Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Low Temperature Dry Reforming of Methane over Plasmonic Ni Photocatalysts Under Visible Light Irradiation

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Material and Preparation. Ga_2O_3 (β-phase, 9.8 m^2g^{-1}, Kojundo Chemical Laboratory Co., Ltd.), Al_2O_3 (γ-phase, 170 m^2 g^{-1}, JRC-ALO-7, the Catalysis Society of Japan), and TiO_2 (anatase, 300 m^2 g^{-1}, JRC-TIO-14, the Catalysis Society of Japan) were used as received without further purification. Precursors used for the metal loading were as follows; $Ni(NO_3)_2·6H_2O$ (Wako, 99%), $AgNO_3$ (Kojundo Chemical Laboratory Co., Ltd., 99.9%), $HAuCl_4·6H_2O$ (Kishida, 99%), $H_2PtCl_6·6H_2O$ (Nacalai Tesque, 99.7%), $PdCl_2$ (Wako, 98%), $RhCl_3·nH_2O$ (Mitsuwa Kagaku Co. Ltd.), $ZnCl_2$ (Kojundo Chemical Laboratory Co., Ltd., 99.9%), $Cu(NO_3)_2·3H_2O$ (Nacalai Tesque, 99%), $Fe(NO_3)_3·9H_2O$ (Wako, 99.9%), or $La(NO_3)_3·6H_2O$ (Nacalai tesque, 99.9%). The metal precursor was impregnated on the metal oxide (Ga_2O_3, Al_2O_3, or TiO_2) powder. Shortly, the metal oxide powder was dispersed in ion-exchanged water (100 mL) containing the metal precursor, and was heated at 353 K to dryness under magnetically stirring. The powder was dried at 373 K overnight, and calcined at 673 K for 2 h.

Photocatalytic activity test. Photocatalytic reaction test was carried out using a fixed-bed flow reactor as described in our previous study.[1] In the present study, the irradiation area of the light was fixed to 4 cm^2 for the photocatalytic activity test by changing the catalyst weight.[2] Typically, catalyst granules of 5 wt% Ni/Al_2O_3 (0.3 g) were filled into a quartz reactor (2 cm × 2 cm × 1 mm). Before the activity test, the sample was heated at 623 K under O_2 gas (100%, total flow rate: 5 ml min^{-1}) for 30 min to remove organic impurities on the catalyst surface, and then reduced by $H_2(10\%)/Ar$ gas (total flow rate: 20 ml min^{-1}) at various temperature of 323–1073 K (typically, 623 K) for 30 min. After the pretreatment, a reactant gas (typically $CO_2/CH_4/Ar=1/1/8$, total flow rate: 20 ml min^{-1}) was flowed into the reactor in the dark at the reaction temperature (typically, 473 K). After 30 min, light irradiation was started using a 300 W Xe lump (Excelitas Technologies, PE300BUV, light intensity: 250 mW cm^{-2} in the range of 254±10 nm). For the visible light irradiation, a long-pass filter (Y-43, Toshiba Co. Ltd., $\lambda > 430$ nm, Fig. S1) was used to remove the UV light. The outlet gas was analysed by online gas chromatography with a thermal conductivity detector (Shimadzu, GC-8A) using a Shincarbon ST column.

Characterization. Ni K-edge XAFS spectra were recorded in a transmission mode at room temperature at the BL12C facility of the Photon Factory, High Energy Accelerator Research Organization (KEK-PF, Tsukuba, Japan) using a Si(111) double crystal monochromator. The Ni/Al_2O_3 samples were sealed in a polyethylene bag immediately after the H_2 pretreatment to minimize the effect of oxidation of the Ni species by the air. XAFS data analysis was performed with the Athena software. UV-Vis Diffuse reflectance spectra (UV-Vis DRS) were recorded on a V-570 instrument (JASCO, Japan). X-ray diffraction (XRD) measurement was carried out on a Lab X XRD-6000 (Shimadzu, Japan). Transmission electron microscope (TEM) measurement was carried out using a JEM 2010 (JEOL, Japan). Thermogravimetric (TG) analysis and differential thermal analysis (DTA) were performed on a Rigaku Thermo plus TG 8120 apparatus at a heating rate of 10 K min^{-1} under a dry air flow condition (200 mL min^{-1}) using Pt pans.

