Operando NMR Spectroscopic Analysis of the Effects of Pt Nanoparticle Size and Crystal Facet Structure on the Alcohol Reforming Reactions

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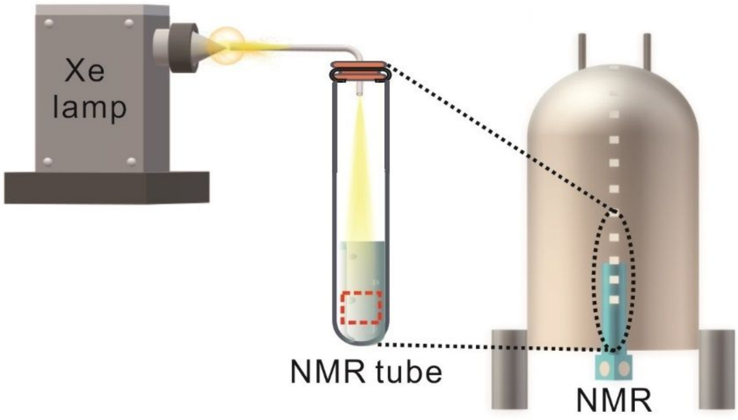

Figure S1. Schematic layout of set-up for operando NMR studies.

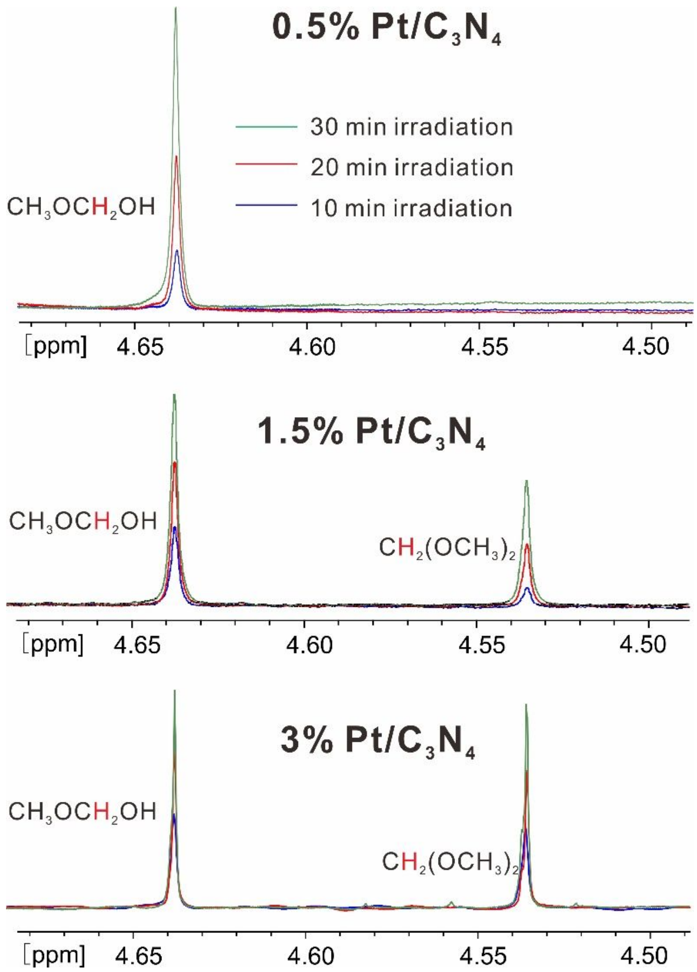

Figure S2. ^1H NMR spectra of methanol reforming products obtained for the Pt/C_3N_4 photocatalyst samples after 10 min, 20 min and 30 min of visible light irradiation (>400 nm, 300 W Xe lamp).

