Supporting Information

**Hotspots on Action: Near-infrared Light Mediated Photo Electrochemical Oxygen Evolution on High Index Facet Plasmonic Gold Nano Architectures.**

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Figure S1. (a) $^1$H-NMR and (b) $^{13}$C-NMR for 1-tetradecyl-1, 10-phenanthroline-1-ium bromide surfactant dissolved in D-chloroform solvent.
Figure S2. Dynamic light scattering analysis spectra of Au 12 tips aqueous solution (DLS, model W3180, Microtrac).
Figure S3. (a) TEM image of one of the sharp tips of Au 12 tips nanostars. (b) HRTEM image, (c) the atomic model of the \{711\} planes projected along the [-1, 1, 1] and [-1, 1, 0] zone axis.

Figure S4. Molar extinction coefficients of Au 12 tips nanostars as a function of wavelengths (The inset shows the optical image of Au 12 tips nanostars-containing aqueous dispersion).
Figure S5. XRD pattern for Au 12 tips nanostars and Au nanoparticles.

Figure S6. (a) TEM image and (b) DLS spectra of Au nanoparticles.
Figure S7. XPS spectra of Au 12 tips nanostars, (a) survey scan (b) high-resolution of Au 4f, and (c) high-resolution of Ag 3d.
Figure S8. (a) EDX elemental mapping for Au 12 tips nanostars, (b) the corresponding EDX elemental spectrum and atomic percentage.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag L</td>
<td>0.37</td>
<td>0.67</td>
</tr>
<tr>
<td>Au L</td>
<td>99.63</td>
<td>99.33</td>
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</tbody>
</table>

Figure S9. Schematic illustration of the formation and growth mechanism of Au 12 tips nanostars.
Figure S10. SEM images (a) without TDPB surfactant and (b) without AgNO₃.

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Intensity ratio of I(111)/I(200)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>3.78</td>
</tr>
<tr>
<td>45</td>
<td>3.73</td>
</tr>
<tr>
<td>30</td>
<td>3.65</td>
</tr>
<tr>
<td>15</td>
<td>3.54</td>
</tr>
<tr>
<td>10</td>
<td>3.17</td>
</tr>
<tr>
<td>5</td>
<td>2.70</td>
</tr>
<tr>
<td>2</td>
<td>1.95</td>
</tr>
</tbody>
</table>

Figure S11. XRD peak intensity ratio (111) / (200) during the formation of Au 12 tips nanostars.
Figure S12. TDPB coated Au NPs. (A) TEM image of Au NPs, (B) DLS size distribution spectra, (C) absorption spectra of NPs. (D) LSV curves corresponding to the photoelectrochemical OER on TDPB-capped Au NPs under dark, 532 nm and 915 nm laser irradiation conditions.
**Figure S13.** LSV curves corresponding to the photoelectrochemical OER on TDPB-capped Au NPs and TDPB-capped Au 12 tips-electrodes under dark and light conditions, respectively.

**Figure S14.** FDTD calculated the local electric field Au 12 tips under 532 nm (a) upper monitor and (b) down the monitor.
Figure S15. Schematic illustration of photocatalytic mechanism of OER on Au 12 tips-electrode.

Figure S16. (a) Stability test performed on Au 12 tips- and Au NPs-electrodes in the dark. (b) Chrono potentiometric curves of Au 12 tips and Au NPs electrodes under laser irradiation, respectively. The externally applied voltage is 0.6 V vs. RHE.
**Figure S17.** TEM images for Au 12 tips nanostars before catalytic performance and after catalytic performance.

**Table S1** High index facets of Au 12 tips nanostars with different projection angles.

<table>
<thead>
<tr>
<th>Angle with {100}</th>
<th>55°</th>
<th>35°</th>
<th>25°</th>
<th>19°</th>
<th>15°</th>
<th>13°</th>
<th>11°</th>
</tr>
</thead>
<tbody>
<tr>
<td>{h11}</td>
<td>{111}</td>
<td>{211}</td>
<td>{311}</td>
<td>{411}</td>
<td>{511}</td>
<td>{611}</td>
<td>{711}</td>
</tr>
</tbody>
</table>

