Electronic Supplementary Information

Hydrogen-treated mesoporous WO_3 as a reduction agent of CO_2 to fuels (CH_4 and CH_3OH) with enhanced photo-thermal catalytic performances

S1

Experimental details

Materials

All the chemical reagents were analytical grade and used without further purification. Deionized water was used in all experiments. N-butanol, tetraethyl orthosilicate (TEOS, $\geqslant$ 99.0%), commercial WO_3 (com-WO_3), silicotungstic acid ($H_4Si_4W_{12}O_4$), hydrochloric acid (HCl, 35%), and Hydrofluoric acid (HF, 40%) were purchased from Sinopharm Chemical Reagent Company. Ltd. Pluronic P-123 ($EO_{20}PO_{70}EO_{20}$) was purchased from Sigma-Aldrich and its average molecular weight (MW) is 5800.

Synthesis of hydrogen-treated mesoporous WO_3

KIT-6 mesoporous silica was synthesized at hydrothermal treatment temperature (120◦C) following a literature procedure.[1] KIT-6 (SiO_2): In a typical experiment, P123 (3g) was dissolved in distilled H_2O (110g) and concentrated HCl (35%) (6g). The solution was stirred for 3h at 35°C and butanol (3g) was added under stirring for another hour. TEOS (6.25g) was finally added and stirred for 24h at the same temperature. The suspension was transferred into an 80 mL Teflon-lined stainless steel autoclave and then placed in an oven at 120°C for 24h. The resulting white powders were collected by filtration, washing, drying at room temperature in air, and calcination at 550°C for 5h (1°C/min). The KIT-6 template was designated as KIT-6-120.

Hydrogen-treated mesoporous WO_3 was prepared according to the following procedures.[2] Silica KIT-6 (0.2g) was dissolved in ethanol with $H_4Si_4W_{12}O_{40}$ (0.6g). After the impregnation, samples were dried and calcined at 350°C for 4 h in air, dried at room temperature in air and calcined at 550°C for 5h. The obtained m-WO_3 powders were treated in pure H_2 (99.999%) flow of 60 mL min^{-1} for 0.5 h under 250◦C, 350◦C, 450◦C and 550◦C. Finally the mesoporous silica was removed with HF. The mesoporous catalyst was separated by centrifugation, washed sequentially with water, ethanol and dried at room temperature. Respectively, the obtained samples were denoted as m-WO_3-H250, m-WO_3-H350, m-WO_3-H450 and m-WO_3-H550, so as to distinguish from the m-WO_3 and com -WO_3.

Characterization

The morphology of the samples was examined using a field emission scanning electron microscope (FESEM, Hitachi S-4800, Japan). The TEM and HRTEM images were obtained by transmission electron microscope (TEM, JEOL-2100F, Japan) equipped with a field emission source at an accelerating voltage of 200 kV. XRD patterns were measured on a powder X-ray diffractometer (PANalytical X'Pert) using Cu Ka radiation (λ=0.154nm) radiation with a nickel filter operating at 40 kV and 40 mA in the 2 range between 0.5◦ and 90◦. The composition of the samples was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo XPS ESCALAB 250Xi, Al Ka radiation (1486.8 eV)). The binding energies were calibrated to the signal for adventitious C1s at 284.8 eV as an internal standard. The nitrogen adsorption/desorption isotherm measurement was carried out at -196◦C by using an automated gas sorption analyzer (Micromeritics, ASAP2020, USA) after having degassed the sample for 10h at 150 ◦C. The specific area was calculated by the Brunauer-Emmett-Teller (BET) method in the P/P_0 range 0.05-0.5. The pore-size distribution was calculated on the desorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) model. UV-visible diffuse reflectance spectra (DRS) of the samples were recorded by using a UV-vis-NIR spectrophotometer (UV-3600; SHIMADZU) with the integration sphere diffuse reflectance attachment. The band gap energy (Eg) of the material was calculated from the absorption data by using the Tauc relation. Raman spectra were collected in the anti-Stokes range of 200-1200 cm^{-1} using a Jobin-Yvon T6400 triple-stage spectro graph source with the spectral resolution of 4 cm^{-1}.

The band gap energy (Eg) of the material was calculated from the absorption data by using the Tauc relation.[3]

$$(\alpha h\nu) = C(h\nu - Eg)^n \qquad (1)$$

Where C is a constant, α is molar extinction coefficient, Eg is the average band gap of the material and n depends on the type of transition. For n = 1/2, Eg in equation (1) is indirect allowed band gap. n=2, Eg in equation (1) is direct allowed band gap. The band gap of WO_3 is the indirect band gap edge absorption.

