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**Supplementary information**

**In situ Constructed Oxygen-vacancy-rich MoO$_{3-x}$/Porous g-C$_3$N$_4$ Heterojunction for Synergistically Enhanced Photocatalytic H$_2$ Evolution**

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Figure S1 XRD patterns of g-C₃N₄, MoO₃ₓ/g-C₃N₄ (calcination at 280 °C), and MoO₃ₓ/g-C₃N₄ (calcination at 350 °C).
Figure S2 XRD pattern of MoO$_3$ (The Mo (OH)$_6$ precursor was calcined at 400 ºC), the illustration shows the crystal structure of MoO$_3$. 
Figure S3 SEM images of pure $g$-$C_3N_4$ and MoO$_{3-x}$/g-$C_3N_4$. 
Figure S4 HR-TEM images of MoO$_{3-x}$/g-C$_3$N$_4$. 
Figure S5 AFM image of pure $g$-$C_3N_4$ nanosheets.
Figure S6 Photocatalytic hydrogen production rates of $g$-$C_3N_4$, 5% MoO$_3$/g-$C_3N_4$ and 5% MoO$_{3-x}$/g-$C_3N_4$. 
Figure S7 UV–vis diffuse reflectance spectra of g-\(\text{C}_3\text{N}_4\) (a) and MoO\(_{3-x}\) (b), the illustrations are their corresponding Tauc’s plot.
Table S1. The N/C ratios of g-C₃N₄ and MoO₃₋ₓ/g-C₃N₄ calculated by XPS.

| g-C₃N₄ | Atomic % | N/C ratio | MoO₃₋ₓ/g-C₃N₄ | Atomic % | N/C ratio |
|--------|----------|-----------|---------------|----------|-----------|
| N1s    | 54.06    |           | N1s           | 45.40    |           |
| O1s    | 4.92     | 1.32      | O1s           | 4.47     | 1.02      |
| C1s    | 41.02    |           | C1s           | 44.08    |           |
|        |          | Mo 3s     | 3.44          | Na 1s    | 1.42      |
|        |          | Cl 2p     | 1.18          |          |           |
Table S2. The ratios of different O species of MoO$_3$ calculated by XPS.

| Species           | Peak BE | FWHM eV | Area (P) CPS. eV | Ratio % |
|-------------------|---------|---------|------------------|---------|
| Lattice oxygen    | 530.5   | 1.34    | 230460.80        | 72.02   |
| Defect oxygen     | 532.2   | 1.67    | 69881.18         | 21.84   |
| Hydroxyl oxygen   | 533.0   | 1.37    | 19636.34         | 6.14    |
Table S3. The ratios of different O species of MoO$_{3-x}$/g-C$_3$N$_4$ calculated by XPS.

| Species            | Peak BE | FWHM eV | Area (P) CPS.eV | Ratio % |
|--------------------|---------|---------|----------------|---------|
| Lattice oxygen     | 531.1   | 1.55    | 17656.19       | 31.67   |
| Defect oxygen      | 532.2   | 1.49    | 27133.34       | 48.67   |
| Adsorbed water     | 535.4   | 3.16    | 10963.82       | 19.66   |
Table S4. Photocatalytic hydrogen production performance of similar photocatalysts reported in recent references.

| Photocatalysts | HER performance /μmol h⁻¹ g⁻¹ | Co-catalyst | Sacrificial agent | Reference |
|---------------|---------------------------------|-------------|-------------------|-----------|
| MoS₂/g-C₃N₄   | 3570.0                          | 2 wt% Pt    | TEOA              | Ref. 1    |
| WO₃/g-C₃N₄   | 982.0                           | 2 wt% Pt    | lactic acid       | Ref. 2    |
| Cu (OH)₂/g-C₃N₄ | 48.7                           | --          | CH₃OH             | Ref. 3    |
| MoO₃ₓ/g-C₃N₄ | 4694.3                          | 2 wt% Pt    | TEOA              | This work |
| MoO₃ₓ/g-C₃N₄ | 821.0                           | 2 wt% Pt    | lactic acid       | This work |
References
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