Efficient photocatalytic hydrogen evolution mediated by defect-rich 1T-PtS_2 atomic layer nanosheets modified mesoporous graphitic carbon nitride

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1. Experimental section

Chemicals

All the reagents were of analytical grade and used without further purification. melemine ($C_3H_5N_6$, 99% purity), ethanol (CH_3CH_2OH, 99% purity), sublimed sulfur powders, platinum powder were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). All the solutions used in the experiments were freshly prepared with ultrapure water (Nanjing Baocheng Biotechnology CO. Ltd., China).

Material characterization.

The fluorescence life time spectra were recorded on a spectrophotometer (FS5, Edinburgh Instruments Ltd.) a Varian Cary Eclipse spectrometer. Decay curves were analyzed at the emission of 434 nm in prepared materials under 406 nm excitation. The decay curves for samples can be fitted based on the following formula:

$$I(t)=B+\sum_{i=1}^{N}(A_i)\exp(-\frac{t}{\tau_i})$$

where N is a number of discrete emissive species, B is a baseline correction, A_i and τ_i are pre-exponential factors. For multi-exponential decays, the average lifetime, $\langle\tau\rangle$, can be formulated as:

$$\langle\tau\rangle=\sum_{i=1}^{N}a_i\tau_i \qquad a_i=\frac{A_1}{\sum A_i}$$

where a_i is the contribution of the decay component.

Photoelectrochemical measurements

Photocurrent measurements were carried out a CHI 660E electrochemical workstation (Chenhua Instrument), including astandard three electrodes system configuration with a platinumwire as counter electrode, an Ag/AgCl wire (saturated KCl solution) as reference electrode, and 0.1 M Na_2SO_4 solution as the electrolyte. The working electrode was prepared as followed: 5 mg of photocatalysts was dispersed in 1 mL ethylene glycol solution. The suspension was then spread on ITO glass substrate and dried under infrared lamp to form MCN and the different mass ratio of UPSMCN modified ITO electrodes. 300 W Xe lamp was used as light source. Electrochemical impedance spectra (EIS) were measured in 0.1 M KCl solution containing 5 mM $Fe(CN)_6^{3-}$/ $Fe(CN)_6^{4-}$.

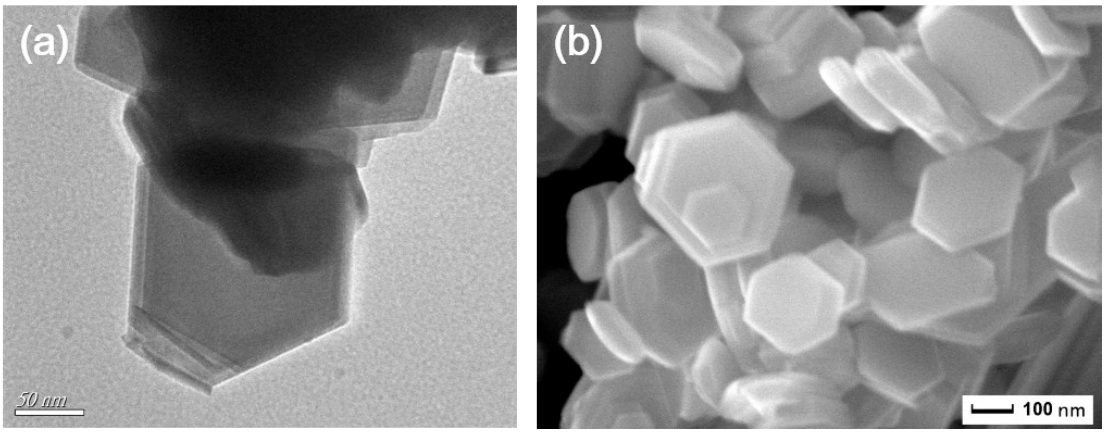

Figure S1. The TEM (a) and SEM (b) images of bulk PtS_2.

