

Supplementary Information

In situ construction of sulfated TiO₂ nanoparticles with TiOSO₄ for enhanced photocatalytic hydrogen production

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The calculation of activation energy

The activation energy of each reaction stage was calculated according to the kinetic formula of the thermal decomposition of solids. At the constant heating rate, the parametric Eq S1¹ is expressed as follows:

$$d\alpha/dT = A/\beta \exp(-E/RT) (1-\alpha)^n \quad (\text{Eq S1})$$

taking logarithms on both sides of the Eq S1 yields the following equation

$$\ln(d\alpha/dT) = \ln[(A/\beta) (1-\alpha)^n] - E/RT \quad (\text{Eq S2})$$

where α is the conversion of the reactant defined by $\alpha_t = (m_0 - m_t)/(m_0 - m_\infty)$, m_0 , m_t , m_∞ represent the initial mass, the mass at time t and the final mass of the samples, respectively, A is the pre-exponential factor (s^{-1}), β is the constant heating rate (K min^{-1}), E is the activation energy of decomposition (kJ mol^{-1}), T is the temperature (K). It can be seen from the Eq S2 that there is a linear correlation between $\ln(d\alpha/dT)$ and $1/T$. Taking $1/T$ as abscissa and $\ln(d\alpha/dT)$ as ordinate, the straight slope $-E/R$ can be obtained.

The calculation of AQE

In our work, the cut-off of the UV light filter is 365 nm, the intensity of light measured at 100 mW cm^{-2} , and the irradiated surface area was approximately 38.5 cm^2 .

$$\begin{aligned} \text{AQE} &= \frac{2 \times \text{the number of generated } H_2 \text{ molecules}}{\text{the number of incident photons}} \times 100\% \\ &= \frac{2 \times n_{H_2} \times N_A \times h \times c}{I \times S \times t \times \lambda} \times 100\% \end{aligned}$$

where Avogadro's number is $6.022 \times 10^{23} \text{ mol}^{-1}$, h is the Planck's constant ($6.626 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}$), c is the speed of light ($3 \times 10^8 \text{ m s}^{-1}$), and λ is the wavelength of the light source (365 nm).

$$\begin{aligned} \text{AQE} &= \frac{2 \times 16.68 \times 50 \times 10^{-6} \times 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 3 \times 10^8}{100 \times 38.5 \times 10^{-3} \times 3600 \times 365 \times 10^{-9}} \times 100\% \\ &= 3.9\% \end{aligned}$$

The cycle test procedure

For the first cycle, 50 mg fresh catalyst was ultrasonically dispersed in 100 mL of aqueous methanol (methanol 20 vol%), and Pt (3 wt%) was used as the cocatalyst. Centrifugally collecting the catalyst after the first cycle, washing with water and ethanol for three times, and dried. For the

second cycle, the used catalyst was tested under the same conditions as described above, except for Pt. The next several cycles follow the same procedure.

Table S1. BET specific surface area, average pore diameter and pore capacity of TS-0CTAC, TS-5CTAC and TS-12.5CTAC.

Samples	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Average pore size (nm)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)
TS-0CTAC	31.4	15.17	0.1435
TS-5CTAC	118.9	6.63	0.2857
TS-12.5CTAC	103.1	7.96	0.3198

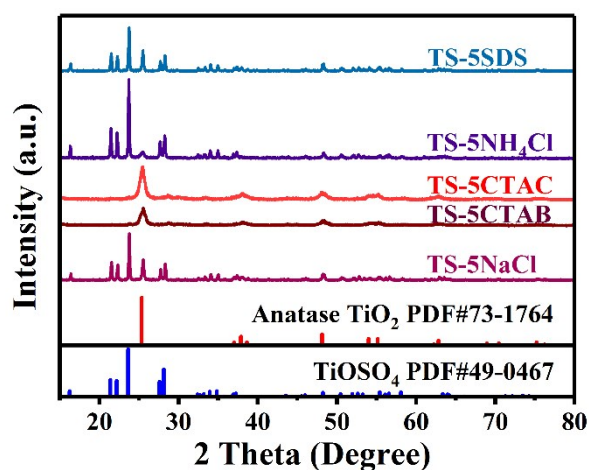


Fig. S1. (a) XRD patterns of the TS-5Y samples prepared with different auxiliaries

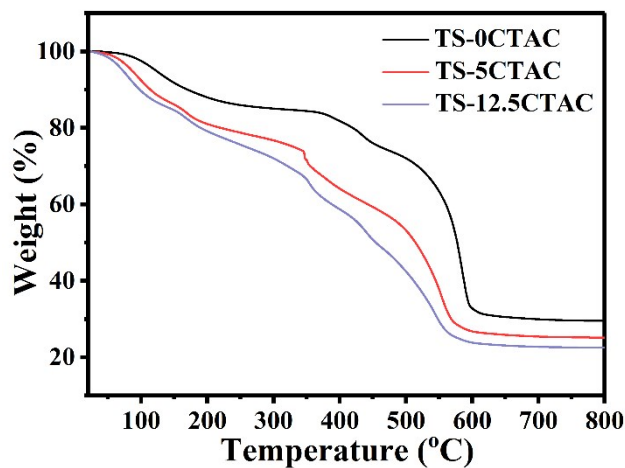


Fig. S2. TGA curves of the precursors of TS-0CTAC, TS-5CTAC and TS-12.5CTAC.

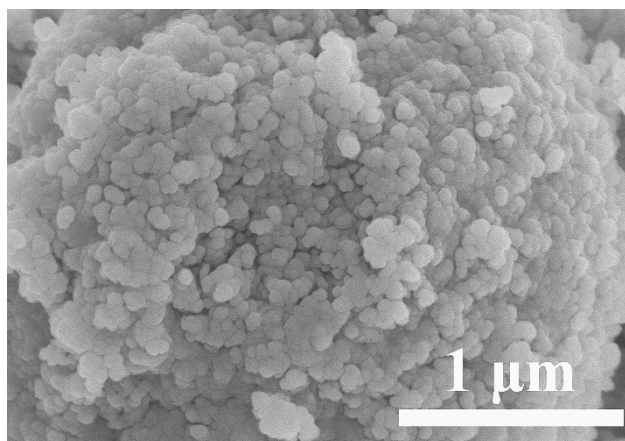


Fig. S3. SEM images of the TS-5CTAC.

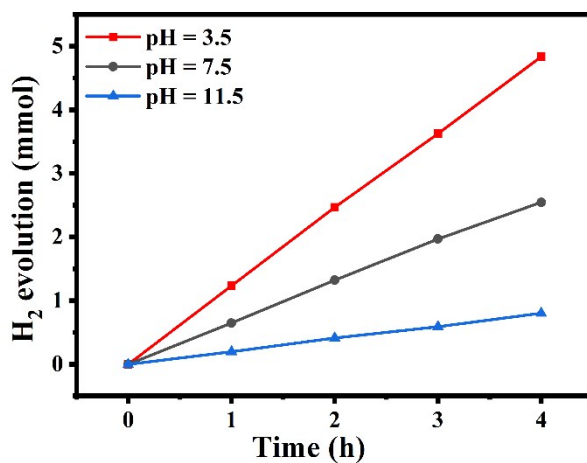


Fig. S4. The comparison of photocatalytic H₂ evolutions of TS-5CTAC sample with different pH values.

