Supporting information for

C_2H_2 Treatment as a Facile Method to Boost the Catalysis of Pd Nanoparticulate Catalysts

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Experimental Section

Synthesis of Pd nanosheets: Pd(II) acetylacetonate ($Pd(acac)_2$, 50.0 mg), poly(vinylpyrrolidone) (PVP, MW=58000, 160.0 mg) and TBAB(160.0 mg) were mixed together with N,N-dimethylformamide (DMF,10 mL) and water (2 mL). The resulting homogeneous yellow solution was transferred to a glass pressure vessel. The vessel was then charged with CO to 1 bar and heated at 60 ℃ for 3.0 h before it was cooled to room temperature.

Synthesis of Pd nanocubes: 8.0 mL of an aqueous solution containing poly(vinyl pyrrolidone) (PVP, *M*W ≈ 55 000, 105 mg), *L*-ascorbic acid (AA, 60 mg), KBr (75 mg) and KCl (141 mg) were placed in a 20 mL vial, and pre-heated in air under magnetic stirring at 80 ℃ for 10 min. Then, 3.0 mL of an aqueous solution containing Na2PdCl4 (57 mg) was added using a pipette. After the vial had been capped, the reaction was allowed to proceed at 80 ℃ for 3 h.

Synthesis of surface-clean Pd nanosheets: A 30 μL 1 mol/L H_2PdCl_4 aqueous solution was added into a glass pressure vessel containing 10 mL dimethyl formamide (DMF). Then 1 atm CO atmosphere was introduced at ambient temperature under stirring. After 15 min, the CO gas was removed. 1 mL of pure H_2O was then injected

into the vessel under stirring. This step also lasted for 15 min. To do catalytic reaction, the surface-clean Pd nanosheets were support on SiO_2. The procedures are as follow: The Pd nanosheets colloidal solution was added dropwise into a SiO_2 suspension in ethanol to give a 5% Pd/SiO_2. The catalyst was then filtrated and dried in vacuum at 40℃.

Catalytic hydrogenation of acetylene: 5 ml DMF dispersion of Pd nanosheets was precipitated by acetone, separated via centrifugation, dispersed in 40 ml ethanol. 5 ml C_2H_2, 10 ml H_2, 20 ml Ar were passed through the ethanol solution of Pd nanosheets at 30℃, and the reaction products were analyzed by GC. Only 5% acetylene converted to ethylene. That's because compare with C_2H_2, H_2 have a much low solubility in ethanol. The mole fraction solubility of C_2H_2 at atmospheric pressure, 25 ℃ is 0.015.[1] While the mole fraction solubility of H_2 at 3.12 MPa, 18 ℃ is only 0.0067.[2] So in ethanol solution the main reaction is C_2H_2 reaction with Pd nanosheets.

C_2H_2 treatment: 5 ml DMF dispersion of Pd nanosheets was transferred to a glass pressure vessel, The vessel was then charged with C_2H_2 to 1 bar and heated at 30 ℃ for different time. The treatment of Pd nanocubes is the same as Pd nanosheets. Except that before treatment the aqueous solution of Pd nanocubes were precipitated by acetone, separated via centrifugation, dispersed in DMF.

Catalytic hydrogenation of styrene: All hydrogenation reactions were carried out under at 30 ℃, 1 atm of H_2. A round-bottom flask, charged with the Pd catalyst (0.25 mg)，1 mmol styrene，10 ml ethanol and a magnetic stirrer, was connected to a gas buret (500 mL) with a flask to balance the pressure. The flask was filled with hydrogen. The reaction was monitored by the volume of gas consumed and by gas chromatography. After the completion of the reaction, the catalyst was filtered from the reaction mixture. The solution was analyzed by GC.

Recycle of the catalyst: The used catalyst was filtrated and washed once with ethanol, it was then put into use again following the same reaction condition.

Catalytic hydrogenation of nitrobenzene: The procedure was the same as catalytic hydrogenation of styrene except the use 0.3 mmol nitrobenzene as substrate.