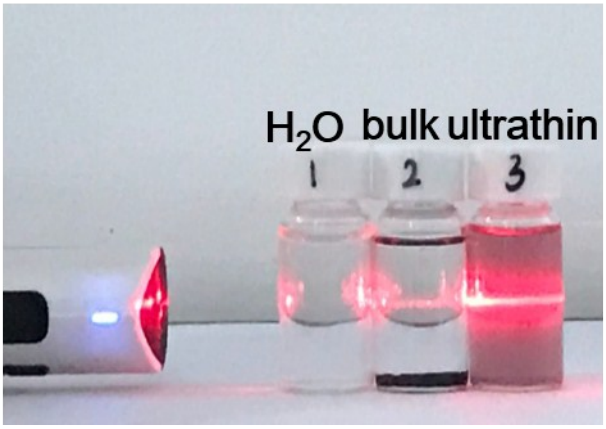

Figure S2. Dispersions of blank, bulk PtS_2 nanosheets and ultrathin PtS_2 catalysts in water (left, middle and right, respectively), and the evaluation of the Tyndall effect.

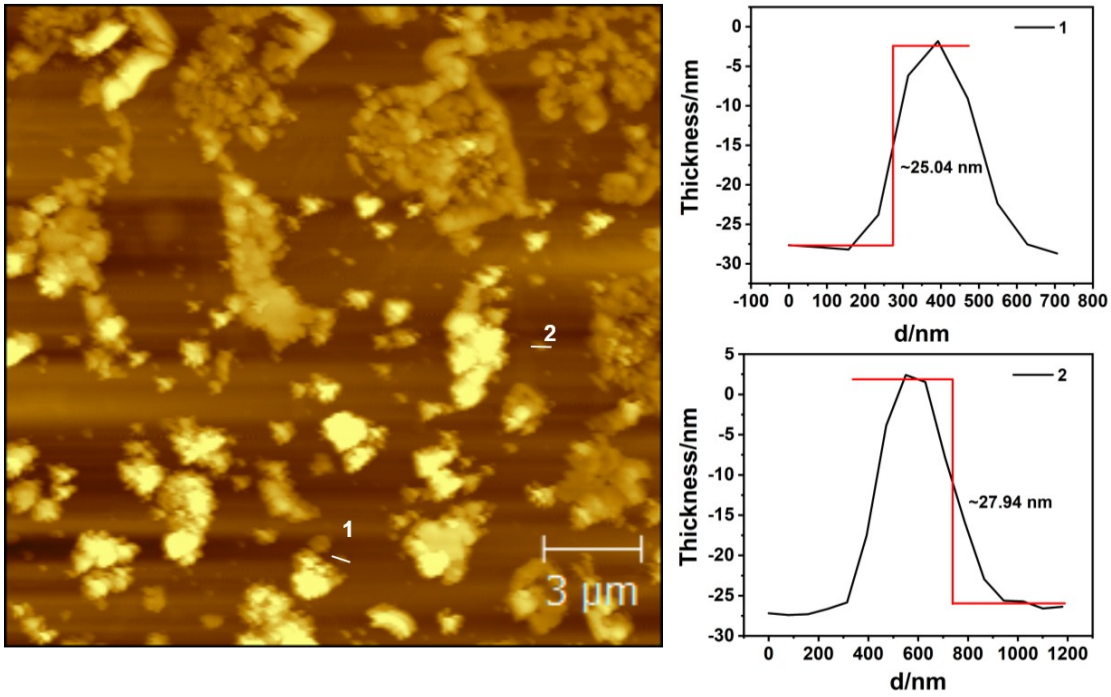

Figure S3. AFM image of bulk PtS_2 nanosheets.

