

**Anchoring RuS<sub>2</sub> on multi-shelled hollow cube CaTiO<sub>3</sub> for ultrahigh hydrogen evolution with the assistance of a photocatalytic biorefinery**

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## Chemicals

Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (99.0%), tetrabutyl titanate (99.0%), NaOH (99.0%), Ruthenium trichloride (RuCl<sub>3</sub>, 45.0 ~ 55.0%), thiourea (99.0%), potassium hydroxide (KOH, 99.0%), Hydrochloric acid (99.0%), Tryptophan (Trp, 99.0%), potassium iodide (KI, 99.0%), benzoquinone (BQ, 99.0%), isopropyl (IPA, 99.0%), rhamnose (98.0%), xylose (98.0%), xylan (85.0%), arabinose (98.0%), mannose (98.0%), fructose (98.0%) and glucose (98.0%) were acquired from Aladdin Chemistry Co., Ltd (Shanghai, China). Lactic acid (99.0%), formic acid (99.0%) and other chemicals were purchased from Dalian Chemical Reagent Factory, China. All the reagents were used as received without further purification.

## Characterization

Transmission electron microscopy (TEM) were recorded on JEM-2100 CXII and scanning electron microscopy (SEM) were explored on Hitachi-4800. The powder X-ray diffraction (XRD) patterns were measured with a Bruker D8 Focus diffractometer (CuK $\alpha$  radiation,  $\lambda = 0.15418$  nm) in the  $\theta$ - $2\theta$  mode. Brunauer-Emmett-Teller (BET) specific surface areas were measured on a Micromeritics ASAP 2020 apparatus. The X-ray photoelectron spectroscopy (XPS) analysis was performed with a Kratos Axis Ultra DLD spectrometer employing an amonochromated AlK $\alpha$  X-ray source (1486.6 eV). The ultraviolet-visible diffuse reflectance spectrum (UV-vis DRS) was achieved on a Cary 5000 spectrophotometer by using BaSO<sub>4</sub> as the reference. The photoluminescence (PL) spectrum was measured by an Edinburgh FLS-920 spectrometer. Electron spin-resonance spectroscopy was used to study

molecules and materials with unpaired electrons, and the 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) was chosen as a spin trap for the detection of hydroxyl radical ( $\cdot\text{OH}$ ) and superoxide ( $\cdot\text{O}_2^-$ ), the 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) was applied to characterize electrons and holes, while the amino-2,2,6,6-tetramethylpiperidine (TEMPONE) was used to detect singlet oxygen. Ultraviolet photoelectron spectroscopy (UPS) was measured by using a He I (21.20 eV) as monochromatic discharge light source and a VG Scienta R4000 analyzer. A sample bias of -5 V was applied to observe the secondary electron cutoff (SEC).

## **Photoelectrochemical Measurements**

Electrochemical measurements were carried out on a CHI760E electrochemical workstation with a standard three-electrodes system. Among them, a Pt wire was used as the counter electrode, and the reference electrode was the saturated Ag/AgCl. The cleaned F-doped tin oxide (FTO) glass was used as the working electrode. 5 mg of corresponding photocatalyst and 20  $\mu\text{L}$  of Nafion (5%) were added into 980  $\mu\text{L}$  of ethanol to form a homogeneous slurry. The homogeneous slurry was ultrasonicated for 30 min and then coated on the FTO glass. The obtained system was dried at 150  $^\circ\text{C}$  for 60 min. The supporting electrolyte was  $\text{Na}_2\text{SO}_4$  solution (0.5 M) with the pH value of 6.8. The incident visible light source was Xe lamp (300 W). The photocurrent-time was investigated in the irradiation of Xe lamp at a bias potential of 0.5 V vs. Ag/AgCl. The electrochemical impedance spectroscopy (EIS) was detected by an AC voltage amplitude of 10 mV at -0.3 V versus Ag/AgCl over the frequency range from 10 kHz to 0.01 Hz. The Mott-Schottky was studied in the electrolyte of

Na<sub>2</sub>SO<sub>4</sub> (0.5 M), and the frequency of the AC potential was set as 500, 800, and 1000 Hz as well as the amplitude was 10 mV.

## **Products Analysis**

The photocatalytic performance was measured with the Perfectlight PCX 50C multi-channel photochemical reaction system under the illumination of 10 W LED lamps.

### **Hydrogen:**

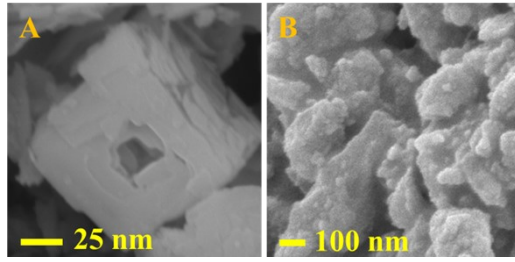
The yield of hydrogen was analyzed by gas chromatography (GC-7900, Ar carrier gas, molecular sieve 5 Å column) equipped with a thermal conductivity detector (TCD).

### **Products of Oxidation Half-reaction:**

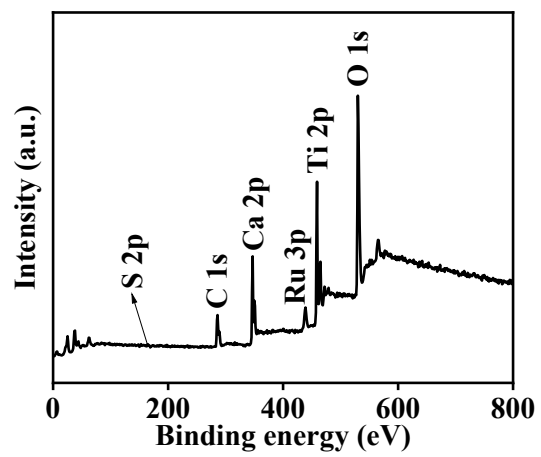
After the reaction, the samples were filtrated with a Millipore filter (0.22 μm) and analyzed by high-performance liquid chromatography (HPLC) with a Bio-Rad Aminex HPX-87H column (300 mm × 7.8 mm × 9 μm). Concentrations of lactic acid was measured by Waters 2414 RI detector. The mobile phase was 5 mmol H<sub>2</sub>SO<sub>4</sub> at a flow rate of 0.5 mL/min. The temperature of column was set at 55 °C and the total time to finish the product analysis was set at 30 min. The conversion and yields of oxidation half-reaction products were calculated as follows:

$$\text{Conversion (\%)} = \frac{\text{Moles of carbon in feedstock consumed}}{\text{Moles of carbon in feedstock input}} \times 100\%$$

$$\text{Product yield (\%)} = \frac{\text{Moles of carbon in organic acid}}{\text{Moles of carbon in feedstock input}} \times 100\%$$



**Fig. S1** SEM images of CaTiO<sub>3</sub> (A) and RuS<sub>2</sub> (B).



**Fig. S2** XPS survey spectra of RuS<sub>2</sub>@CaTiO<sub>3</sub>-10.

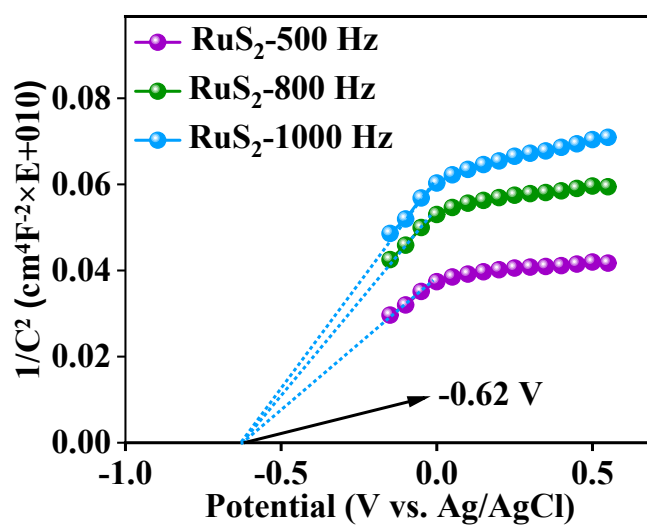
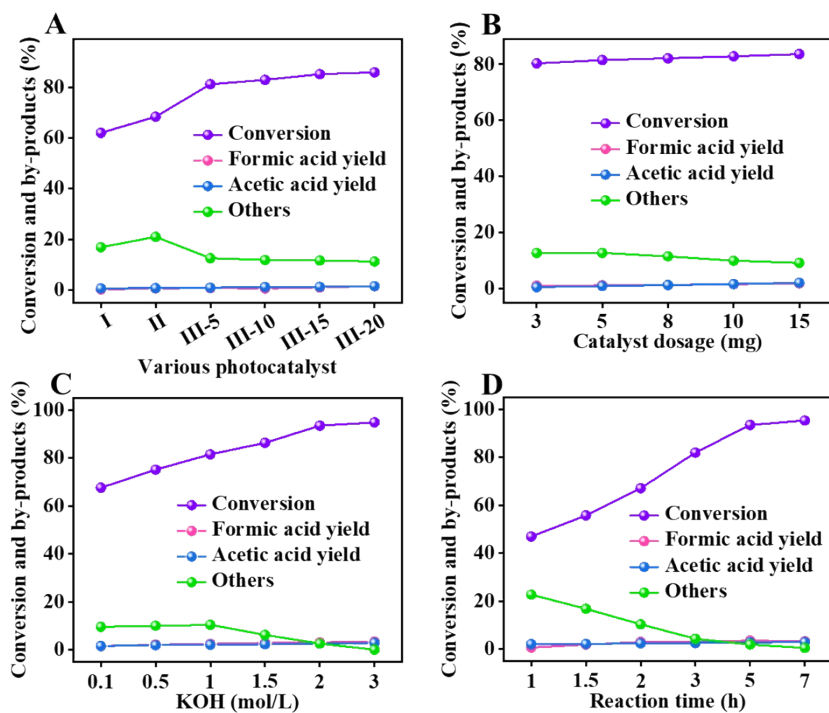
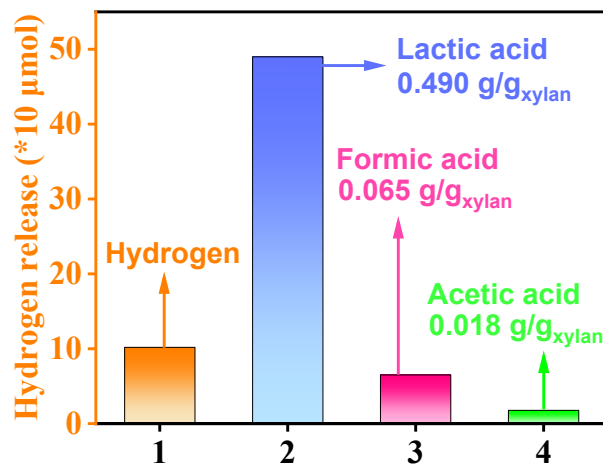


Fig. S3 Mott-Schottky plots of RuS<sub>2</sub>.

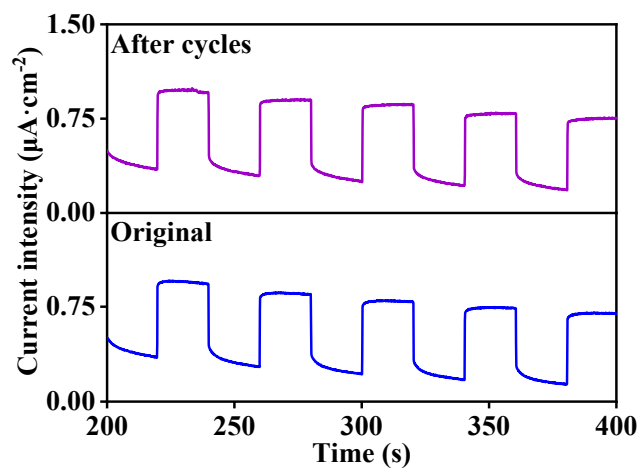


**Fig. S4** The effect of different different photocatalysts (I:  $\text{CaTiO}_3$ , II:  $\text{RuS}_2$ , III:  $\text{RuS}_2@\text{CaTiO}_3$ ) (A), catalyst dosage (B), KOH concentrations (C) and irradiation time (D) on the xylose conversion and the yields of by-products (formic acid and acetic acid).





**Fig. S5** When xylan as substance for photocatalytic synthesis of value-added chemicals and hydrogen via RuS<sub>2</sub>@CaTiO<sub>3</sub>-10.



**Fig. S6** transient photocurrent response of before and after cycles.

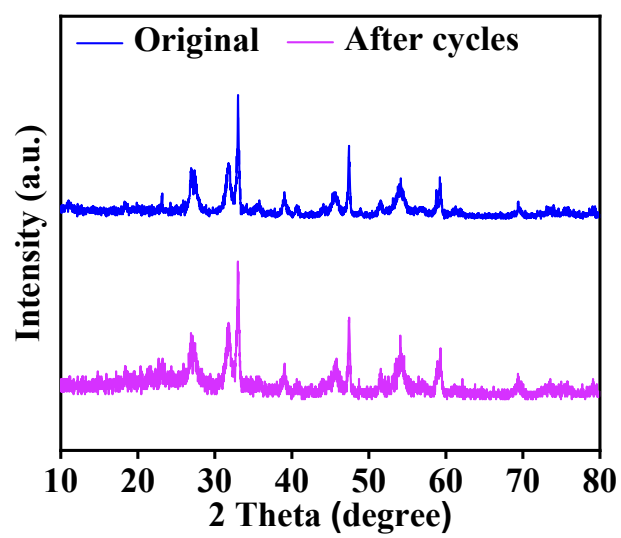
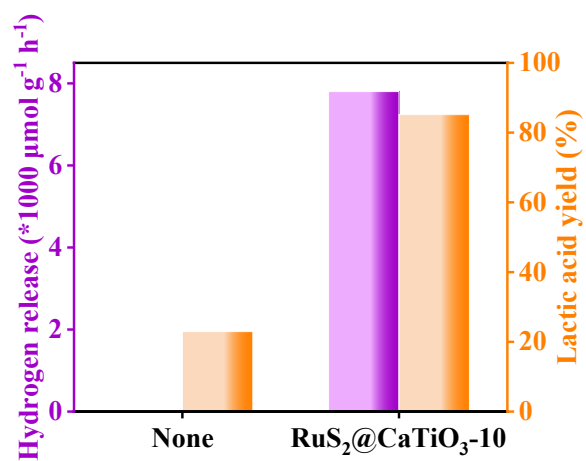
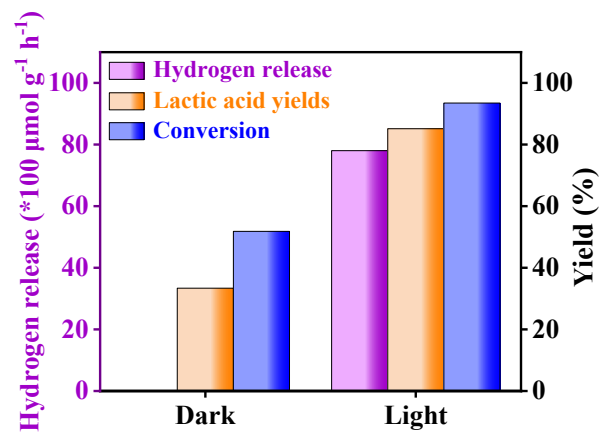


Fig. S7 XRD of before and after cycles.



**Fig. S8** The effects of RuS<sub>2</sub>@CaTiO<sub>3</sub>-10 on co-production of hydrogen and lactic acid.



**Fig. S9** The effects of illumination on co-produced of hydrogen and lactic acid.

**Table S1.** The effects of different CaTiO<sub>3</sub> based photocatalysts on the hydrogen evolution.

Entry	Photocatalysts	Catalyst Dosage (mg)	Sacrificial Agents	Light Source	Hydrogen Release (mmol g <sup>-1</sup> h <sup>-1</sup> )	Ref.
1	CdSe/CaTiO <sub>3</sub>	25	NaS <sub>2</sub> , Na <sub>2</sub> SO <sub>3</sub>	300 W Xe lamp	3.014	[1]
2	g-C <sub>3</sub> N <sub>4</sub> /CaTiO <sub>3</sub>	50	methanol	300 W Xe lamp	0.189	[2]
3	MoS <sub>2</sub> /CaTiO <sub>3</sub>	50	vitamin C (VC)	300 W LED lamp	0.622	[3]
4	Bi <sub>12</sub> O <sub>17</sub> Cl <sub>2</sub> /CaTiO <sub>3</sub>	50	vitamin C (VC)	300 W Xe lamp	0.784	[4]
5	Ca <sub>0.94</sub> Ag <sub>0.03</sub> La <sub>0.03</sub> TiO <sub>3</sub>	50	TEOA	300 W Xe lamp	1.064	[5]
6	CaTiO <sub>3</sub> /Cu	20	methanol	500 W Xe lamp	0.251	[6]
7	AgCl/Ag/CaTiO <sub>3</sub>	50	methanol	300 W Xe lamp	0.227	[7]
8	RuS <sub>2</sub> @CaTiO <sub>3</sub> -10	5	xylose	10 W visible light	7.939	This work

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