

## **Ternary Nanocomposites of CdS/WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> for Hydrogen Production**

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### **1.1 Characterization of the catalysts**

X-ray diffraction (XRD) analysis of the catalysts was carried out using a PANalytical diffractometer with Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at a scan rate of  $10^\circ/\text{min}$  and a beam current and voltage of 30 mA and 50 kV, respectively. For transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) measurements, all samples were sonicated using a C<sub>2</sub>H<sub>5</sub>OH solution and suspended on a copper grid (400-mesh, with 3.5-mm diameter) with a high-resolution transmission electron microscope (H-7600; Hitachi Inc., Japan) accelerating 120 kV microscope. The binding energies of all synthesized samples were tested as referenced to C 1s at 284.7 eV. A scanning electron microscope (SEM) (SEM HITACHI S-4800) was used for the microstructural and surface morphology characterizations. The N<sub>2</sub> adsorption-desorption isotherms were measured using a Micromeritics ASAP 2420 surface area analyzer. Before gas adsorption, the samples were degassed at 150 °C for 3h. The chemical valences of elements were analyzed by X-ray photoelectron spectra (XPS) using a Thermo Scientific k- $\alpha$  surface analyzer equipped with a AlK $\alpha$  X-ray source ( $h\nu = 1486 \text{ eV}$ ) using C 1s (284.5 eV) as a reference to calibrate binding energies. The ultra-violet-visible (UV-Vis) spectroscopy was carried out on a Cary 5000 apparatus in the 200 – 800 nm wavelength.

## 1.2 Photocatalytic test

The photocatalytic hydrogen production experiment was conducted in a quartz flask (150 mL) containing 10 mg of catalyst and certain amount of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (3 wt% Pt relative to the catalyst) as co-catalyst were added in 45 mL of DI water, 5 mL of TEOA as a sacrificial agent, and at room temperature. The opening of the flask was airtight with a silicone rubber septum. A Xenon light source ( $\lambda > 420$  nm, 300 W MAX-303 model) was used as the light source. Before illuminations, the system was evacuated and bubbled with  $\text{N}_2$  for 30 min to remove the dissolved air molecules. The  $\text{H}_2$  gas evolved was estimated using an off-line gas chromatograph (YL-6500 instrument) equipped with a thermal conductivity detector (TCD) and He is a carrier gas. Photocatalytic tests were performed with 20 mg of as-prepared photocatalysts suspended in 100 mL of dye aqueous solution with the concentration of MG dye of 5 mg/L under visible light irradiation. Before conducting the photocatalytic test, the mixture was stirred in the dark for 30 min to obtain the adsorption-desorption equilibrium. Under illuminations, at certain time intervals, 3-mL solution was collected from the reactor and centrifuged and then tested by using UV-Visible spectroscopy.

## 1.3 Electrochemical measurements

The photocurrent was measured and electron impedance spectroscopy (EIS) was performed using a three-electrode cell in which Ag/AgCl was employed as the reference electrode and a platinum coil was used as the counter electrode at an ambient temperature. A fluorine doped Tin oxide (FTO) glass substrate was used as the working electrode. The preparation method of the working electrode was as follows: 10 mg of the sample was mixed with 450  $\mu\text{L}$  of DI water and 50  $\mu\text{L}$  of Nafion to create a slurry which was applied on the ITO glass substrate using a drop-casting method. Then, the working electrode was heated to 90 °C for overnight. The photocurrent measurements were conducted using a 300-W Xenon lamp with 80  $\text{mW}/\text{cm}^2$  of light intensity. EIS was performed over a frequency of from 100 MHz to 1 MHz at the open

circuit. All the electrochemical experiments were performed on an SP-200 Bio-logic workstation in 0.5 Na<sub>2</sub>SO<sub>4</sub>.