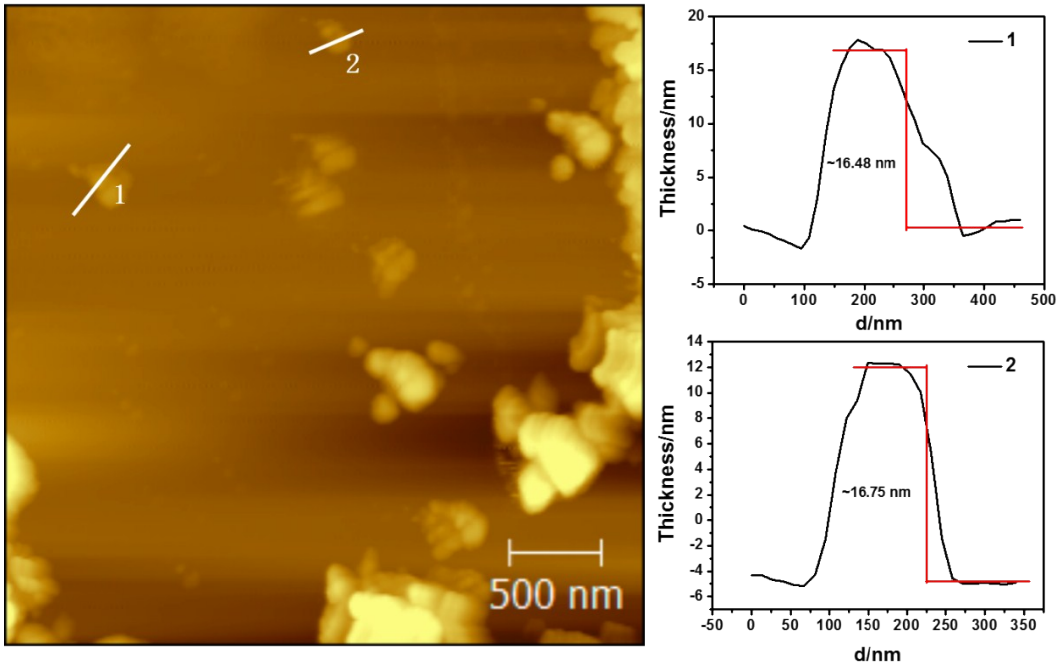

Figure S4. AFM image of PtS_2-500 nanosheets.

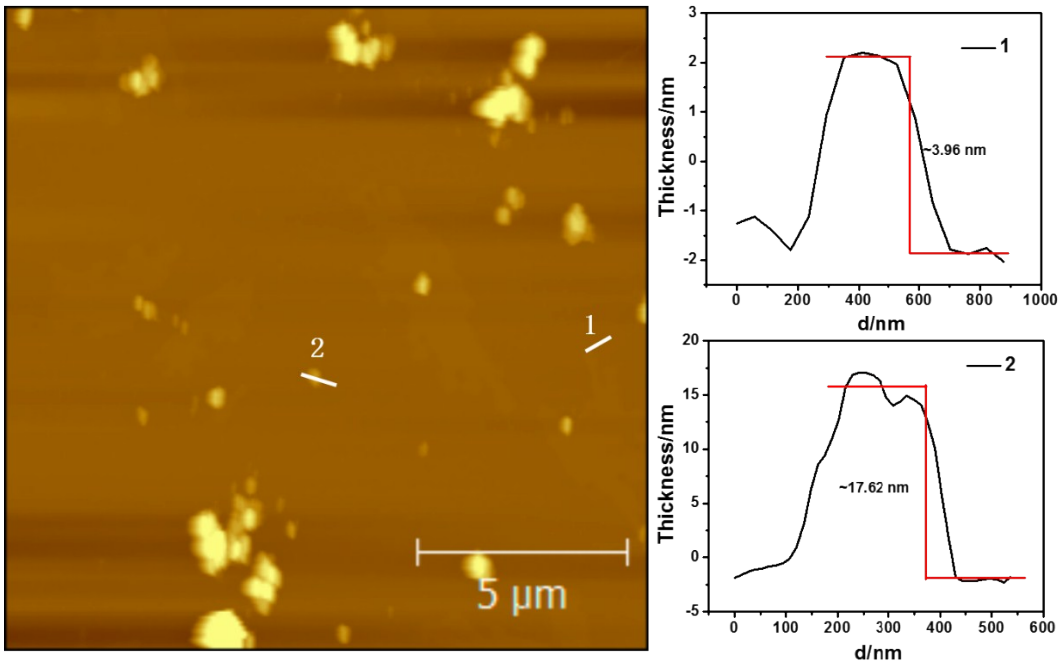

Figure S5. AFM image of PtS_2-3000 nanosheets.

