Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

Pd@C core-shell nanoparticles on carbon nanotube as highly stable and selective catalysts for hydrogenation of acetylene to ethylene

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Experiment Section

1. Catalyst synthesis

The synthesis of oxidized Carbon nanotube (CNT) supported Pd catalyst. CNT supported Pd catalyst was prepared by a deposition-precipitation method. First, the pH values of $Pd(NO_3)_2$ solution were adjusted using 0.25 M Na_2CO_3 solution to about 7, and the pH values of CNT solutions were adjusted to about 10 using the 0.25 M Na_2CO_3 solution. Second, the $Pd(NO_3)_2$ solutions were added to the carbon supports solutions dropwise under stirring at 100 °C. After stirring for 1 h, the mixtures were cooled to room temperature, filtrated and washed. Afterwards, the solids were dried at 100 °C and reduced with H_2 at 200 °C for 2 h. This sample was labeled as Pd/CNT.

Preparation of core-shell Pd@C nanoparticle supported on CNT (Pd@C/CNT). First, Pd/CNT was modified with an nitrogen-containing ionic liquid (IL), 1-ethyl-3-methylimidazolium dicyanamide ([Emim][DCA]), by dispersing Pd/CNT into the IL phase and removing the excess IL with centrifugation. Then the IL modified Pd/CNT was annealed at 350

˚C for 1h in vacuum, followed by being annealed at higher temperature in Ar atmosphere for 1h. The obtained sample was labeled as Pd@C/CNT.

2. Characterization

Transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) images were obtained by using an FEI Tecnai G^2 F20 microscope equipped with EDAX and HAADF detectors. X-ray diffraction (XRD) patterns of the catalysts were acquired using an X-ray diffractometer (D/MAX-2400) with Cu K_α source at a scan rate of 2° min^{-1}. X-ray photoelectron spectroscopy (XPS) spectra were carried out by ESCALAB 250 instrument with Al K_α X-rays (1489.6 eV, 150 W, 50.0 eV pass energy). The quasi in situ XPS analyses were performed on a PHI5000 Versaprobe-II Scanning XPS Microprobe system. This system also employed an Al K_α X-rays, and the pass energy was 46.95 eV. The binding energy (BE) was relative to the adventitious C1 s line at 284.6 eV.

3. Thermal treatment

In order to investigate the effect of *in situ* formed N-doped carbon layers, a control experiment was performed by annealing the as-prepared catalysts Pd/CNT in tubular furnace under flowing Ar gas conditions at 700 ˚C for 1h, which is same with the annealing condition of IL-modified Pd/CNT. To further study the thermal stability of Pd nanoparticles (NPs), Pd/CNT and Pd@C/CNT were annealed with an *in situ* heating TEM holder and a tubular furnace under flowing Ar gas conditions, respectively. The *in situ* heating experiments were carried out in vacuum condition by DENSsolutions heating TEM holder, from room temperature (RT) via 350 ˚C for 1h, 500 ˚C for 1h to 700 ˚C for 1h, respectively. Actual metal loadings of the as-prepared catalysts were quantified on a Leeman Laboratories Prodigy inductively coupled plasma mass spectrometry (ICP-MS).

4. Reaction test

The partial hydrogenation of acetylene in excess ethylene was conducted in a fixed-bed flow quartz reactor. The feed gas consisted of 2.99% H_2, 20.11% C_2H_4, 0.504% C_2H_2 with He as the balance gas from Dalian Special Gases Co., Ltd.. The total flow rate was kept at 20 ml/min, which was controlled by mass flow controller. The amount of uncoated Pd/CNT catalyst was 5 mg, while the amount of carbon layers coated Pd@C/CNT catalyst was 20 mg. The reaction was conducted in a temperature-programmed mode, ramping at 1 ˚C/min. The gas composition from the microreactor outlet was analyzed by online gas chromatography (Agilent Technologies 7890A) equipped with a FID detector.

Acetylene conversion and selectivity to ethylene were calculated as follows:

$$Conversion = \frac{C_2H_2(feed) - C_2H_2}{C_2H_2(feed)} \times 100\%$$

$$Selectivity = (1 - \frac{C_2H_6 + 2 \times C_4}{C_2H_2(feed) - C_2H_2}) \times 100\%$$

C_4 represents butane and dibutene.

