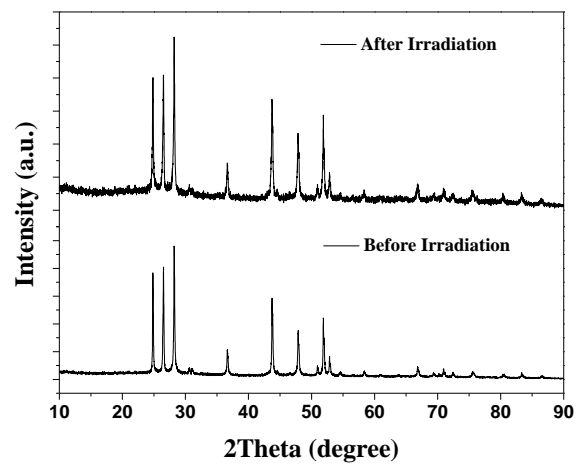


# **High Efficiency and Stable Tungsten Phosphide Cocatalyst for Photocatalytic Hydrogen Production**

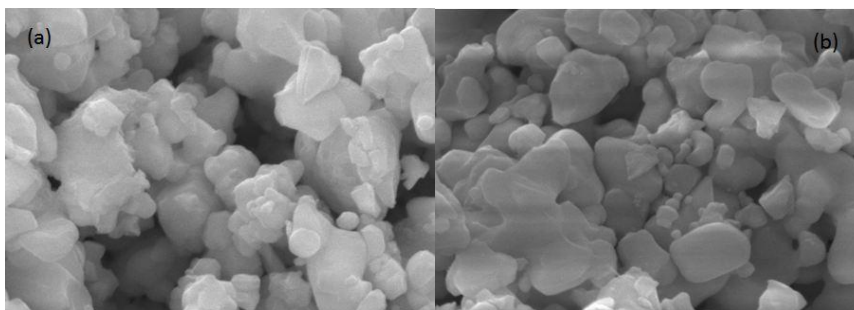
## **Supporting Information**

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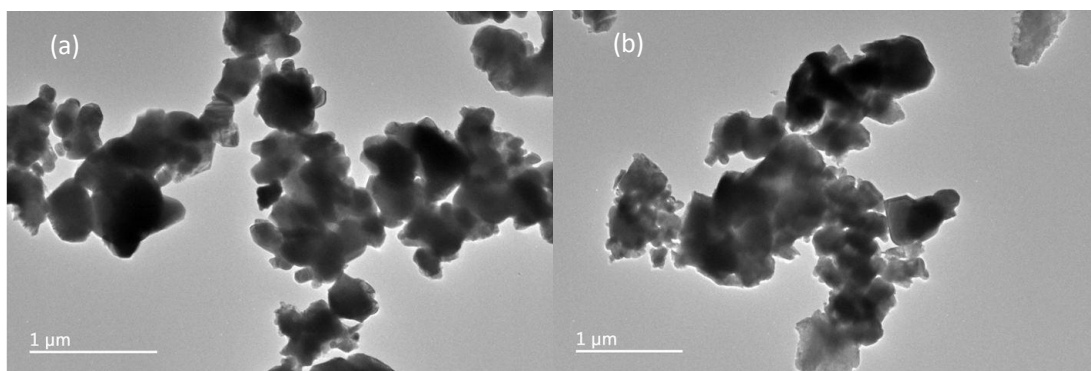
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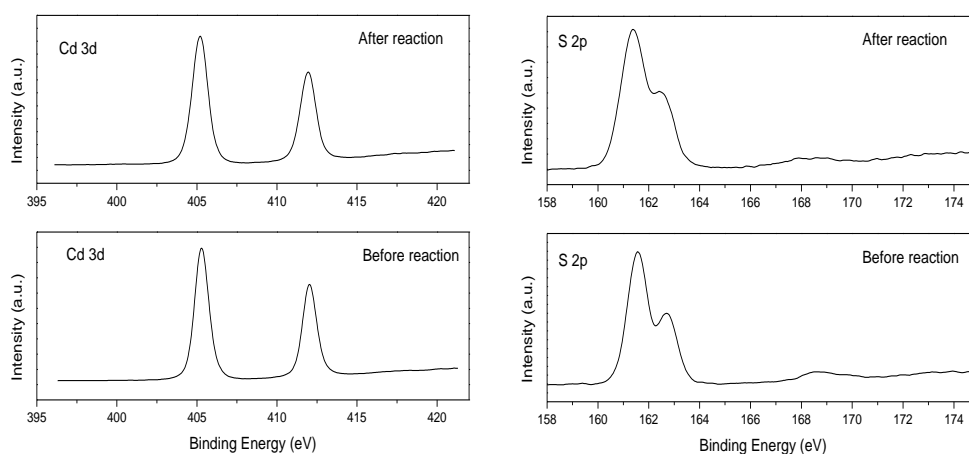
**Figure S1.** XRD patterns of 4.0 wt.% WP/CdS photocatalyst before and after photocatalytic hydrogen production under visible light irradiation ( $\lambda > 420$  nm).



