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Supporting Information

Light-driven Conversion of Greenhouse Gases over Plasmonic Metal-carbide Nanocomposites

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Contents

Synthetic procedures

Reagents used for the synthesis: Anhydrous Cobalt (11) Chloride ($CoCl_2$, Aldrich, > 98.0%), anhydrous Tantalum pentachloride ($TaCl_5$, STREM, resublimed 99.99+%-Ta PURATREM), Diethylene glycol dimethyl ether (anhydrous, 99.5%, Aldrich), $LiBH(C2H_5)_3$ (super-hydride, 1M in THF, Aldrich), Hexane (anhydrous, 95%, Aldrich) and acetonitrile (99.8%, Aldrich).

Synthesis of Co@TaC Nanocomposites: Co@TaC nanocomposites was synthesized by co-reduction of metal precursors in Diethylene glycol dimethyl ether (diglyme). 100 mg of $CoCl_2$ and 100mg of $TaCl_5$ were weighed in a 50 mL round bottom flask and 30 ml of diglyme was then added to the vessel, stirred the mixture for 20 min. to dissolve the reactants. Super-hydride (3.3 mL) was then added to the reaction mixture, allowed to stir for 15 min., heated the reaction mixture at 200°C in an oil bath for 3h under an argon pressure of 0.5 MPa, cooled to room temperature. The product was then transferred to a centrifuge tube under argon atmosphere. The precipitate was separated from diglyme by centrifuging at 12000 rpm for 10 min. The product was washed several times with hexane and acetonitrile to remove the by-products. The product was dried under vacuum for 1 h. The as prepared product was annealed at 900°C for 15 h under vacuum. All the above steps were performed under complete inert conditions.[1]

Synthesis of Cobalt (Co) Metal: Cobalt acetate ($Co(CH_3COO)_2$ (200 mg) powder was directly annealed under Argon+ Hydrogen (5%) atmosphere at 600°C for 4h. Along with Co metal, minute amount of oxide impurity was also obtained.

Synthesis of 2.5 Wt% Co/Al_2O_3: Cobalt nitrate hexa hydrate (12.5 mg $Co(NO_3)_2.$ $6H_2O$ Aldrich) was dissolved in 20 mL ethanol and stirred at room temperature. To the clear pink solution added $100mg\ \gamma$- Al_2O_3 nano powder (Aldrich) and stirring continued for 4 h. This turbid solution was allowed to heat slowly at 80°C on a hot plate. The dry powder was further heated at 100°C for 6h and annealed under Argon+ Hydrogen ($Ar+H_2$ (5%)) atmosphere at 600°C for 4h.[2]

Characterization

Powder X-ray diffractometry (*p*XRD): The *p*XRD measurements were performed using Cu *Kα* radiation (λ =0.15418 nm; X'Pert Powder Diffractometer, Panalytical) with an increment of 0.02 degrees in a range of diffraction angles from 10 to 90 degrees. An obliquely finished Si crystal (non-reflection Si plate) was used as a sample holder to minimize the background.

Hard X-ray photoemission spectroscopy (HAXPES): HAXPES measurements were performed using X-rays with a photon energy of 5.95 keV, at the undulator beamline BL15XU of SPring-8, Japan. Samples for HAXPES measurements were prepared by dispersing Co@TaC sample in ethanol and 10 μl of the sample was dropped onto the Si substrate and dried under vacuum. The core-level states of the samples were examined at room temperature in UHV using a hemispherical electron energy analyser (VG SCIENTA R4000). The total energy resolution was set to 220 meV. The binding energy was referenced to the Fermi edge of an Au thin film.

Transmission electron Microscopy: We used a 200 kV transmission electron microscope (TEM and/or STEM, JEM-2100F, JEOL) equipped with two aberration correctors (CEOS GmbH) for the image- and probe-forming lens systems and an X-ray energy-dispersive spectrometer (JED-2300T, JEOL) for elemental mapping. The samples for TEM were prepared by dropping an ethanol suspension of the sample powder onto a commercial TEM grid coated with a collodion film. The sample was thoroughly dried in vacuum prior to observation. Details about EELS needed from Fujita Sensei.