Supporting Figures

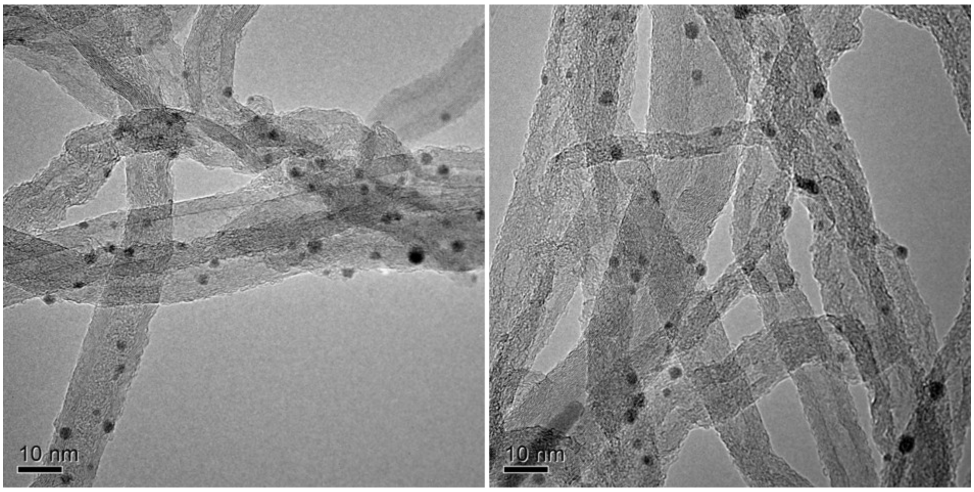

Figure S1. TEM images of Pd/CNT.

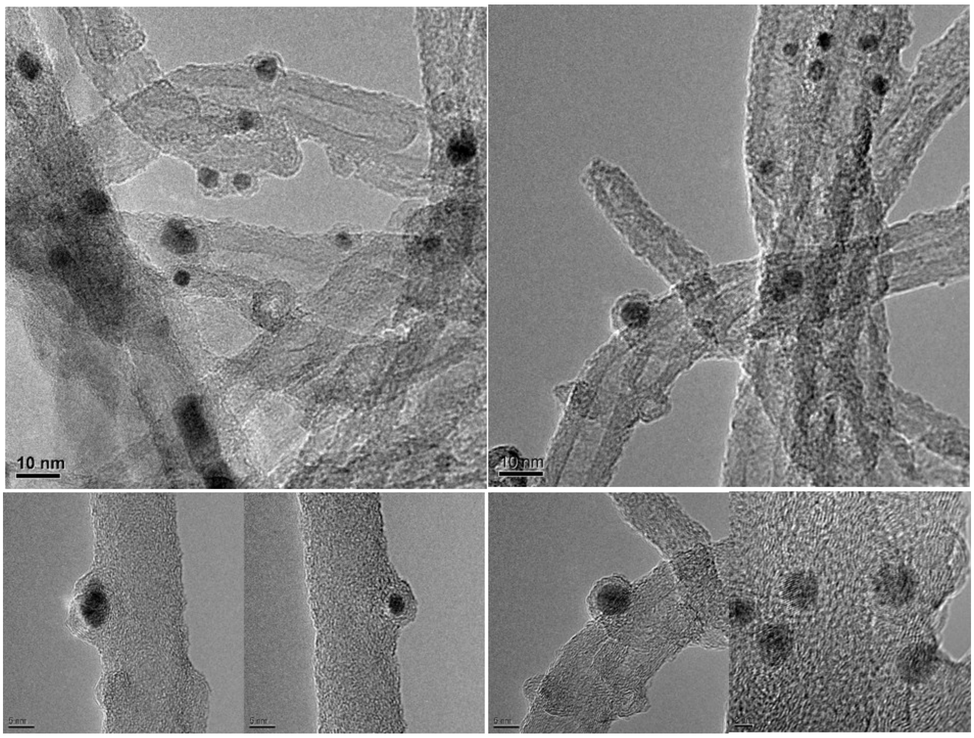

Figure S2. TEM images of Pd@C/CNT.

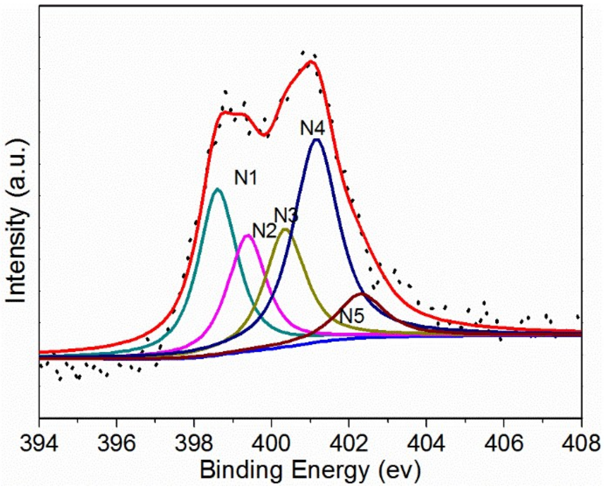

Figure S3. N 1s XPS core level spectrum of Pd@C/CNT.

