Supplementary Information

Bimetallic palladium nickel nanoparticles loaded on ammonia-alkalized multi-walled carbon nanotubes for efficient dehydrogenation of formic acid

1. Chemicals:

Multi-walled carbon nanotubes (Shandong Dazhan nano materials Co., Ltd, 97%), O-phenylenediamine (OPDA, Shanghai Macklin Biochemical Co., Ltd, >98%), acetone (Yantai Yuandong Fine Chemical Co., Ltd, >99.5%), potassium chloropalladite (K_2PdCl_4, Shanghai Macklin Biochemical Co., Ltd, >98%), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, Tianjin Bodhi Chemical Co., Ltd, >98%), sodium borohydride ($NaBH_4$, Shanghai Shanpu Chemical Co., Ltd, ≥96.0%), formic acid (FA, Shanghai Macklin Biochemical Co., Ltd, >98%), and deionized water.

2. Characterization

X-ray diffraction (XRD) was performed using a Rigaku D/MAX/2500 PC powder X-ray diffractometer containing Cu-K (40kv, 40mA) radiation. Infrared (IR) spectrograms were obtained with a Thermo Fisher Nicolet IS10 infrared spectrometer. Transmission electron microscopy (TEM) maps and high-resolution transmission electron microscopy (HR-TEM) maps were measured on a Tecnai G2 F30 S-Twin instrument in conjunction with a 200Kv field emission gun. The scanning electron microscope (SEM) model JSM-6700F was used to obtain the topography and energy dispersive spectra (EDS). X-ray photoelectron spectroscopy (XPS) was acquired with an ESCALAB 250Xi spectrophotometer. GC-8A (Molecular Sieve 5A, carrier gas Ar as carrier gas) and GC-8A (Porapack N, He as carrier gas) analyzers (Shimadzu) were used to analyze the gases collected after at least three times of the reactor with argon.

3. Calculation methods

The turnover frequency (TOF) reported here is an apparent TOF value based on the number of metal atoms in catalyst, which is calculated from the equation as follow:

$$TOF= P_0V/(2RTn_Mt)$$

Where P_0 is the atmospheric pressure (101325 Pa), V is the final generated volume of (H_2+CO_2) gas, R is the universal gas constant (8.3145 m^3 Pa mol^{-1} K^{-1}), T is the room temperature (298 K), n_M is the total mole number of Pd and Ni atoms in the catalyst and t is the completion time of the reaction in hour.

4. Durability testing of the catalysts

After the first decomposition of formic acid by catalyst $Pd_{0.7}Ni_{0.3}$/OPDA-MWCNTs at 323 K, an equal amount of 6 mmol of formic acid was added to the flask. The cycle test performance of the catalyst was obtained by repeating the operation five times.
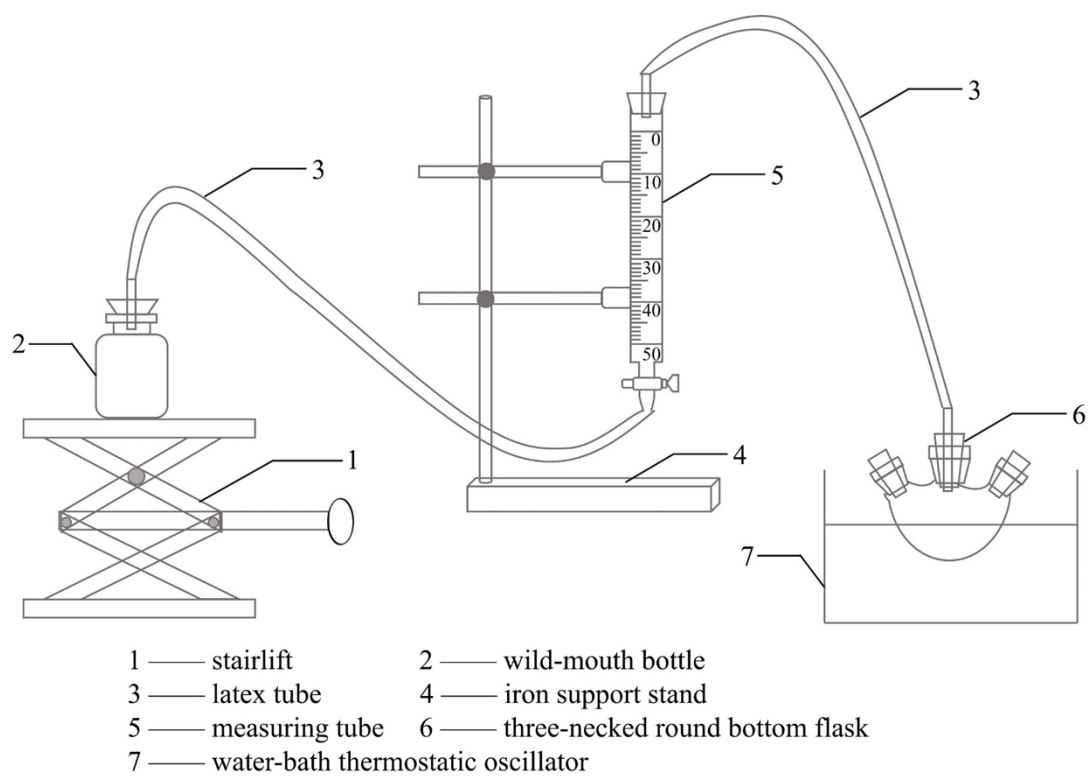
1 —— stairlift   2 —— wild-mouth bottle
3 —— latex tube   4 —— iron support stand
5 —— measuring tube   6 —— three-necked round bottom flask
7 —— water-bath thermostatic oscillator