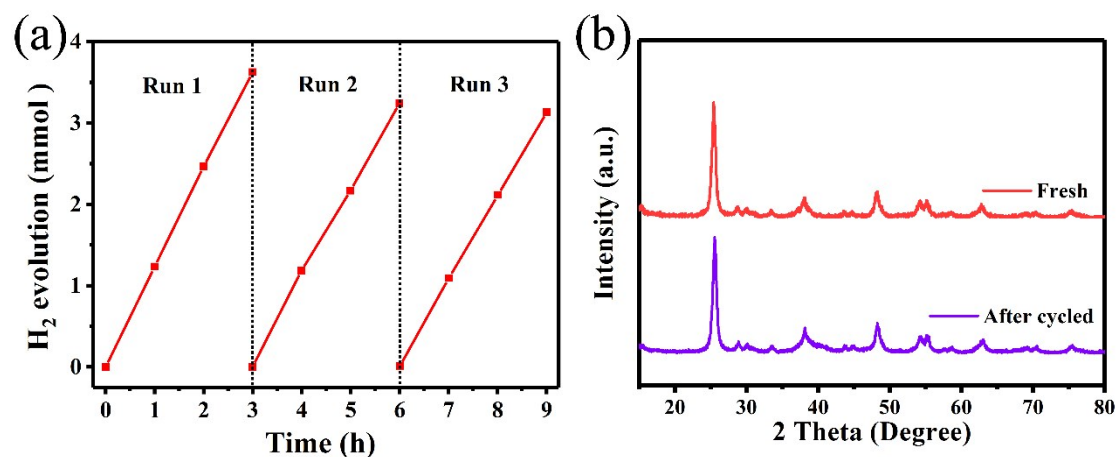


Fig. S5. (a) The durability test under continuous illumination for 9 h and (b) the comparison of XRD patterns of TS-5CTAC before and after the reaction 9 h.

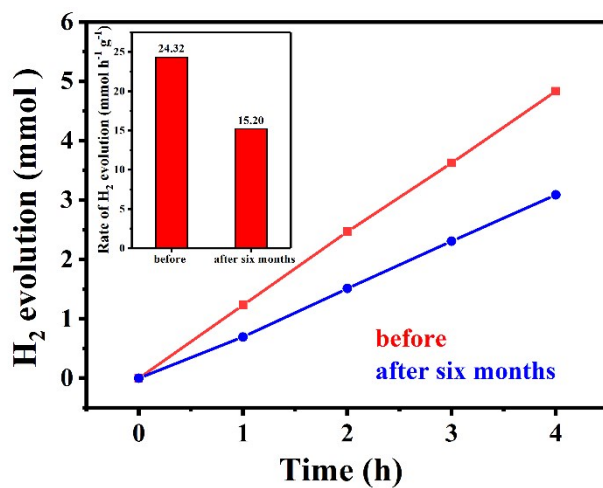


Fig. S6. The comparison of photocatalytic H₂ evolutions and photocatalytic H₂ evolution rates (inset) of TS-5CTAC before and after six months.

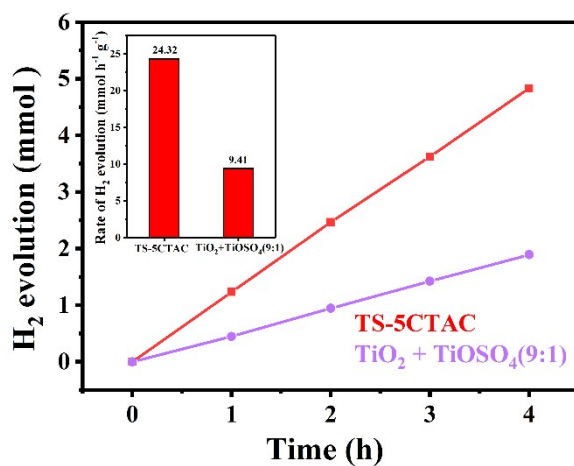


Figure S7. The comparison of photocatalytic H₂ evolutions and photocatalytic H₂ evolution rates (inset) of TS-5CTAC and the physical mixture of TiO₂ and TiOSO₄ (9:1).

Table S2. S content of TS-5CTAC in fresh, 1st and 3rd cycle

TS-5CTAC Sample	S content (%)
Fresh	2.022
1st cycle	1.351
3rd cycle	0.221

Table S3. Photocatalytic H₂ production of different catalysts.

Catalysts	Amount of catalysts (mg)	H ₂ evolution (mmol h ⁻¹ g ⁻¹)	Light source Wavelength (nm)	Reference
TiO ₂ (B)/anatase	20	5.01	300 W Xe lamp simulated sunlight	²
Sulfate anchored N-TiO ₂	50	5.08	125 W Hg lamp (> 400 nm)	³
Au/S, N-TiO ₂	50	5.35	125 W Hg lamp (> 400 nm)	⁴
Pt/Cu/TiO ₂	14	27.20	300 W Xe lamp (350–400 nm)	⁵
Ag/N-TiO ₂	20	4.70	300 W Xe lamp simulated sunlight	⁶
Au/SrTiO ₃ /TiO ₂	100	0.47	300 W Xe lamp simulated sunlight	⁷
SO ₄ ²⁻ -TiO ₂	50	24.32	300 W Xe lamp simulated sunlight	This work

References

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