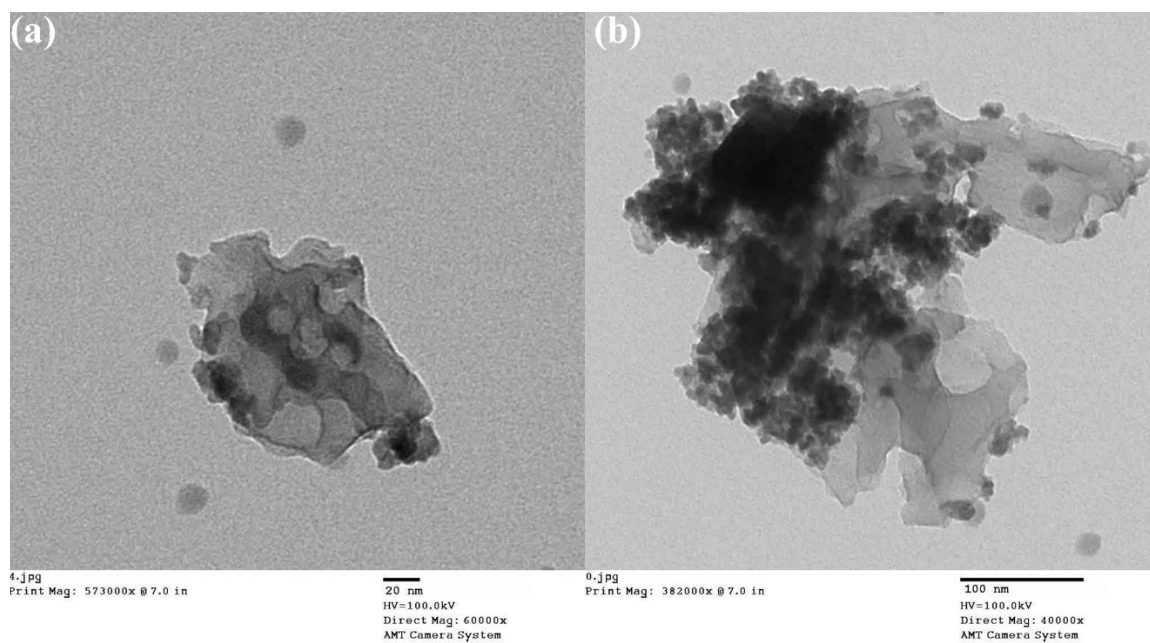


Fig. S1 HRTEM images of (a) CN and (b) CNW catalysts.

