Supporting Information

$\text{Bi}_2\text{Te}_3$ nanosheets promoted Pd for ethylene glycol electrooxidation in both dark and visible light irradiation

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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/Bi$_2$Te$_3$-20% catalyst with 20 wt% Pd. While for Pd/Bi$_2$Te$_3$-25% and Pd/Bi$_2$Te$_3$-30% catalysts, the synthesis process was not changed just by using 2.78 and 3.58 mL of H$_2$PdCl$_4$ 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 Kα 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 μL of ethanol and 50 μL of Nafion solution (5 wt%) with ultrasonic treatment to form a homogeneous catalyst ink. Afterward, 2 μL 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 N$_2$ 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$_2$Te$_3$ and Pd/Bi$_2$Te$_3$.

Fig. S2 CV curves of Bi$_2$Te$_3$ 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/Bi$_2$Te$_3$ with different loading of Pd for EG oxidation under dark (a) and visible light irradiation (b) conditions. Mass activity of Pd/C and Pd/Bi$_2$Te$_3$ 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/Bi$_2$Te$_3$ 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.
Pd + (CH$_2$OH)$_2$$_{\text{solution}}$ → Pd-(CH$_2$OH)$_2$$_{\text{ads}}$  \hspace{1cm} (1)
Pd + (CH$_2$OH)$_{\text{ads}}$ + 4OH$^-$ → Pd-(HCO)$_{\text{ads}}$ + 4H$_2$O + 4e$^-$  \hspace{1cm} (2)
Pd-(HCO)$_{\text{ads}}$ + 4OH$^-$ → Pd-(HCOO)$_{\text{ads}}$ + 2H$_2$O + 4e$^-$  \hspace{1cm} (3)
Pd-HCOO$_{\text{ads}}$ + e$^-$ → Pd-CO$_{\text{ads}}$ + OH$^-$  \hspace{1cm} (4)
Pd-(HCOO)$_{\text{ads}}$ + e$^-$ → Pd-CO$_{\text{ads}}$ + OH$^-$  \hspace{1cm} (5)
Pd-OH$^-$ → Pd + OH$_{\text{ads}}$ + e$^-$  \hspace{1cm} (6)
Pd-CO$_{\text{ads}}$ + Pd + OH$_{\text{ads}}$ → 2Pd + CO$_2$ + H$^+$ + e$^-$  \hspace{1cm} (7)
Bi$_2$Te$_3$ + H$_2$O → Bi$_2$Te$_3$-OH$_{\text{ads}}$ + H$^+$ + e$^-$  \hspace{1cm} (8)
Pd-CO$_{\text{ads}}$ + Bi$_2$Te$_3$-OH$_{\text{ads}}$ → Pd + Bi$_2$Te$_3$ + CO$_2$ + H$^+$ + e$^-$  \hspace{1cm} (9)

$\text{Bi}_2\text{Te}_3 + h\nu \rightarrow \text{Bi}_2\text{Te}_3 + e^- + h^+$  \hspace{1cm} (10)
$\text{h}^+ (\text{Bi}_2\text{Te}_3) + \text{OH}^- \rightarrow \text{OH}$  \hspace{1cm} (11)
(CH$_2$OH)$_2$ + 10(\text{OH}) → 2CO$_2$ + 8H$_2$O + 5e$^-$  \hspace{1cm} (12)
Intermediates (CO$_{\text{ads}}$) + ·OH → CO$_2$ + H$^+$ + e$^-$  \hspace{1cm} (13)

**Scheme S1** The photoelectrocatalytic process of EG oxidation over Pd/Bi$_2$Te$_3$ catalyst.

**Table S1.** Binding energy (B.E.) of Te 3d and Bi 4f obtained from curve-fitted XPS spectra for Bi$_2$Te$_3$ and Pd/Bi$_2$Te$_3$ samples.

<table>
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<tr>
<th>Catalysts</th>
<th>Te 3d$_{5/2}$</th>
<th>Te 3d$_{3/2}$</th>
<th>Bi 4f$_{7/2}$</th>
<th>Bi 4f$_{5/2}$</th>
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<tr>
<td></td>
<td>Peak</td>
<td>B.E. (eV)</td>
<td>Peak</td>
<td>B.E. (eV)</td>
</tr>
<tr>
<td>Bi$_2$Te$_3$</td>
<td>Te$^{2-}$</td>
<td>571.6</td>
<td>Te$^{2-}$</td>
<td>582.0</td>
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<td>Te$^{4+}$</td>
<td>575.5</td>
<td>Te$^{4+}$</td>
<td>585.9</td>
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<td>Pd/Bi$_2$Te$_3$</td>
<td>Te$^{2-}$</td>
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<td>Te$^{2-}$</td>
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<tr>
<td></td>
<td>Te$^{4+}$</td>
<td>575.7</td>
<td>Te$^{4+}$</td>
<td>586.1</td>
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Table S2. Comparison with other Pd-based catalysts for EGOR.

<table>
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<tr>
<th>Catalysts</th>
<th>Electrolyte</th>
<th>Mass activity [mA mg&lt;sub&gt;Pd&lt;/sub&gt;⁻¹]</th>
<th>Reference</th>
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<tr>
<td>Pd-PPy/NGE</td>
<td>1.0 M KOH + 1.0 M EG</td>
<td>2176.7</td>
<td>[1]</td>
</tr>
<tr>
<td>Pd-Bi&lt;sub&gt;2&lt;/sub&gt;Te&lt;sub&gt;3&lt;/sub&gt;-1/C</td>
<td>1.0 M KOH + 1.0 M EG</td>
<td>2420.0</td>
<td>[2]</td>
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<tr>
<td>Pd-Cu₂S</td>
<td>1.0 M KOH + 1.0 M EG</td>
<td>3254.0</td>
<td>[3]</td>
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<tr>
<td>PdPbAg NDs</td>
<td>1.0 M KOH + 1.0 M EG</td>
<td>3867.0</td>
<td>[4]</td>
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<tr>
<td>Pd/CoTe-C</td>
<td>1.0 M KOH + 1.0 M EG</td>
<td>3917.3</td>
<td>[5]</td>
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<tr>
<td>PdSn/rGO</td>
<td>0.1 M KOH + 0.5 M EG</td>
<td>4340.0</td>
<td>[6]</td>
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<tr>
<td>Pd/Bi&lt;sub&gt;2&lt;/sub&gt;Te&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.0 M KOH + 1.0 M EG</td>
<td>5620.0</td>
<td>This work</td>
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References