UV-Visible Absorbance Measurements: The diffuse reflection spectra of catalysts were measured by UV-3600 UV-Vis-NIR spectrophotometer (SHIMADZU Co., Japan) from 220 nm to 1200 nm. Reflectance data was translated to absorbance using Kobelka-Munk method.

Catalytic performance tests

DRM reaction was conducted in a fixed-bed flow reactor under atmospheric pressure. A 0.0200 g portion of catalyst without dilution was uniformly placed on a porous alumina pan (4 mm diameter). Both TC-1000 temperature controller (S. T. Japan Inc.) and 150 W Xe lamp (Hayashi Watch Works Ltd.) were employed to provide the energy input. The light spectrum of the Xe lamp in the present study was measured by a spectro-radiometer (Ushio Ltd. USR-45) and shown below. Its integrated light intensity was 150 kWm^{-2}. Mixed synthetic gas of $CH_4/CO_2/Ar$ = 1/1/98 (volume ratio) was introduced into the reactor at a total flowrate of 10.0 mL/min (STP) using a mass-flow controller. Gas flow was passed through powder catalyst and porous alumina pan and finally exhausted to a vent, to which a micro gas chromatograph was connected (Micro GC, Inficon Ltd. 3000 Micro GC Gas Analyzer equipped with TCD (thermal conductivity detector). The micro GC can quantitatively detect effluent gas (CH_4, CO, CO_2 and H_2) every 10 minutes with a sampling volume of 1.0 μL using automatic gas injector.

Verification of the energy conversions

The light-to-chemical energy transformation efficiencies and related values were verified using reported thermodynamical data such as standard Gibbs free energy.[3] It was assumed that the greenhouse-to-synthetic gas conversion (GTS conversion) proceeded in two pathways including the dry-reforming-of-methane (DRM) pathway and the inverse-gas-shift (IGS) pathway.

DRM pathway: $CH_4 + CO_2 \Rightarrow 2CO + 2H_2$ (eq.1)

IGS pathway: $CO_2 + H_2 \Rightarrow CO + H_2O$ (eq.2).

Provided that the total turnovers of DRM and IGS are defined respectively as n^{DRM} (mol sec^{-1}) and n^{IGS} (mol sec^{-1}), the production rates of CO and H_2 are described as

n^{CO} (mol sec^{-1}) = $2 \times n^{DRM} + n^{IGS}$ (eq.3)

n^{H_2} (mol sec^{-1}) = $2 \times n^{DRM} - n^{IGS}$ (eq.4)

considering the eq.1 and eq.2.

The total gain of chemical energy via the two parallel pathways is calculated as

$\Delta G = \Delta G^{DRM} \times n^{DRM} + \Delta G^{IGS} \times n^{IGS}$ (eq.5)

where ΔG^{DRM} and ΔG^{IGS} correspond to the energy gains via the DRM pathway (eq.1) and IGS pathway (eq.2), respectively. These values are calculated as ΔG^{DRM} = +171.2 $kJmol^{-1}$ and ΔG^{IGS} = +28.4 $kJmol^{-1}$ from the reported formation Gibbs free energies for CH_4 (-50 $kJmol^{-1}$), H_2O (-229.0 $kJmol^{-1}$), CO_2 (-394.4 $kJmol^{-1}$) and CO (-137.0 $kJmol^{-}$

^{1}).[3] Summarizing the equations 3-5, the energy gain is obtained as a function of n^{CO} and $n^{H}{}_{2}$ as

$\Delta G = 57.0 \text{ x } n^{CO} + 28.6 \text{ x } n^{H}{}_{2}$ (kW) (eq.6).

