Electronic Supplementary Information for

Carbon-rich nanofiber framework based on conjugated arylacetylene polymer for photocathodic enzymatic bioanalysis

Junyan Tang [1], Xiaoya Liu [1], Chengwei Yang [1], Zhening Zhang [1], Rui Sun [1], Hongmei Li [1], Caolong Li [1,2*] and Fei Wang [1]

[1] *Key Laboratory of Biomedical Functional Materials, School of Science, China Pharmaceutical University, Nanjing, 211198, P. R. China.*

[2] *Tibetan Medicine Research Institute, Tibetan Traditional Medical College, Tibet, 850000, P. R. China*

Supplementary experiment details for the synthesis of bulk PTEB in solution and the fabrication process of the bulk PTEB modified ITO electrode.

The synthesis of bulk PTEB was based on the reported method by Xu *et al.* [1].

300 mg 1,3,5-triethynylbenzene (TEB) was dissolved in 350 mL methanol and then 5 mL $NH_3 \cdot H_2O$ was slowly added into the methanol solution at 0 °C. 40 mg CuBr was dispersed in 50 mL methanol and the suspension was carefully dropped into the above solution under vigorous stirring (600 rpm). After warming up to 25 °C, the reaction was proceeded in dark for 72 h and the yellow insoluble product precipitated from the solution gradually. The precipitate was collected by filtering using a polyvinylidene fluoride (PVDF) microporous membrane (220 nm), washed with 1M HCl (500 mL), deionized water (250 mL), methanol (250 mL) successively and followed by Soxhlet extraction with methanol (~24 hours) and deionized water (~6 hours), respectively. Finally, the product was dispersed in methanol again and the suspension was centrifuged at 8000 rpm to obtain the yellow powder of bulk PTEB.

For the fabrication of the photoelectrode, 5 mg bulk PTEB was dispersed in 1 mL 0.05 wt% Nafion to form 1 mg mL^{-1} suspension. The photoelectrode based on bulk PTEB was prepared by drop-casting 100 μL of the suspension on the ITO surface, and dried in air as working electrode. The followed photoelectrochemical test was consistent with that of PTEB nanofiber film.

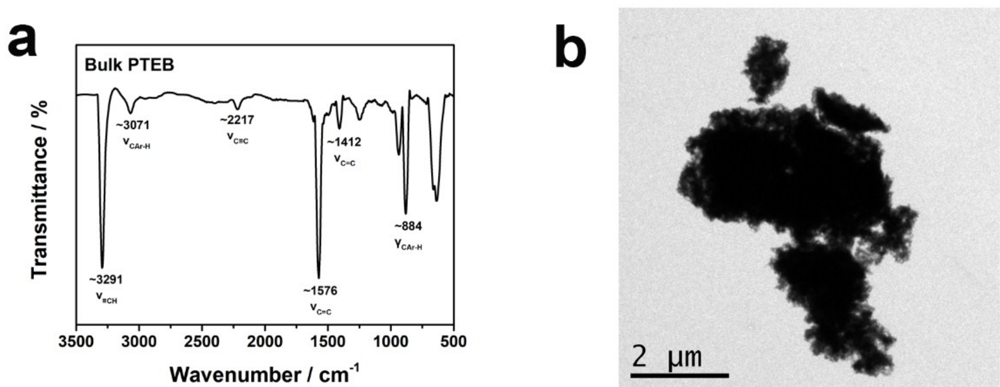

Fig. S1. (a) FT-IR spectra and (b) TEM image of bulk PTEB which show aggregated sheet-like morphology.

