Supplementary Information

DFT study on Ag loaded 2H-MoS$_2$ for mechanism of improved photocatalytic reduction of CO$_2$

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As shown in Figure S1, the symmetry of our choice of molybdenum disulfide is \( P_{6_3}^{\text{mc}} \)mc, which is a stable 2H semiconductor state \(^1\). The interlayer distance of 2H-MoS\(_2\) after full optimization is 6.406 Å, which is consistent with previous reports \(^2,3\). In our experiments, 2H-MoS\(_2\) (002) has the best photocatalytic activity and the Ag nanoparticles were approximately 100-200 Å in average diameter \(^4\). Considering the possibility of preparing much smaller nanoparticles, we tracked the Ag preparation methods and found the diameter of Ag nanoparticles prepared by chemical reduction of citric acid to be at 40-800 Å \(^5\). These diameters of Ag nanoparticles are much larger than the interlayer distance of 2H-MoS\(_2\) (002). Therefore, Ag nanoparticles cannot enter 2H-MoS\(_2\). Based on the above analyses, this work chooses loading Ag atoms on a single layer of 2H-MoS\(_2\) nanosheets.
Figure S2. PDOS of (a) 2H-MoS$_2$ and (b) Ag/2H-MoS$_2$.

Figure S3. Hirshfeld charges population to (a) 2H-MoS$_2$, (b) Ag/2H-MoS$_2$ in a 3×3×1 supercell. Yellow: sulfur, blue: molybdenum, and gray: silver.

Figure S4. Optical absorption behaviors of (a) 2H-MoS$_2$ and (b) Ag/2H-MoS$_2$. 
Figure S5. PDOS of different loadings of Ag atoms on 2H-MoS$_2$. 
We construct four structures as I-type, II-type, III-type and IV-type for 20wt% Ag/2H-MoS₂ and show them in Figure S6(a)-(d). Among them, I-type is a structure of three Ag atoms in triangular arrangement, II-type and III-type are polyline structures, and IV-type has a structure of three Ag atoms in line. It is worth noting that II-type and III-type also change to the triangular arrangement after the structure optimization, so the triangular structure is more stable than the polyline structure. Our calculation results show that the binding energies required to form I-type and II-type are very similar, respectively -1.633 eV and -1.687 eV, as shown in Figure S6(e), the difference is only
0.054 eV. But after the structure optimization, there are only two Ag-S bonds in the three Ag atoms of II-type, so we explored the bond populations and bond lengths of I-type and II-type in Table S4, where the bond populations of the three Ag-S bonds and the bond lengths in I-type are relatively uniform and stable at about 2.7 Å, respectively. However, the three Ag atoms in the II-type interacted with the four nearby S atoms, and their bond populations of Ag 1- S 12 and Ag 2- S 4 are 0.03 and 0.05 respectively, which are obviously smaller than those of the rest Ag-S bonds. Thus, it is reasonable to speculate some chemical bonds in II-type are weaker than those in I-type. Additionally, the bond lengths of Ag 1- S 12 and Ag 2- S 4 in II-type are also extended to 2.9 Å, which makes these Ag-S bonds in II-type to be easier to break, thus the II-type seems only two chemical bonds between three loaded Ag atoms and the 2H-MoS2 carrier. In summary, I-type is conducive to the stability of the structure. Therefore, we abandoned II-type and chose to use I-type in our work for follow-up research.

![Figure S7. Structural model corresponding to FH path of 2H-MoS2.](image1)

![Figure S8. Gibbs free energy of hydrogen evolution reaction (HER) on 2H-MoS2 and 20wt%Ag /2H-MoS2.](image2)

As shown in Figure S8, The Gibbs free energy changes of the HER on 2H-MoS2 and 20wt%Ag /2H-MoS2 are lower than that of the potential-limiting step of CO2 reduction, manifesting that the HER side reaction are easier to perform in low pH areas. However, it is experimentally possible to prevent HER by adjusting the pH of the electrolyte or using a non-aqueous solvent such as acetonitrile, DMF, etc. Therefore, the effects of the HER side reaction are minimized through regulation in the experiment.
Table S1. The ratio of the number of atoms based on the weight ratio and molar ratio of Ag atoms to S atoms in the experiment.