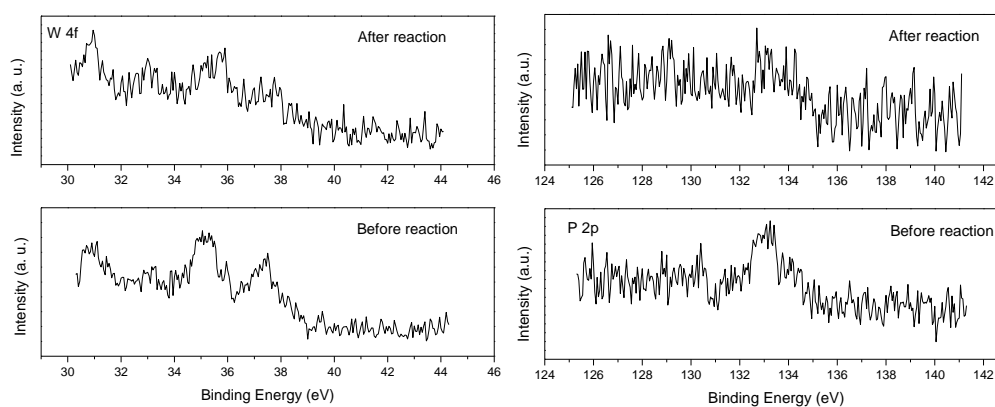
**Figure S2.** SEM images of WP/CdS before (a) and after (b) photocatalytic hydrogen production.



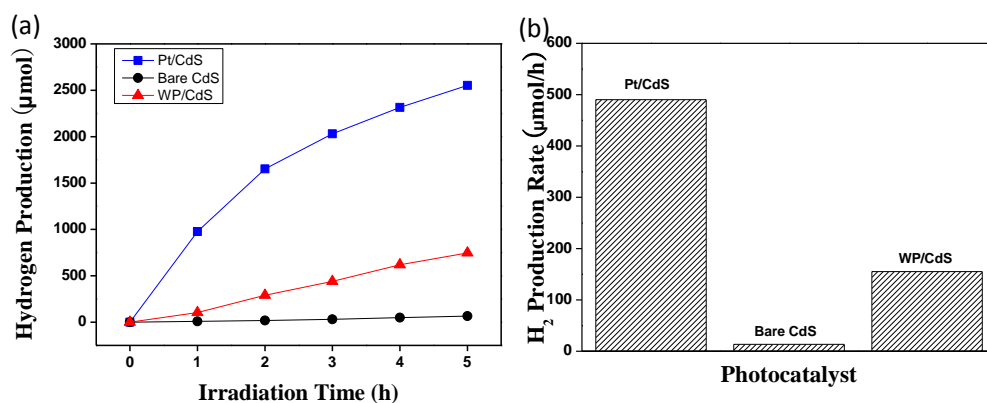
**Figure S3.** TEM images of WP/CdS before (a) and after (b) photocatalytic hydrogen production.



**Figure S4.** Cd 3d (left) and S 2p XPS (right) spectra of 4.0 wt.% WP/CdS photocatalyst before and after photocatalytic hydrogen production



**Figure S5.** W 4f (left) and P 2p (right) XPS spectra of 4.0 wt.% WP/CdS photocatalyst before and after photocatalytic hydrogen production.



**Figure S6.** (a) Hydrogen production and (b) Rate of hydrogen production from WP/CdS, bare CdS and Pt/CdS photocatalysts under visible light. (Reaction temperature: room temperature; Light Source: visible light ( $\lambda > 420$  nm); Catalyst weight: 50 mg; Photolyte: 100 mL of 1.0 M  $(\text{NH}_4)_2\text{SO}_3$  solution).