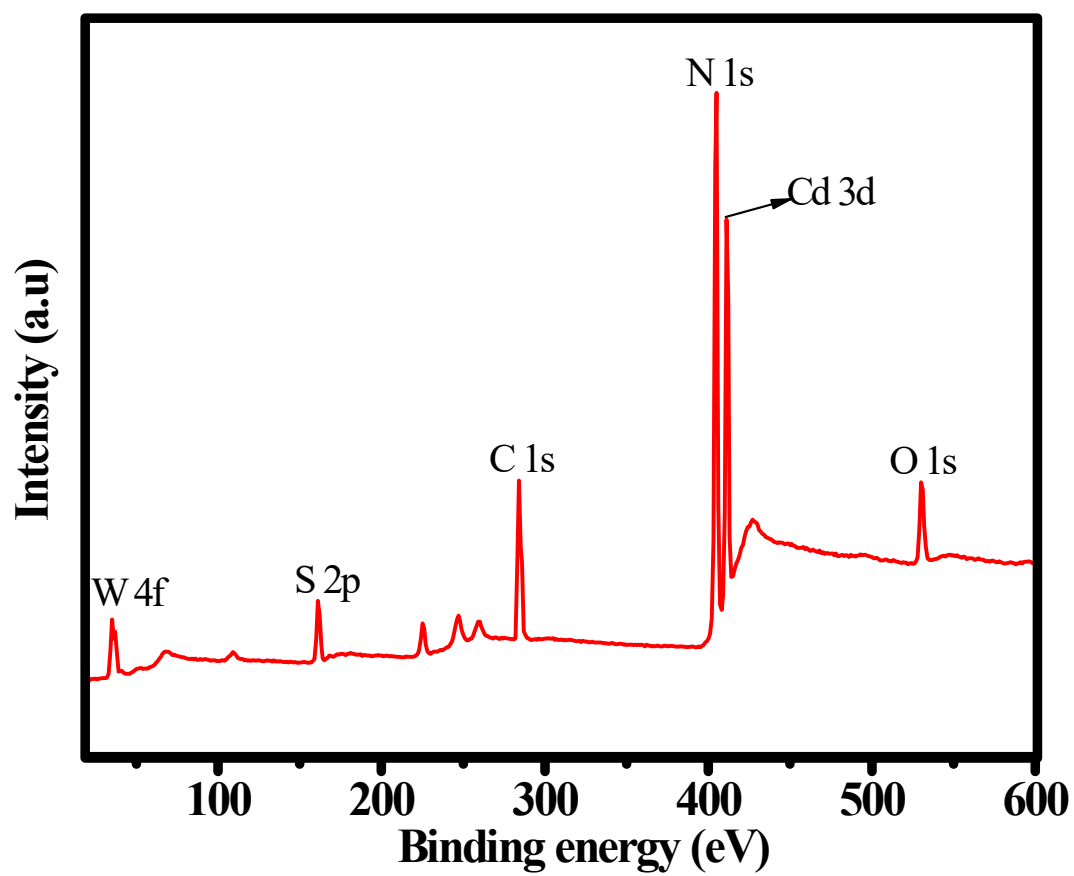


Fig. S2 XPS survey of 3C-CNW nanostructure catalyst.

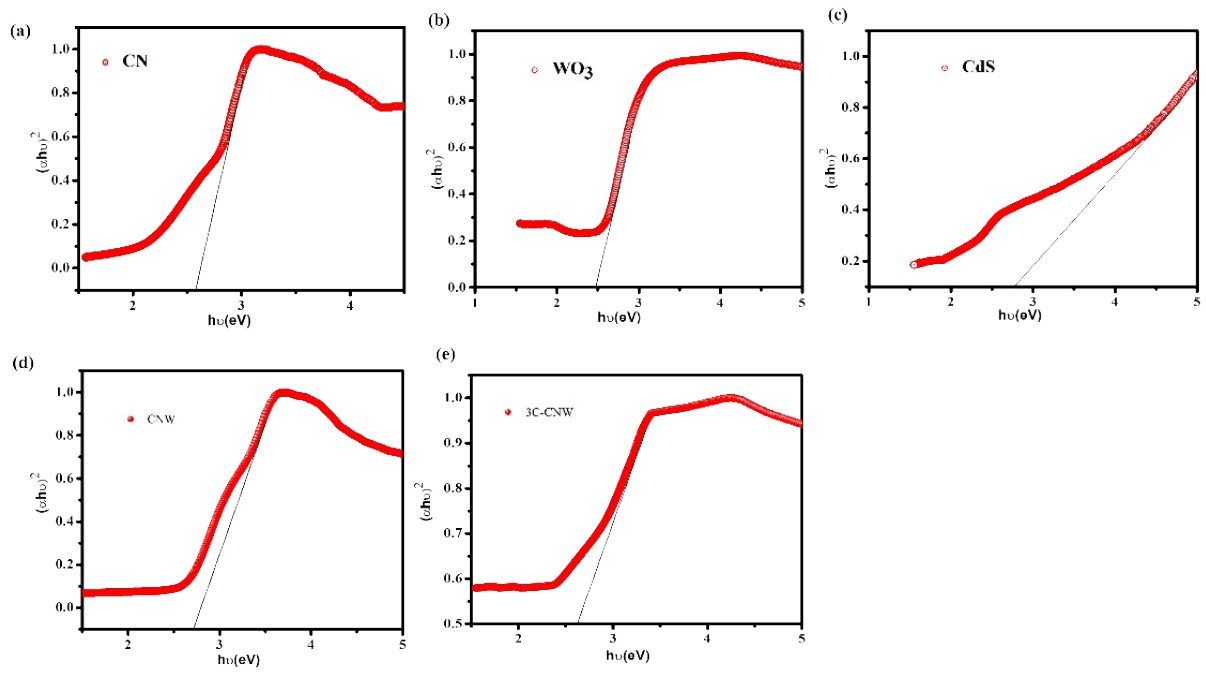


Fig. S3 (a-e) Estimated band gaps from Tauc plots of CN, WO<sub>3</sub>, CdS, CNW and 3C-CNW samples.

