer/Graphene Networks: Toward Sensitive Photocathodic Enzymatic Bioanalysis

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## This material includes:

# EXPERIMENTAL SECTION

**Chemicals and Apparatus.** The ITO slices (type N-STN-S1-10 with ITO coating 180±20nm, sheet resistance 8.1±0.6 $\Omega cm^{-2}$) were purchased from China Southern Co. Ltd, Shenzhen, China. Graphene oxide was bought from Graphenea S.A. Conjugated polymer poly[(9,9-dioctylfluorenyl-2,7-diyl)-*co*-(1,4-benzo-{2,1,3}-thiadazole)] (PFBT) and poly(diallyldimethylammonium chloride) (PDDA, 20%, w/w in water, MW=200,000-350,000) were obtained from Sigma-Aldrich (U.S.A). Poly (styrene-*co*-maleic anhydride) (PSMA) and Tris (hydroxymethyl) aminomethane (Tris) were obtained from Tianjin Heowns Biochem LLC (China). Sarcosine oxide (SOx, 10 kU) was purchased from Bioss Co., Ltd (China). Sarcosine was bought from BBI Life Sciences Corporation. Tetrahydrofuran (THF) (≥ 99.0%), phenylalanine, cysteine, lysine, aspartate, ascorbic acid, D-(+)-glucose, urea and arginine were supplied from Sinopharm Chemical Reagent Co., Ltd. (China). Other chemicals were all of analytical reagent grade and were used as received. All aqueous solutions were prepared using ultrapure water (18.2 $M\Omega\ cm^{-1}$ resistivity at 25°C) which was obtained from a Milli-Q water purification system.

Ultraviolet-visible (UV-vis) absorption spectrum was obtained from a Shimadzu UV-3600 UV/vis spectrophotometer. Field-emission scanning electron microscopy (FE-SEM) was performed on a Hitachi S-4800 scanning electron microscope (Hitachi Co., Japan). Transmission electron microscopy (TEM) was conducted on a JEOL model 2000 instrument operating at 200 kV accelerating voltage. The freeze-dried 3D graphene was obtained from Labconco Freeze dryer. The X-ray photoelectron

spectrum (XPS) was monitored on an ESCALAB 250 spectrometer (Thermo-VG Scientic Co. USA) with an ultrahigh vacuum generator. Fourier-transform infrared spectra (FTIR) of samples in solid state (KBr matrix) was measured with a Perkin Elmer Spectrometer. XRD spectra were measured on powder X-ray diffraction (XRD, X'TRA, Cu Kα; ARL Co., Switzerland). PEC measurements were performed with a homemade PEC system equipped with a 5 W LED lamp of 450 nm excitation light. Photocurrent was measured on a CHI 660C electrochemical workstation (China), and a modified indium tin oxide (ITO) electrode with geometrical area of 0.25 $cm^2$, a Pt wire, a saturated Ag/AgCl electrode were respectively used as working, counter, and reference electrode in this work.

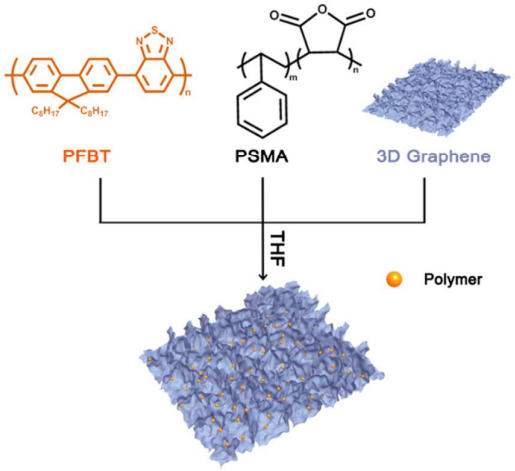
**Preparation of Three-dimensional (3D) Graphene.** Firstly, graphene hydrogels were synthesized by one-step hydrothermal treatment. Specifically, 4mg/mL of graphene oxide (GO) solution was dispersed in water and subsequently sonicated for 30 min to obtain a homogeneous suspension. Afterwards, the suspension above was transferred into a Teflon-sealed autoclave and heated at 180 ºC for 12 h.[1] Then the desired 3D graphene was obtained by freeze-dry for 2 days.

**Synthesis of 3D Semiconducting Polymer/Graphene (SP/G) Hybrid.** Specifically, 3 mg/mL of the PFBT polymer, 4 mg/mL of PMSA and 2 mg/mL 3D graphene were dispersed together in THF. After magnetic stirred overnight and sonicated for an hour, the 3D SP/G hybrid was obtained in a form of a homogeneous dark green suspension. Significantly, the PFBT polymer, PMSA and 3D graphene could not be dissolved in the ultrapure water.

**Fabrication of the 3D SP/G Networks-Based Photocathode.** Firstly, 15 μL of the as-prepared 3D SP/G suspension was assembled onto the ITO electrode. Followed by dried at room temperature, the modified electrodes were able to be used for further photocurrent detection.