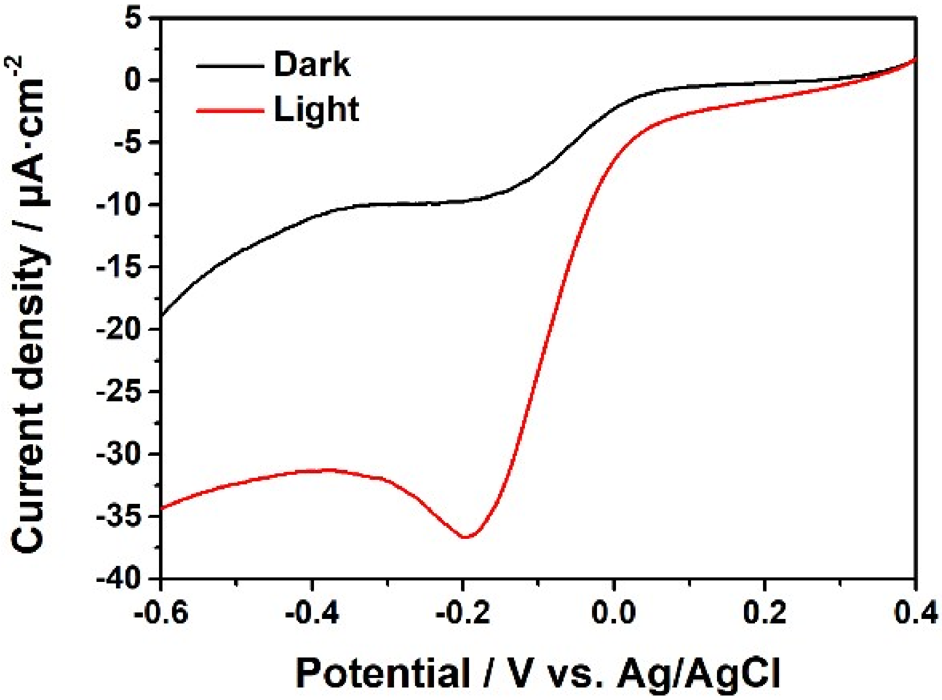

Fig. S2. Linear sweep voltammetry (LSV) curves of PTEB nanofiber film under dark and simulated sunlight irradiation (λ≥420 nm, 80 mW cm^{-2}).

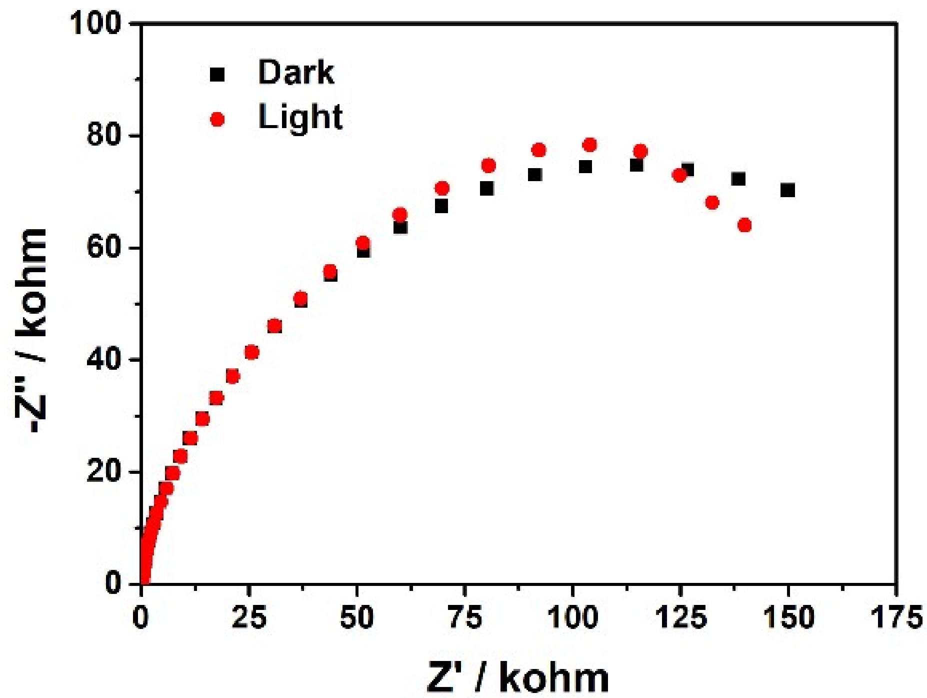

Fig. S3. Nyquist plot of bulk PTEB under dark and illumination in pH 7.0, 0.1 M PBS (bias: -0.3 V *vs*. Ag/AgCl, amplitude: 5 mV, frequency range: 100 kHz ~ 0.01 Hz).

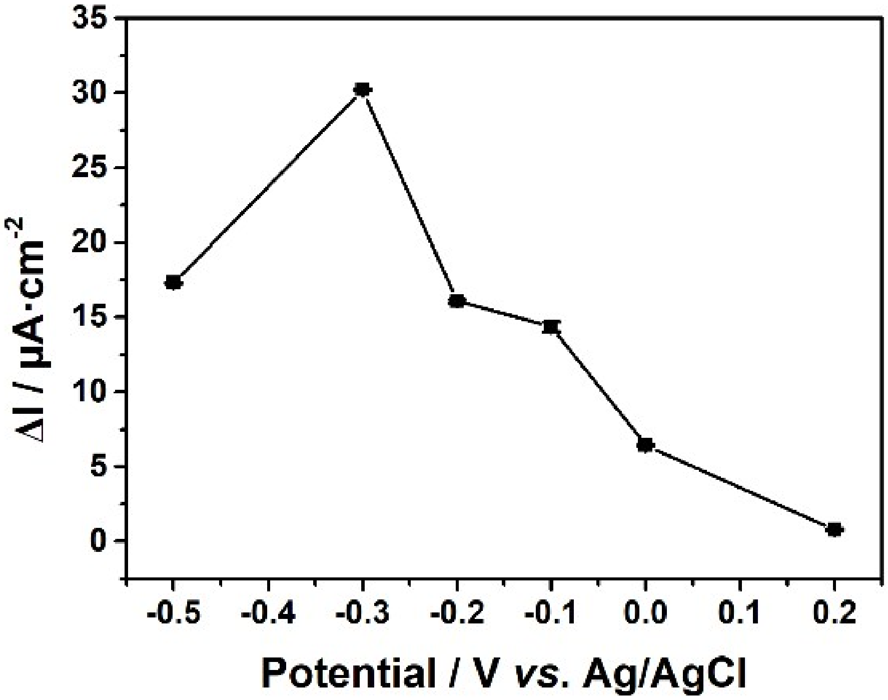

Fig. S4. The corresponding plot of photocurrent density of PTEB photocathode *vs*. various bias potential from 0.2 V to -0.5 V (*vs*. Ag/AgCl).

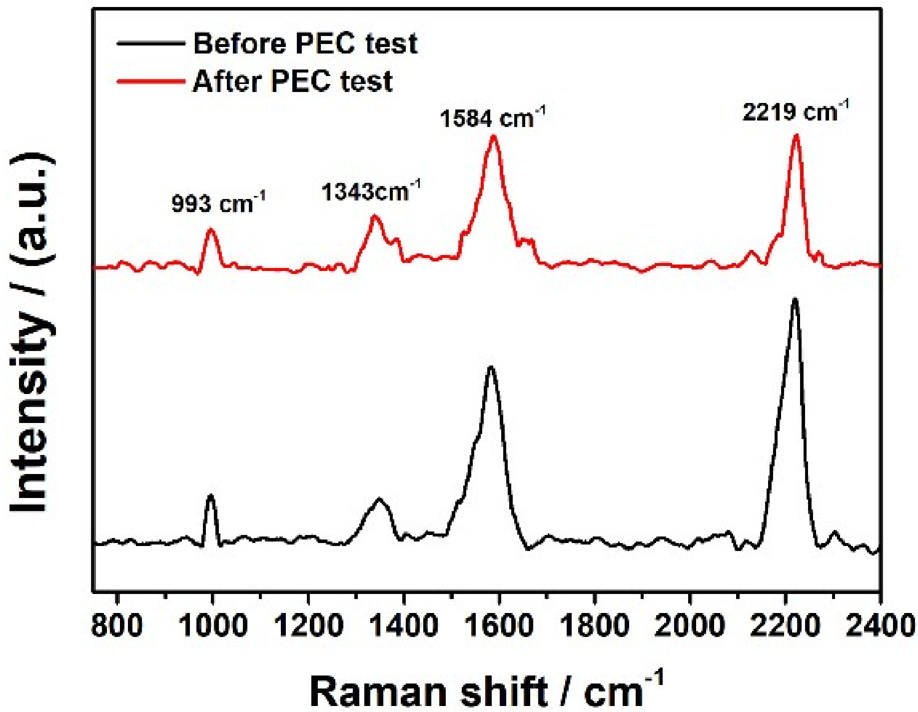

Fig. S5. Raman spectra of PTEB nanofiber film coated on ITO substrate before (black) and after (red) 1 h of continuous illumination in PEC test.

