Supporting Information

for

DFT calculations of the structure and stability of copper clusters on MoS$_2$

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Additional computational data
DOS Plots

Density of state plots for all Cu$_n$ adsorption configurations are given below.
Figure S1: DOS plots of Cu$_1$ and Cu$_2$ adsorption structures. Black = total DOS, blue = DOS projected onto Mo d orbitals, red = DOS projected onto S p orbitals, cyan = DOS projected onto Cu d orbitals. The contribution of the Cu d orbitals has been increased by a factor of 5 for the ease of comparison.
Figure S2: DOS plots of Cu$_3$ adsorption structures. Black = total DOS, blue = DOS projected onto Mo d orbitals, red = DOS projected onto S p orbitals, cyan = DOS projected onto Cu d orbitals. The contribution of the Cu d orbitals has been increased by a factor of five for the ease of comparison.
Figure S3: DOS plots of Cu₄ adsorption structures. Black = total DOS, blue = DOS projected onto Mo d orbitals, red = DOS projected onto S p orbitals, cyan = DOS projected onto Cu d orbitals. The contribution of the Cu d orbitals has been increased by a factor of five for the ease of comparison.
Figure S4: DOS plots of Cu₁ and Cu₄ adsorption structures on defective MoS₂. Black = total DOS, blue = DOS projected onto Mo d orbitals, red = DOS projected onto S p orbitals, cyan = DOS projected onto Cu d orbitals. The contribution of the Cu d orbitals has been increased by a factor of five for the ease of comparison.
Charge Density Distribution after adsorption of Cu

The charge density difference after adsorption of the most favourable Cu\textsubscript{n} is shown below.

<table>
<thead>
<tr>
<th>A</th>
<th>Cu\textsubscript{1} Site 2</th>
<th>B</th>
<th>Cu\textsubscript{2} Neighbouring Site 2</th>
<th>C</th>
<th>Cu\textsubscript{2} Neighbouring Site 3</th>
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<tbody>
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<tr>
<td>D</td>
<td>Cu\textsubscript{2} 3D Triangle Site 1</td>
<td>E</td>
<td>Cu\textsubscript{3} 3D Triangle Site 2</td>
<td>F</td>
<td>Cu\textsubscript{4} Rhombus Site 1</td>
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<tr>
<td>G</td>
<td>Cu\textsubscript{4} Tetrahedron Site 1</td>
<td>H</td>
<td>Cu\textsubscript{1} Site 1 S vacancy</td>
<td>I</td>
<td>Cu\textsubscript{4} Rhombus Site 2 S vacancy</td>
</tr>
</tbody>
</table>

**Figure S5:** Charge density difference after adsorption of the most favourable Cu\textsubscript{n} on pristine (A–G) and defective (H, I) MoS\textsubscript{2}.

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**Cu atom repelled from ML**

An example of a Cu atom that is repelled from the MoS$_2$ ML is shown in Figure S6. This occurred during the relaxation of several Cu$_4$ structures on the MoS$_2$ monolayer with an S vacancy.

*Figure S6:* A Cu atom is repelled from the surface during the geometry relaxation.