Catalytic hydrogenation of 4-nitrophenol (4-NP): The reduction reactions of 4-NP by $NaBH_4$ were chosen as model reactions to test the catalytic activity of Pd nanosheets before and after C_2H_2 treatment. Pd nanoparticles suspension in water (0.05 mL, 0.03 $mgmL^{-1}$) was added to $NaBH_4$ aqueous solution (3 mL, 0.03 M), and the mixture was stirred for 10 min at room temperature. 4-NP(0.04 mL, 0.01 M) was then added to the mixture. After that, the solution were quickly added into quartz cuvettes. UV/Vis spectra were recorded at regular intervals to monitor the progress of the reaction.

Raman spectroscopy: Raman spectra were acquired with a laser Raman microscope (RAMAN-11; Nanophoton Co., Osaka, Japan) through a line-shaped 532 nm laser at 1mW power. Scan mode: xy-imaging, the exposure time of each line was 2s and total exposure time was 330 s.

References:

(1) McKinnis, A. *Industrial & Engineering Chemistry* **1955**, *47*, 850.

(2) Wainwright, M. S.; Ahn, T.; Trimm, D. L.; Cant, N. W. *Journal of Chemical and Engineering Data* **1987**, *32*, 22.

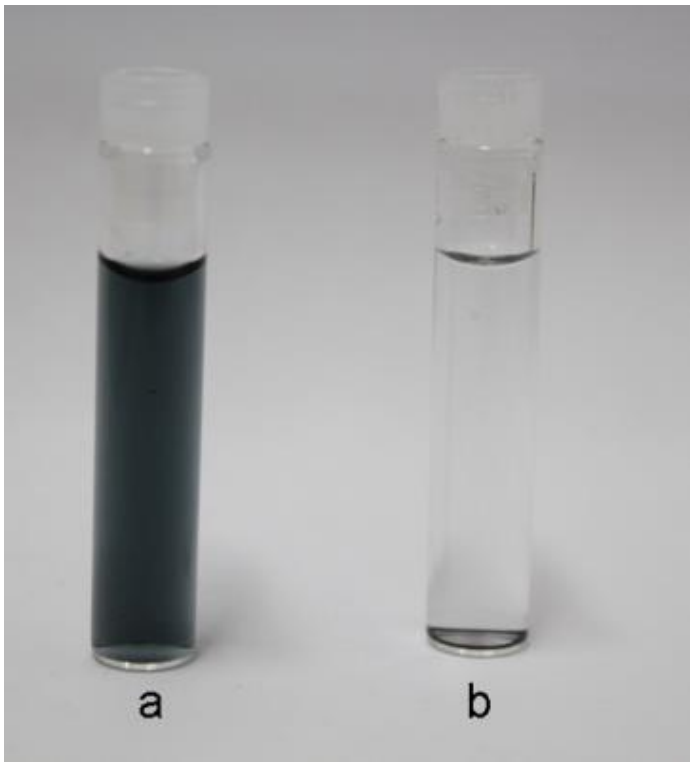

Figure S1. Photos of Pd nanosheets dispersed in ethanol solution: (a) before and (b) after the catalytic hydrogenation of C_2H_2.