Activity tests

The catalytic experiment was carried out in a gas-closed circulation system. The volume of the reaction system was about 120 mL. 0.05g of the tested catalyst was put in a glass reactor. The reaction setup was vacuum-treated several times, and the high purity CO_2 (≥99.999%) was flown through the whole system for 5 min to ensure complete from the system and the maximum adsorption of CO_2 molecules onto the active sites of the catalyst water vapor mixture into the reactor that has a quartz window at constant temperature. A positive pressure of CO_2 was maintained at 25 kPa inside the system. The catalytic activity evaluation was performed at 250◦C, which kept through the heating jacket in out of the reactor and the temperature control device. A 300 W Xe lamp (PLS-SXE300, Beijing Zhongjiaojinyuan Technology Co, Ltd) with a UV-light filter (λ >420 nm) was employed as the light source, which was kept 8-10 cm away from the upper surface of the catalyst. The total light intensity ranging from 420 nm to 780 nm on the surface of quartz window was detected to be 320 mW/cm^2 by an irradiato-meter at the central point. Taking samples per hour and qualitatively analyzed by GS-Tek (Echromtek A90) equipped with a capillary column (HP-PLOTQ), using Pure N_2 (99.999%) as carrier gas. The quantification of CH_4 and CH_3OH products was based on the external standard and the use of calibration curve.
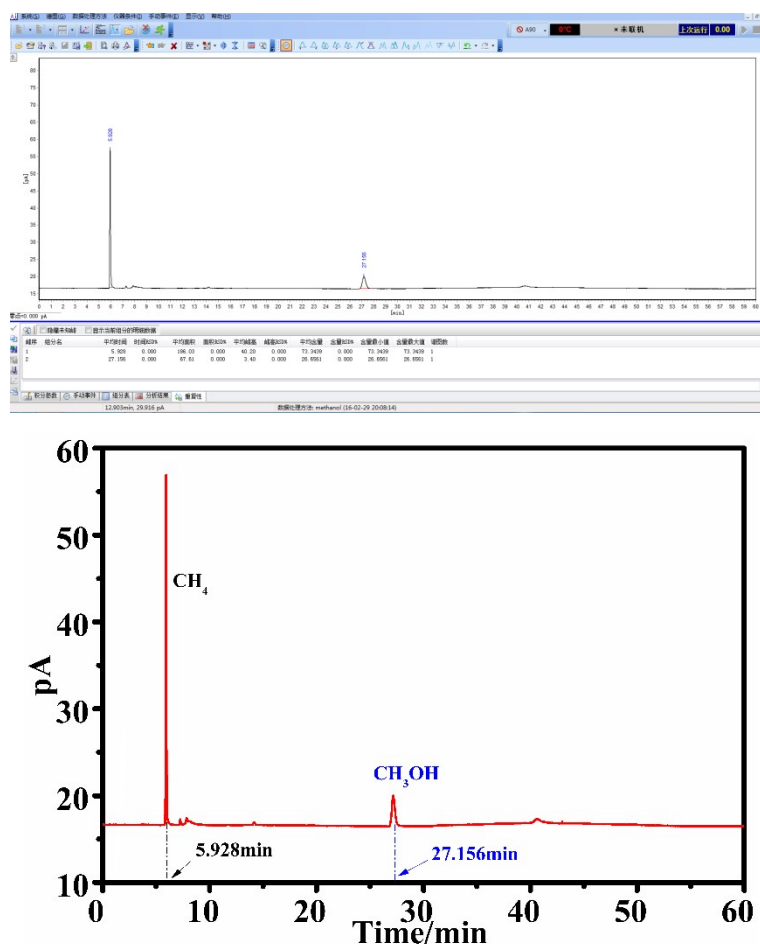
S2 Original GC data

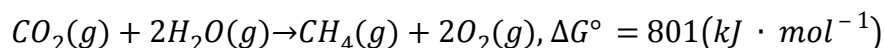Figure S1. The original GC data of H250 under photo-thermal condition for 5 h

S3 Energy efficiency discussion

A 300 W high-pressure Xe lamp (CEL-HXUV300, spectral output 420-760nm, overall radiant output 50 W) was used as the light source and the distance from a point source of light to the catalyst surface is 10 cm. The power of incident light was obtained by a CEL-NP2000 (Beijing CEAULight, China). Solar-to-Methane (or Methanol) (STM) energy conversion efficiency was estimated using the following equation:
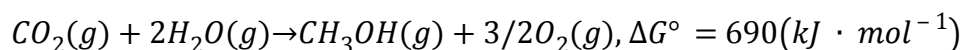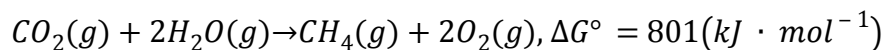
$$STM\ efficiency\ (\%) = \frac{Methane\ (mol)(Or\ Methanol(mol)) \times \Delta G° \ (kJ \cdot mol^{-1})}{P_{total}(mW \cdot cm^{-2}) \times Electrode\ erea\ (cm^2)}$$

Where $\Delta G°$ is the Gibbs free energy for conversion of gaseous CO_2 to Methane (or Methanol) (801kJ·mol^{-1}, 690kJ·mol^{-1}), Electrode erea (4cm^2) and P_{total} is the power of incident light (145 mW·cm^{-2}). $\Delta G°$ was estimated based on the following chemical reaction:

(1)Photo-catalytic:

$$CO_2(g) + 2H_2O(g) \rightarrow CH_4(g) + 2O_2(g), \Delta G° = 801(kJ \cdot mol^{-1})$$

(2)Photo and thermal coupling:

$$CO_2(g) + 2H_2O(g) \rightarrow CH_4(g) + 2O_2(g), \Delta G° = 801(kJ \cdot mol^{-1})$$

$$CO_2(g) + 2H_2O(g) \rightarrow CH_3OH(g) + 3/2O_2(g), \Delta G° = 690(kJ \cdot mol^{-1})$$

For example: CO_2: $V_{(input)}$=150ml, n=150ml/22.4mol=6696.4285umol;

Catalyst: m=50mg, n=0.05g/231.85 (g/mol) =215.6566uoml.

The quantification of CH_4 yield was based on the external standard and the use of calibration curve. The average area of CH_4 (100%) is 756900 (V=0.1ml), the average area of CH_3OH (100%) is 13093**(V=0.1ul*(1ml/11ml)/1000(ml), 1ml of methanol and mixed 10ml H$_2$O extracting the mixture 0.1ul)**. At the same conditions, the average area of CH_4 evolved from m-WO$_3$-H550 is 30 under photo-catalytic conditions after 12h, the average area of CH_4 evolved from m-WO$_3$-H550 is 248.95 under photo- thermal coupling after 12h **(Every time, the volume of taking samples injected into the system is V=0.5ml (The volume of gas is mingle gas volume.))**. The total volume of CH_4 (100%) evolved from m-WO$_3$-H550 is 1.17ul under photo-catalytic conditions through mathematical computation. The total volume of CH_4

(100%) evolved from m-WO$_3$-H550 is 9.75ul under photo-thermal coupling through mathematical computation. The total volume of CH$_3$OH (100%) evolved from m-WO$_3$-H550 is 0.06ul under photo-thermal coupling through mathematical computation.

The total amount of CH$_4$ evolved from m-WO$_3$-H550 after 12h irradiation is 0.1561 μmolg^{-1} under photo-catalytic conditions (CH$_3$OH was the not detected by GC under photo-catalytic conditions). The total amount of CH$_4$, CH$_3$OH evolved from m-WO$_3$-H550 after 12h irradiation is 25.7724 μmolg^{-1}, 2.561μmolg^{-1} under photo- thermal coupling.

(1) photo-catalytic conditions:

Yield (Moles of product (CH$_4$) per 100 moles of carbon dioxide) =
$$1.17ul/22.4/6696.4285*100=0.078\%$$

TON (Turnover number = number of moles of product per mol of catalyst precursor.)=1.17ul/22.4/215.6566uoml=0.0002

(2) photo- thermal coupling:

Yield (Moles of product (CH$_4$ or CH$_3$OH) per 100 moles of carbon dioxide) = (9.75ul+0.06ul)/22.4/6696.4285*100=0.654%

TON (Turnover number = number of moles of product per mol of catalyst precursor.)= (9.75ul+0.06ul)/22.4/215.6566uoml=0.002

Sample	CH$_4$			
	Photo-catalytic			
	Yield[a] (%)	TON[b]	STM efficiency (%)	Selectivity (%)
com-WO$_3$	0.018	0.00	0.0015	100
m-WO$_3$	0.031	0.00623	0.0028	100
m-WO$_3$-H250	0.034	0.0005	0.0037	100
m-WO$_3$-H350	0.050	0.0008	0.0042	100
m-WO$_3$-H450	0.066	0.0015	0.0045	100
m-WO$_3$-H550	0.078	0.0020	0.0049	100

[a]Moles of product (CH$_4$ or CH$_3$OH) per 100 moles of carbon dioxide
[b]Turnover number = number of moles of product per mol of catalyst precursor.

Sample	CH$_4$		CH$_3$OH		Yield[a]	TON[b]
	Photo and thermal coupling:					
	STM efficiency (%)	Selectivity (%)	STM efficiency (%)	Selectivity (%)		
com-WO$_3$	0.03	43.67	0.03	56.33	0.081	0.0006
m-WO$_3$	0.09	54.73	0.06	45.27	0.101	0.0008
m-WO$_3$-H250	0.18	39.86	0.24	60.14	0.189	0.0009
m-WO$_3$-H350	0.45	64.17	0.21	35.83	0.304	0.0014
m-WO$_3$-H450	0.65	75.82	0.17	24.18	0.426	0.0017
m-WO$_3$-H550	0.82	90.96	0.07	9.04	0.654	0.0020

References

1   J. H. Wang, Y. Li, Z. S. Zhang and Z. P. Hao, *J. Mater. Chem. A*, 2015, **3**, 8650.
2   X. Z. Cui, J. L. Shi, H. R. Chen, L. X. Zhang and L. M. Guo, *J. Phys. Chem. B*, 2008, **112**, 12024.
3   J. Tauc, A. Menth, *J. Non-Cryst. Solids.*, 1972, **569**, 8-10