

Supporting Information

Bi₂Te₃ nanosheets promoted Pd for ethylene glycol electrooxidation in both dark and visible light irradiation

*Fangfang Ren^a, Zhenghao Fei^a, Yun Yang^{*b}, Shuli Wang^c, Ligang Feng^{*c}*

a. College of Chemical and Environmental Engineering, Yancheng Teachers University, Yancheng, 224007, PR China.

b. Nanomaterials and Chemistry Key Laboratory, Wenzhou University, Wenzhou, China. E-mail: bachier@163.com

c. School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, 225002, PR China. E-mail: ligang.feng@yzu.edu.cn, fenglg11@gmail.com

Experimental section

Chemicals

Palladium chloride (PdCl₂, AR), ethanol (CH₃CH₂OH, AR, ≥99.7%), ethylene glycol (EG, AR, ≥99.5%), sodium hydroxide (NaOH, AR, ≥96.0%) and potassium hydroxide (KOH, AR, ≥85.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Polyvinyl pyrrolidone (PVP, K30, GR), bismuth (III) oxide (Bi₂O₃, 99.9%), tellurium dioxide (TeO₂, 99.99%) and commercial Pd/C (10 wt%, contains 40-60% H₂O) catalyst were purchased from Aladdin. Nafion (5 wt%, contains 45 ± 3% H₂O) was purchased from Shanghai Hesen Electric Co., Ltd. All solutions were prepared using ultrapure water and the chemicals were purchased and used without further purification.

Synthesis of Bi₂Te₃

In a typical synthesis, 0.4 g of PVP was added into a flask containing 18 mL of EG. Then, the mixture was sonicated for about 15 min to obtain a uniform suspension. After that, 0.2298 g of Bi₂O₃ and 0.2394 g of TeO₂ were added in and thoroughly stirred. Subsequently, 0.32 g of NaOH completely dissolved in 2 mL of ultrapure water was added dropwise into the above solution with continuous stirring. After stirring for 30 min at room temperature, the mixture was transferred into the Teflon-lined stainless steel with a volume capacity of 30 mL, sealed and reacted at 200 °C for 4 h. The product was collected through centrifugation, washed with ultrapure water and ethanol three times and dried in a vacuum oven at 60 °C.

Synthesis of Pd/Bi₂Te₃

The Pd catalyst anchored over Bi₂Te₃ was synthesized by a solvothermal method. Typically, 20 mg of Bi₂Te₃ obtained above was ultrasonically dispersed in a mixture containing 40 mL of ethanol and 40 mL of ultrapure water to form a uniform suspension. Under stirring, 2 mL of H₂PdCl₄ solution (22.6 × 10⁻³ M) was added to the suspension. Then, the pH of the suspension was adjusted to about 9 ~ 10 by NaOH solution (5 M). Subsequently, the resultant mixture was transferred into the Teflon-

lined stainless steel with a volume capacity of 100 mL, sealed and reacted at 140 °C for 4 h. After naturally cooled to room temperature, the mixture was filtered and washed several times with ethanol and water, respectively. At last, the resulting solid was transferred into a vacuum oven and dried overnight at 60°C to obtain the Pd/Bi₂Te₃-20% catalyst with 20 wt% Pd. While for Pd/Bi₂Te₃-25% and Pd/Bi₂Te₃-30% catalysts, the synthesis process was not changed just by using 2.78 and 3.58 mL of H₂PdCl₄ solution, respectively.

Physical characterizations

Power X-ray diffraction (XRD) was measured on a Rigaku Ultimate IV X-ray diffractometer operating at 40 mA and 40 kV. Scanning electron microscopy (SEM) image was acquired using a FEI Nova NanoSEM 450. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and element mapping analysis were conducted on a JEM-2100F electron microscope. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB250Xi spectrometer with an Al K α radiation source.