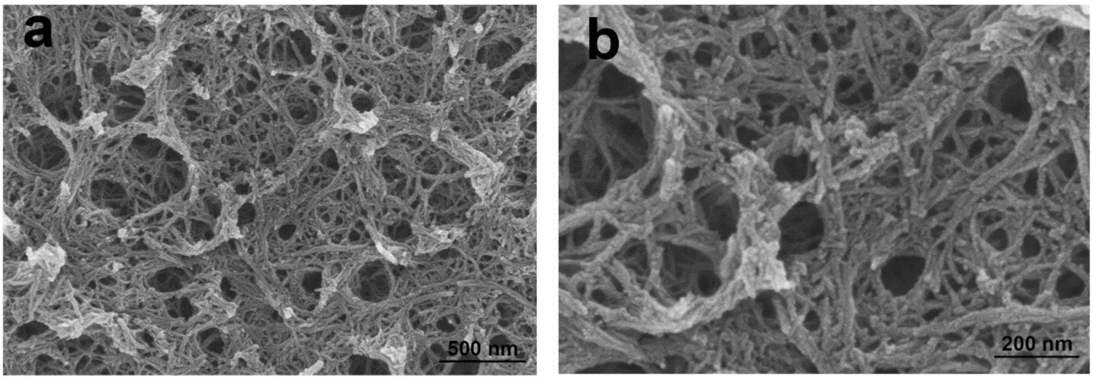

Fig. S6. (a) Top view and (b) magnified SEM images of PTEB nanofiber framework after 1 h of continuous illumination in PEC test.

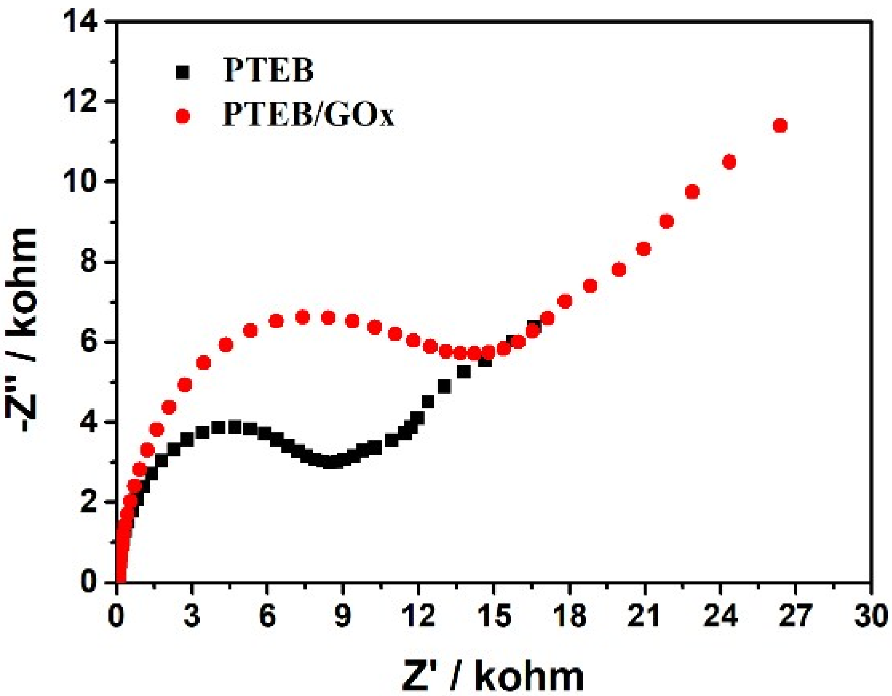

Fig. S7. Nyquist plots of PTEB photocathode before (black) and after (red) GOx modification in pH 7.0, 0.1 M PBS (bias: -0.3 V *vs*. Ag/AgCl, amplitude: 5 mV, frequency range: 100 kHz ~ 0.01 Hz).