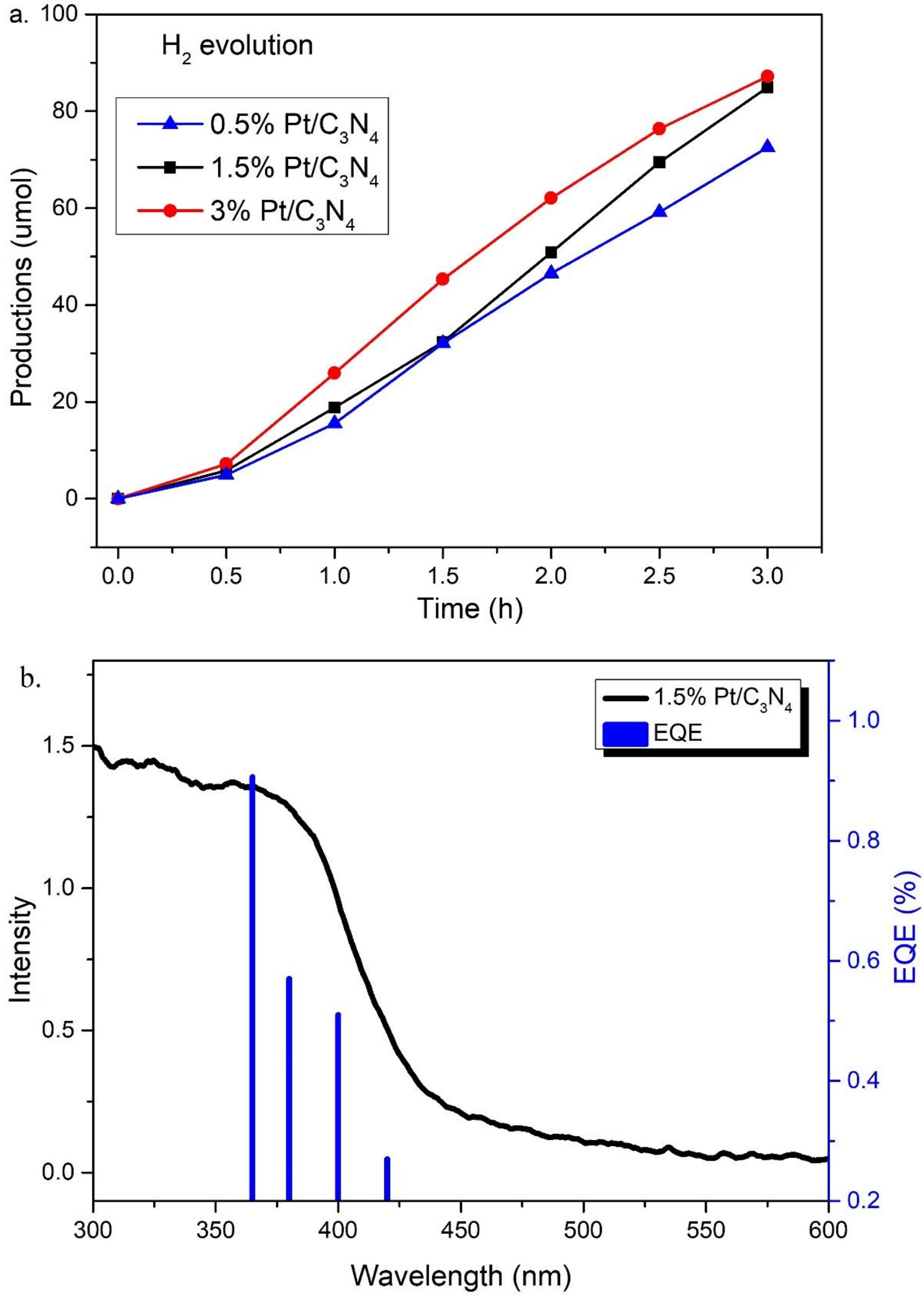

Figure S3. a. Photocatalytic H_2 evolution over Pt/C_3N_4 catalysts (20 mg) and CH_3OH (50 mL) under visible light irradiation observed by GC chromatography. b. The wavelength-dependent external quantum efficiency (EQE) of 1.5% Pt/C_3N_4 at 365 nm, 380 nm, 400 nm and 420 nm.