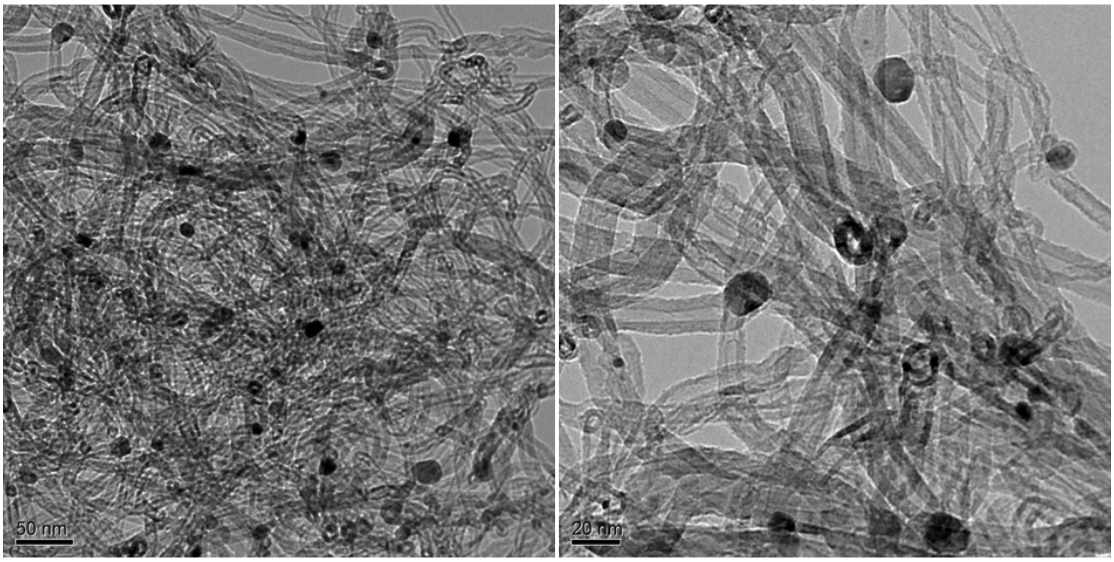

Figure S4. TEM images of Pd/CNT-700, which was obtained by annealing Pd/CNT at 700 ˚C in Ar atmosphere.