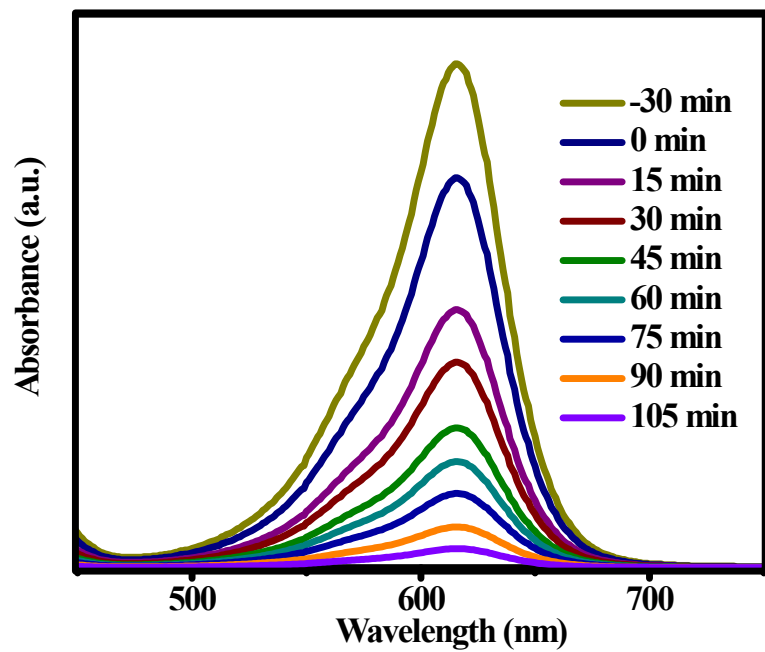


Fig. S4 UV-Vis absorption spectra of 3C-CNW nanostructure over MG dye under visible light irradiation.

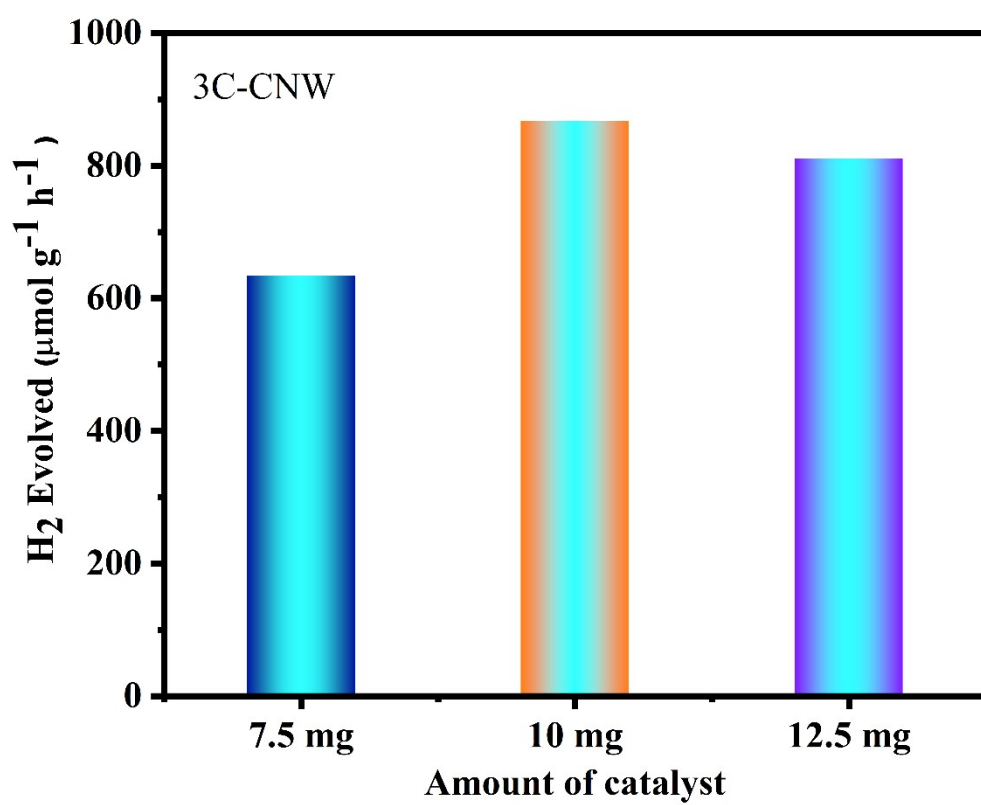


Fig. S5 Influence of amount of catalysts over 3C-CNW nanostructure catalyst.