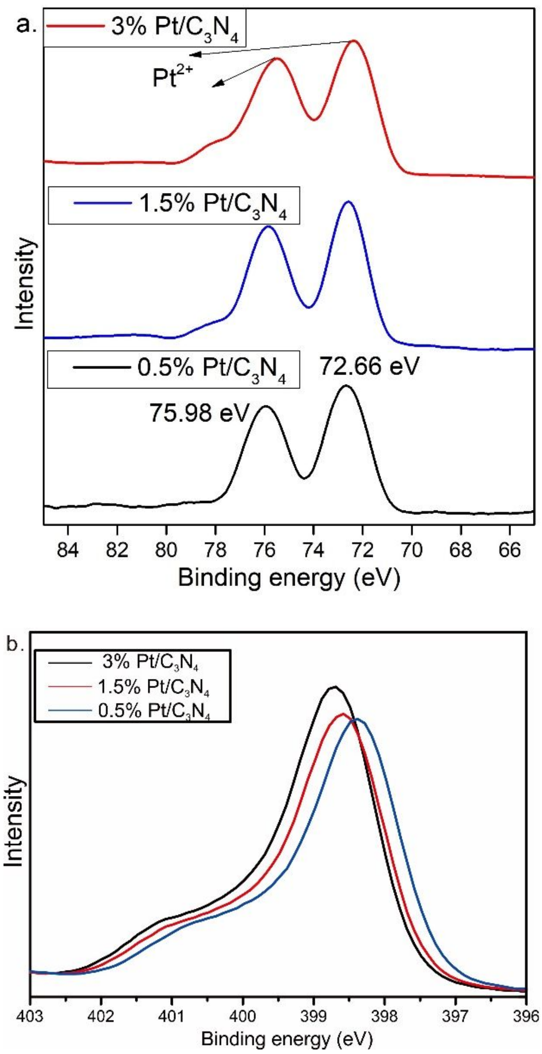

Figure S4. High resolution of XPS analysis of (a) Pt_{4f} and (b) N_{1s} of 0.5% Pt/C_3N_4, 1.5% Pt/C_3N_4, and 3% Pt/C_3N_4 samples.