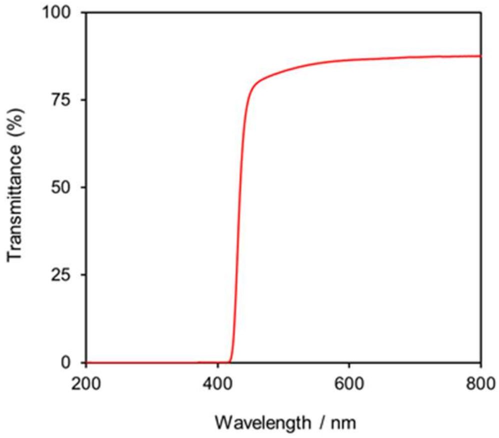


Fig. S1 Absorption property of a Y-43 long-pass filter used in the photo-DRM activity test. The spectrum was obtained in a transmission mode by the UV-Vis absorption spectrometer.

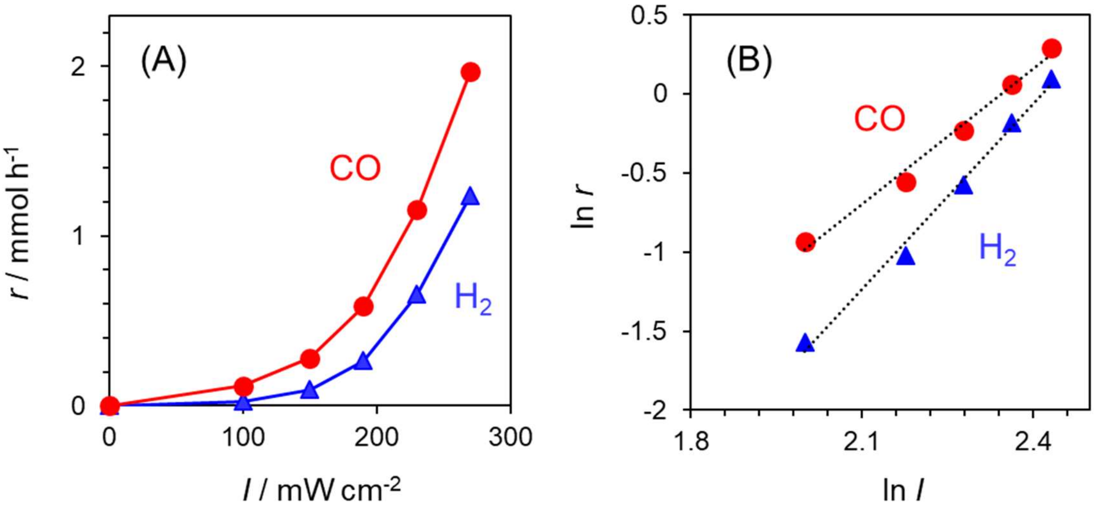


Fig. S2 Effect of the light intensity on the production rates (r) of CO and H_2 in the photo-DRM reaction at 473 K under visible light irradiation (A) and the double logarithmic plots (B). The light intensity was measured in the range of 254±10 nm without using any filter.

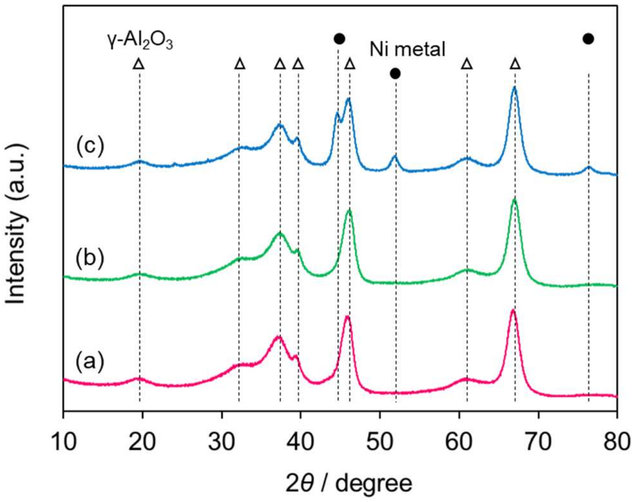


Fig. S3 XRD patterns of the 5 wt% Ni/Al_2O_3 samples before (a) and after the H_2 pretreatment at 623 K (b) and 1073 K (c).