As shown in Fig.3A and 3B, the average CO- and H_2 concentrations contained in the effluent gas over the Co@TaC were 594 and 84 ppm under the light illumination, which corresponded to the time range from 95 to 105 min. The average CO- and H_2 concentrations in the effluent gas decreased to 301 and 32 ppm when the light was off. The *energy yields* with or without light illumination were then calculated using the eq.6 as

$\Delta G^{(Light+Heat)} = (57.0 \text{ x } 594 + 28.6 \text{ x } 84) \text{ x } 10^{-6} \text{ x } (10 \text{ (ml min}^{-1}) \text{ x } 10^{-3} / 22.4 \text{ (l)} / 60) = 270\ (\mu W)$ (eq.7)

$\Delta G^{(Heat)} = (57.0 \text{ x } 301 + 28.6 \text{ x } 32) \text{ x } 10^{-6} \text{ x } (10 \text{ (ml min}^{-1}) \text{ x } 10^{-3} / 22.4 \text{ (l)} / 60) = 135\ (\mu W)$ (eq.8).

The energy gain that is purely attributed to the light illumination (*i.e.* the light yield) was finally obtained as

$\Delta G^{(Light)} = \Delta G^{(Light+Heat)} - \Delta G^{(Heat)} = 135\ (\mu W)$ (see the left panel of Fig.3) (eq.9).

The *energy fraction*, which is a descriptor showing how much of the total chemical energy originated from the provided light energy, is then calculated as

$\Delta G^{(Light)} / \Delta G^{(Light+Heat)} \text{ x } 100 = 50\ (\%)$ (see the right panel of Fig.3) (eq.10).

On the grounds of the same procedures from the eq.6 through 11, the light yield and energy fraction for the Co/Al_2O_3 are calculated as shown below by using these experimentally determined values: CO- and H_2 concentrations in the effluent gas under the light illumination = 2146 and 867 ppm; CO- and H_2 concentrations in the effluent gas in the dark = 2109 and 735 ppm (see Fig.S5 and S6).

$\Delta G^{(Light+Heat)} = (57.0 \text{ x } 2146 + 28.6 \text{ x } 867) \text{ x } 10^{-6} \text{ x } (10 \text{ (ml min}^{-1}) \text{ x } 10^{-3} / 22.4 / 60) = 1095\ (\mu W)$ (eq.12)

$\Delta G^{(Heat)} = (57.0 \times 2109 + 28.6 \times 735) \times 10^{-6} \times (10\ (\mathrm{ml\ min^{-1}}) \times 10^{-3} / 22.4 / 60) = 1051\ (\mu W)$ (eq.13)

$\Delta G^{(Light)} = \Delta G^{(Light+Heat)} - \Delta G^{(Heat)} = 44\ (\mu W)$ (see the left panel of Fig.3) (eq.14).

$\Delta G^{(Light)} / \Delta G^{(Light+Heat)} \times 100 = 4\ (\%)$ (see the right panel of Fig.3) (eq.15).

Table 1

	Total GHSV (h^{-1})	CH_4/CO_2 Conversions (%)	Selectivity/Yield for CO (%)	Selectivity/Yield for H_2 (%)	CH_4/CO_2 Consumption (mmol min^{-1})	H_2/CO Formation (mmol min^{-1})
Under Light	15000	1.2/8.9	78/3.9	53/0.6	0.054/0.40	0.057/0.36
In Dark	15000	1.4/4.4	58/1.7	14/0.2	0.063/0.20	0.018/0.15

Calculation method:

(1) CH_4 Conversion (%) = $CH_{4\ \mathit{converted}} / CH_{4\ \mathit{input}}$

(2) CO_2 Conversion (%) = $CO_{2\ \mathit{converted}} / CO_{2\ \mathit{input}}$

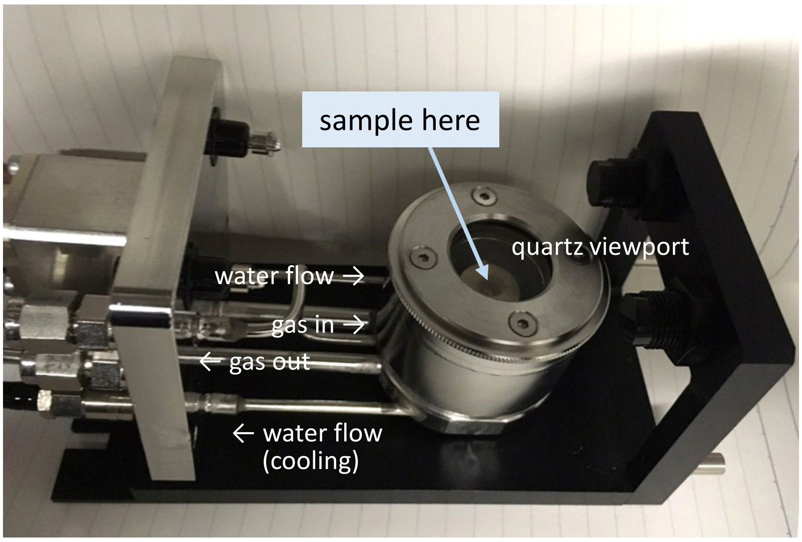
(3) CO Selectivity (%) = $CO_{\mathit{output}} / (CH_{4\ \mathit{converted}} + CO_{2\ \mathit{converted}})$

(4) CO Yield (%) = $CO_{\mathit{output}} / (CH_{4\ \mathit{input}} + CO_{2\ \mathit{input}})$

(5) H_2 Selectivity (%) = $H_{2\ \mathit{output}} / (2 \times CH_{4\ \mathit{converted}})$

(6) H_2 Yield (%) = $H_{2\ \mathit{output}} / (2 \times CH_{4\ \mathit{input}})$

(7) The Consumption and Formation concentration were calculated based on the GC area.



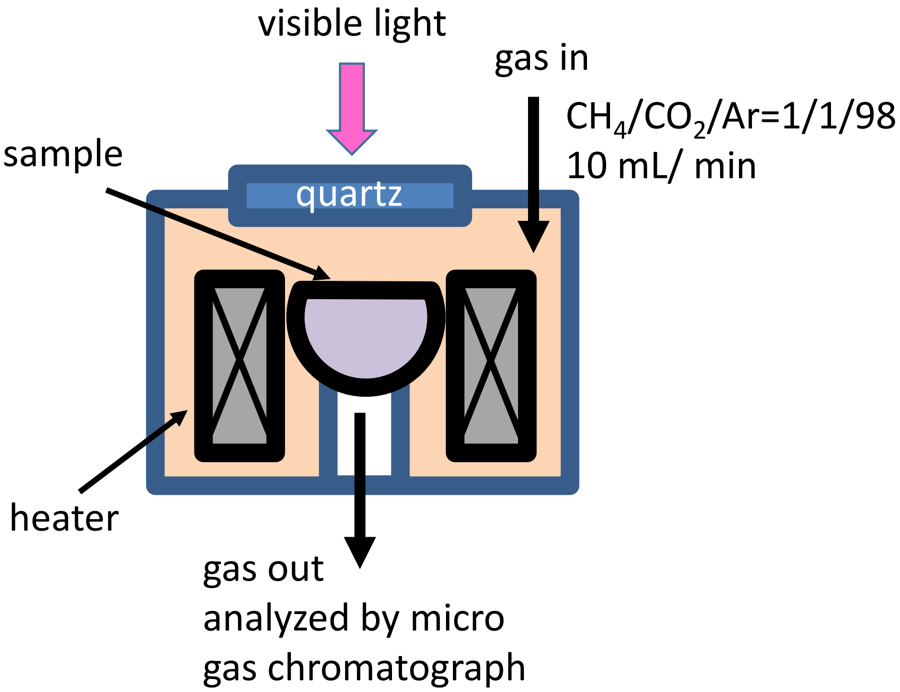


Fig.S1. Experimental setup (top) and the layout (bottom) for the catalytic tests.