Photoelectrochemical measurements

All photoelectrochemical measurements were performed in a conventional three-electrode system by a CHI 660E electrochemical workstation. An L-glassy carbon electrode (L-GCE) with a diameter of 3.0 mm coated by catalyst was employed as the working electrode, an Hg/HgO (1 M KOH) electrode was used as the reference electrode and a platinum foil electrode was used as the counter electrode, respectively. The working electrode was prepared by dispersing 5 mg of catalyst powders into the mixture containing 950 μ L of ethanol and 50 μ L of Nafion solution (5 wt%) with ultrasonic treatment to form a homogeneous catalyst ink. Afterward, 2 μ L of the catalyst ink was dripped onto the L-GCE as the working electrode and then dried in air before electrochemical measurements. All of the potentials were in regard to the Hg/HgO. The electrolyte was saturated by N₂ for 15 min before measurements.

Cyclic voltammetry (CV) was carried out in a 1.0 M KOH solution or a mixed solution of 1.0 M KOH and 1.0 M EG at a potential range between -0.6 ~ 0.3 V with a

scan rate of 50 mV s^{-1} . Chronoamperometry (CA) was performed in a mixed solution of 1.0 M KOH and 1.0 M EG at -0.05 V for 3600 s . CO stripping voltammetry was measured in a 1.0 M KOH solution at 20 mV s^{-1} . CO was bubbled into the 1.0 M KOH solution for 30 min to form a CO monolayer adsorption onto the catalyst. Then, the excess CO in the electrolyte was removed by bubbling N_2 into the solution for 15 min .

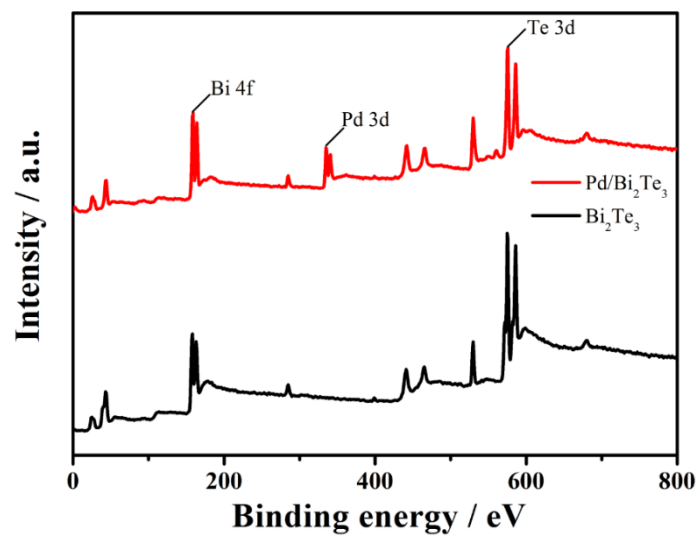


Fig. S1 XPS survey spectra of Bi_2Te_3 and $\text{Pd}/\text{Bi}_2\text{Te}_3$.

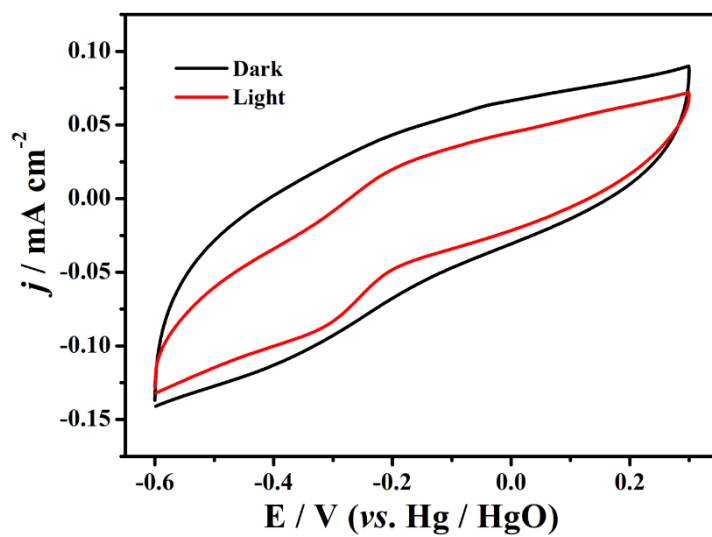


Fig. S2 CV curves of Bi_2Te_3 in 1.0 M EG + 1.0 M KOH solution under dark and visible light irradiation conditions at 50 mV s^{-1} .