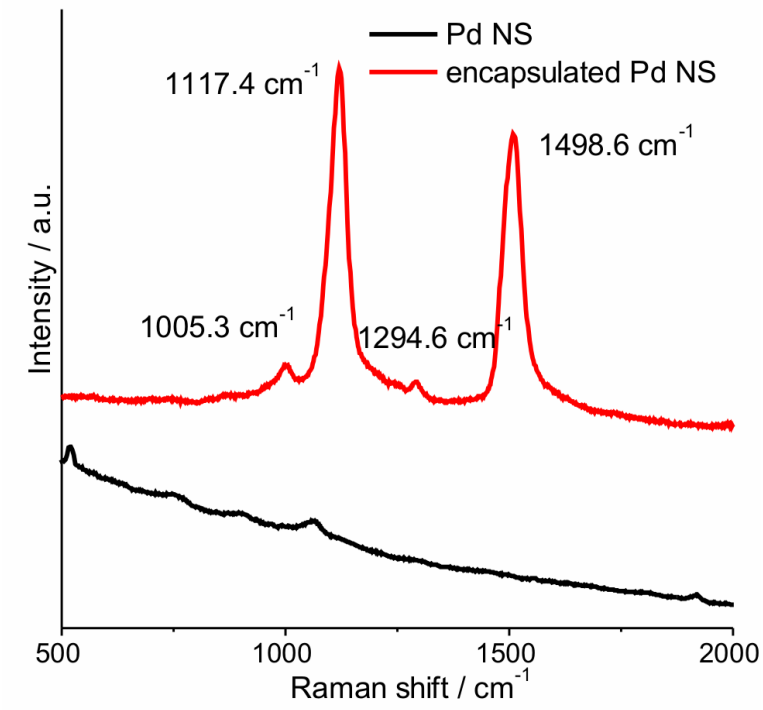

Figure S2. Raman spectra of Pd nanosheets before and after catalytic hydrogenation of C_2H_2.

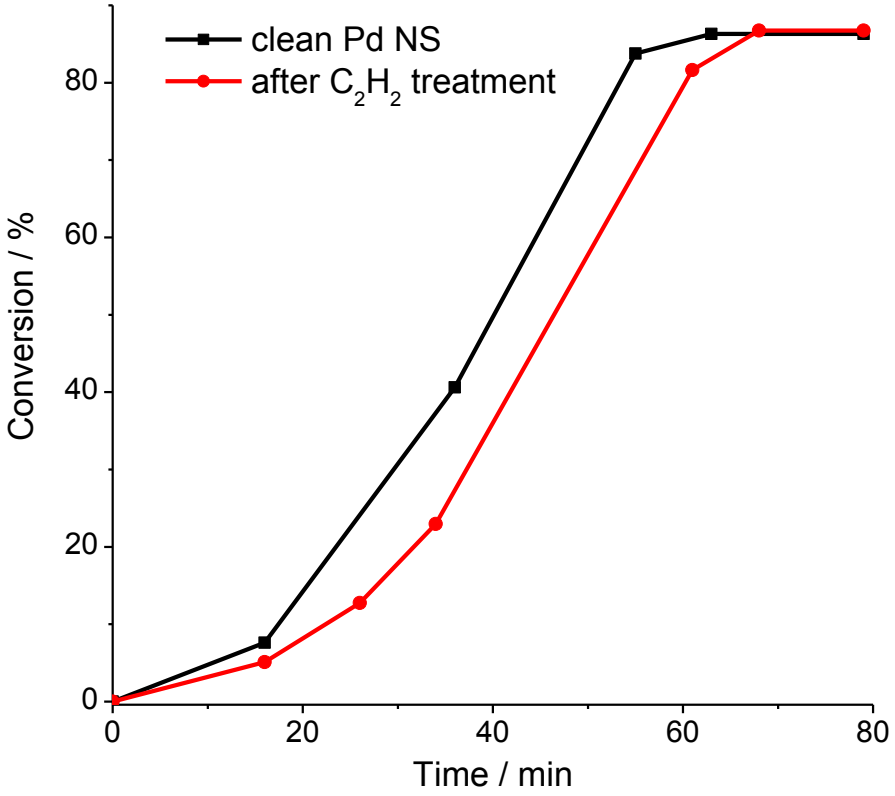

Figure S3. Catalytic hydrogenation of cis-2-butene-1,4-diol by Pd nanosheets before and after the C_2H_2 treatment. Catalytic conditions: 1 mmol cis-2-butene-1,4-diol, 0.25 mg Pd, 10 ml ethanol, 1 atm, 30 °C. The Pd nanosheets used in the studies were surface-clean without PVP.