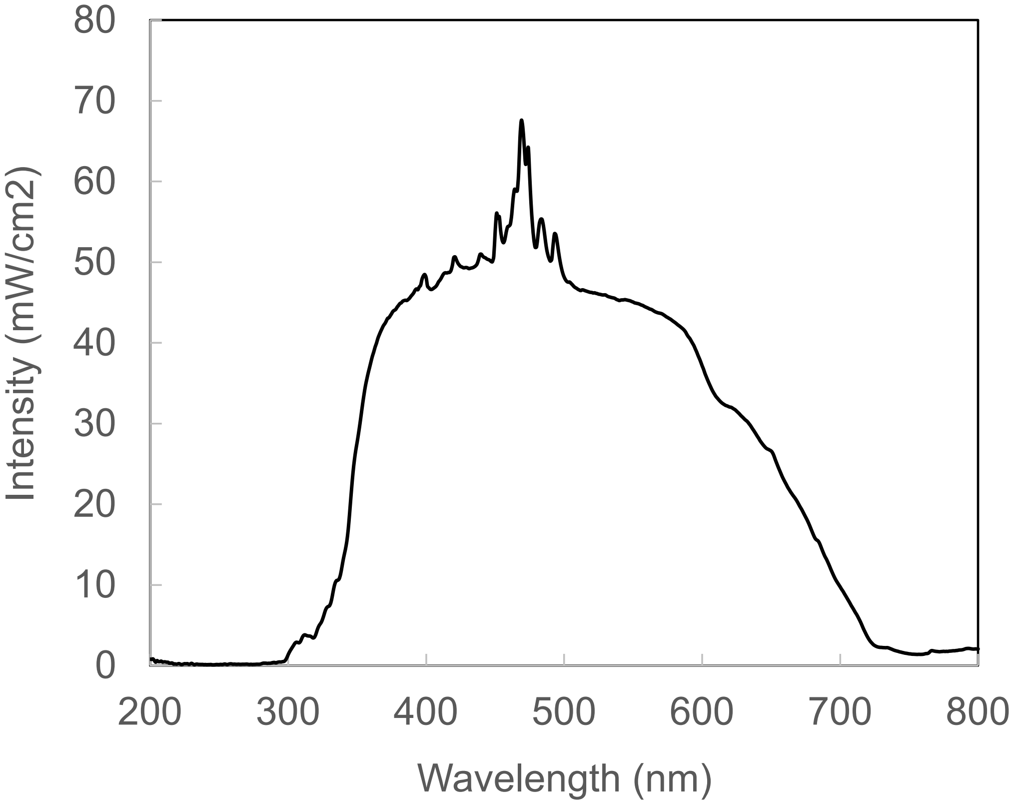


Fig.S2. Emission spectrum for a Xe lamp used for the catalytic tests. Acquired with a spectro-radiometer.