Carbon deposition during the reaction

XRD measurement was carried out to characterize the Ni/Al_2O_3 catalyst after reaction (Fig. S4). After reaction for 100 h, new XRD peaks appeared at $2\theta = 26.1$ and 51.9 degrees, which can be attributed to graphic carbon[3] and Ni metal,[4] respectively. Thus, the XRD result indicates that carbon deposition and formation and/or aggregation of Ni metal species proceeded during the reaction under visible light irradiation although clear change was not confirmed by TEM observation (Fig. S5). To support the carbon deposition, we performed TG-DTA (Fig. S6). In the Ni/Al_2O_3 catalyst after the reaction for 100 h, two steps of weight loss were observed around 330 and 830 K. The former was observed in all the samples tested, and would be assignable to desorption of water. On the other hand, the later was not observed in the Ni/Al_2O_3 after H_2 pretreatment at 623 K. In addition, a physical mixture of the Ni/Al_2O_3 photocatalyst after H_2 pretreatment and active carbon (10 wt%, Nacalai Tesque) showed the weight loss in the same temperature range around 830 K. These results revealed that carbon species was deposited on the Ni/Al_2O_3 photocatalyst after the reaction for 100 h under visible light irradiation. The content of the carbon was estimated to be 3.8 wt% after reaction for 100 h based on the weight loss. Besides, in the UV-Vis adsorption around 300-800 nm increased after the reaction (Fig. S6), which also supports the carbon deposition and formation and/or aggregation of Ni metal species

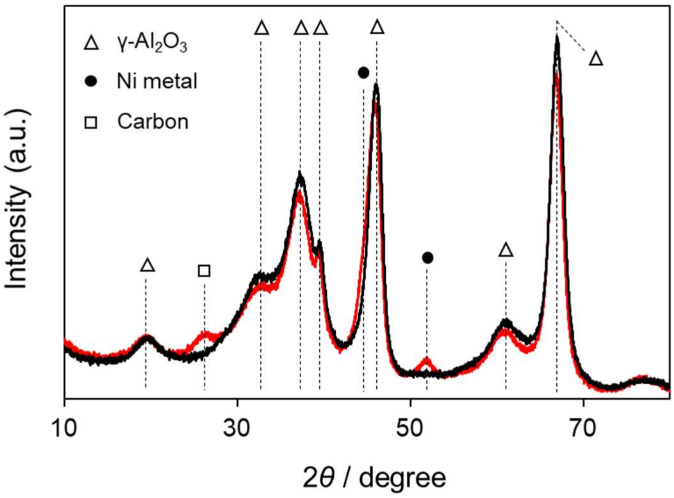


Fig. S4 XRD patterns of Ni/Al_2O_3 after H_2 pretreatment (black), and after reaction for 100 h (red). Ni loading: 5wt%, H_2 pretreatment temperature: 623 K.

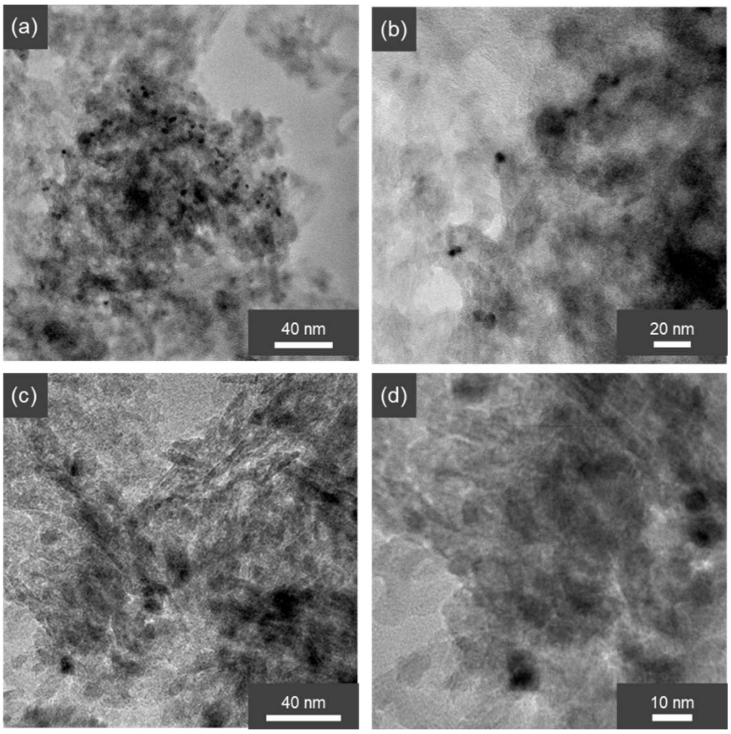


Fig. S5 TEM images of the Ni/Al_2O_3 photocatalysts after H_2 pretreatment (a, b) and after reaction for 100 h (c, d). Ni loading: 5wt%, H_2 pretreatment temperature: 623 K.

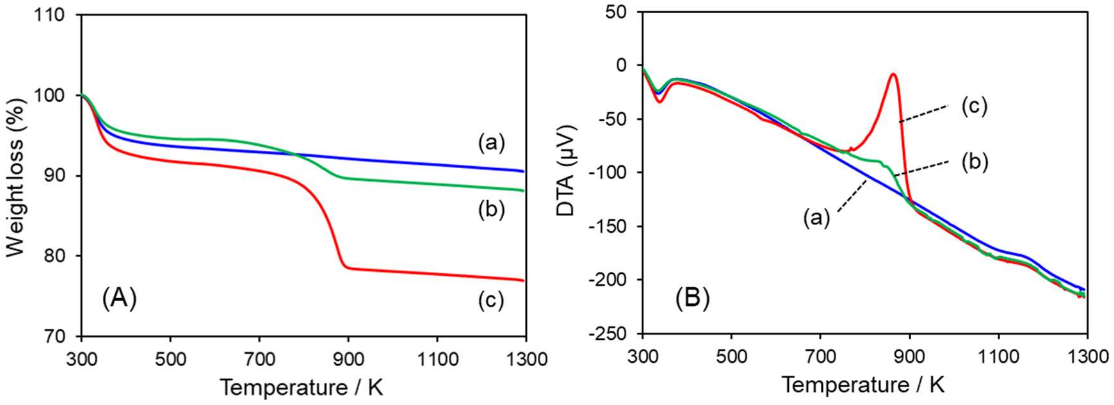


Fig. S6 TG-DTA profiles of Ni/Al_2O_3 before reaction (a), and after reaction for 100 h (b), and physical mixture of Ni/Al_2O_3 and active carbon (10 wt%) (c).

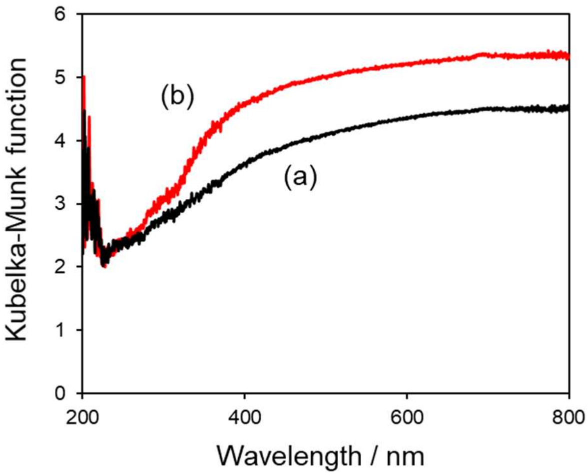


Fig. S7 UV-vis diffuse reflectance spectra of the Ni/Al_2O_3 photocatalysts after H_2 pretreatment (a) and after reaction for 100 h (b). Ni loading: 5wt%, H_2 pretreatment temperature: 623 K.

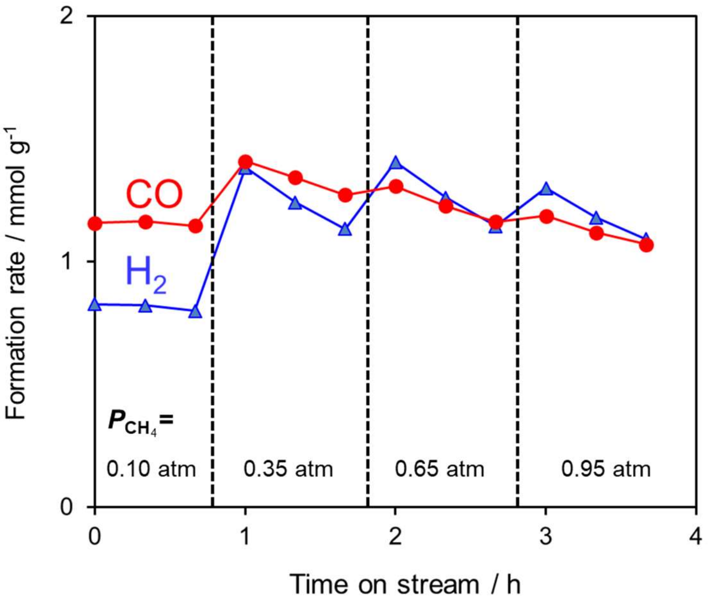


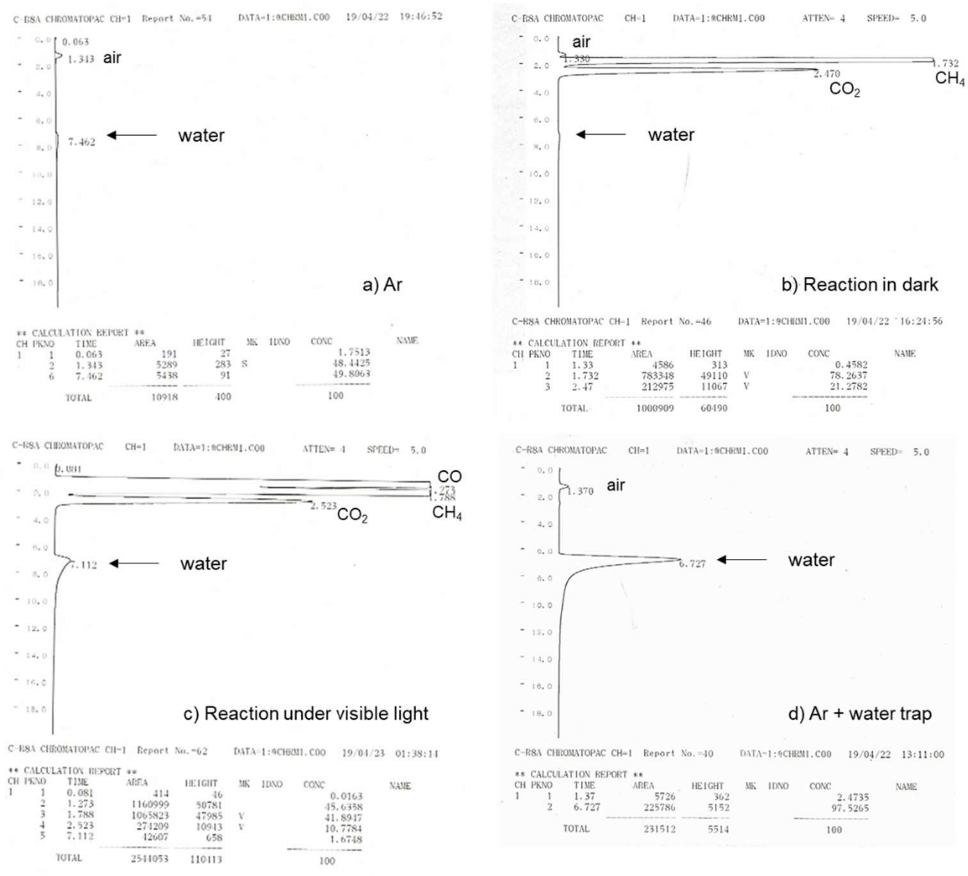
Fig. S8 Time course of the formation rates of CO and H_2 at 473 K at various P_{CH4} pressures using the 5wt% Ni/Al_2O_3 catalyst. P_{CO2}: 0.05 atm, H_2 pre-treatment temperature: 623 K.

Quantification of water

Generation of water was confirmed using a gas chromatography with thermal conductivity detector (GC-8A, Shimadzu, Japan) using a Porapak Q column (GL science, Japan). The reaction gas was sampled by using a gastight syringe (2.0 mL). The charts of the gas chromatography were shown in Fig. S9. A small peak of water was observed in the dark condition and it was also observed using a pure Ar gas as shown in (a) and (b), suggesting the peak would be due to contamination of water from the air or stainless lines. When visible light irradiation was applied at 473 K, the peak intensity increased as shown in (c), clearly indicating the formation of water. By bubbling Ar gas into water, we made a calibration curve considering the amount of the water contamination, and the amount of water was estimated to be 0.24 mmol h^{-1} based on the peak area. At that time, the production rates of CO and H_2 were 1.50 and 0.92 mmol h^{-1}, respectively. When we assume only DRM, RWGS, and Sabatier reactions (eqs. 1, 3, and 4), the formation rate of water is expressed as follows

$r_{H2O} = (r_{CO} - r_{H2})/2$

Here, r_x means formation rate of x (x = H_2O, CO or H_2). The calculated value (0.29 mmol h^{-1}) was almost similar to the experimental one (0.24 mmol h^{-1}), which strongly supports the RWGS and Sabatier reactions.



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      2    1.343        5289         283   S            48.4425
      6    7.462        5438          91                49.8063
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         TOTAL         10918         400                   100
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      2    1.732      783348       49110   V            78.2637
      3    2.47       212975       11067   V            21.2782
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** CALCULATION REPORT **
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      2    1.273     1160999       50781                45.6358
      3    1.788     1065823       47985   V            41.8947
      4    2.523      274209       10913   V            10.7784
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      2    6.727      225786        5152                97.5265
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         TOTAL        231512        5514                   100
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Fig. S9 Results of GC analysis in the photo-DRM reaction under visible light irradiation at 473 K. The samples are as follows: (a): Ar, (b) reaction in the dark, (c): reaction under visible light, and (d) Ar + water vapor.

References

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