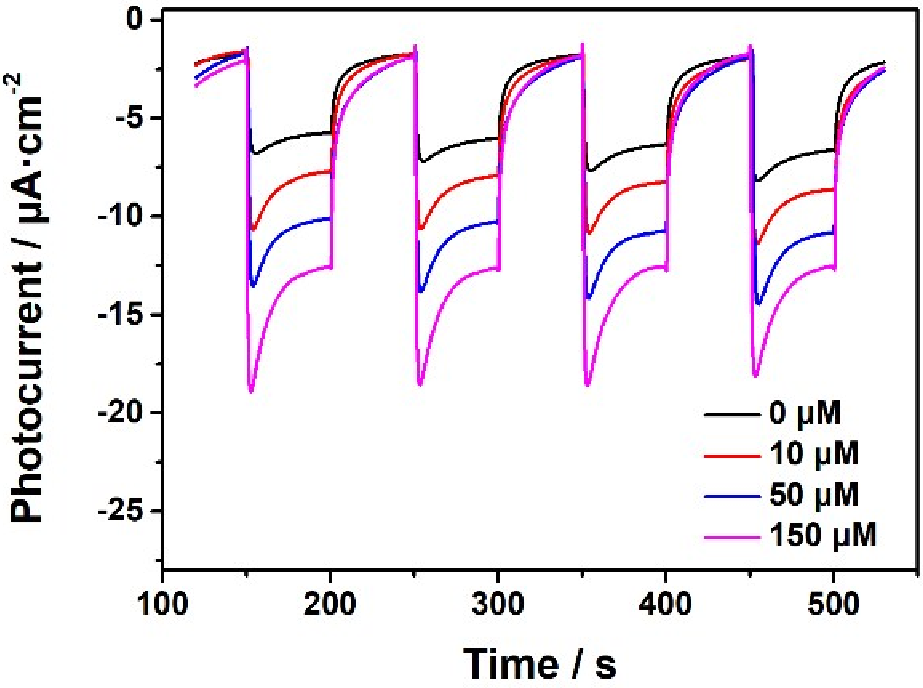

Fig. S8. Transient photocurrent density *vs*. time of photocathode based on PTEB film at a bias potential of -0.3 V (*vs*. Ag/AgCl) under intermittent irradiation in deoxygenated 0.1 M Na_2SO_4 containing various concentrations of Cu^{2+} as the electron scavenger.

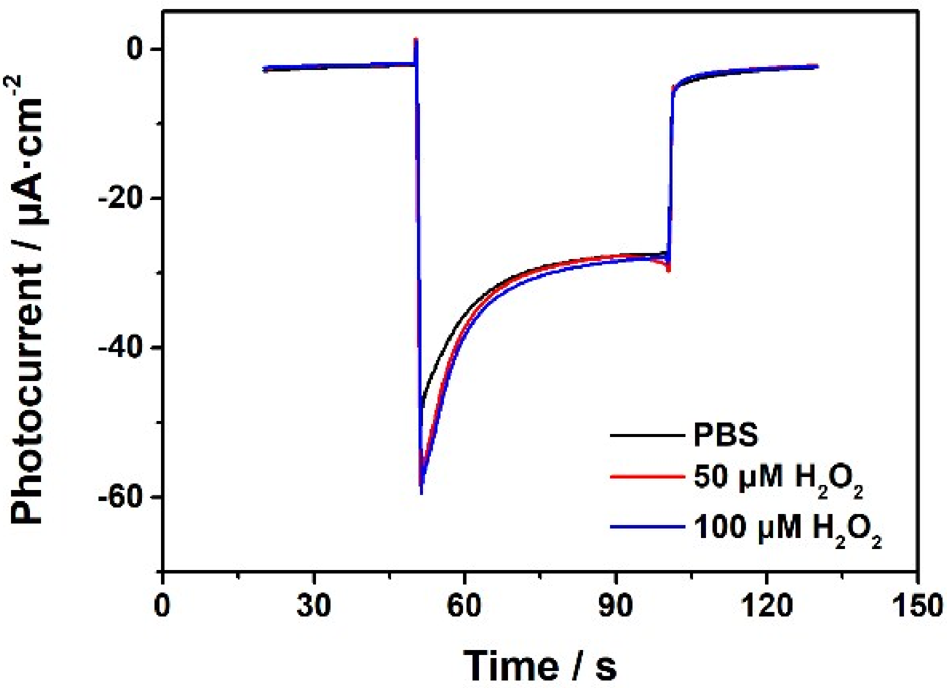

Fig. S9. The photocurrent response of PTEB photocathode to H_2O_2 in air-saturated 0.1 M PBS (pH 7.0).

