Copper Coordination Polymer Electrocatalyst for Strong Hydrogen Evolution Reaction Activity in Neutral Medium: Influence of Coordination Environment and Network Structure

Pandi Muthukumar,^[a] Dohyun Moon,*^[b] and Savarimuthu Philip Anthony*^[a]

Figure S1. Molecular structure of green crystal. C (grey), N (blue), O (red), H (white) and Cu (orange).
Figure S2. Different structural motifs of Cu-PDA CPs and complexes with different coordination geometry and mode. C (grey), N (blue), O (red), H (white) and Cu (orange).
Figure S3. (a) Different coordination geometry of Cu and coordination mode of PDA in Cu PDA-1 with elemental labelling, (b) 1D coordination polymeric network and (c) Asymmetric unit of Cu PDA-1 with included DABCO and water molecule in the crystal lattice of Cu PDA-1. C (grey), N (blue), O (red), H (white) and Cu (orange).
Figure S4. (a) H-bonding interaction between protonated DABCO and carboxylate oxygen (b) molecular packing in the crystal lattice of Cu PDA-1. C (grey), N (blue), O (red), H (white) and Cu (orange); H-bonds (broken line). $d_{D\cdots A}$ distances are marked (Å).

Figure S5. 1D coordination network structure with different coordination geometry of Cu and PDA coordination mode in the crystal lattice of Cu PDA-2. C (grey), N (blue), O (red), H (white) and Cu (orange).
Figure S6. 1D coordination network structure in the crystal lattice of (a) Cu PDA-3 and (b) Cu PDA-4. C (grey), N (blue), O (red), H (white) and Cu (orange).

Figure S7. H-bonding interactions between coordinated water molecules and carboxylate oxygen in the crystal lattice of Cu PDA-3. C (grey), N (blue), O (red), H (white) and Cu (orange); H-bonds (broken line). $d_{\text{D}...\text{A}}$ distances are marked (Å).
Figure S8. Molecular packing in the crystal lattice of (a) Cu PDA-3 and (b) Cu PDA-4. C (grey), N (blue), O (red), H (white) and Cu (orange).

Figure S9. Molecular structure in the crystal lattice of (a) Cu PDA-5 and (b) Cu PDA-6. C (grey), N (blue), O (red), H (white) and Cu (orange).
Figure S10. H-bonding interactions between coordinated water molecules and carboxylate oxygen in the crystal lattice of Cu PDA-6. C (grey), N (blue), O (red), H (white) and Cu (orange); H-bonds (broken line). $d_{\text{D}...\text{A}}$ distances are marked (Å).
Figure S11. TGA analysis of Cu PDA-1 to Cu PDA-3.
Figure S12. TGA analysis of Cu PDA-4 to Cu PDA-6.
Figure S13. Comparison of simulated and experimental PXRD of Cu PDA-1 and Cu PDA-2.
Figure S14. Comparison of simulated and experimental PXRD of Cu PDA-3 and Cu PDA-4.
Figure S15. Comparison of simulated and experimental PXRD of Cu PDA-5 and Cu PDA-6.
Figure S16. Absorption spectra of Cu PDA-1 and 3 in different water medium after immersing in 1h.
Table S2. HER electrocatalytic activities of CPs/MOFs in presence of conducting composites. (*0.5M H₂SO₄ was used as electrolyte for all catalysts)

<table>
<thead>
<tr>
<th>Catalyst (*)</th>
<th>Overpotential [mV] @ 10 mA/cm²</th>
<th>Tafel slope [mV/dec]</th>
<th>Stability tests</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>(GO 8 wt%) Cu-MOF</td>
<td>209 (30 mA/cm²)</td>
<td>84</td>
<td>N/A</td>
<td>1</td>
</tr>
<tr>
<td>1.7 wt% AB &amp;Cu.BTC</td>
<td>208</td>
<td>80</td>
<td>2000 cycles and 18h</td>
<td>2</td>
</tr>
<tr>
<td>AB&amp;CTGU-5 (1:4) (Co)</td>
<td>44</td>
<td>45</td>
<td>96 h</td>
<td>3</td>
</tr>
<tr>
<td>AB&amp;CTGU-9 (3:4) (Co)</td>
<td>128</td>
<td>87</td>
<td>2000 cycle and 21h</td>
<td>4</td>
</tr>
<tr>
<td>Gr(4wt%) &amp;Co-MOF</td>
<td>125</td>
<td>91</td>
<td>1000 cycle</td>
<td>5</td>
</tr>
<tr>
<td>UiO-66-NH2-Mo-5 (Zr&amp; Mo)</td>
<td>200</td>
<td>59</td>
<td>5000 cycles and 7h</td>
<td>6</td>
</tr>
<tr>
<td>MSZIF-900 (Co)</td>
<td>233</td>
<td>N/A</td>
<td>2.5 h</td>
<td>7</td>
</tr>
</tbody>
</table>
Figure S17. HER Polarization curves of two more batch prepared Cu PDA-3 in 1.0 M KOH and 1.0 M PBS.
Figure S18. HER polarization curves of Cu PDA-3 in 0.5 M H₂SO₄.

Figure S19. High resolution XPS spectrum of Cu²⁺ after catalysis of Cu PDA-3 in 1.0 M PBS.
Figure S20. Current–time chronoamperometric response of Cu PDA-1, Cu PDA-2, Cu PDA-4, Cu PDA-5 and Cu PDA-6 in 1.0 M KOH.
Figure S21. Current–time chronoamperometric response of Cu PDA-1, Cu PDA-2, Cu PDA-4, Cu PDA-5 and Cu PDA-6 in 1.0 M PBS.
Figure S22. Possible H-bonding site of water molecule with Cu PDA-3 is shown in blue circle whereas crossed red circle shows the absence of such H-bonding site in Cu PDA-4.

References: