RuS₂@CN-x with exposed (200) facet as a high-performance photocatalyst for selective C-C bond cleavage of biomass coupling with H-O bond cleavage of water for co-produce chemical and H₂

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Chemicals

Ruthenium trichloride (RuCl₃, 45.0 ~ 55.0%), melamine (99.0%), thiourea (99.0%) and potassium hydroxide (KOH, 99.0%) were provided by Macklin biochemical Co., Ltd (Shanghai, China). 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) was recorded on JEM-2100 CXII and scanning electron microscopy (SEM) was explored on Hitachis-4800. The powder Xray diffraction (XRD) patterns were measured with a Bruker D8 Focus diffractometer (CuK α radiation, $\lambda = 0.15418$ nm) in the θ -2 θ 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 AlKR X-ray source (1486.6 eV). The ultraviolet-visible diffuse reflectance spectrum (UV-vis DRS) was achieved on a Cary 5000 spectrophotometer by using BaSO₄ 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 OH) and superoxide (\cdot O₂ \cdot), the 2,2,6,6-tetramethylpiperidine-1-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 stand 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 μ L of Nafion (5%) were added into 980 μ 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 °C for 60 min. The supporting electrolyte was Na₂SO₄ 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 Na₂SO₄ (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 μ m) and analyzed by high-performance liquid chromatography (HPLC) with a Bio-Rad Aminex HPX-87H column (300 mm × 7.8 mm × 9 μ m). Concentrations of lactic acid was measured by Waters 2414 RI detector. The mobile phase was 5 mmol H₂SO₄ 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:

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

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

Computational Details

All of the mode structures were computed with the DMol³ program in Materials Studio 7.0 software package [1]. To describe electron exchange interaction, the generalized gradient approximation (GGA) was selected and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [2]. For Ru elements, the core electrons were replaced by the density functional semicore pseudopotential (DSPP) [3], and H, C and O were treated as in the all-electron case. The double numerical plus polarization (DNP) basis set was adopted for the valence electron wave function of atoms [4]. The total energy was converged to be less than 1.0×10^{-4} hartree, while the forces imposed on each atoms were converged to be less than 0.02 hartree Å⁻¹ and the displacement convergence was less than 0.05 Å. The vacuum region was set to 15 Å to separate the slabs in the direction perpendicular to the surface.



Fig. S1 SEM images of CN (A) and RuS_2 (B).



Fig. S2 TEM image of RuS₂@CN-2.



Fig. S3 XPS survey spectra of $RuS_2@CN-2$.



Fig. S4 UV-vis DRS of CN, $RuS_2@CN-0.5$, $RuS_2@CN-1$, $RuS_2@CN-2$ and $RuS_2@CN-3$.



Fig. S5 Relative band alignment of CN and RuS₂@CN-2.



Fig. S6 The effect of different RuCl₃ content photocatalyst (A), catalyst dosage (B), KOH concentrations (C) and irradiation time (D) on the conversion of xylose and the yields of by-products (formic acid and acetic acid).



Fig. S7 When xylan as substance for photocatalytic synthesis of value-added chemicals and hydrogen via $RuS_2@CN-2$.

Entry	Photocatalysts	Catalyst Dosage (mg)	Sacrificial Agent	Light Source	Hydrogen Release (mmol g ⁻¹ h ⁻¹)	Ref.
1	15%ReS ₂ @CN	20	TEOA	300 W Xe lamp	3.46	[5]
2	CuInS ₂ /g-C ₃ N ₄	50	NaS ₂ , NaSO ₄	300 W Xe lamp	1.29	[6]
3	NV-g-C ₃ N ₄	20	TEOA	3 W LED lamp	0.171	[7]
4	g-C ₃ N ₄ /OLC	25	TEOA	300 W Xe lamp	3.086	[8]
5	PC-CN	50	TEOA	300 W Xe lamp	1.01	[9]
6	g-C ₃ N ₄ / UFR-NC	50	TEOA	300 W Xe lamp	1.686	[10]
7	Co/P/CN-sc	20	TEOA	300 W Xe lamp	0.35	[11]
8	GD/g-C ₃ N ₄	50	TEOA	350 W Xe lamp	0.792	[12]
9	Cd/Mo(0.38)- VC	40	Lactic acid	300 W Xe lamp	2.267	[13]
10	CdS/FePc	10	Lactic acid	300 W Xe lamp	7.301	[14]
11	RuS ₂ @CN-2	50	Arabinose	10 W visible light	8.698	This work

 Table S1. Photocatalytic water splitting to hydrogen.

Entry	Photocatalysts	Catalyst Dosage (mg)	Sacrificial Agent	Light Source	Hydrogen Release (mmol g ⁻¹ h ⁻¹)	Oxidation products and selectivity	Ref.
1	Zn _{0.5} Cd _{0.5} S-P	1	5- hydroxymethylf urfural (HMF)	White LED light	0.786	2,5- diformylfuran (DFF) 65%	[15]
2	Ni/CdS	10	Furfural alcohol	450 nm LED Lamp	2.006	Furfural 92.6%	[16]
3	Co ₉ S ₈ /CdS	5	Benzyl alcohol (BA)	LED lamp (450 nm)	4.316	Benzaldehyde (BAD) > 99.9%	[17]
4	Pt _{0.21} -C ₃ N ₄	10	Glucose	40 W LED lamp	3.39	Lactic acid 86%	[18]
5	Zn _{0.6} Cd _{0.4} S	10	Glucose	300 W Xe lamp	0.718	Lactic acid 87%	[19]
6	RuS ₂ @CN-2	50	Arabinose	10 W visible light	8.698	Lactic acid 91.5%	This work

 Table S2. Photocatalytic water splitting coupling with sacrificial agents oxidation.

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