Supplementary Material (ESI) for Energy & Environmental Science
This journal is © The Royal Society of Chemistry 2010

Supplementary Information

Nafion Layer-Enhanced Photosynthetic Conversion of CO_2 into Hydrocarbons on TiO_2 Nanoparticles

Wooyul Kim, Taehong Seok and Wonyong Choi*

School of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang, 790-784, Korea

E-mail: wchoi@postech.edu

1. Experimental Details

1) Materials and Chemicals. TiO_2 powder (Degussa P25) was used as received as a base material. Nafion (perfluorinated ion-exchange resin) was purchased from Aldrich as 5 wt% solution in a mixture of alcohol and water. The following reagents were used as received: sodium carbonate (SIGMA-Aldrich, ACS reagent), sodium carbonate-^{13}C (SIGMA-Aldrich, 99 atom%), palladium (II) chloride (SIGMA-Aldrich, 99.999%), and methanol (J. T. Baker, HPLC solvent). Concentrated $HClO_4$ and NaOH solutions were used for the pH adjustment of aqueous suspensions. Deionized ultrapure water (18 MΩ·cm) was used and prepared by a Barnstead purification system.

2) Preparation of catalyst. Palladium nanoparticles were loaded onto TiO_2 particles using a photo-deposition method.[1] The deposition of palladium nanoparticles was carried out in an aqueous suspension of TiO_2 (0.5 g/L) in the presence of methanol (electron donor, 1.25 M) and palladium chloride ($PdCl_2$, 46.98 μM) under UV irradiation for 30 min (with a 200-W mercury lamp). After irradiation, the palladized catalysts (Pd-TiO_2) were filtered and washed with distilled water. A typical Pd loading was estimated to be ca. 1.0 wt%. Nafion solution was prepared according to previous reports.[2] 20 g of 5 wt% Nafion solution in a mixture of alcohol and water (Aldrich) was added to 300 mL of deionized water. The solution was heated to 70–80℃ on a hot-plate until the total volume was reduced to 50 mL, and then diluted to 300 mL. This procedure was repeated three times to remove aliphatic alcohols from the solution. The total volume of the final solution was diluted to 100 mL. Pd-TiO_2 powder was thoroughly mixed to the appropriate volume of the above Nafion solution (final concentration: 4.2 – 13 mg-Nafion/g-TiO_2) and subsequently dried at 80℃ for overnight. Although Nf/Pd-TiO_2 powder was not initially well suspended because of the hydrophobic nature of Nafion, vigorous stirring for 30 min was enough to obtain a well-suspended slurry.

3) Photocatalysts Characterization. The high-resolution transmission electron micrographs (HRTEM) and energy-filtered transmission electron micrographs (EFTEM) of Nf/Pd-TiO_2 were obtained using a JEM-2200FS microscope with Cs-

corrected. X-ray photoelectron spectra (XPS, Kratos XSAM 800pci) of Nf/Pd-TiO_2 and Pd-TiO_2 powder were obtained using the Mg Kα line (1253.6 eV) as the excitation source. The zeta potentials of both catalyst particles in aqueous suspension were measured using an electrophoretic light scattering spectrophotometer (ELS 8000, Otsuka).

4) **Photosynthetic Experiments.** A quartz reactor (54 mL) was used for photoreaction. Prior to the CO_2 photoreduction experiment, the aqueous suspension of Pd-TiO_2 (or Nf/Pd-TiO_2) was dispersed using ultra-sonication and magnetic stirrer, and the resulting suspension was illuminated for 16 h under Ar to remove carbon residues on the surface of Pd-TiO_2 (or Nf/Pd-TiO_2). The photosynthetic experiments were carried out in the presence of sodium carbonate, and CO_2 was purged for 30 min prior to irradiation. The initial pH of the suspension was adjusted to different values (pH 1, 3, and 11). A 300-W Xe arc lamp (Oriel) was used as a light source. Light passed through a 10-cm IR water filter and a cutoff filter ($\lambda > 300$ nm).