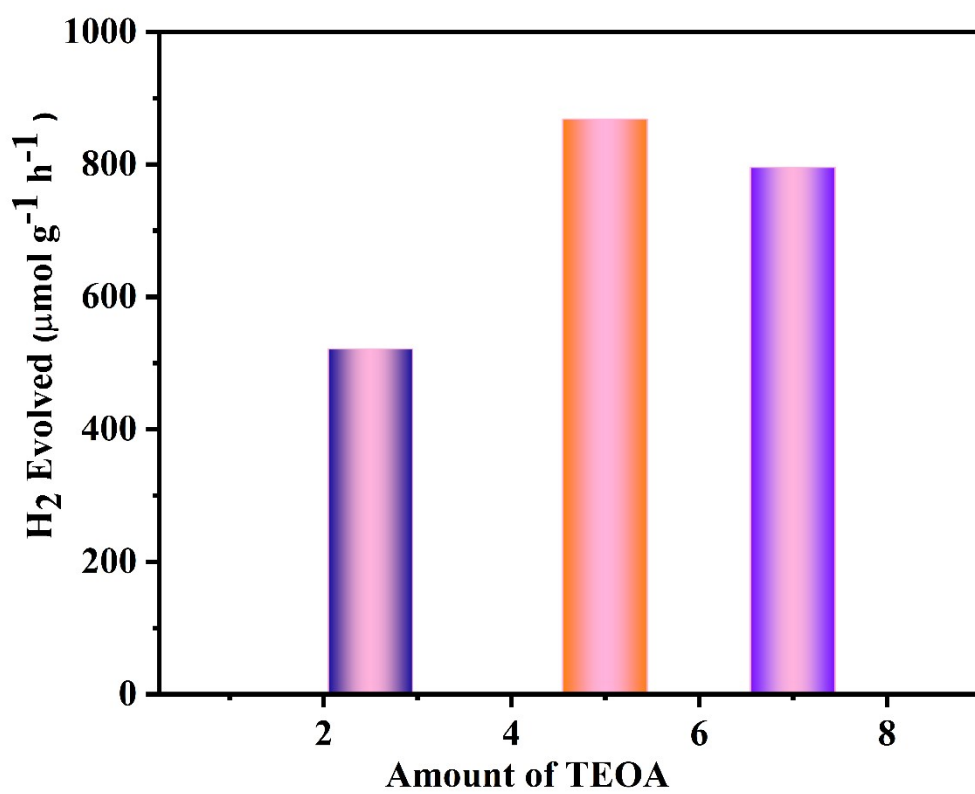
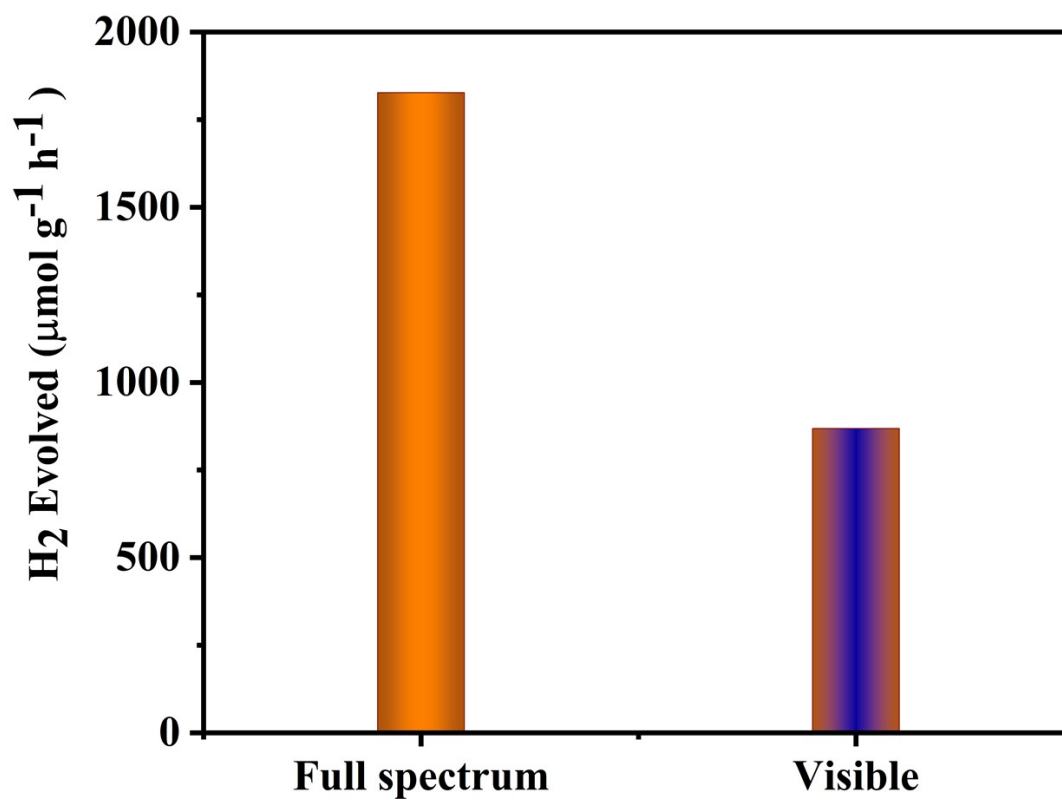