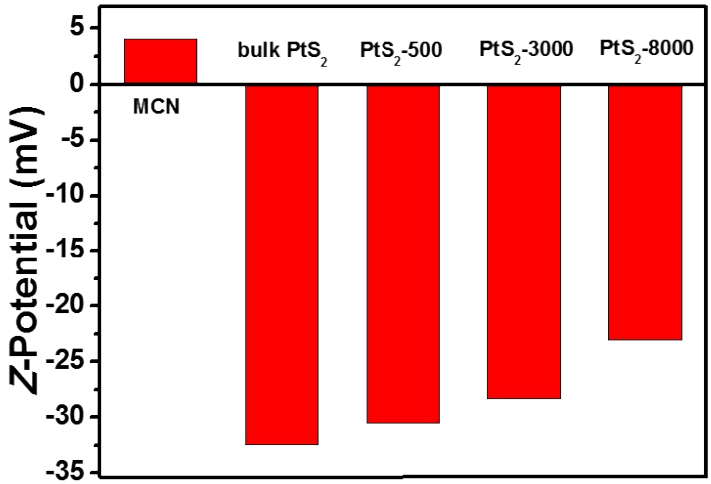

Figure S6. Z-potentials of mpg-C_3N_4 and the different centrifugal speeds of PtS_2 in aqueous solution.

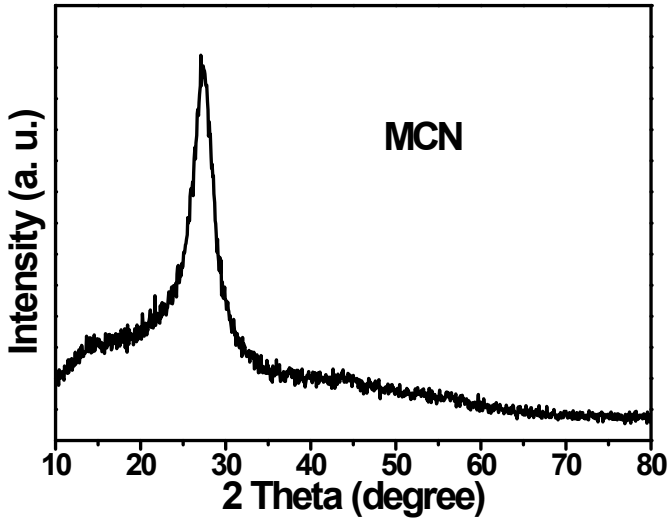

Figure S7. The XRD patterns of MCN.

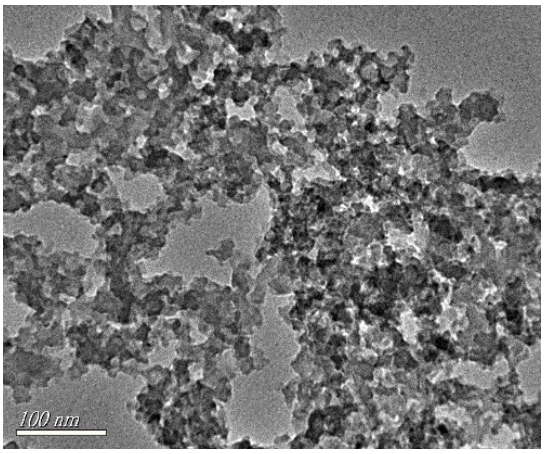

Figure S8. The TEM of pure MCN.