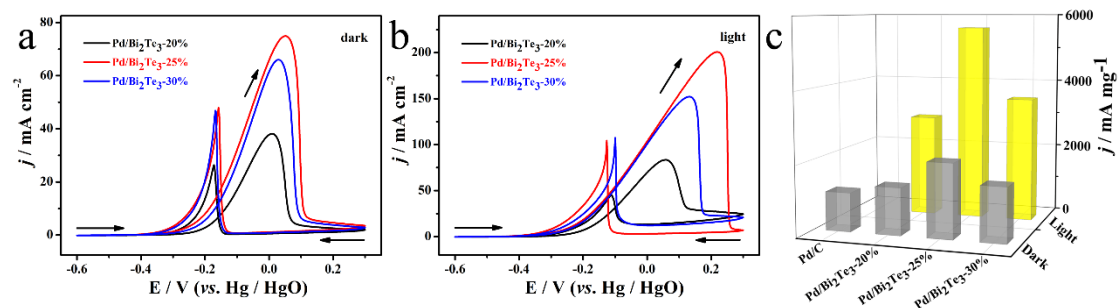


Fig. S3 CV curves of Pd/Bi₂Te₃ with different loading of Pd for EG oxidation under dark (a) and visible light irradiation (b) conditions. Mass activity of Pd/C and Pd/Bi₂Te₃ with different loading of Pd in 1.0 M EG + 1.0 M KOH solution at 50 mV s⁻¹ (c).

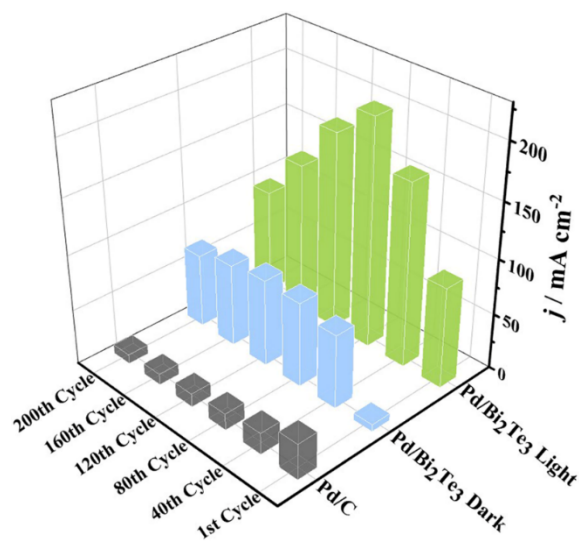


Fig. S4 The histogram of forward peak current density of Pd/C and Pd/Bi₂Te₃ vs. scanning cycles.

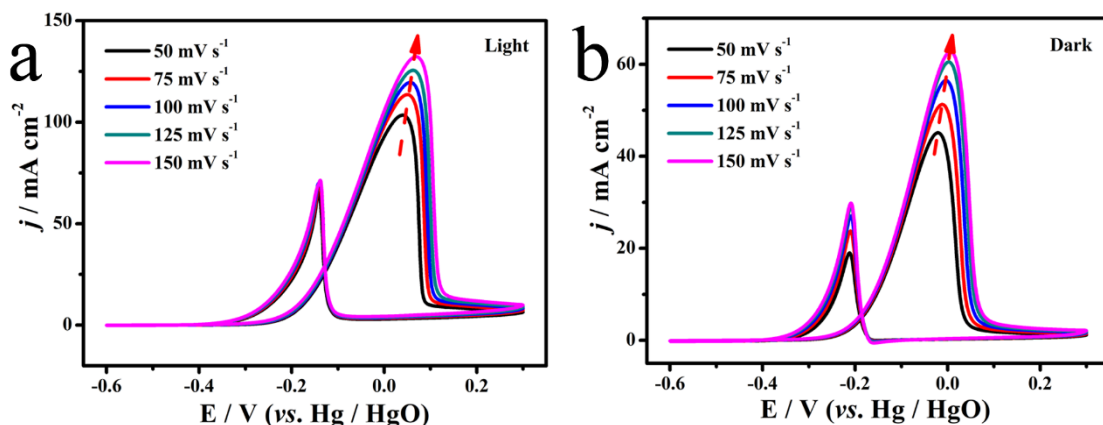


Fig. S5 CV curves of Pd/Bi₂Te₃ with (a) and without (b) visible light irradiation in 1.0 M EG + 1.0 M KOH solution at different scan rate.