Fig. S6 Comparison of H<sub>2</sub> generation rate with different amount of TEOA scavenger over 3C-CNW nanostructure catalyst.





**Fig. S7** amount of H<sub>2</sub> generated over 3C-CNW nanostructure under visible light ( $\lambda > 420$  nm) and full spectrum light [with same light intensity: 80 mW/cm<sup>2</sup>, light type: MAX 303, 300 W].

**Table 1** Comparison of photocatalytic H<sub>2</sub> generation rate over g-C<sub>3</sub>N<sub>4</sub> based photocatalysts

Photocatalyst (Co-catalyst)	Sacrificing agent	Light source*	H <sub>2</sub> production rate	Reference
Bulk-g-C <sub>3</sub> N <sub>4</sub>	TEOA, Pt as cocatalyst	300W, >420 nm	10.7 μmol h <sup>-1</sup>	[1]
TiO <sub>2</sub> /MoS <sub>2</sub> /graphene (0.5%)	25 vol% EtOH/H <sub>2</sub> O	350 W, Xe lamp	2066 μmol g <sup>-1</sup> h <sup>-1</sup>	[2]
g-C <sub>3</sub> N <sub>4</sub> /TiO <sub>2</sub>	100 mL of TEOA, 3 wt.% Pt as a cocatalyst	300W, Xe λ>420nm	40 μmol h <sup>-1</sup>	[3]
CdS/g-C <sub>3</sub> N <sub>4</sub>	Methanol, Pt as cocatalyst	Xe lamp (λ > 400 nm)	172.7 μmol g <sup>-1</sup> h <sup>-1</sup>	[4]
MoS <sub>2</sub> /CdS/TiO <sub>2</sub> (1%)	10 vol% lactic acid	300 W, Xe lamp	280 μmol h <sup>-1</sup>	[5]
Black TiO <sub>2</sub> /MoS <sub>2</sub> /TiO <sub>2</sub>	20 vol% methanol/H <sub>2</sub> O	300 W, Xe lamp	560 μmol g <sup>-1</sup> h <sup>-1</sup>	[6]
CdS/MOS <sub>2</sub> /graphene	20 vol% lactic acid	300 W, Xe lamp	1.8 mmol h <sup>-1</sup>	[7]
Meso-TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Methanol, Pt as cocatalyst	Xe lamp (λ > 420 nm)	983.56 μmol g <sup>-1</sup> h <sup>-1</sup>	[8]
NGQDs-Zn/C <sub>3</sub> N <sub>4</sub>	Methanol, Pt as cocatalyst	Xe lamp (λ > 420 nm)	340.9 μmol g <sup>-1</sup> h <sup>-1</sup>	[9]
Ti <sub>3</sub> C <sub>2</sub> (TiO <sub>2</sub> )/CdS/MoS <sub>2</sub>	-	300W, Xe lamp	317 μmol g <sup>-1</sup> h <sup>-1</sup>	[10]
Pt/g-C <sub>3</sub> N <sub>4</sub> nanowire bundles (CN NWB)	-	Xe, >420 nm	3.6 μmol h <sup>-1</sup>	[11]
MoS <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	TEOA	Xe lamp (λ > 400 nm)	252 μmol g <sup>-1</sup> h <sup>-1</sup>	[12]
CN	5 vol%TEOA, Pt-cocatalyst	300 W, Xe >420 nm	12.6 μmol g <sup>-1</sup> h <sup>-1</sup>	Current work
CNW	5 vol%TEOA, Pt-cocatalyst	300 W, Xe >420 nm	248.06 μmol g <sup>-1</sup> h <sup>-1</sup>	Current work
3C-CNW	5 vol%TEOA, Pt-cocatalyst	300 W, Xe >420 nm	868.23 μmol g <sup>-1</sup> h <sup>-1</sup>	Current work

TEOA is triethanolamine.

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