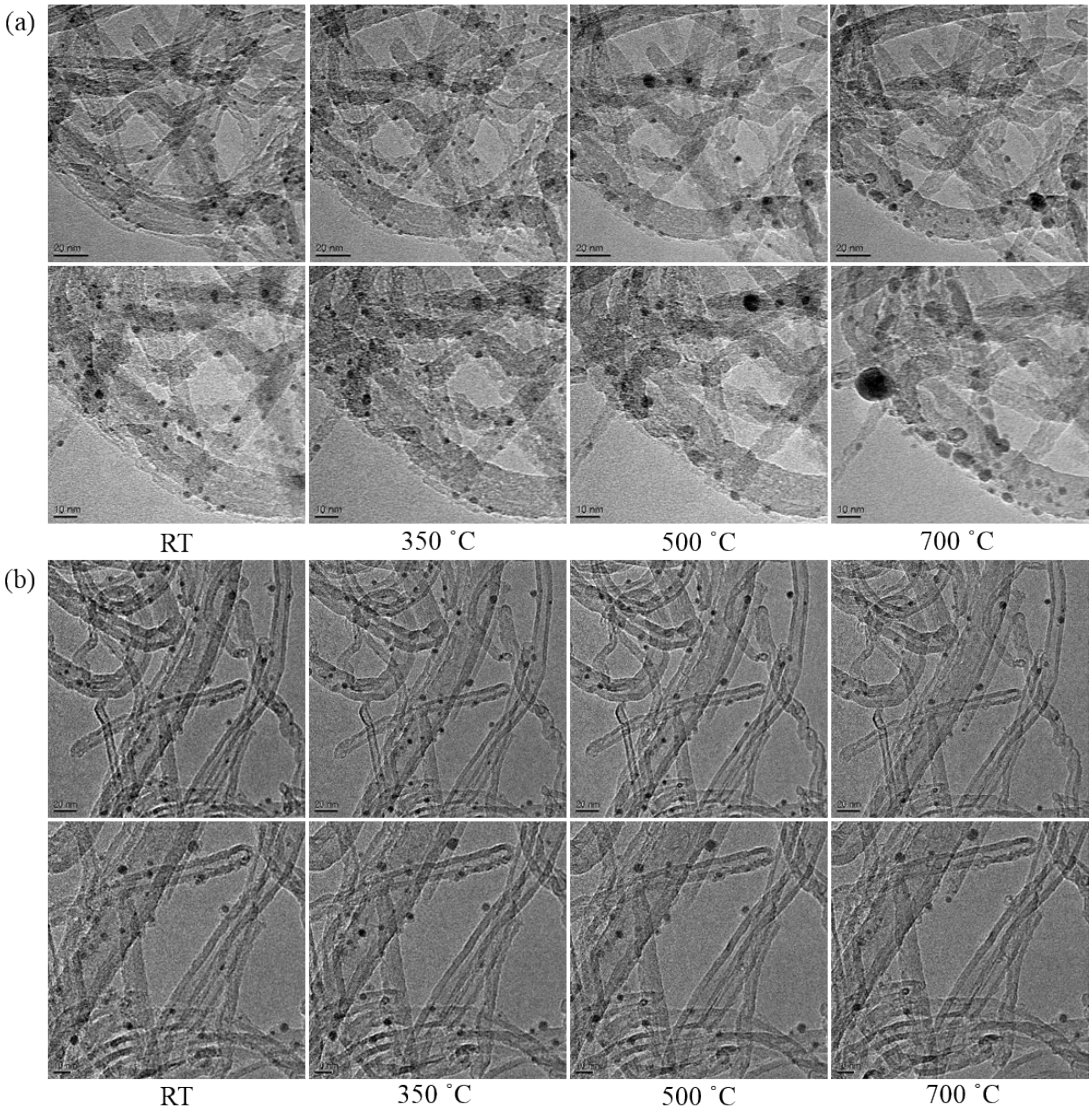

Figure S5. TEM images of Pd/CNT (a) and Pd@C/CNT (b) annealed using an *in situ* heating TEM holder at RT, 350 ˚C for 1h, 500 ˚C for 1h, and 700 ˚C for 1h.

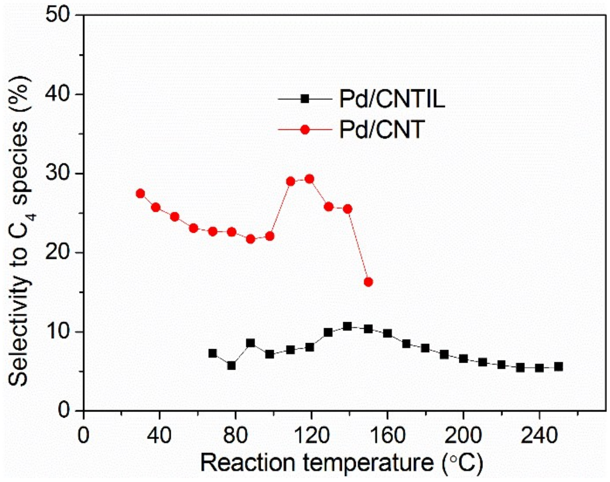

Figure S6 C_4 species selectivity as a function of reaction temperature over Pd/CNT and Pd@C/CNT.