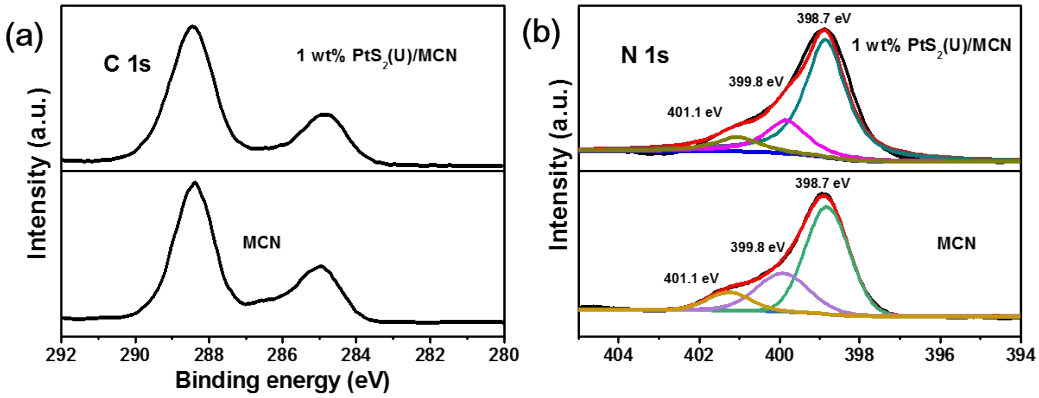

Figure S9. (a) The high-resolution XPS of C 1s and of (b) N 1s of PtS_2(U)/MCN composites and pure MCN.

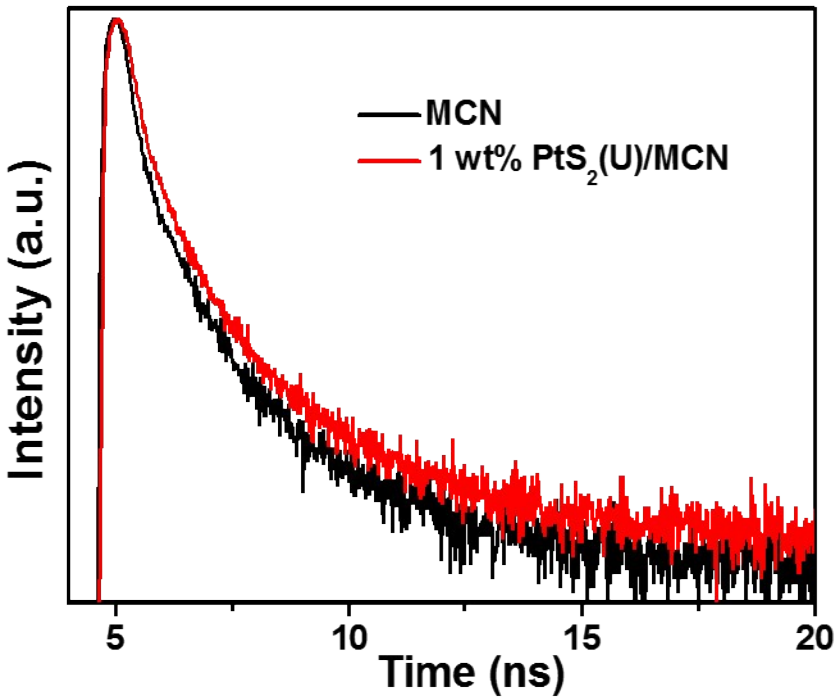

Figure S10. Time-resolved transient FL decay of MCN and the 1 wt% PtS_2(U)/MCN composite.