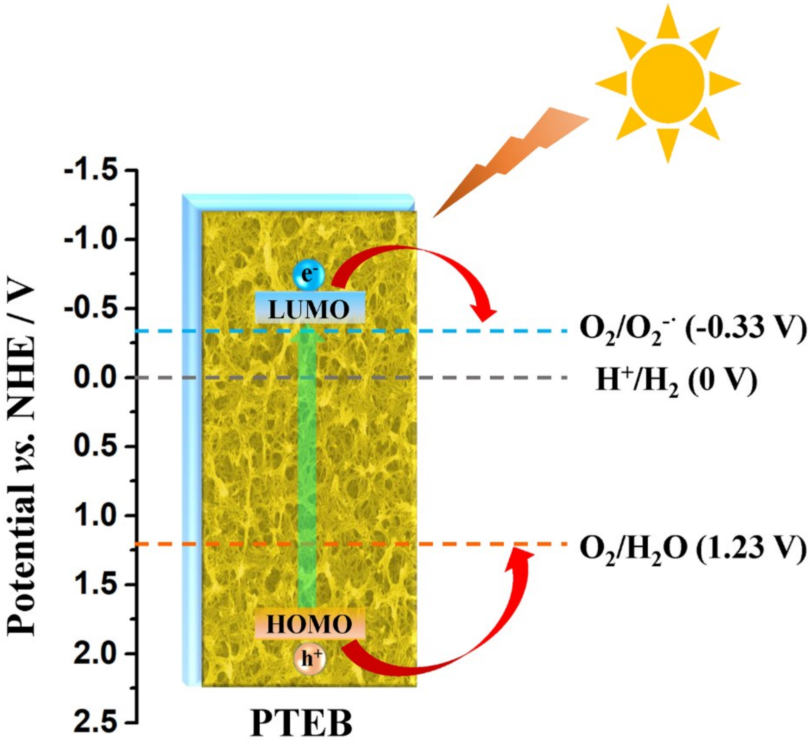

Fig. S10. Band structure diagram of PTEB nanofiber and the charge transfer process under light illumination.

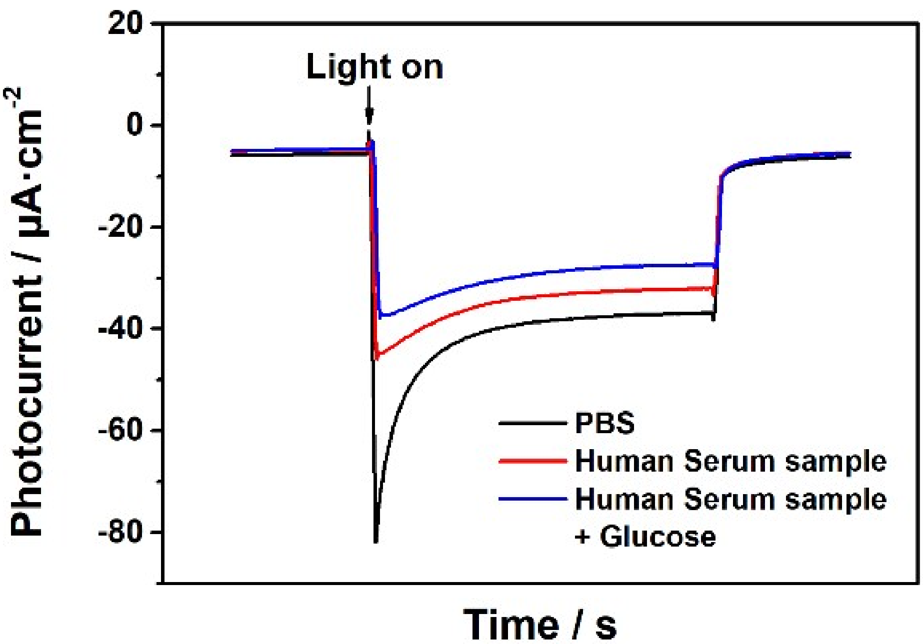

Fig. S11. The depressed cathodic photocurrent of PTEB photocathode with the addition of human serum sample and glucose in 0.1 M PBS (pH 7.0).

Table S1. Comparison of photoelectrochemical (PEC) sensing performance of PTEB-based transducer with some other previously reported PEC glucose sensors.