The amount of hydrogen sampled from the headspace of reactor was analyzed using a gas chromatograph (GC, HP6890A) equipped with a thermal conductivity detector and a 5Å molecular sieve column. CH_4, C_2H_6, and C_3H_8 were analyzed using a Varian CP-3800 gas chromatograph equipped with a CP-PoraPLOT Q capillary column (25 m × 0.25 mm) and a flame ionization detector. An isotope experiment was carried out with using $Na^{13}CO_3$ to detect the production of $^{13}CH_4$: the headspace gas sampled from the reactor was ionized by 70 eV electron impact and subsequently analyzed by a quadrupole mass spectrometer (QMI 422, Pfeiffer Vacuum) under a vacuum (1.0×10^{-5} mbar).

The incident photon intensity (I_{in}) was measured to be 2.3×10^{-3} Einstein·min^{-1}·L^{-1} using ferrioxalate actinometry.[3] APE is defined as: $APE(\%)= ((2P_{H2} + 8P_{CH4} + 14P_{C2H6})/I_{in})\times100$ where P_{H2}, P_{CH4}, and P_{C2H6} (mol·min^{-1}·L^{-1}) represent the rate of hydrogen, methane, and ethane production, respectively.

5) **Solar Experiments.** The outdoor solar experiments were carried out on the roof of the Environmental Engineering building at POSTECH (Pohang, Korea: 36°N latitude) from 10 am to 4 pm under clear sky condition on June 8th, 2011. The solar light intensity was recorded every minute by using a pyranometer (Apogee, PYR-P). A flat circular quartz reactor (diameter 5.5 cm, volume 63 mL) was used for the experiment.

References

1. O. Ishitani, C. Inoue, Y. Suzuki and T. Ibusuki, *J. Photochem. Photobiol., A: Chem.*, 1993, **72**, 269-271.

2. M. Hara and T. E. Mallouk, *Chem Commun.*, 2000, 1903-1904.

3. C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, 1956, **235**, 518.

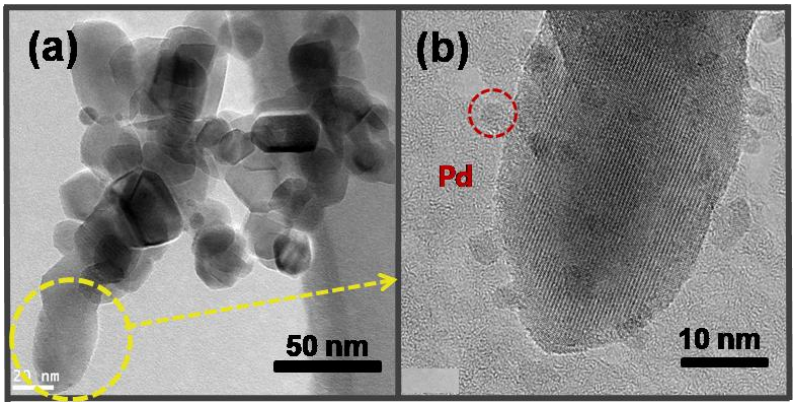

Fig. S1. (a) TEM image and (b) high-resolution TEM images of Nf/Pd-TiO_2.