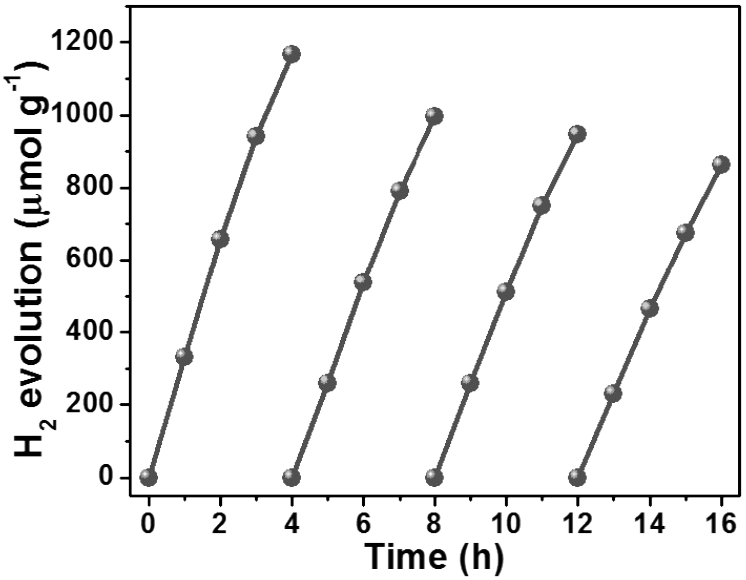

Figure S11. Stability test of 1 wt% PtS_2(U)/MCN for the photocatalytic H_2 evolution.

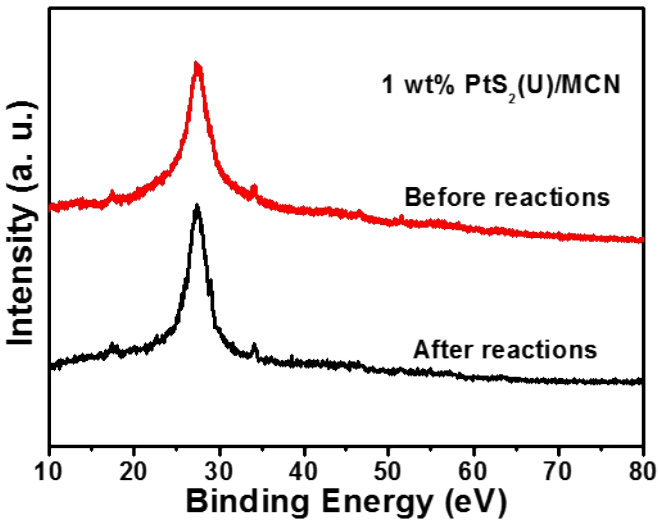

Figure S12. XRD patterns of the 1 wt% PtS_2(U)/MCN materials before and after the cycling photocatalytic experiments.