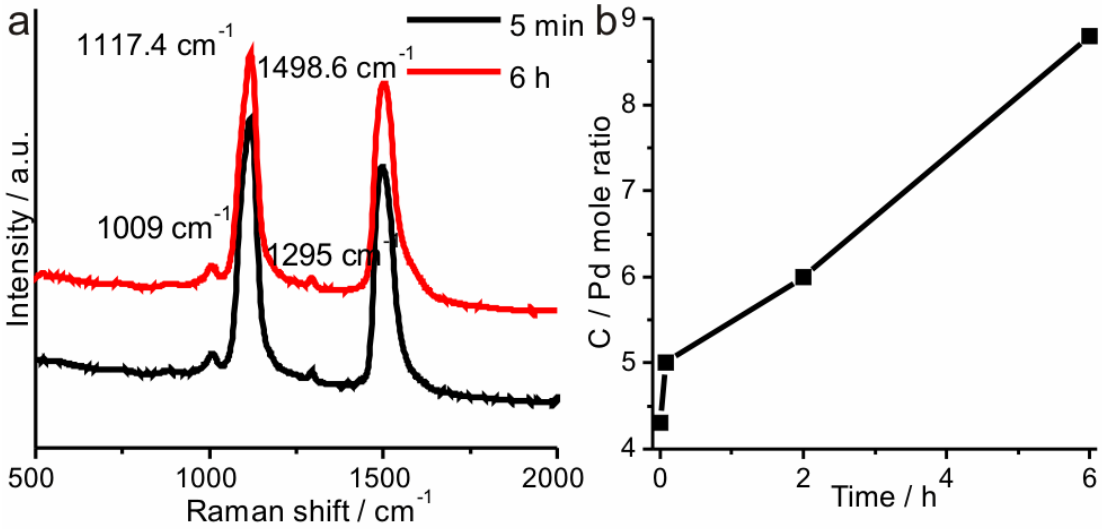

Figure S4. (a) Raman of Pd nanosheets treated with C_2H_2 for different time. (b) The relation between C/Pd mole ratio and C_2H_2 treatment time.

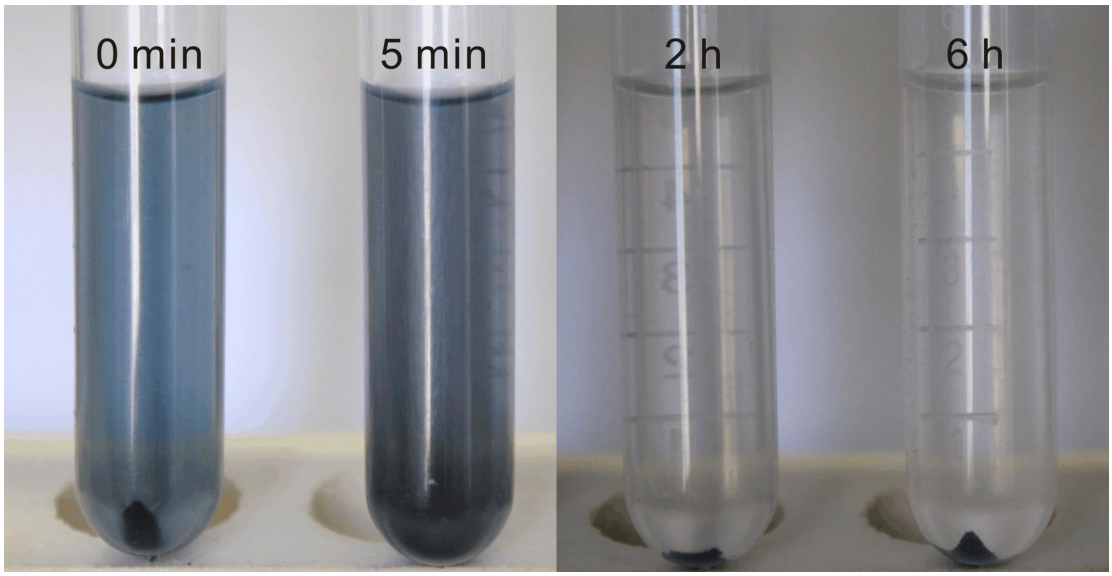

Figure S5. Photos of samples by centrifugal separation after catalytic reaction: the time is C_2H_2 treatment time.