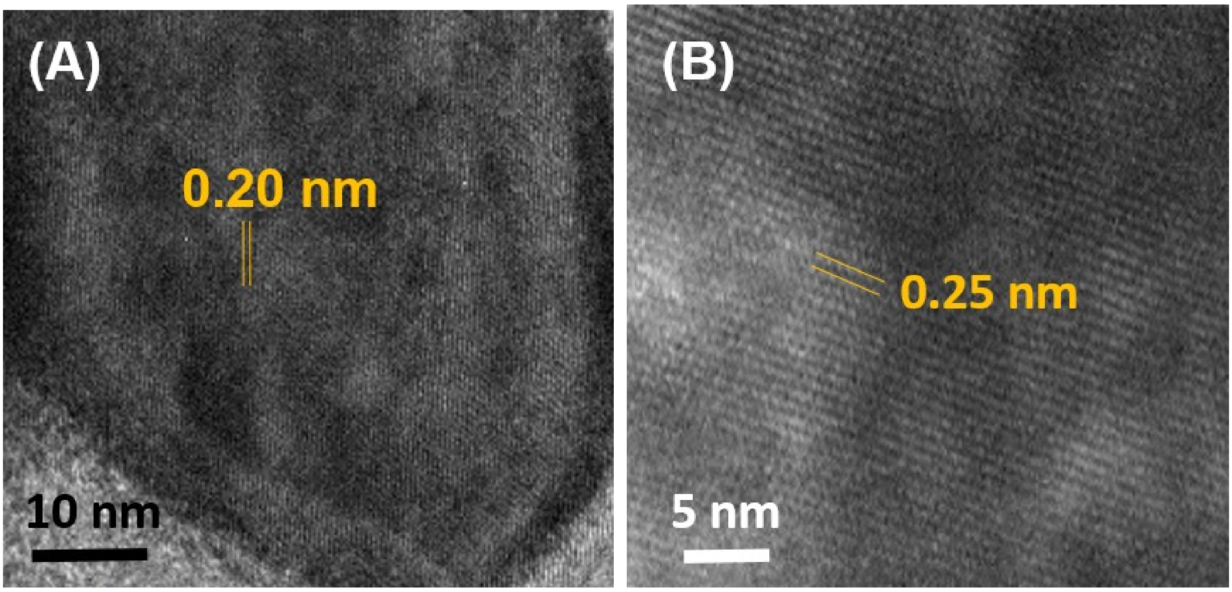


Fig.S3. (A) High-resolution TEM images for the Co part (A) and the TaC part of the Co@TaC.

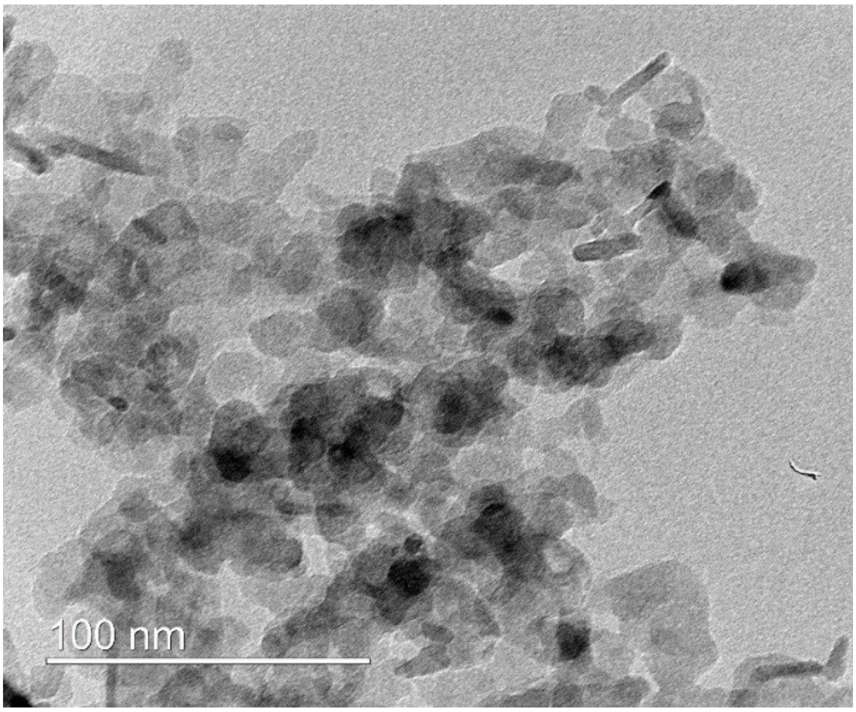
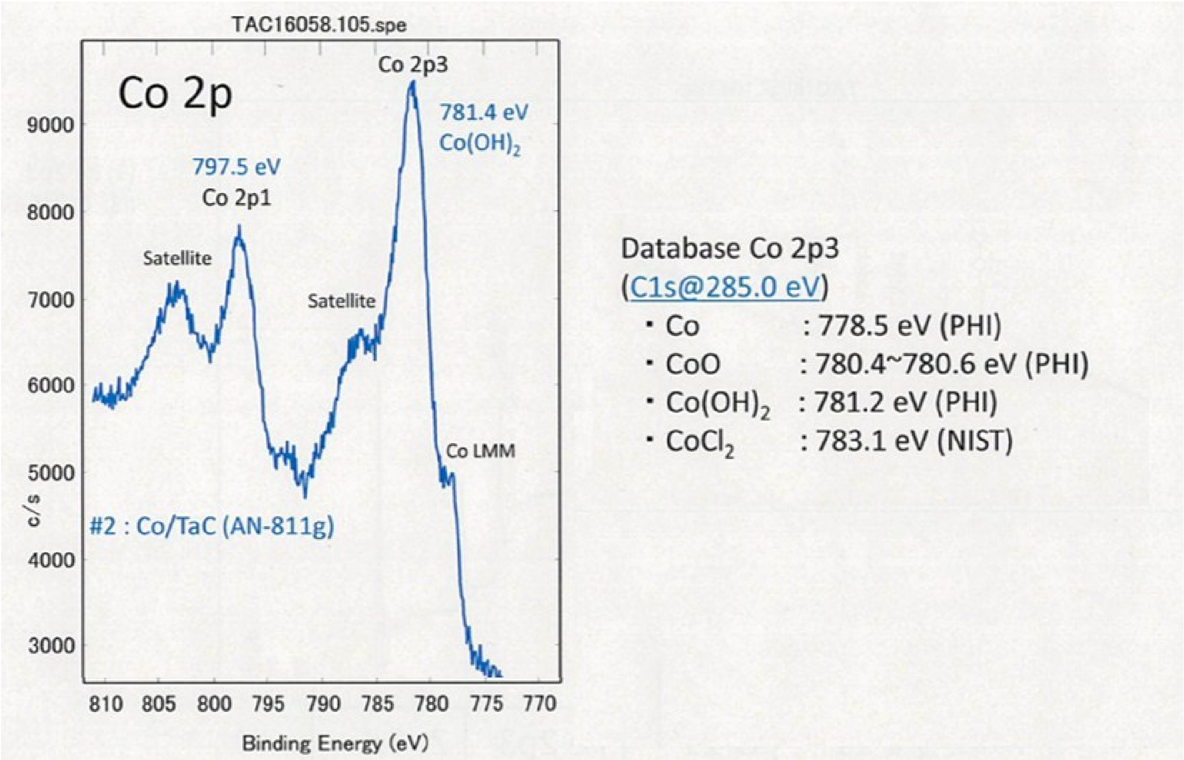