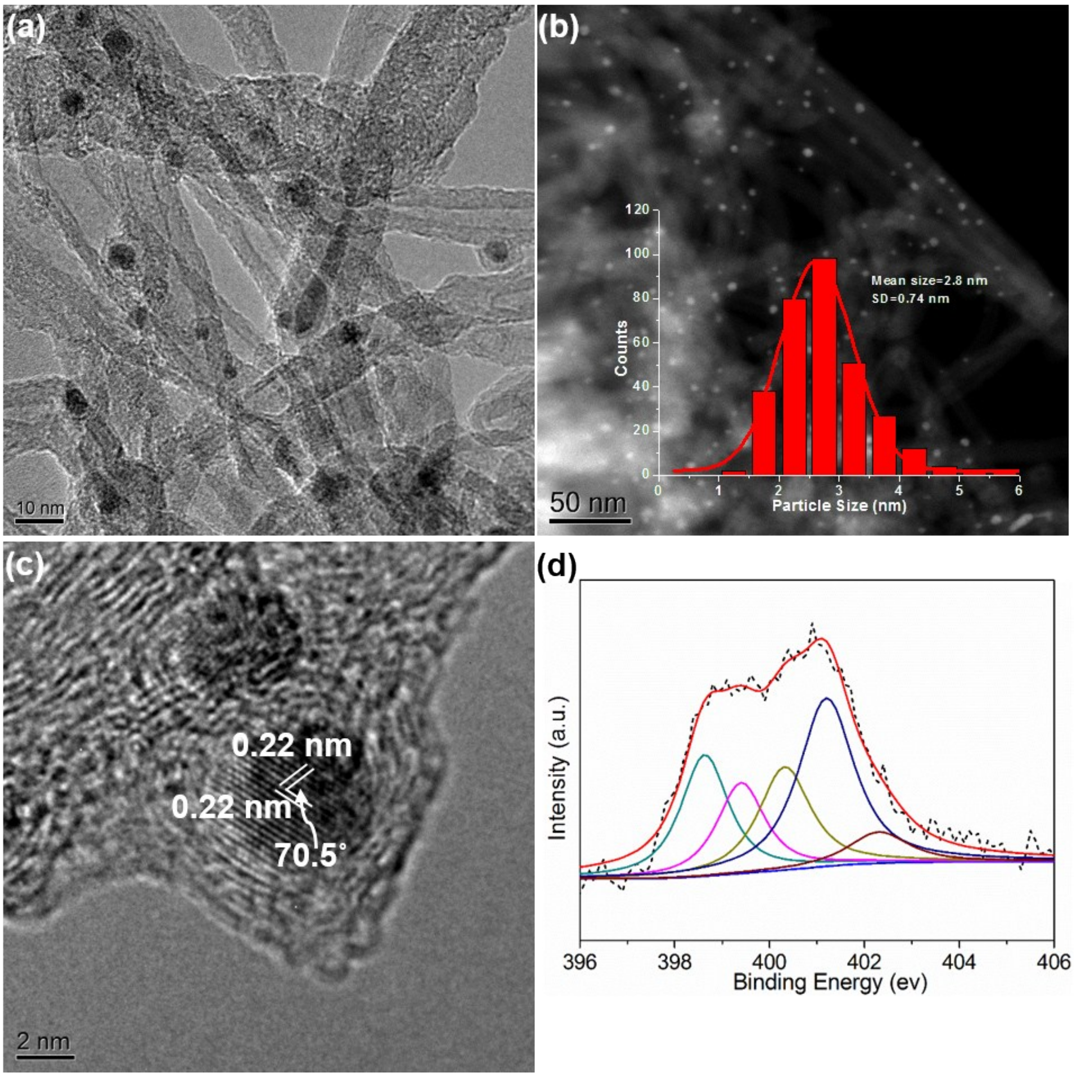

Figure S7 (a) TEM image, (b) HAADF-STEM image, (c) HRTEM image, (d) N1s XPS spectrum of used Pd@C/CNT, the inset in (b) is the corresponding histogram of particle size distribution.

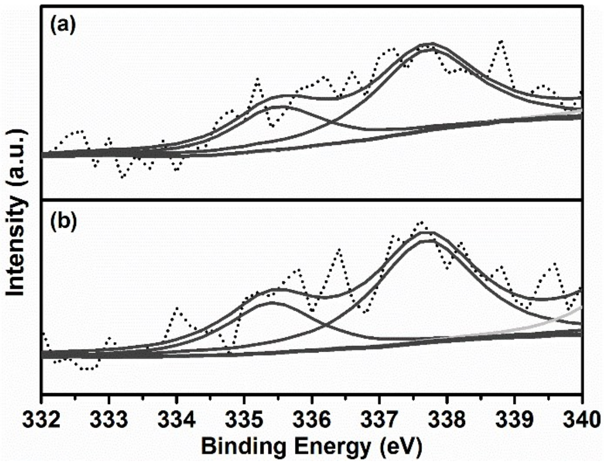

Figure S8 Deconvolution results of Pd 3d XPS core level spectra of (a) fresh Pd@C/CNT and (b) used Pd@C/CNT at 150 °C, obtained by quasi-in situ XPS technique.

Supporting Table

Table S1. Elemental analysis of Pd/CNT and Pd@C/CNT.

Samples	Carbon content [at. %] [a]	Oxygen content [at. %] [a]	Nitrogen content [at. %] [a]	Palladium content [at. %] [a]	Palladium weight loading [wt. %][b]
Pd/CNT	94.66	4.50	0.39	0.45	2.0
Pd@C/CNT	87.58	6.73	5.41	0.28	1.5

[a] Determined by XPS; [b] Determined by ICP-MS.