## Supplementary data

# Ni-CdS composited with ZnO for improved surface reaction and

## charge efficiency for photocatalytic hydrogen production from formic

## acid

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Fig. S1. The EDS spectrum of Ni-CdS@ZnO-10.



**Fig. S2.** The UV-Vis adsorption spectra and photographs of Ni-CdS@ZnO-X (X=5, 20, 30).



Fig. S3. The XRD and TEM of Ni-CdS@ ZnO-10 photocatalyst after photocatalytic reaction.



**Fig. S4.** The gas chromatography results of photocatalytic formic acid decomposition over Ni-CdS@ZnO-10.



Fig. S5. In situ ATR infrared spectra of Ni-CdS@ZnO (a) and Ni-CdS (b) for photocatalytic formic acid decomposition.



Fig. S6. The valence band of ZnO, Ni-CdS and Ni-CdS@ ZnO-10.

Regions	Integral area	
	Ni-CdS@ZnO-10	Ni-CdS
Туре І	20.0	21.3
Type II	22.8	9.1
Type III	14.3	6.0

**Table S1.** H<sub>2</sub>O-TPD integral area statistics of Ni-CdS@ZnO-10 and Ni-CdS.

#### **Experiments**

#### 1. Synthesis of Ni-CdS

In detail, 1 mmol CdCl<sub>2</sub>·2.5H<sub>2</sub>O was dispersed in 110 mL water and heated at 80  $^{\circ}$ C with powerful stirring. Subsequently, an excessive amount of Na<sub>2</sub>S (5 mmol) was dissolved in 10 mL of deionized water and injected into the reactor quickly. After stirring at 80  $^{\circ}$ C for 2 hours, 0.6 mmol nickel acetate were added into the reactor for another hour. After that, the metal-modified cadmium sulfide was obtained via centrifugation and drying, and noted as Ni-CdS.

### 2. Photocatalytic hydrogen evolution from formic acid

The specific experimental parameters are as follows: the light intensity was 135 mW/cm<sup>2</sup>, and the stirring rate was 300 r/min. 5 mg photocatalyst was added into 30 mL formic acid solution (5 mol/L), followed by 10 min degas operation with argon to discharge other gases in this system. Subsequently, the prepared reactor was put into a multichannel photochemical reaction system to decompose formic acid. The generated gases (H<sub>2</sub>, CO and CO<sub>2</sub>) were detected via gas chromatograph (Techcomp GC-7900, China, Ar carrier gas) and calculated with the external standard method. The recycling test was carried out according to the same test condition above.