Fig.S4. TEM image of Co/Al_2O_3.



Database Co 2p3
(C1s@285.0 eV)

- Co : 778.5 eV (PHI)
- CoO : 780.4~780.6 eV (PHI)
- $Co(OH)_2$: 781.2 eV (PHI)
- $CoCl_2$: 783.1 eV (NIST)

Fig.S5. XPS spectrum for TaC-supported Co nanoparticles.

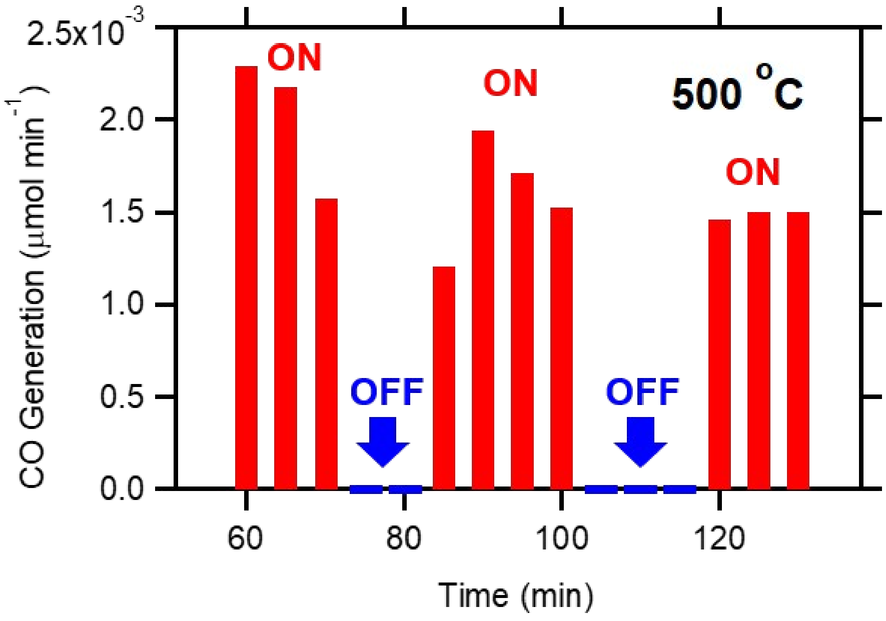


Fig.S6. H_2 production over the Co@TaC at different temperatures under the illumination of visible light: the H_2 production was evaluated right after the sample was illuminated with light.