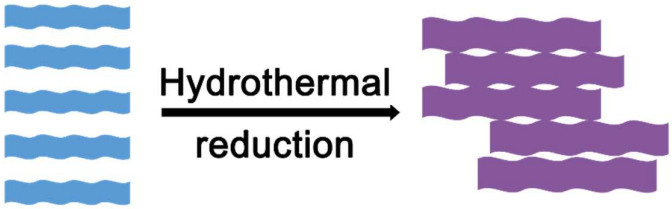
**Development of SOx biosensor.** SOx was immobilized onto the 3D SP/G modified electrode by alternately immersing the electrode into a solution of 2% PDDA containing 0.5 M NaCl and the SOx aqueous solution for 15 min.[2] This process was repeated for three times to make sure the good bioconjugation of SOx onto the electrode. Particularly, the electrodes were carefully washed with Milli-Q water after each dipping step.

**Scheme S1. The Synthesis of 3D SP/G Hybrid**




As shown in Scheme S1, the 3D SP/G hybrid was prepared by the mixture of 3D graphene, PFBT polymer and PSMA in THF. Followed by magnetic stirred overnight and sonicated for an hour, the as-obtained 3D SP/G solution were dropped onto the ITO electrode. Subsequently, the as-prepared photocathodic electrode was dried at the room temperature prior to use.

**Scheme S2. The Formation Mechanism of Graphene Hydrogel**




The formation mechanism of graphene hydrogel was illustrated in Scheme S2. After hydrothermal reaction with high pressure and high temperature, the graphene hydrogel was formed with the formation of π-conjugated and hydrophobic structures.[1]

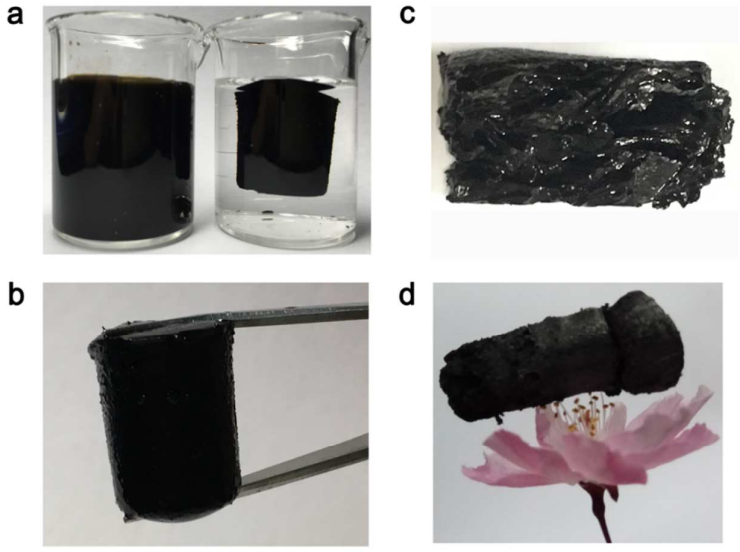



**Figure S1.** (a) Photographs of the GO solution before and after hydrothermal reaction; (b) Photogragh of the graphene hydrogel. (c) Photograph of the sectional graphene hydrogel. (d) Photogragh of the 3D graphene.

As shown in Figure S1a, the bulk sample was acquired after the high pressure and high temperature by hydrothermal reaction and called graphene hydrogel. As shown in Figure S1b, the as-obtained graphene hydrogel was strongly interconnected due to a large amount of π-π stacking. After cut longitudinally, Figure S1c showed the sectional view of graphene hydrogel with porous and water-contained. Another flower begonia was introduced to validate the low density of 3D graphene in Figure S1d. As

shown, the 3D graphene could easily be placed on the flower.

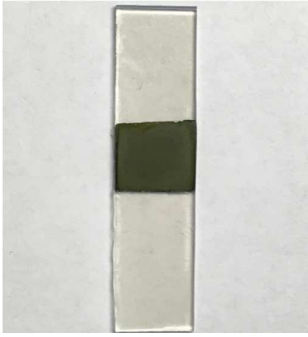


**Figure S2.** The photograph of the 3D SP/G networks-based photocathode.

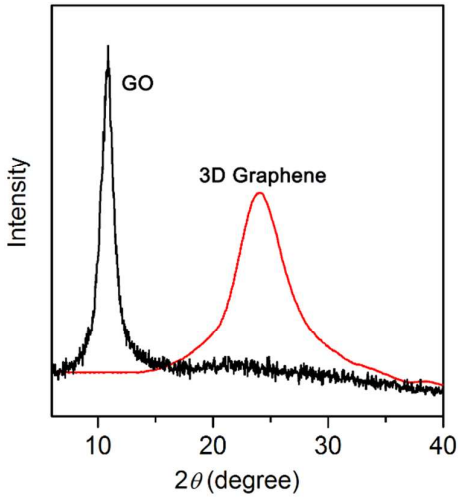



**Figure S3.** XRD patterns of the GO and 3D graphene.

The photograph of the 3D SP/G networks-based photocathode was shown in Figure S2. It can be seen that the 3D SP/G hybrid was uniformly covered onto the ITO electrode. The Figure S3 further demonstrated the successful preparation of 3D SP/G hybrid.[3] Compared with GO, the X-ray diffraction (XRD) spectrum of 3D graphene displayed a broader peak with the (002) peak shifted from 10.4° to 24.3°,[4] which further demonstrated the good reduction of GO by hydrothermal reaction.

## REFERENCES

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