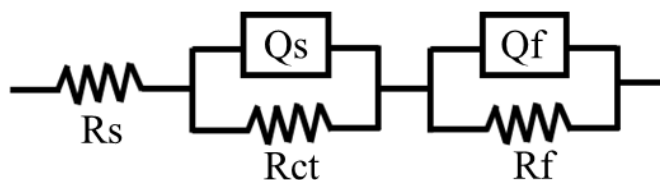


Fig. S6 Equivalent circuit for EIS analysis. For the equivalent circuit, R_s is the uncompensated solution resistance, R_{ct} represents the charge-transfer resistance arising from alcohol oxidation and R_f stands for the film resistance. Q_s represents double-layer capacitance and Q_f corresponds to the film capacitance.

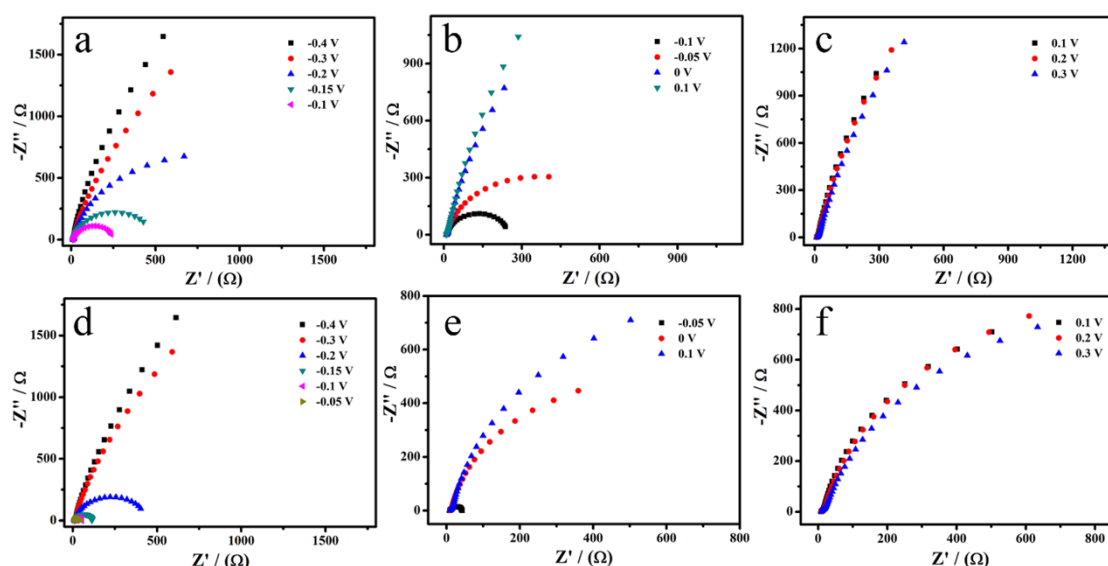
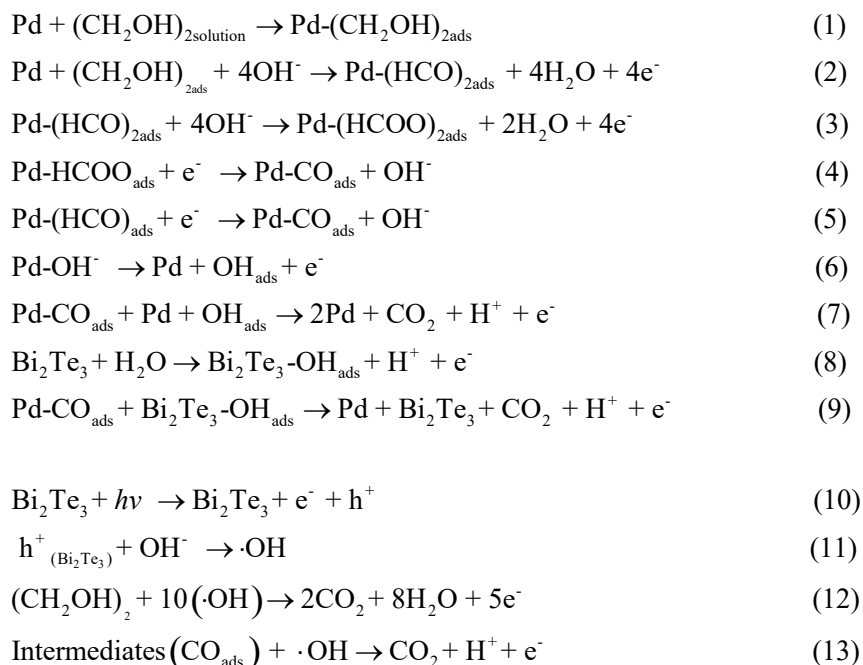