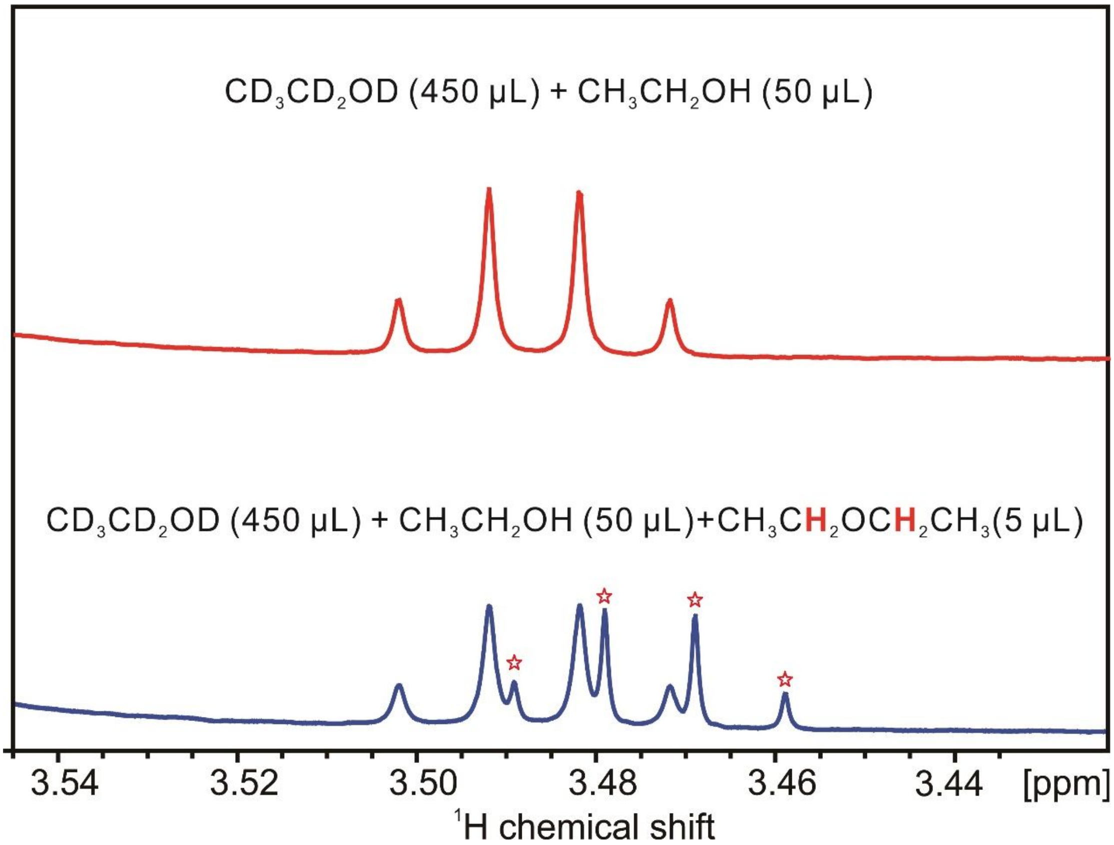

Figure S5. [1]H NMR spectra of CD_3CD_2OD (450 μL) + CH_3CH_2OH (50 μL) + $CH_3CH_2OCH_2CH_3$ (5 μL) and CD_3CD_2OD (450 μL) + CH_3CH_2OH (50 μL). The quadruple peak (1:2:2:1) in the red spectrum represents CH_2 of CH_3CH_2OH, and the new quadruple peak (1:2:2:1) in the blue spectrum is the CH_2 signal of additional $CH_3CH_2OCH_2CH_3$.