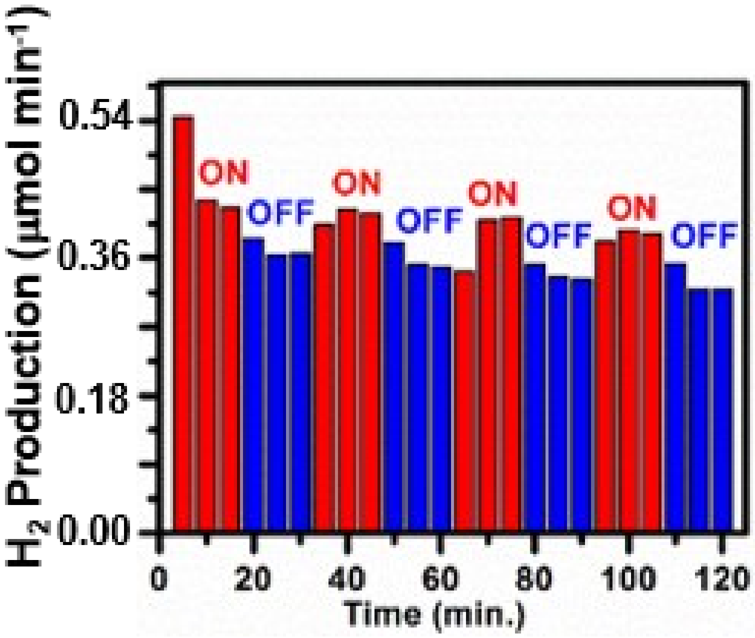


Fig.S7. H_2 production over Co/Al_2O_3 at 600 °C under the light illumination (ON, red) and in the dark (OFF, blue).

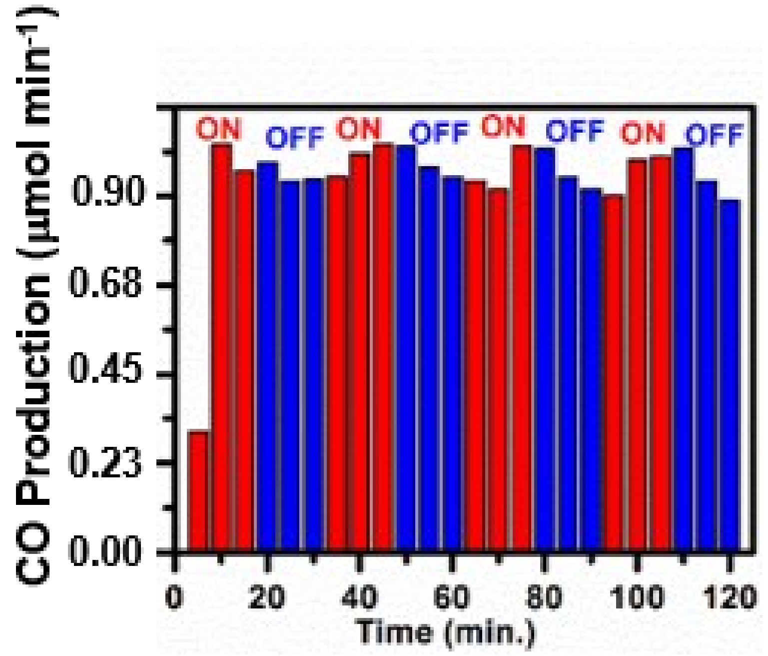


Fig.S8. CO production over Co/Al_2O_3 at 600 °C under the light illumination (ON, red) and in the dark (OFF, blue).

References :

(1) D. Zeng, M. J. Hampden-Smith, *Chem. Mater.* 1993, **5,** 681.

(2) X. Liao, R. Gerdts, S.F. Parker, L. Chi, Y. Zhao, M. Hill, J. Guo, M. O. Jones, Z. Jiang, *Phys. Chem. Chem. Phys.,* 2016, **18,** 17311.

(3) http://kinetics.nist.gov/janaf