Supporting Information (SI)

Amorphous MoS$_x$ modified g-C$_3$N$_4$ composite for efficient photocatalytic hydrogen evolution

Fig. S1 TEM image of MoS$_x$/MoS$_2$

Mo Ka1  S Ka1
Table S1 Summary of photocatalytic activity of g-C$_3$N$_4$/MoS$_2$ composite

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Light source</th>
<th>Sacrificial reagent</th>
<th>H$_2$ yield ($\mu$mol h$^{-1}$ g$^{-1}$)</th>
<th>Reaction time</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 mg MoS$_x$/UCN</td>
<td>300 W Xe lamp, $\lambda&gt;$400 nm</td>
<td>10% triethanolamine in water</td>
<td>1586</td>
<td>5h</td>
<td>This work</td>
</tr>
<tr>
<td>20 mg MoS$_2$/mpg-CN</td>
<td>300 W Xe lamp, $\lambda&gt;$420 nm</td>
<td>10% triethanolamine in water</td>
<td>1030</td>
<td>4h</td>
<td>[1]</td>
</tr>
<tr>
<td>100 mg MoS$_2$/C$_3$N$_4$ (1 wt% Pt)</td>
<td>300 W Xe lamp, $\lambda&gt;$400 nm</td>
<td>25% methano in water</td>
<td>231</td>
<td>6h</td>
<td>[2]</td>
</tr>
<tr>
<td>Samples</td>
<td>UCN</td>
<td>MoSₓ/UCN</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------</td>
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</tr>
<tr>
<td>SA/m²·g⁻¹</td>
<td>89.29</td>
<td>72.56</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Pore volume (m³/g)</td>
<td>0.31</td>
<td>0.18</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Both the ultrasonic power and time can affect the degree of exfoliation. We synthesized samples with different time and power to research their effects on the performance of hydrogen evolution. In the first group, MoS\textsubscript{x}/UCN (7 wt\%) was prepared with different ultrasonic power (120 W, 210 W, 300 W), and ultrasonic time was fixed at 2h, the results are shown in Fig. S4(a). In the second group, MoS\textsubscript{x}/UCN (7 wt\%) was prepared with different ultrasonic time (10 min, 60 min, 120 min, 240 min), and ultrasonic power was fixed at 300 W, the results are shown in Fig. S4(b). It can be seen that proper increase of time and power is beneficial to the improvement of performance, but excess ultrasonic time and ultrasonic power will not be beneficial to the performance.

In the photocatalytic hydrogen evolution system, the sacrificial agent is a good electron donor, which can effectively improve the quantum efficiency of photocatalysis. The choice of sacrificial agent will greatly affect the photocatalytic results. Currently, researchers prefer to choose triethanolamine and lactic acid as sacrificial agents in the photocatalytic hydrogen evolution system of g-C\textsubscript{3}N\textsubscript{4}. We found that MoS\textsubscript{x}/UCN (7 wt\%) show better photocatalytic performance under aqueous solution containing triethanolamine than under aqueous solution containing lactic acid (see Fig. S5). Therefore,
we use triethanolamine as sacrificial reagent in this study.

In order to research the hydrothermal temperature and reaction precursor of influence on the formation of molybdenum sulfide, we prepared MoS\textsubscript{x} samples under different conditions. On the basis of preparing MoS\textsubscript{x}, we prepared 1-MoS\textsubscript{x} by setting the hydrothermal temperature at 200 °C, prepared 2-MoS\textsubscript{x} by reducing the mole ratio of CH\textsubscript{3}CSNH\textsubscript{2} : Na\textsubscript{2}MoO\textsubscript{4} \cdot H\textsubscript{2}O to 3 : 1, prepared 3-MoS\textsubscript{x} by removing H\textsubscript{4}SiO\textsubscript{4}(W\textsubscript{3}O\textsubscript{9})\textsubscript{4} from the precursor. And the hydrogen evolution performance of samples was shown in figure S6. The results suggest that change of the hydrothermal temperature shows little influence on the co-catalytic performance of MoS\textsubscript{x}, ratio of CH\textsubscript{3}CSNH\textsubscript{2} to Na\textsubscript{2}MoO\textsubscript{4} \cdot H\textsubscript{2}O and the presence of H\textsubscript{4}SiO\textsubscript{4}(W\textsubscript{3}O\textsubscript{9})\textsubscript{4} shows great influence on the co-catalytic performance of MoS\textsubscript{x}. High ratio of CH\textsubscript{3}CSNH\textsubscript{2} to Na\textsubscript{2}MoO\textsubscript{4} \cdot H\textsubscript{2}O and presence of H\textsubscript{4}SiO\textsubscript{4}(W\textsubscript{3}O\textsubscript{9})\textsubscript{4} are beneficial to the co-catalytic performance of MoS\textsubscript{x}. By comparing XPS of various MoS\textsubscript{x} (figure S7), we think that the change of hydrothermal temperature did not cause obvious change in structure of MoS\textsubscript{x}. High ratio of CH\textsubscript{3}CSNH\textsubscript{2} to Na\textsubscript{2}MoO\textsubscript{4} \cdot H\textsubscript{2}O and presence of H\textsubscript{4}SiO\textsubscript{4}(W\textsubscript{3}O\textsubscript{9})\textsubscript{4} can increase the percent of S atoms with high binding energy in MoS\textsubscript{x}, which is a reason why MoS\textsubscript{x} and 1-MoS\textsubscript{x} show better co-catalytic performance than 2-MoS\textsubscript{x} and 3-MoS\textsubscript{x}. The TEM images (figure S7) of various MoS\textsubscript{x} are show in figure S8. It can find that the size of 4-MoS\textsubscript{x} is bigger than MoS\textsubscript{x}, 2-MoS\textsubscript{x} and 3-MoS\textsubscript{x}, which suggests that H\textsubscript{4}SiO\textsubscript{4}(W\textsubscript{3}O\textsubscript{9})\textsubscript{4} can reduce the size of the MoS\textsubscript{x}. 

Fig. S6. The photocatalytic H\textsubscript{2} evolution rate of samples:(a) MoS\textsubscript{x}/UCN(7 wt%) (b) 1-MoS\textsubscript{x}/UCN(7 wt%) (c) 2-MoS\textsubscript{x}/UCN(7 wt%) (d) 3-MoS\textsubscript{x}/UCN(7 wt%)
Fig. S7. High-resolution XPS spectra of S 2p

Fig. S8. TEM images: (a) MoS$_x$ (b) 1-MoS$_x$ (c) 2-MoS$_x$ (d) 3-MoS$_x$. 
References