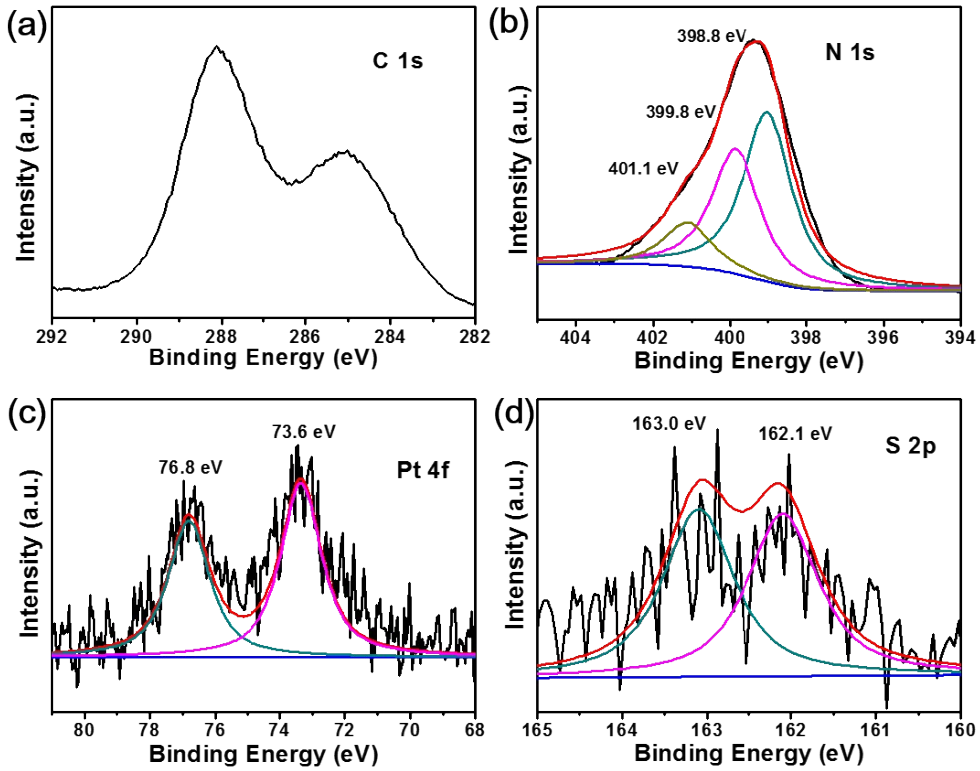

Figure S13. The high resolution XPS spectra for C 1s (a), N 1s (b), Pt 4f (c) and S 2p (d) of PtS_2(U)/MCN after photocatalytic reaction.

The External Quantum Efficiency (EQE) is analyzed at different wavelength (405, 420, 450 and 550 nm, λ ± 10 nm) in the 300 W Xenon lamp (PLS-SXE 300C (BF), PerfectLight, Beijing). The other experimental condition is similar to the photocatalytic hydrogen evolution measurement as described before. The light intensity is obtained with an optical power meter (CEL-NP2000, *CEAULIGHT*, Beijing). For example, if 405 nm is used, the average light intensity is 25.26 mW. The number of incident photons (*N*) is 1.92×10^{20} calculated by equation (1). The amount of H_2 molecules generated in 1 h are 6.06 μmol. The EQE is then calculated in equation (2).

$$N = \frac{E\lambda}{hc} = \frac{25.26 \times 10^{-3} \times 1 \times 3600 \times 420 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 1.92 \times 10^{20} \quad (1)$$

$$EQE = \frac{the\ number\ of\ reacted\ electrons}{the\ number\ of\ incident\ photons} \times 100\% \quad (2)$$

$$= \frac{2 \times 6.02 \times 10^{23} \times 1.12 \times 10^{-6}}{1.92 \times 10^{20}} \times 100\% = 0.7\%$$

Table S1 The calculated External Quantum Efficiency (EQE) at different wavelength.

Wavelength	H_2 Evolved	Light Intensity	EQE
λ=405 nm	1.84 μmol	25.26 mW	1.16 %
λ=420 nm	1.12 μmol	26.12 mW	0.7 %
λ=450 nm	0.69 μmol	27.02 mW	0.38 %
λ=550 nm	0 μmol	28.18 mW	--

λ=405 nm

$$N = \frac{E\lambda}{hc} = \frac{26.12 \times 10^{-3} \times 1 \times 3600 \times 405 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 1.92 \times 10^{20} \quad (1)$$

$$EQE = \frac{the\ number\ of\ reacted\ electrons}{the\ number\ of\ incident\ photons} \times 100\% \quad (2)$$

$$= \frac{2 \times 6.02 \times 10^{23} \times 1.84 \times 10^{-6}}{1.92 \times 10^{20}} \times 100\% = 1.16\ \%$$

λ=450 nm

$$N = \frac{E\lambda}{hc} = \frac{27.02 \times 10^{-3} \times 1 \times 3600 \times 450 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 2.20 \times 10^{20} \quad (1)$$

$$EQE = \frac{\textit{the number of reacted electrons}}{\textit{the number of incident photons}} \times 100\% \quad (2)$$

$$= \frac{2 \times 6.02 \times 10^{23} \times 0.69 \times 10^{-6}}{2.20 \times 10^{20}} \times 100\% = 0.38\%$$