ELECTRONIC SUPPLEMENTARY INFORMATION

Tailoring ORR and HER electrocatalytic performances of gold nanoparticles through metal-ligand interfaces

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Fig. S1 FTIR spectra of the four pure ligands used in this work.

Fig. S2 XPS survey spectra of the different ligand-stabilized AuNPs on ITO supports.
Fig. S3 DPVs curves obtained for GC electrodes modified with different ligand-stabilized AuNPs in N₂-saturated (A) and O₂-saturated (B) 0.5 M KOH at 0.1 V·s⁻¹.

Fig. S4 Hysteresis effect during measurements with rotating disk electrode of GC electrodes modified with different ligand-stabilized AuNPs at same rotating rate of 2500 rpm. Scan rate: 10 mV·s⁻¹.
**Fig. S5** Rotating-disk voltammograms for AuNPs@Citrate (A), AuNPs@CTAB (B), AuNPs@PSS (C) and AuNPs@MUA (D) modified GC electrodes at different rotation rates in O$_2$-saturated 0.5 M KOH. Scan rate 10 mV·s$^{-1}$.

**Fig. S6** Linear sweep voltammograms, without $iR$-correction, of GC electrodes modified with different ligand-stabilized AuNPs in N$_2$-saturated 0.5 M H$_2$SO$_4$ at rotation rate of 1600 rpm. Scan rate: 2 mV·s$^{-1}$. 


Fig. S7 (A) Chronopotentiometry measurements at $J = -10 \, \text{mA} \cdot \text{cm}^{-2}$ for the different ligand-stabilized AuNPs. (B) LSV curves, without iR-correction, of the different ligand-stabilized AuNPs before (solid lines) and after (dash-dotted lines) the long-term stability test.

Fig. S8 Faradaic efficiency plot of AuNPs@Citrate for HER at $a = -270 \, \text{mV}$ (E vs. RHE).
Fig. S9 High-resolution XPS spectra of Au 4f (A), C 1s (B) and O 1s (C) for AuNPs@Citrate, before and after ORR and HER measurements.

Fig. S10 High-resolution XPS spectra of Au 4f (A), C 1s (B) and N 1s (C) for AuNPs@CTAB, before and after ORR and HER measurements.
Fig. S11 High-resolution XPS spectra of Au 4f (A), C 1s (B), O 1s (C) and S 2p (D) for AuNPs@PSS, before and after ORR and HER measurements.

Fig. S12 High-resolution XPS spectra of Au 4f (A), C 1s (B) and S 2p (C) for AuNPs@MUA, before and after ORR and HER measurements.
Fig. S13 High-Resolution XPS spectra of Au 4f for AuNPs@Citrate (A), AuNPs@CTAB (B), AuNPs@PSS (C) and AuNPs@MUA (D), including schematic representation of the spatial distribution of each capping ligand on AuNPs surface. Scheme is not drawn to scale.
<table>
<thead>
<tr>
<th>Catalyst(^a)</th>
<th>Substrate</th>
<th>Mass density (mg/cm(^2))</th>
<th>Reaction</th>
<th>(\eta_{\text{onset}}) (V)</th>
<th>Tafel slope (mV/dec)</th>
<th>(J_{\text{dl}}) (mA/cm(^2))</th>
<th>Overpotential</th>
<th>Electrolyte</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au@Pd(_{1.0})</td>
<td>GCE (vs RHE)</td>
<td>101.9</td>
<td>ORR</td>
<td>0.93</td>
<td>68.1</td>
<td>4.91</td>
<td>-</td>
<td>0.1 M KOH</td>
<td>S1</td>
</tr>
<tr>
<td>Au@Pd(_{1.0})</td>
<td>GCE (vs RHE)</td>
<td>0.357</td>
<td>HER</td>
<td>-0.29</td>
<td>66.0</td>
<td>-</td>
<td>0.116 V at 20 mA/cm(^2)</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>S1</td>
</tr>
<tr>
<td>NCN-1000-5</td>
<td>RDE (vs RHE)</td>
<td>0.2</td>
<td>ORR</td>
<td>0.95</td>
<td>86.0</td>
<td>6.43</td>
<td>-</td>
<td>0.1 M KOH</td>
<td>S2</td>
</tr>
<tr>
<td>NCN-1000-5</td>
<td>RDE (vs RHE)</td>
<td>0.2</td>
<td>HER</td>
<td>-0.03</td>
<td>43.0</td>
<td>-</td>
<td>0.090 V at 20 mA/cm(^2)</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>S2</td>
</tr>
<tr>
<td>CoSAs/PTFs-600</td>
<td>RRDE (vs RHE)</td>
<td>-</td>
<td>ORR</td>
<td>0.88</td>
<td>57.0</td>
<td>6.14</td>
<td>-</td>
<td>0.1 M KOH</td>
<td>S3</td>
</tr>
<tr>
<td>CoSAs/PTFs-600</td>
<td>RRDE (vs RHE)</td>
<td>-</td>
<td>HER</td>
<td>-0.02</td>
<td>50.0</td>
<td>-</td>
<td>0.094 V at 10 mA/cm(^2)</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>S3</td>
</tr>
<tr>
<td>Co(_{1-x}) S/NC</td>
<td>RRDE (vs RHE)</td>
<td>0.204</td>
<td>ORR</td>
<td>70.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1 M KOH</td>
<td>S4</td>
</tr>
<tr>
<td>Co(_{1-x}) S/NC</td>
<td>RRDE (vs RHE)</td>
<td>0.204</td>
<td>HER</td>
<td>-0.03</td>
<td>71.0</td>
<td>-</td>
<td>0.073 V at 10 mA/cm(^2)</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>S4</td>
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<tr>
<td>Mo(_2)C@NC nanomesh</td>
<td>RDE (vs RHE)</td>
<td>0.5</td>
<td>ORR</td>
<td>1.00</td>
<td>50.1</td>
<td>4.50</td>
<td>-</td>
<td>0.1 M KOH</td>
<td>S5</td>
</tr>
<tr>
<td>Mo(_2)C@NC nanomesh</td>
<td>RDE (vs RHE)</td>
<td>0.5</td>
<td>HER</td>
<td>-0.02</td>
<td>33.7</td>
<td>-</td>
<td>0.036 V at 10 mA/cm(^2)</td>
<td>S5</td>
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</table>

\(^a\)The most proficient version of the electrocatalysts.
\(^b\)Diffusion-limiting current density.
References