**Table S1.** Summary hydrogen production rates and quantum efficiencies for non-noble metal based cocatalysts.

| Non-noble metal Cocatalyst/Photocatalyst                   | Sacrificial Agent                                  | H <sub>2</sub> Production Rate               | Quantum Efficiency | Ref.                       |
|--|--|--|--------------------|----------------------------|
| 2.0 wt.% NiS <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub> | TEOA*  | 4.06 μmol·h <sup>-1</sup>                    | N/A                | C. Xue et al. <sup>1</sup> |
| 0.33 mg CdS + 0.75 mg Co <sub>2</sub> P                    | DL-mandelic acid                                   | 19373 μmol·h <sup>-1</sup> ·g <sup>-1</sup>  | 6.8%               | Y Chen et al. <sup>2</sup> |
| 16.7 wt.% MoP/CdS  | Lactic acid  | 163.2 μmol·h <sup>-1</sup> ·mg <sup>-1</sup> | 5.6% at 450 nm     | P. Du et al. <sup>3</sup>  |
| 5.0 wt.% FeP/CdS   | Lactic acid  | 202000 μmol·h <sup>-1</sup> ·g <sup>-1</sup> | Over 35% at 520 nm | Y Chen et al. <sup>4</sup> |
| 0.5 wt.% Ni <sub>2</sub> P/CdS                             | Na <sub>2</sub> S+ Na <sub>2</sub> SO <sub>3</sub> | 553 μmol·h <sup>-1</sup> ·mg <sup>-1</sup>   | 41% at 450 nm      | P. Du et al. <sup>5</sup>  |
| 1.25 wt.% NiS/C <sub>3</sub> N <sub>4</sub>                | TEOA   | 48.2 μmol·h <sup>-1</sup>                    | 1.9% at 440 nm     | R. Xu et al. <sup>6</sup>  |
| 5.0 mol% CoS <sub>x</sub> /TiO <sub>2</sub>                | CH <sub>3</sub> CH <sub>2</sub> OH                 | 838.9 μmolh <sup>-1</sup> ·g <sup>-1</sup>   | N/A                | Y. Li et al. <sup>7</sup>  |
| 60.0 wt.% CdS + WS <sub>2</sub> -40.0 wt.%                 | Lactic acid  | 373.41 μmol·h <sup>-1</sup> ·g <sup>-1</sup> | 25.03% at 420 nm   | Y Wu et al. <sup>8</sup>   |
| MoS <sub>2</sub> /TiO <sub>2</sub> /E Y**                  | TEOA   | 16.7 mmol·h <sup>-1</sup> ·g <sup>-1</sup>   | N/A                | P. Du et al. <sup>9</sup>  |
| 4.0 wt.% WP/CdS  | (NH <sub>4</sub> ) <sub>2</sub> SO <sub>3</sub>    | 155.17 μmol·h <sup>-1</sup>                  | 10.2% at 420 nm    | This work                  |

\*Triethanolamine; \*\*Eosin Y.

**Table S2.** EDX and XPS element content analysis of WP/CdS

| Element | Atom content (atom%) |       |        |       |
|---------|----------------------|-------|--------|-------|
|         | XPS                  |       | EDX    |       |
|         | Before               | After | Before | After |
| Cd      | 58.2                 | 56.2  | 48.3   | 47.7  |
| S       | 40.0                 | 41.7  | 44.8   | 44.0  |
| W       | 0.3                  | 0.3   | 4.7    | 5.4   |
| P       | 1.5                  | 1.7   | 2.3    | 2.9   |

**Table S3.** Summary hydrogen evolution reaction (HER) activities in acid media for WP based electrocatalysts.

| Catalyst     | Tafel Slope<br>(mV dec <sup>-1</sup> )      | Current<br>density<br>j (mA/cm <sup>2</sup> ) | Overpotential at<br>the corresponding j<br>(mV) | Ref.                     |
|--------------|---|---|---|--------------------------|
| WP           | 127 (0.5 M H <sub>2</sub> SO <sub>4</sub> ) | 10  | 435   | This work                |
| Amorphous WP | 54 (0.5 M H <sub>2</sub> SO <sub>4</sub> )  | 10  | 120   | R E.Schaak <sup>10</sup> |
| WP NPs@NC*   | 58 (0.5 M H <sub>2</sub> SO <sub>4</sub> )  | 10  | 102   | X Liu <sup>11</sup>      |
| WP NAs/CC**  | 69 (0.5 M H <sub>2</sub> SO <sub>4</sub> )  | 10  | 130   | X Sun <sup>12</sup>      |
|              | 125 (1.0 M PBS <sup>***</sup> )             | 10  | 200   |                          |
|              | 102 (1.0 M KOH)                             | 10  | 150   |                          |

\* Nitrogen-doped carbon; \*\* Nanorod arrays on carbon cloth. \*\*\* Phosphate Buffered Saline.

**Table S4.** Specific BET surface areas of pure CdS, 4.0 wt.% WP/CdS and 0.5 wt.% Pt/CdS photocatalysts

| Photocatalyst   | S <sub>BET</sub> [m <sup>2</sup> ·g <sup>-1</sup> ] |
|-----------------|---|
| Pure CdS        | 3.6   |
| 4.0 wt.% WP/CdS | 4.7   |
| 0.5 wt.% Pt/CdS | 4.3   |

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