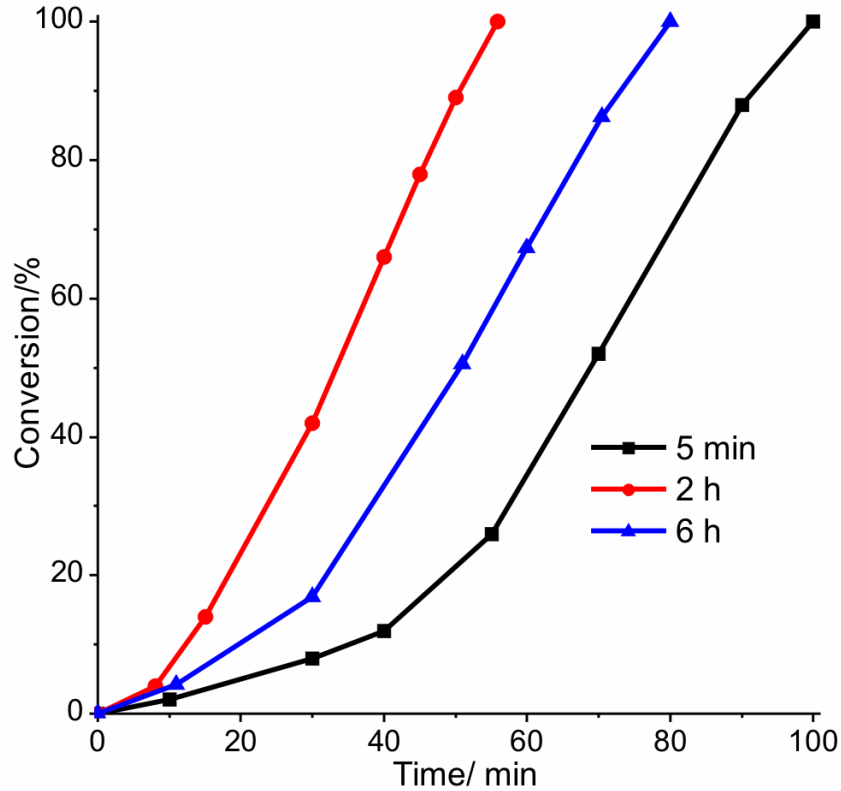

Figure S6. Catalytic hydrogenation of styrene by Pd nanosheets treated with C_2H_2 for different time.

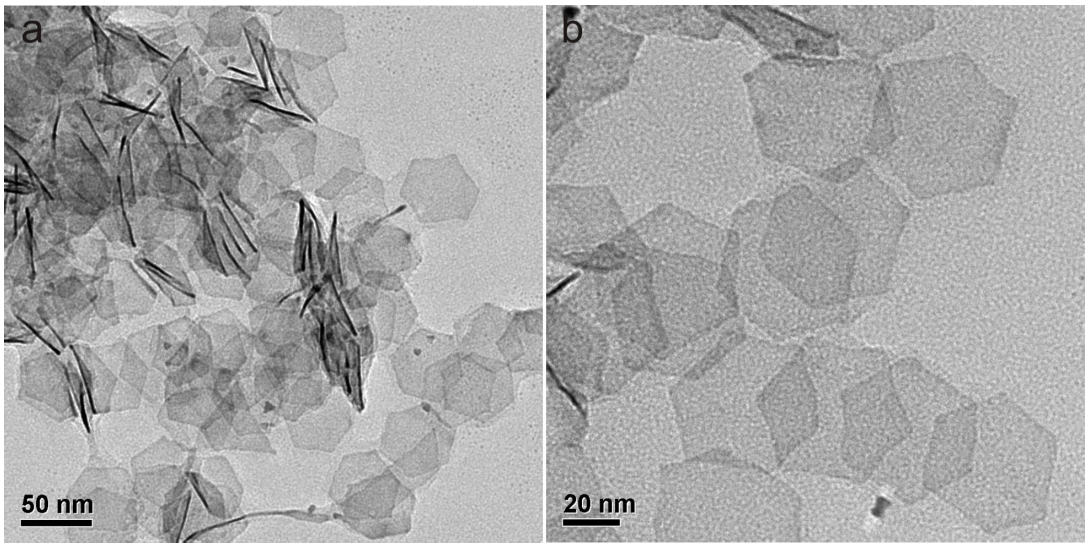

Figure S7. TEM of the Pd nanosheets after 6 cycles of catalytic tests.