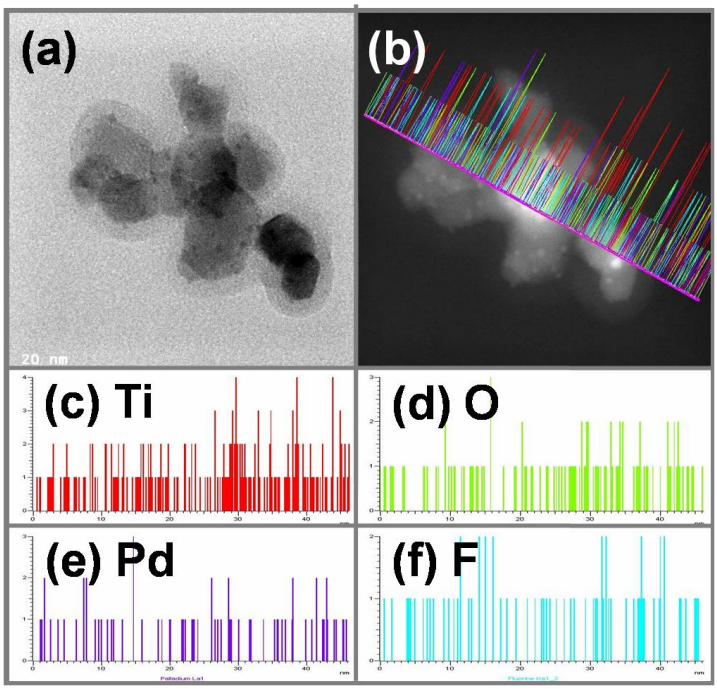

Fig. S2. (a) TEM image and (b) Line Energy Dispersive X-ray microanalysis (EDX) image (high-angle annular dark field image) and the elemental mapping of (c) Ti, (d) O, (e) Pd, and (f) F on Nf/Pd-TiO_2 sample.

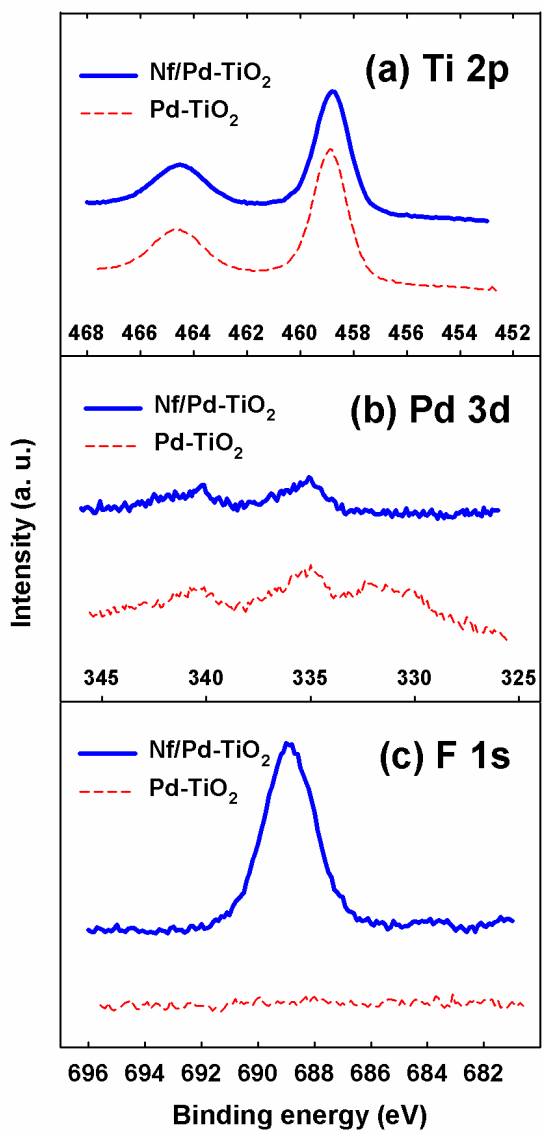

Fig. 3S XPS spectra of Nf/Pd-TiO_2 (blue) and Pd-TiO_2 (red) powder, showing (a) Ti 2p, (b) Pd 3d, and (b) F 1s band regions.