Material	Linear range	Detection limit	Reference
GOx/MoS_2-TiO_2	0.1 – 19.5 mM	0.015 mM	2
GOx/g-C_3N_4/TiO_2	0.05 – 16 mM	0.01 mM	3
GOx/BiOI/NiO	5 μM – 10 mM	1.6 μM	4
Nafion/GOx/ZnO/rGO	0 – 4.0 mM	0.5 μM	5
GOx/MoS_2	8 nM – 5 μM	0.61 nM	6
NiO/CdS/GOx	0.05 – 7.1 mM	0.015 mM	7
GOx/CdTe QDs	0.1 – 11 mM	0.04 mM	8
Rutile/Anatase TiO_2	1 – 20 mM	0.019 mM	9
Au/CuS/TiO_2	0.1 – 3 μM	0.01 μM	9
Ni/CdS/TiO_2	0.1–2 mM, 3–6 mM	7.9 μM	10
Amorphous-MoS_x/RGO[a]	0.15 – 16 mM	0.098 mM	11
CdS/Graphene	0.1 – 4.0 mM	7.0 μM	12
Fe_2O_3-NB-PDA-GDH[b]	0 – 2 mM	25.2 μM	13
$BiVO_4$	0 – 5 mM	0.13 μM	14
$BaTiO_3$	0.1 μM – 1 mM	7.94 μM	15
PTEB	5 μM– 8 mM	1.7 μM	This work

[a] RGO: Reduced graphene oxide

[b] NB-PDA-GDH: Nile Blue-Polydopamine-Glucose dehydrogenase

Reference

1. L. Wang, Y. Y. Wan, Y. J. Ding, S. K. Wu, Y. Zhang, X. L. Zhang, G. Q. Zhang, Y. J. Xiong, X. J. Wu, J. L. Yang and H. X. Xu, *Adv Mater*, 2017, **29**, 1702428.
2. X. Q. Liu, X. H. Huo, P. P. Liu, Y. F. Tang, J. Xu, X. H. Liu and Y. M. Zhou, *Electrochim Acta*, 2017, **242**, 327-336.
3. P. P. Liu, X. H. Huo, Y. F. Tang, J. Xu, X. Q. Liu and D. K. Y. Wong, *Anal Chim Acta*, 2017, **984**, 86-95.
4. L. Zhang, Y. F. Ruan, Y. Y. Liang, W. W. Zhao, X. D. Yu, J. J. Xu and H. Y. Cheng, *Acs Appl Mater Inter*, 2018, **10**, 3372-3379.
5. F. Zhou, W. X. Jing, Y. X. Xu, Z. Chen, Z. D. Jiang and Z. Y. Wei, *Sensor Actuat B-Chem*, 2019, **284**, 377-385.
6. S. Y. Wu, H. Huang, M. X. Shang, C. C. Du, Y. Wu and W. B. Song, *Biosens Bioelectron*, 2017, **92**, 646-653.
7. G. L. Wang, K. L. Liu, Y. M. Dong, X. M. Wu, Z. J. Li and C. Zhang, *Biosens Bioelectron*, 2014, **62**, 66-72.
8. W. J. Wang, L. Bao, J. P. Lei, W. W. Tu and H. X. Ju, *Anal Chim Acta*, 2012, **744**, 33-38.
9. B. D. Yan, Y. Zhuang, Y. L. Jiang, W. Xu, Y. J. Chen, J. C. Tu, X. H. Wang and Q. Wu, *Appl Surf Sci*, 2018, **458**, 382-388.
10. H. H. Huo, Z. D. Xu, T. Zhang and C. L. Xu, *J Mater Chem A*, 2015, **3**, 5882-5888.
11. M. X. Shang, H. Qi, C. C. Du, H. Huang, S. Y. Wu, J. L. Zhang and W. B. Song, *Sensor Actuat B-Chem*, 2018, **266**, 71-79.
12. X. Y. Zhang, F. Xu, B. Q. Zhao, X. Ji, Y. W. Yao, D. P. Wu, Z. Y. Gao and K. Jiang,

Electrochim Acta, 2014, **133**, 615-622.
13. G. M. Ryu, M. Lee, D. S. Choi and C. B. Park, *J Mater Chem B*, 2015, **3**, 4483-4486.
14. S. Wang, S. P. Li, W. W. Wang, M. T. Zhao, J. F. Liu, H. F. Feng, Y. M. Chen, Q. Gu, Y. Du and W. C. Hao, *Sensor Actuat B-Chem*, 2019, **291**, 34-41.
15. S. Selvarajan, N. R. Alluri, A. Chandrasekhar and S. J. Kim, *Sensor Actuat B-Chem*, 2016, **234**, 395-403.