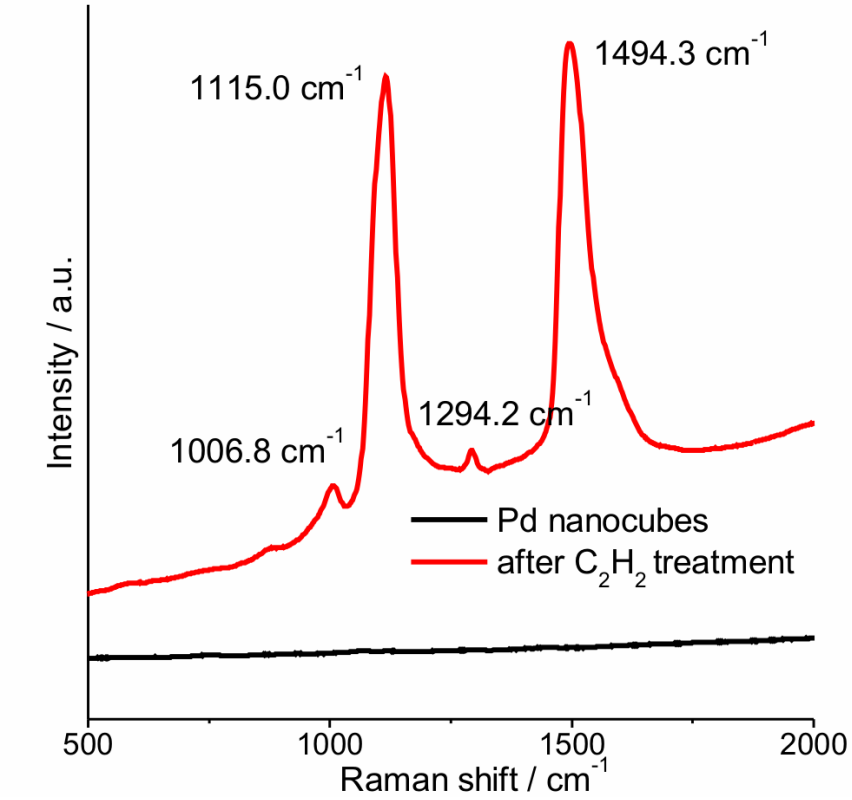

Figure S8. Raman spectrum of Pd nanocubes before and after the C_2H_2 treatment.

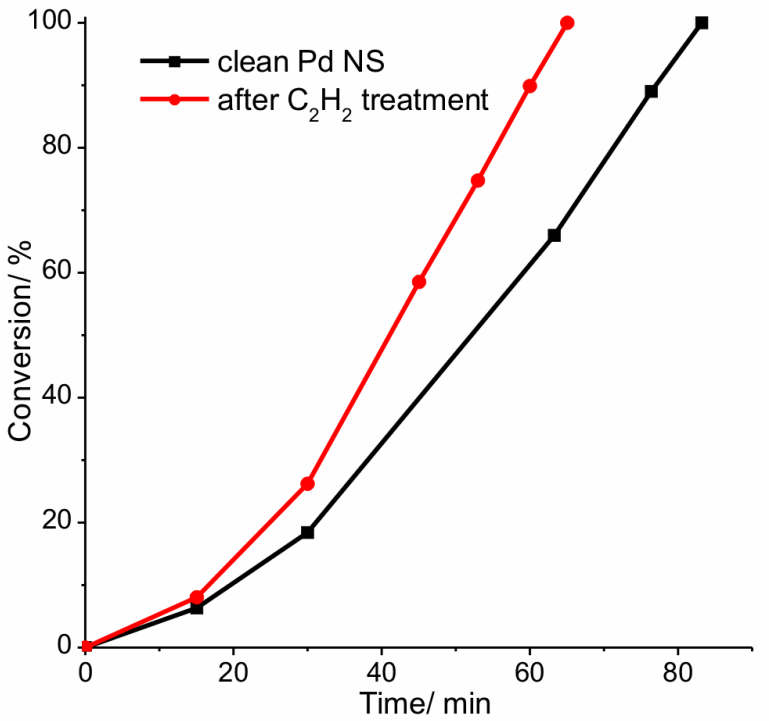

Figure S9. Catalytic hydrogenation of styrene by surface-clean Pd nanosheets before and after the C_2H_2 treatment.