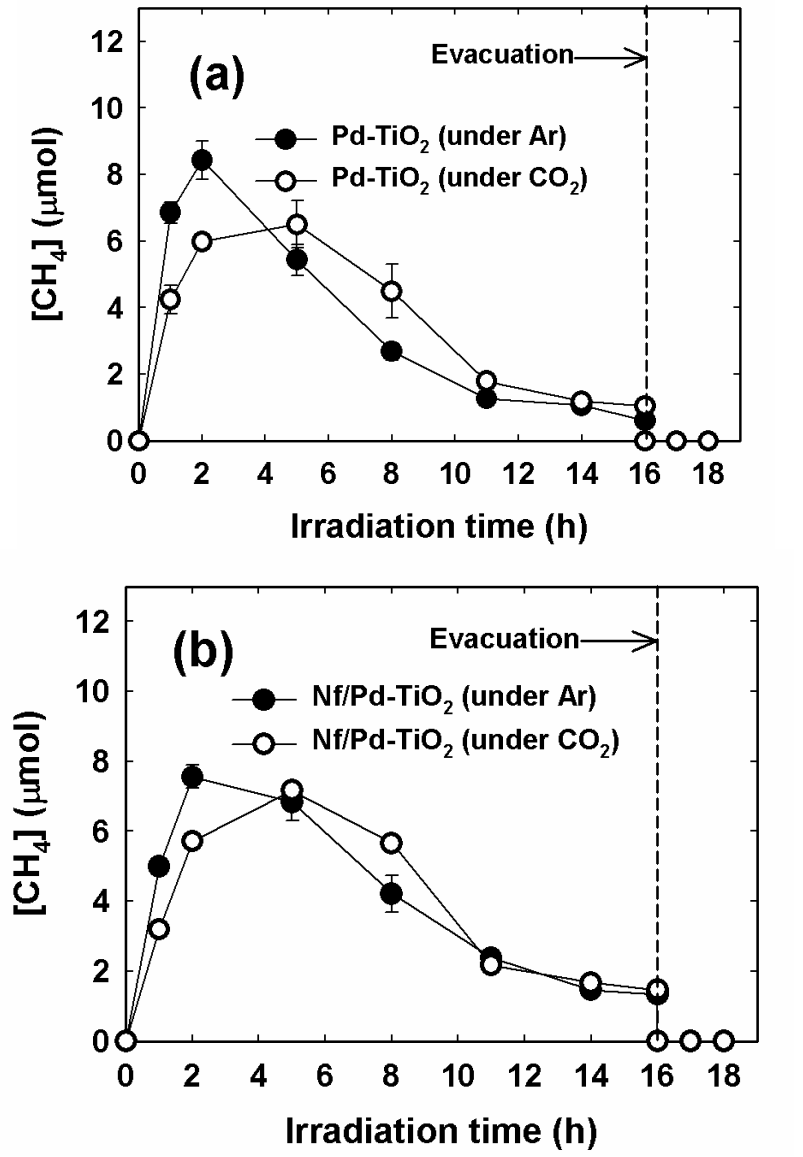

Fig. S4 Time profiles of methane production in the UV-irradiated suspension of (a) Pd-TiO_2 and (b) Nf/Pd-TiO_2 **without pre-cleaning** of the catalysts. The photo-irradiation experiments were compared between Ar- and CO_2-purged conditions. The experimental conditions were [catalyst] = 1.5 g L^{-1} (with 1.0 wt% Pd), pH_i = 5.3 (not adjusted), $\lambda > 300$ nm, and initially Ar or CO_2-saturated.

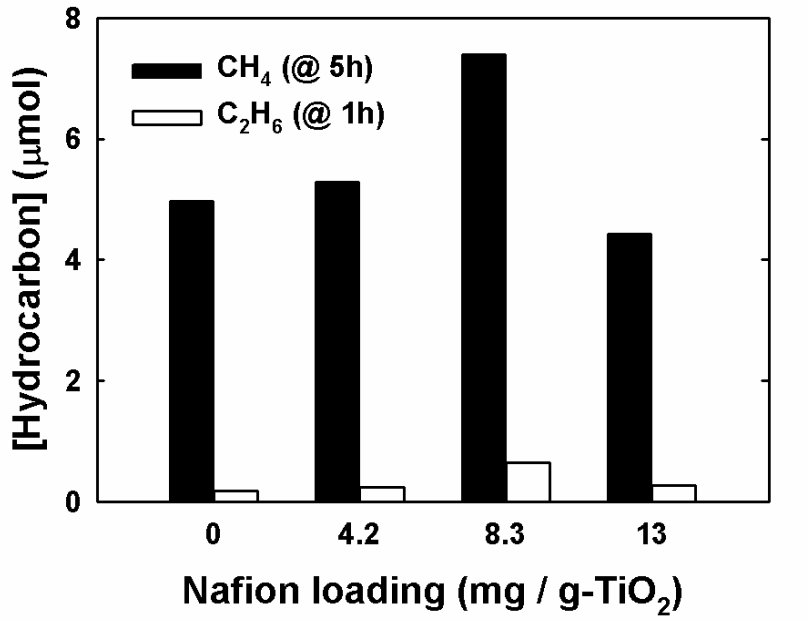

Fig. S5 The amounts of methane and ethane generated after 5 h and 1 h of continuous illumination, respectively, as a function of Nafion loading. The experimental conditions were [catalysts] = 1.5 gL^{-1} (with 1.0 wt% Pd and 0.42 - 1.3 wt% Nafion), $\lambda > 300$ nm, and initially CO_2-saturated with adding 0.2 M sodium carbonate and subsequent acidification to $pH_i = 3$.

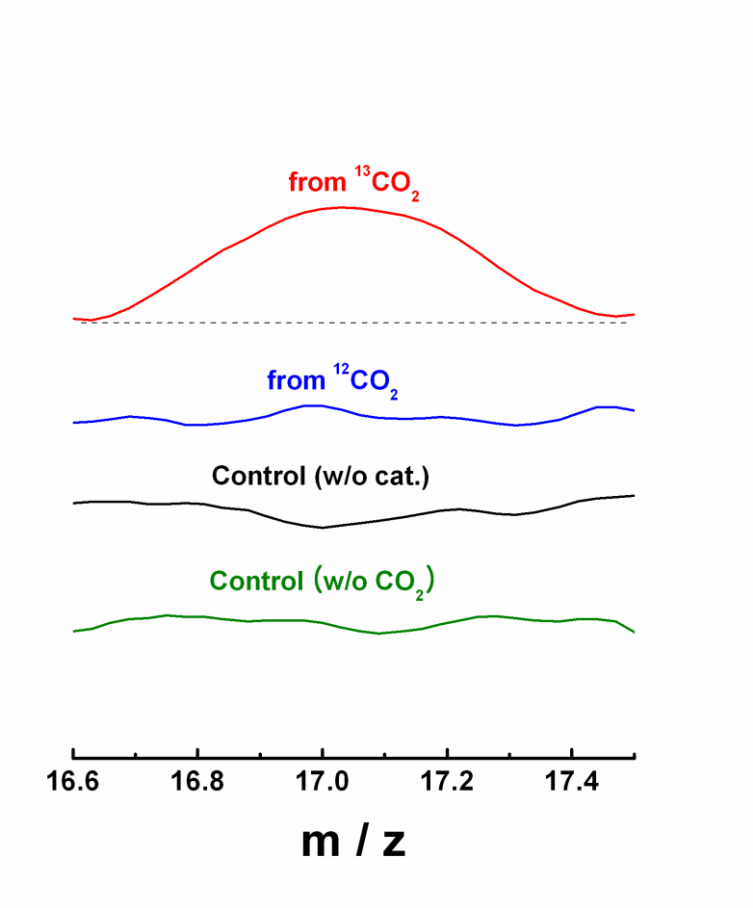

Fig. S6. Mass spectra of isotopically labelled methane ($^{13}CH_4$: m/e = 17.0) produced from $^{13}CO_2$ in the UV-illuminated suspension of Nf/Pd-TiO_2 in 5 h. The mass spectra obtained from a normal experiment using $^{12}CO_2$, and control experiments (i.e., w/o catalyst, and w/o CO_2) were also shown for comparison. The experimental conditions were [catalyst] = 1.5 gL^{-1} (with 1.0 wt% Pd and 0.83 wt% Nafion), pH_i = 1, λ > 300 nm, and initially CO_2-saturated with carbonate addition and subsequent acidification.