<table>
<thead>
<tr>
<th>Composite</th>
<th>10wt% Ag/2H-MoS₂</th>
<th>15wt% Ag/2H-MoS₂</th>
<th>20wt% Ag/2H-MoS₂</th>
<th>25wt% Ag/2H-MoS₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight Ratio</td>
<td>0.1</td>
<td>0.15</td>
<td>0.2</td>
<td>0.25</td>
</tr>
<tr>
<td>Molar ratio</td>
<td>0.148</td>
<td>0.223</td>
<td>0.297</td>
<td>0.371</td>
</tr>
<tr>
<td>Atomic Ratio</td>
<td>1.332</td>
<td>2.007</td>
<td>2.672</td>
<td>3.339</td>
</tr>
</tbody>
</table>

Table S2. Calculated Gibbs free energies of CO₂ reduction into CH₄ on 2H-MoS₂ and 20wt%Ag /2H-MoS₂ in the fast hydrogenation (FH) pathway.

| Intermediate products | Gibbs free energy (eV) | | |
|-----------------------|------------------------| | |
|                       | 2H-MoS₂                | 20wt%Ag /2H-MoS₂ | |
| Surface+ CO₂          | -0.299                 | -0.272            | |
| Surface+*COOH         | 2.395                  | 0.653             | |
| Surface+*CO           | -1.605                 | -0.272            | |
| Surface+*COH          | 3.075                  | 2.313             | |
| Surface+*CHO          | 1.225                  | 0.653             | |
| Surface+*CHOH         | 0.653                  | 0.680             | |
| Surface+*CH₂O         | -1.524                 | -0.680            | |
| Surface+*OCH₃         | 1.333                  | -0.354            | |
| Surface+*CH₂OH        | 0.844                  | 0.245             | |
| Surface+*CH₃OH        | -1.714                 | -0.599            | |
| Surface+*CH₃         | 0.653                  | 0.245             | |
| Surface+ CH₄          | -1.442                 | -1.143            | |

Table S3. Calculated Gibbs free energies of CO₂ reduction into CH₄ on 2H-MoS₂ and 20wt%Ag /2H-MoS₂ in the fast deoxygenation (FO) pathway.

| Intermediate products | Gibbs free energy (eV) | | |
|-----------------------|------------------------| | |
|                       | 2H-MoS₂                | 20wt%Ag /2H-MoS₂ | |
| Surface+ CO₂          | -0.299                 | -0.272            | |
| Surface+*COOH         | 2.395                  | 0.653             | |
| Surface+*CO           | -1.605                 | -0.272            | |
| Surface+*C (FO)       | 4.299                  | 3.701             | |
| Surface+*CH (FH)      | -1.605                 | -1.742            | |
| Surface+*CHO          | 1.225                  | 0.653             | |
| Surface+*CH (FO)      | 1.469                  | 1.306             | |
| Surface+*CH₂ (FH)     | -2.014                 | -1.986            | |
| Surface+*CH₃          | -1.197                 | -0.708            | |
| Surface+*CH₂OH        | -0.653                 | -0.245            | |
| Surface+ CH₄          | -2.095                 | -1.388            | |
Table S4. Bond populations and lengths of I-type and II-type for 20wt% Ag/2H-MoS₂.

<table>
<thead>
<tr>
<th>Load configuration</th>
<th>Bond</th>
<th>Population</th>
<th>Length(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20wt% Ag/2H-MoS₂</td>
<td>Ag 1- S 6</td>
<td>0.14</td>
<td>2.737</td>
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<tr>
<td>of I-type</td>
<td>Ag 2- S 4</td>
<td>0.11</td>
<td>2.742</td>
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<td></td>
<td>Ag 3- S 12</td>
<td>0.13</td>
<td>2.766</td>
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<tr>
<td>20wt% Ag/2H-MoS₂</td>
<td>Ag 1- S 10</td>
<td>0.12</td>
<td>2.856</td>
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<tr>
<td>of II-type</td>
<td>Ag 1- S 12</td>
<td>0.03</td>
<td>2.920</td>
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<td>Ag 2- S 4</td>
<td>0.05</td>
<td>2.921</td>
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<td>Ag 3- S 6</td>
<td>0.14</td>
<td>2.794</td>
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</tbody>
</table>

References

4 Yinan Zheng, Xiaohong Yin, Yue Jiang, Junsong Bai, Yuan Tang, Yongli Shen, Ming Zhang, Energy Technol., 2019, 1900582.
6 Yawei Li, Haibin Su, Siew Hwa Chan, Qiang Sun, ACS Catal., 2015, 5, 11, 6658-6664.
7 Haoming Shen, Yawei Li, Qiang Sun, J. Phys. Chem. C., 2017, 121, 3963-3969.