**Table S2** Summary of recent developments regarding oxygen evolution reaction (OER) using plasmonic photoelectrodes.

<table>
<thead>
<tr>
<th>Plasmonic Photoelectrode</th>
<th>Electrolyte</th>
<th>Light Source</th>
<th>Photocurrent density (mA/cm²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au@TiO₂ nanotube arrays</td>
<td>1.0 M KOH</td>
<td>150 W Xenon lamp cutoff filter &gt;415 nm</td>
<td>0.1 mA/cm² vs. RHE</td>
<td>S1</td>
</tr>
<tr>
<td>Au@BiVO₄</td>
<td>0.1 M PBS</td>
<td>300 W Xenon lamp AM 1.5 Filter 100 mW cm⁻²</td>
<td>0.6 mA/cm² vs. RHE</td>
<td>S2</td>
</tr>
<tr>
<td>Au@WO₃</td>
<td>0.5 M Na₂SO₄</td>
<td>150 W Xenon lamp AM 1.5 Filter 100 mW cm⁻²</td>
<td>0.8 mA/cm² vs Ag/AgCl</td>
<td>S3</td>
</tr>
<tr>
<td>System Description</td>
<td>Reaction Solution</td>
<td>Light Source</td>
<td>Incident Light Intensity</td>
<td>Current Density</td>
</tr>
<tr>
<td>--------------------</td>
<td>-------------------</td>
<td>--------------</td>
<td>--------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>SiO2 @Ag/BiVO₄</td>
<td>0.5 M KH₂PO₄</td>
<td>300 W Xenon lamp AM 1.5 Filter 100 mW cm⁻²</td>
<td>5.0 mA/cm² vs. Ag/AgCl</td>
<td>S4</td>
</tr>
<tr>
<td>Au NPs@Ti₃C₂Tx</td>
<td>1.0 M KOH</td>
<td>525 nm laser 100 mW cm⁻²</td>
<td>8.0 mA/cm² vs. RHE</td>
<td>S5</td>
</tr>
<tr>
<td>BiVO₄/Co(OH)x-Ag</td>
<td>0.5 M Na₂SO₄</td>
<td>300 W Xenon lamp AM 1.5 Filter 100 mW cm⁻²</td>
<td>4.0 mA/cm² vs. RHE</td>
<td>S6</td>
</tr>
<tr>
<td>Ag@BiVO₄</td>
<td>0.5 M Na₂SO₄</td>
<td>300 W Xenon lamp AM 1.5 Filter 100 mW cm⁻²</td>
<td>1.7 mA/cm² vs. RHE</td>
<td>S7</td>
</tr>
<tr>
<td>Au NRs</td>
<td>1.0 M KOH</td>
<td>808 nm laser, 200 mW cm⁻²</td>
<td>0.5 mA/cm² vs. RHE</td>
<td>S8</td>
</tr>
<tr>
<td>Au 12 tips-electrode</td>
<td>0.1 M KOH</td>
<td>915 nm laser 300 mW cm⁻²</td>
<td>1.8 mA/cm² vs. RHE</td>
<td>Current work</td>
</tr>
</tbody>
</table>

**TDPB surfactant crystal structure information**

Apple white powder; ¹H NMR (600 MHz, CDCl₃): δ 10.33 (s, 1 H), 9.40 (d, J= 12.0 Hz, 1 H), 9.18 (s, 1 H), 8.54 (d, J= 6.0 Hz, 1 H), 8.50 (d, J= 6.0 Hz, 1H), 8.34 (d, J= 6.0 Hz, 1H), 8.21 (d, J= 12.0 Hz, 1H), 7.87 (d, J= 12.0 Hz, 1H), 6.13 (t, J= 6.0 Hz, 2H), 2.09-2.06 (m, 2H), 1.56-1.54 (m, 2H), 1.34-1.32 (m, 2H), 1.24 – 1.18 (m, 20 H), 0.81 (t, J= 6.0 Hz, 3 H).

¹³C NMR (150 MHz, CDCl₃): 150.8, 149.1, 146.7, 139.2, 137.4, 135.8, 132.2, 131.5, 130.4, 126.9, 124.8, 124.6, 63.8, 31.4, 31.2, 28.9, 28.9, 28.8, 28.6, 28.5, 25.7, 21.9, and 13.4.

**ORTEP diagram of the solid product surfactant**

![ORTEP diagram](image-url)
Crystal data and structure refinement for mo_160548LT_0m.

Identification code: mo_160548LT_0m

Empirical formula: C26 H39 Br N2 O

Formula weight: 475.50

Temperature: 100(2) K

Wavelength: 0.71073 Å

Crystal system: Triclinic

Space group: P -1

Unit cell dimensions:
\[ a = 8.6383(17) \text{ Å} \quad a = 102.453(5)^\circ. \]
\[ b = 11.793(2) \text{ Å} \quad b = 91.642(5)^\circ. \]
\[ c = 25.970(6) \text{ Å} \quad g = 108.802(5)^\circ. \]

Volume: 2431.8(9) Å³

Z: 4

Density (calculated): 1.299 Mg/m³

Absorption coefficient: 1.710 mm⁻¹

F(000): 1008

Crystal size: 0.15 x 0.10 x 0.10 mm³

Theta range for data collection: 0.808 to 26.532°.

Index ranges: -10<=h<=9, -14<=k<=14, -31<=l<=32

Reflections collected: 37218

Independent reflections: 10037 [R(int) = 0.0679]

Completeness to theta = 25.242°: 100.0 %

Absorption correction: Semi-empirical from equivalents

Max. and min. transmission: 0.9485 and 0.8634

Refinement method: Full-matrix least-squares on F²

Data / restraints / parameters: 10037 / 0 / 543

Goodness-of-fit on F²: 0.993

Final R indices [I>2sigma(I)]: R1 = 0.0396, wR2 = 0.0845

R indices (all data): R1 = 0.0759, wR2 = 0.1012

Extinction coefficient: n/a

Largest diff. peak and hole: 0.438 and -0.439 e.Å⁻³

Supporting reference:


