Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Rapid Detection of the Donor-dependent Photocatalytic Hydrogen Evolution Reaction from NMR Spectroscopy

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Materials and Methods

All the chemicals were used without further purification. Methanol, ethanol, 2-propanol, D_2O, H_2PtCl_6 and $NaBH_4$ were obtained from Wako. Tetramethyl silane was obtained from TCI. TiO_2 nanoparticle, P-25, was obtained from the Aeroxide.[1]

Preparation of Pt-TiO_2

Pt-TiO_2 was prepared by conventional method. 0.132 g of H_2PtCl_6 $6H_2O$ (1.93 mmol) was added to the 500 mL of water. 5 g of P-25 was added to the Pt solution and dispersed for 1.5 h. 0.0997 g of $NaBH_4$ (2.60 mmol) was dissolved to the 3 mL of chilled water. The $NaBH_4$ solution was rapidly added to the TiO_2 suspension containing H_2PtCl_6. The suspension was stirred for 3 hours. The suspension was sintered and filtered. The sample was dried at 110°C before the measurements.

NMR measurements

NMR measurements were conducted by using the 600 MHz NMR, Avance III HD, Bruker. All the chemical shifts were referenced to the tetramethyl silane (TMS). The NMR spectrum were processed via Topspin software. PFG NMR was measured by the magnetic field gradients.

Reaction

All the photocatalytic hydrogen evolution reactions were conducted in the NMR tube. Outer diameter was 5 mm. Inner diameter was 4.2 mm. Typical length of the NMR tube was 17.8 cm. Typically, 5 mL of D_2O and 5 mL of alcohol were mixed and bubbled for 15 min. 5 mg of catalysts was loaded in NMR tube. Under the Ar flow, 0.6 mL of the solution was additionally introduced to the NMR tube. Then, NMR cap was tightly closed. The dead volume of the NMR tube is approximately 1.7 mL. The suspension was sonicated for 10 min for the colloidal dispersion of catalyst. All the data shown in here was measured by the three individual experiments. Sample was placed at approximately 25 cm from the light source (xenon lamp, 100 W, Asahi spectra). Infrared region of light source was filtered by passing the water to avoid the heating effect from light source.
The solution samples were set at the NMR coils. The hydrogen molecules in the gas phase were not detected. The highest concentration of H_2 molecules were 1 mmol/L in our experimental condition. The highest concentration is still below the solubility limits of typical alcohol-water mixture, 5 mmol/L (see references).

Estimation of number of electrons from the NMR measurements

The number of electrons were calculated as following. Number of product molecules are calculated based on the calculation of the number of alcohol molecules. The trace amount of air-oxidized products were included in the initial condition. Increase of the oxidized product was estimated by considering the intial condition. The calculations for the half reactions were following.

$$2H^+ + 2e^- \rightarrow H_2 \quad (1)$$
$$CH_3OH + H_2O \rightarrow HOCH_2OH + 2H^+ + 2e^- \quad (2)$$
$$2CH_3OH \rightarrow CH_3OCH_2OH + 2H^+ + 2e^- \quad (3)$$
$$2CH_3OH \rightarrow HCO_2CH_3 + 4H^+ + 4e^- \quad (4)$$
$$CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + 2e^- \quad (5)$$
$$CH_3CH_2OH + H_2O \rightarrow CH_3CO_2H + 4H^+ + 4e^- \quad (6)$$
$$(CH_3)_2CHOH \rightarrow (CH_3)_2CO + 2H^+ + 2e^- \quad (7)$$

The equation 1 represents the hydrogen evolution reaction. The equations 2-4 represent the oxidation reaction of methanol. The equation 5-6 represent the oxidation reaction of ethanol. The equation 7 represents the oxidation reaction of 2-propanol.

TEM measurements

TEM measurements were conducted by using JEM-2100F under 200 kV as acceleration voltage. Approximately 0.5 mg of sample was dispersed in 0.5 mL ethanol. The solution was drop casted on the collodion film over TEM grid.

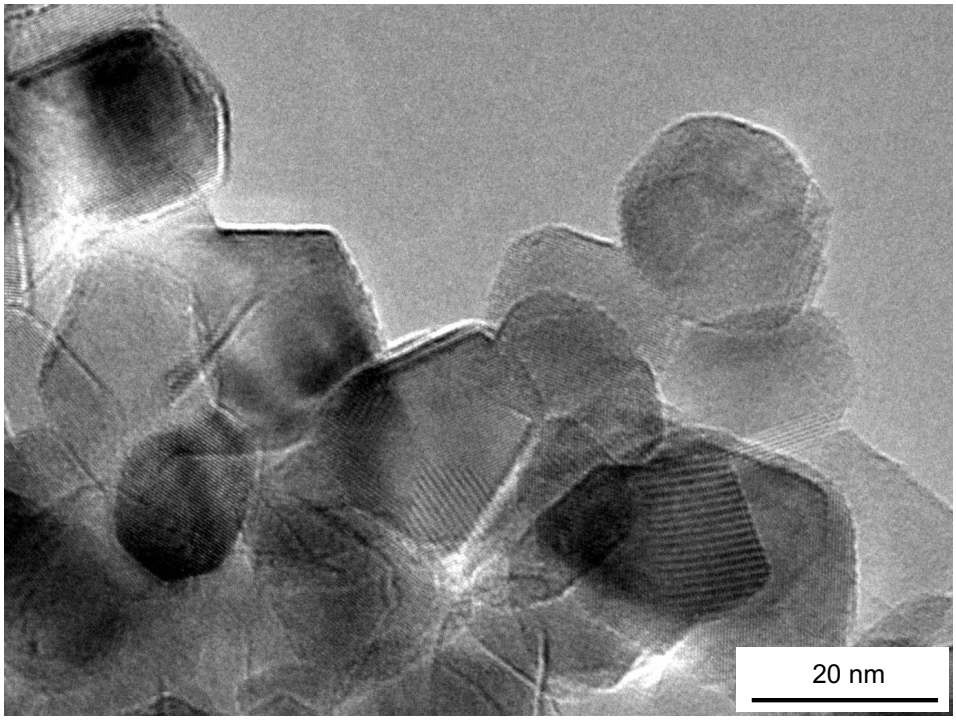

Figure S1. TEM image of the TiO_2.

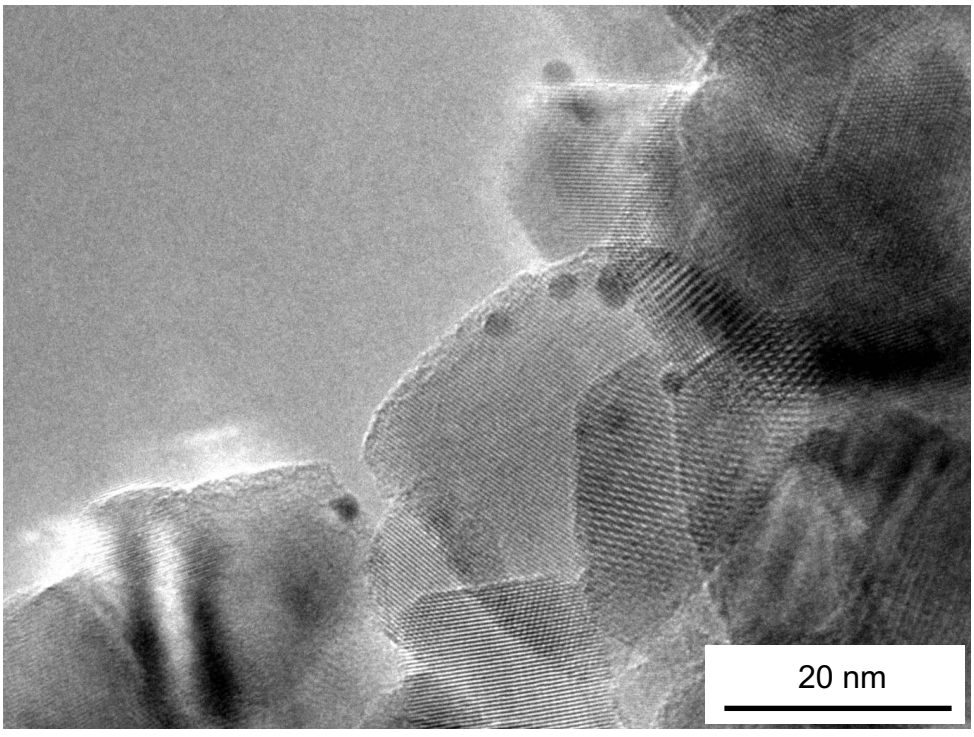

Figure S2. TEM image of the Pt-TiO_2.

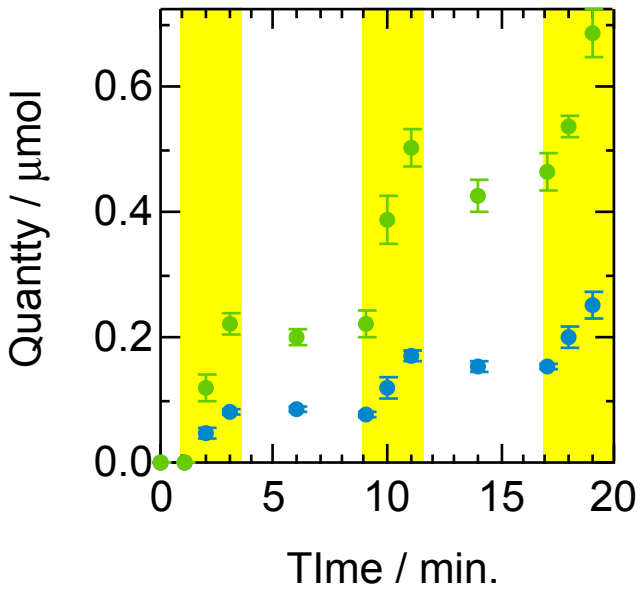

Figure S3. Photo irradiation-response of the evolved H_2 (blue) and HD (green) from Pt-TiO_2 in ethanol/D_2O 1:1 mixture. Light was turned on in the yellow region.

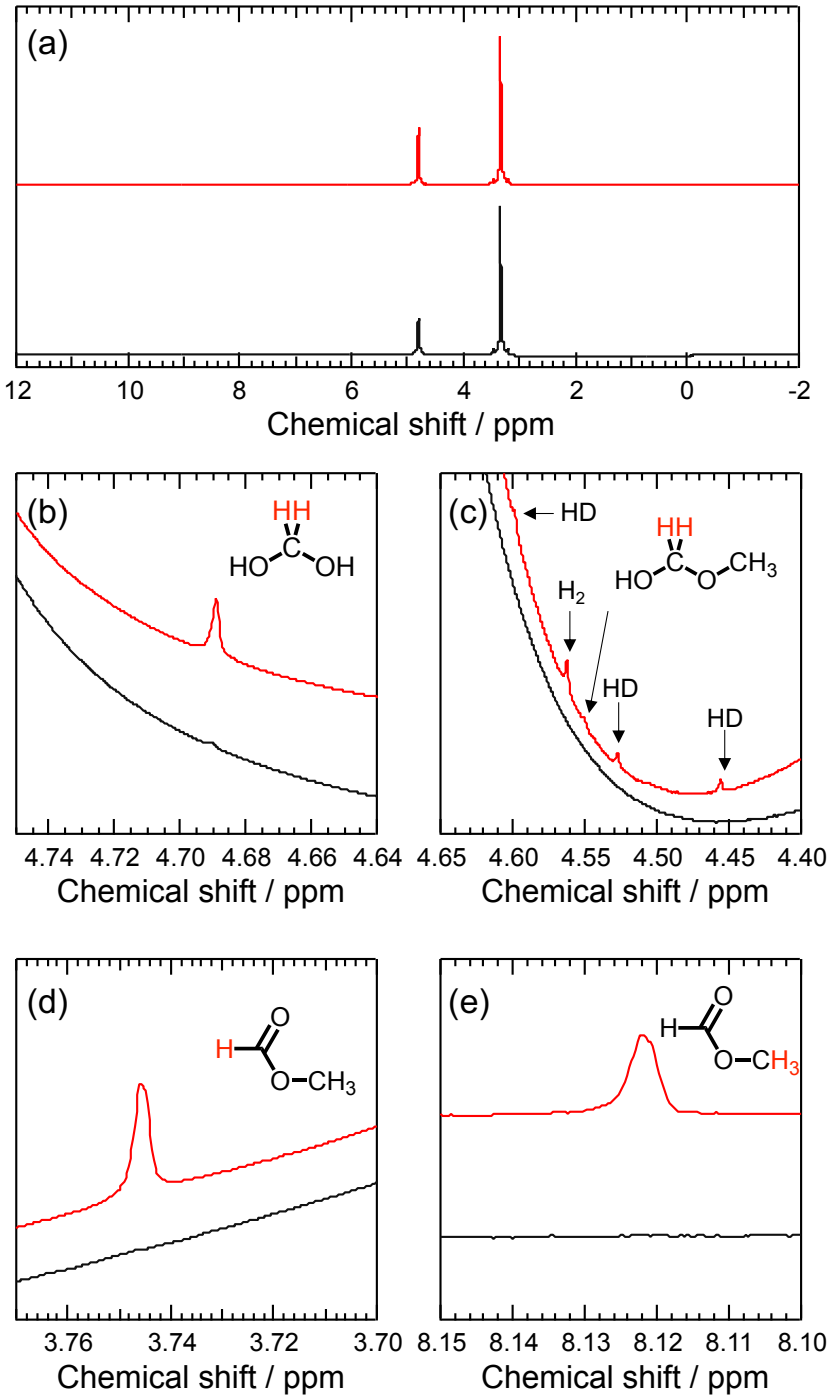

Figure S4. ^{1}H NMR spectra of Pt-TiO_2 / methanol / D_2O. Black line represents 1H NMR spectra before light irradiation. Red line represents 1H NMR spectra after light irradiation for 15 min. (a) Full spectrum. Enlarged area of (b) methylene glycol, (c) 1-methoxy-methanol, H_2, HD and (d,e) methyl formate.

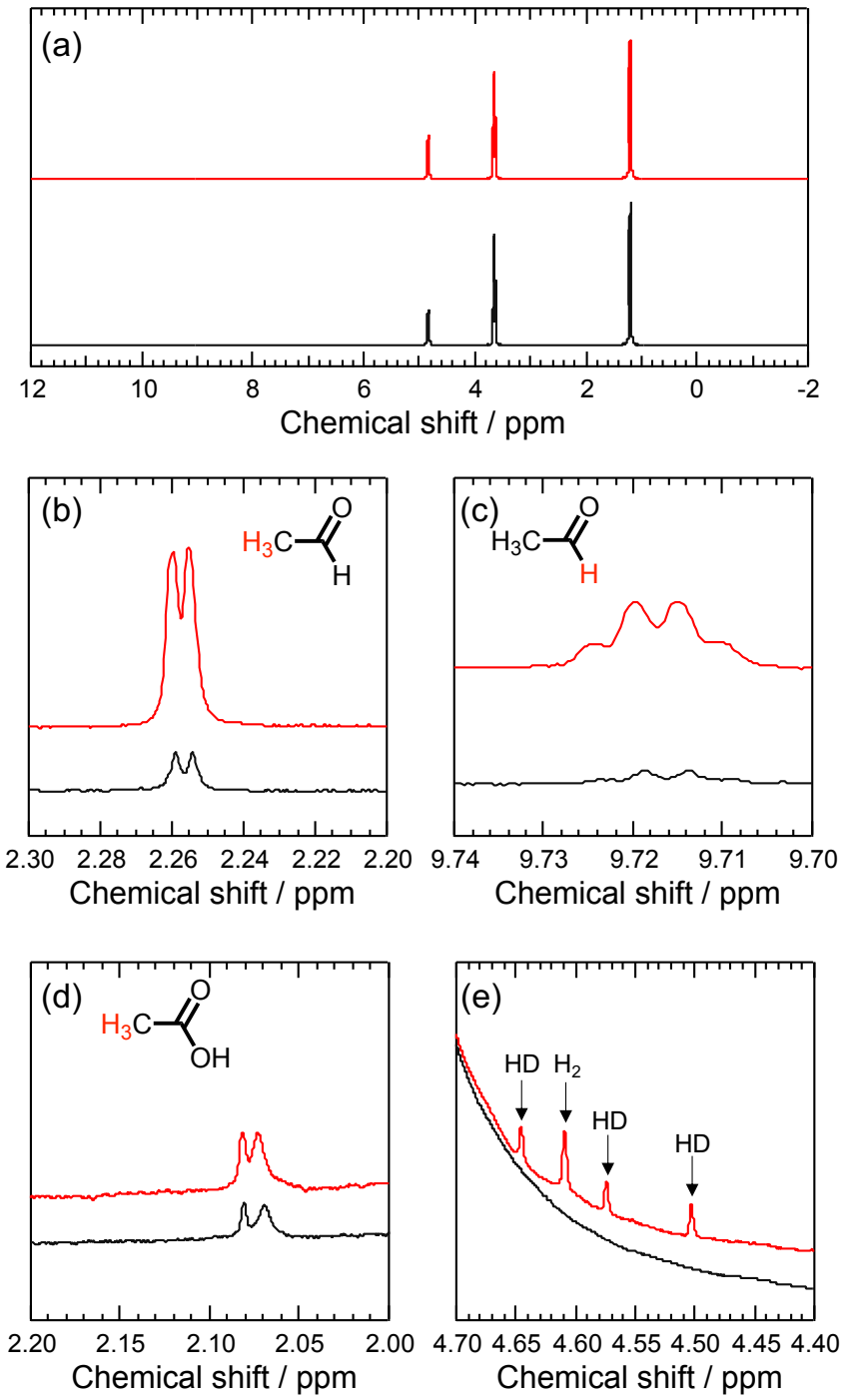

Figure S5. ^{1}H NMR spectra of Pt-TiO_2 / ethanol / D_2O. Black line represents 1H NMR spectra before light irradiation. Red line represents 1H NMR spectra after light irradiation for 15 min. (a) Full spectrum. Enlarged area of (b,c) acetaldehyde, (d) acetic acid, and (e) H_2, HD.

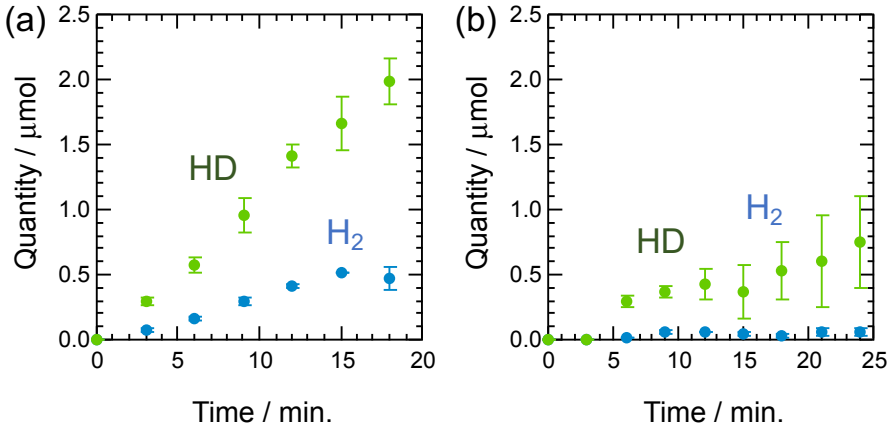

Figure S6. Evolution of reduction product of 2-propanol / D_2O by using Pt-TiO_2 as a photocatalyst. The solution rate was (a) 1:1, (b) 3:1 mixture between D_2O and 2-propanol.

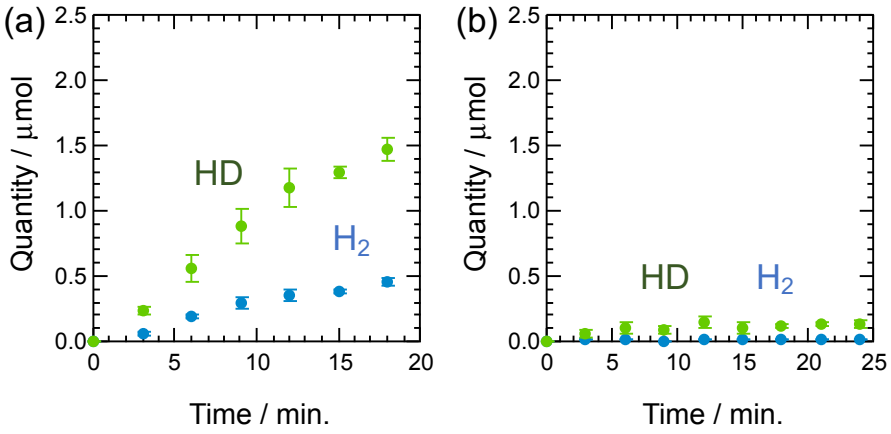

Figure S7. Evolution of reduction product of ethanol / D_2O by using Pt-TiO_2 as a photocatalyst. The solution rate was (a) 1:1, (b) 3:1 mixture between D_2O and ethanol.

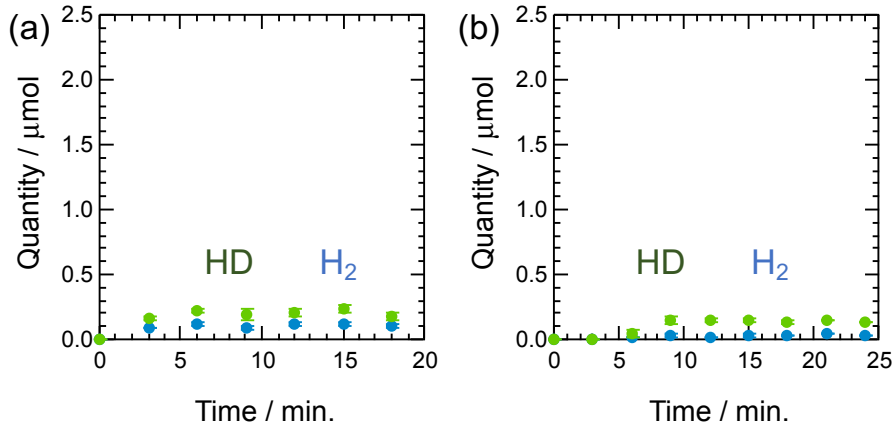

Figure S8. Evolution of reduction product of methanol / D_2O by using Pt-TiO_2 as a photocatalyst. The solution ratio was (a) 1:1, (b) 3:1 mixture between D_2O and methanol.

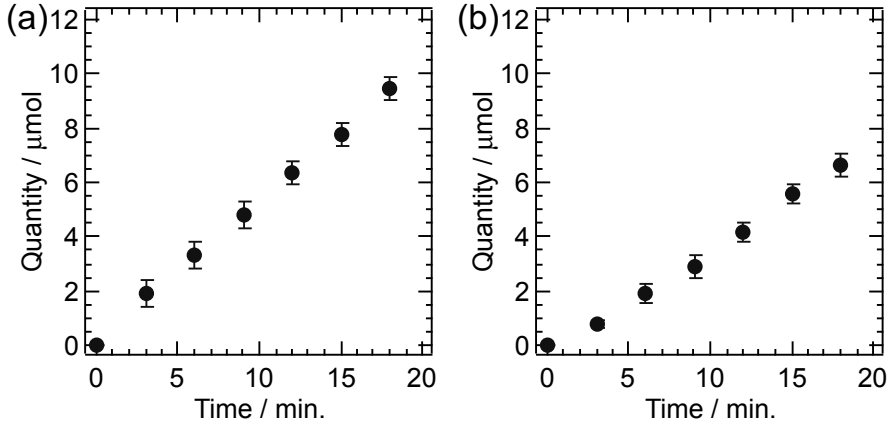

Figure S9. Oxidation product 2-propanol / D_2O. The solution ratio was (a) 1:1, (b) 3:1 mixture between D_2O and 2-propanol.

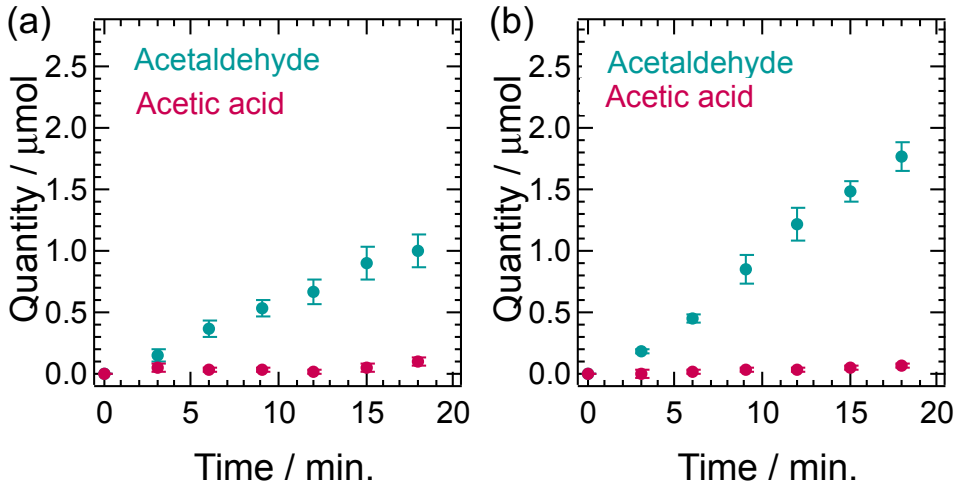

Figure S10. Oxidation product ethanol / D_2O. The solution ratio was (a) 1:1, (b) 3:1 mixture between D_2O and ethanol.

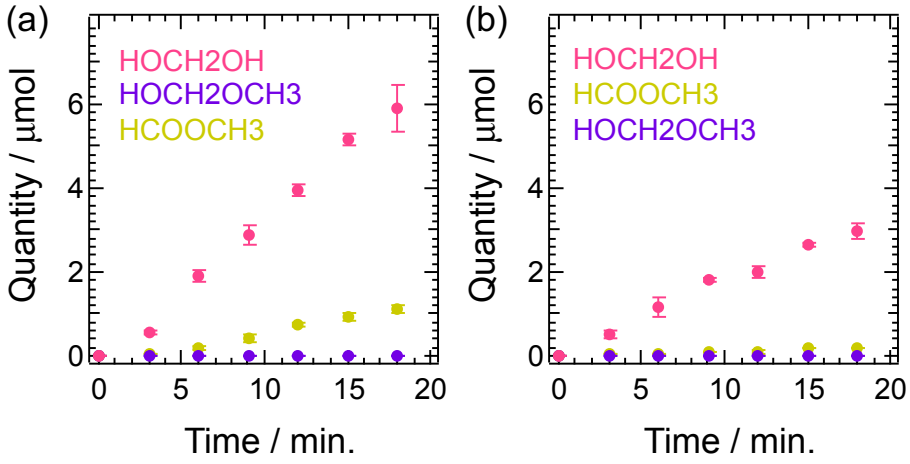

Figure S11. Oxidation product methanol / D_2O. The solution ratio was (a) 1:1, (b) 3:1 mixture between D_2O and ethanol.

Table S1. Diffusion coefficient of D_2O and alcohol mixture (1:1) in the presence of Pt-TiO_2 nanoparticle

	Methanol / D_2O		Ethanol / D_2O		2-Propanol / D_2O	
	Methanol	HDO	Ethanol	HDO	2-Propanol	HDO
D / 10^{-9} m^2 s^{-1}	0.76	1.5	0.69	1.1	0.40	1.0

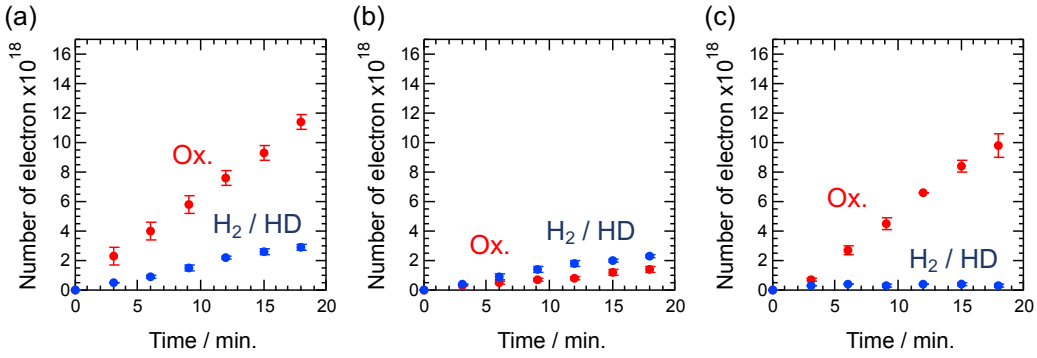

Figure S12. Time-dependent quantity of number of electron for the oxidation and reduction reaction from Pt-TiO_2 with 1:1 (a) 2-propanol / D_2O, (b) ethanol / D_2O, and (c) methanol / D_2O under light irradiation. Number of electrons were calculated based on the half reaction of each product.

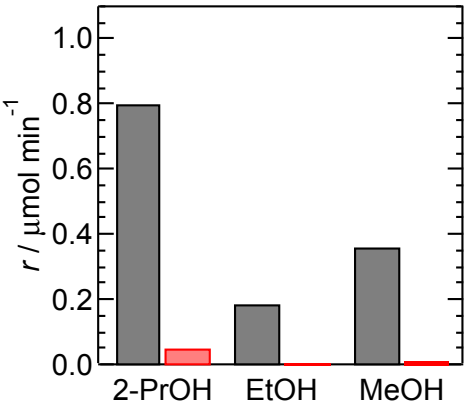

Figure S13. Rate of the oxidation reaction (black) and hydrogen evolution reaction (red) from photocatalytic hydrogen evolution reaction by using 3:1 mixture of D_2O and corresponding alcohol.

References

1. B. Ohtani, O. O. Prieto-Mahaney, D. Li and R. Abe, *Journal of Photochemistry and Photobiology A: Chemistry*, 2010, **216**, 179-182.