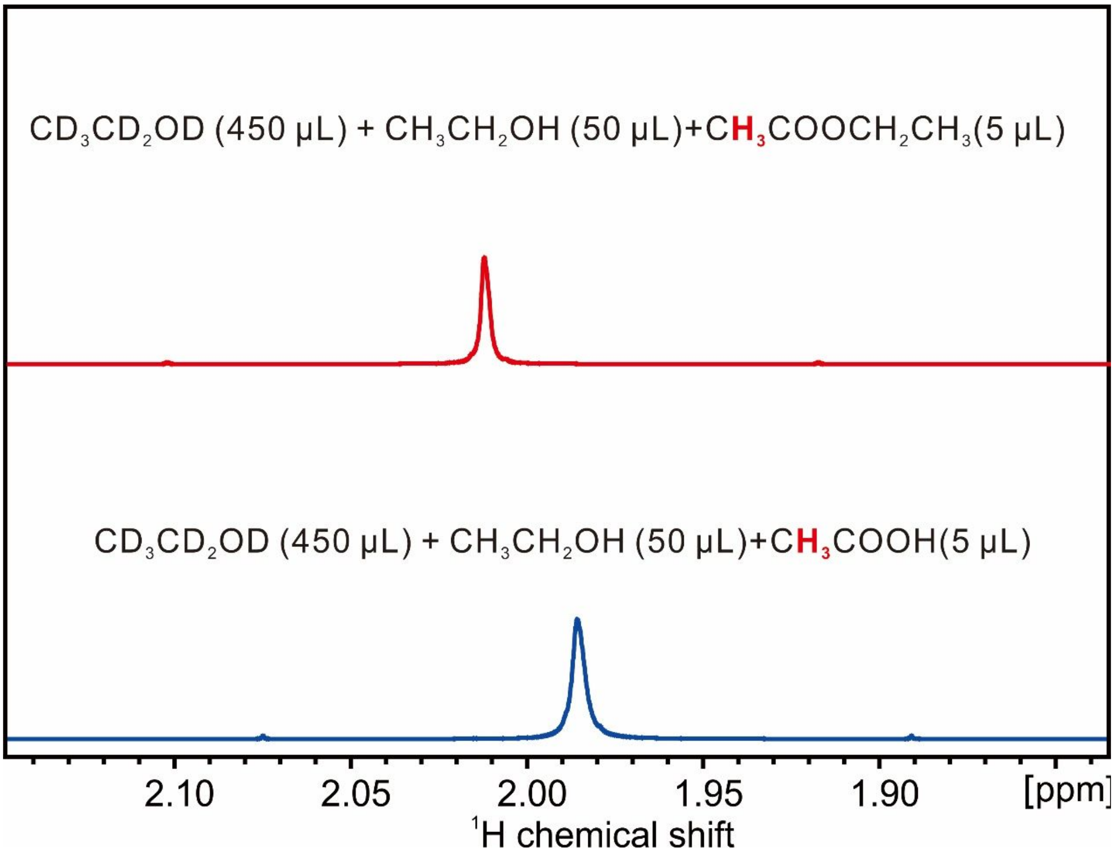

Figure S6. ^{1}H NMR spectra of CD_3CD_2OD (450 μL) + CH_3CH_2OH (50 μL) + CH_3COOH (5 μL) and CD_3CD_2OD (450 μL) + CH_3CH_2OH (50 μL) + $CH_3COOCH_2CH_3$ (5 μL).

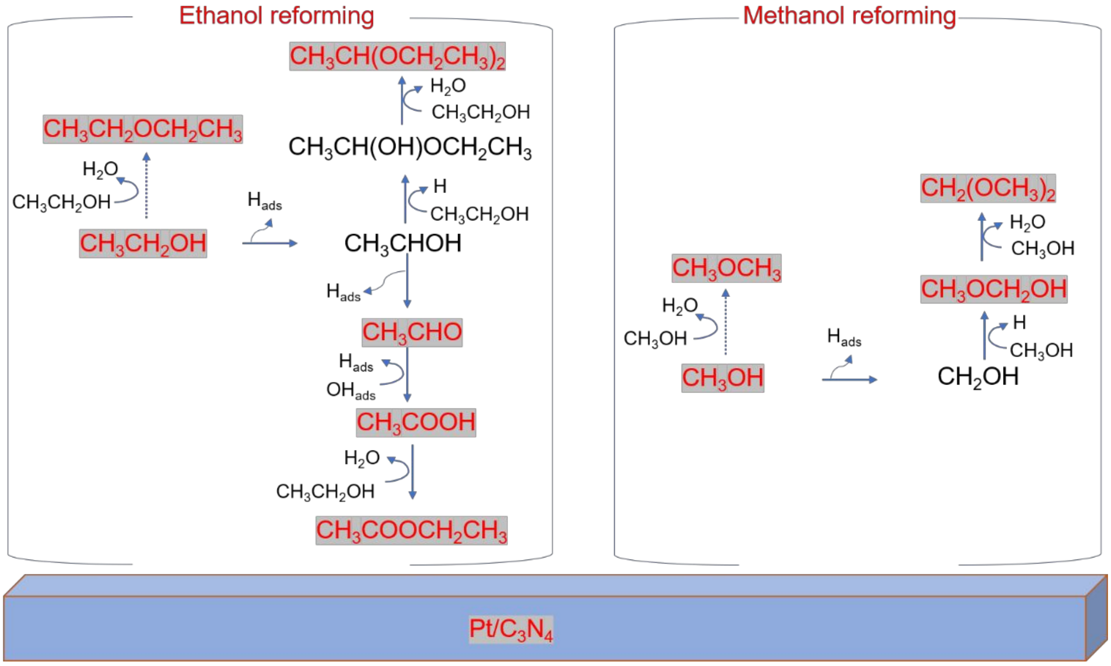

Figure S7. Methanol and ethanol reforming reaction pathways on Pt/C_3N_4 catalysts, proposed on the basis of literature data and our previous reports[1-2].

1. Kim, I.; Han, O. H.; Chae, S. A.; Paik, Y.; Kwon, S.-H.; Lee, K.-S.; Sung, Y.-E.; Kim, H., Catalytic Reactions in Direct Ethanol Fuel Cells. *Angew. Chem. Int. Ed.* **2011,** *50*, 2270-2274.
2. Xu, B.-B.; Zhou, M.; Zhang, R.; Ye, M.; Yang, L.-Y.; Huang, R.; Wang, H. F.; Wang, X. L.; Yao, Y.-F., Solvent Water Controls Photocatalytic Methanol Reforming. *J. Phys. Chem. Lett.* **2020**, *11*, 3738-3744.