Fig. S7 EIS spectra of Pd/Bi₂Te₃ catalyst at different potentials in 1.0 M EG + 1.0 M KOH solution under dark (a-c) and visible light illumination (d-f) conditions.



Scheme S1 The photoelectrocatalytic process of EG oxidation over Pd/Bi₂Te₃ catalyst.

Table S1. Binding energy (B.E.) of Te 3d and Bi 4f obtained from curve-fitted XPS spectra for Bi₂Te₃ and Pd/Bi₂Te₃ samples.

Catalysts	Te 3d _{5/2}		Te 3d _{3/2}		Bi 4f _{7/2}		Bi 4f _{5/2}	
	Peak	B.E. (eV)	Peak	B.E. (eV)	Peak	B.E. (eV)	Peak	B.E. (eV)
Bi ₂ Te ₃	Te ²⁺	571.6	Te ²⁺	582.0	Bi ₂ Te ₃	157.0	Bi ₂ Te ₃	162.3
	Te ⁴⁺	575.5	Te ⁴⁺	585.9	Bismuth oxide	158.5	Bismuth oxide	163.8
Pd/Bi ₂ Te ₃	Te ²⁺	573.4	Te ²⁺	583.8	Bi ₂ Te ₃	158.0	Bi ₂ Te ₃	162.4
	Te ⁴⁺	575.7	Te ⁴⁺	586.1	Bismuth oxide	158.7	Bismuth oxide	164.0

Table S2. Comparison with other Pd-based catalysts for EGOR.

Catalysts	Electrolyte	Mass activity [mA mg _{Pd} ⁻¹]	Reference
Pd-PPy/NGE	1.0 M KOH + 1.0 M EG	2176.7	[1]
Pd-Bi ₂ Te ₃ -1/C	1.0 M KOH + 1.0 M EG	2420.0	[2]
Pd-Cu ₂ S	1.0 M KOH + 1.0 M EG	3254.0	[3]
PdPbAg NDs	1.0 M KOH + 1.0 M EG	3867.0	[4]
Pd/CoTe-C	1.0 M KOH + 1.0 M EG	3917.3	[5]
PdSn/rGO	0.1 M KOH + 0.5 M EG	4340.0	[6]
Pd/Bi ₂ Te ₃	1.0 M KOH + 1.0 M EG	5620.0	This work

References

- [1] S. Xie, L. Deng, H. Huang, J. Yuan, J. Xu, R. Yue, *J. Colloid Interface Sci.* 2022, 608, 3130-3140.
- [2] H. Xu, B. Huang, Y. Zhao, G. He and H. Chen, *Inorg. Chem.*, 2022, **61**, 4533-4540.
- [3] H. Gao, C. Zhai, C. Yuan, Z. Liu, M. Zhu, *Electrochim. Acta*, 2020, **330**, 135214.
- [4] X. Lao, X. Zhang, T. Sun, A. Fu, Y. Zhang, Z. Li, L. Yang, C. Chen, X. Liao, J. Wang, W. Ye, P. Guo, *Chem. Mater.* 2024, **36**, 2124-2137.
- [5] F. Ren, Z. Zhang, Z. Liang, Y. Shen, X. Wang, Q. Chen, Y. Du, *J. Colloid Interface Sci.*, 2022, **616**, 316-325.
- [6] S. Mondal, V.S.K. Choutipalli, B.K. Jena, V. Subramanian, C.R. Raj, *J. Phys.Chem.C* 2020, **124**, 9631-9643.