Fig. S1. The schematic diagram of the experimental set-up for catalytic performance testing.
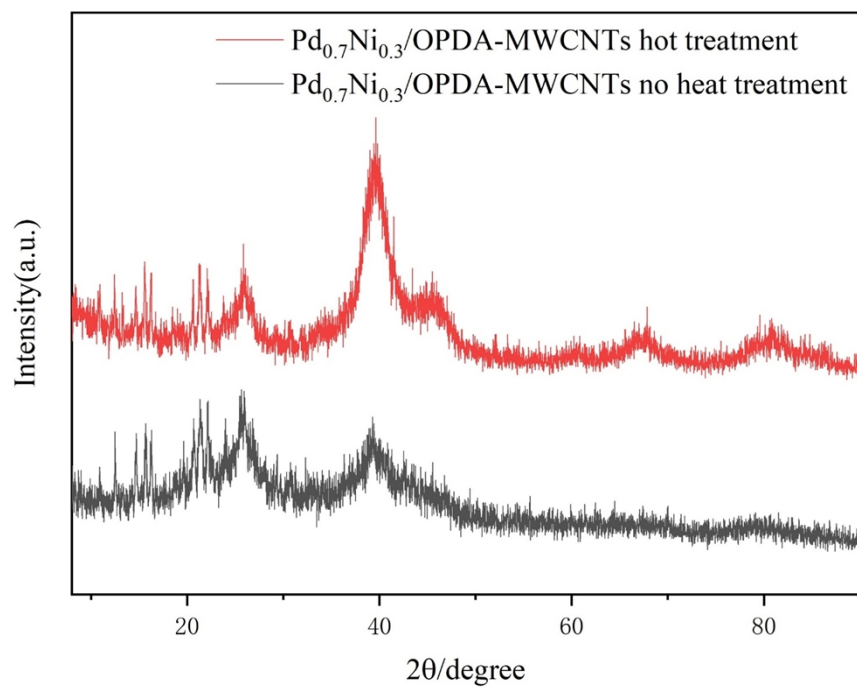
Fig. S2. The XRD comparison of the catalyst $Pd_{0.7}Ni_{0.3}$/OPDA-MWCNTs with and without heat treatment.
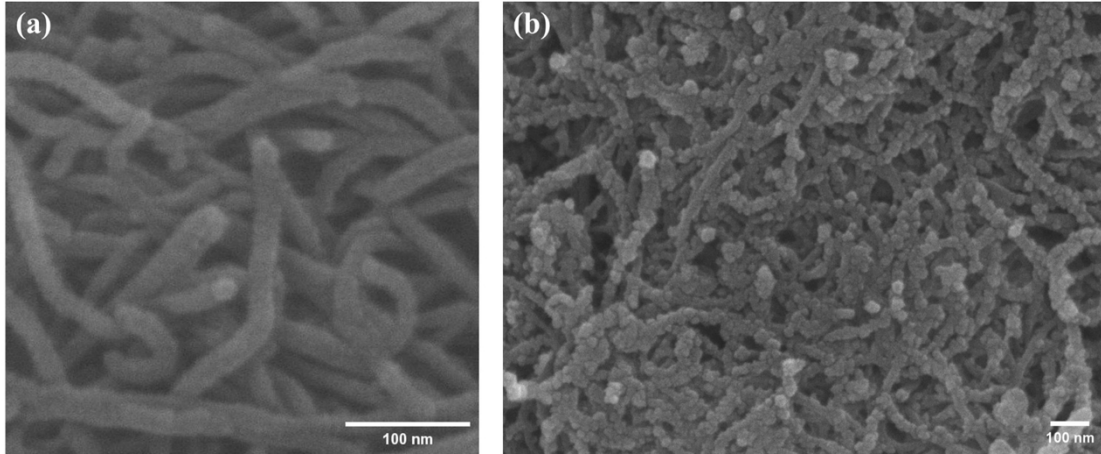
Fig. S3. SEM images of (a) MWCNTs and (b) $Pd_{0.7}Ni_{0.3}$/OPDA-MWCNTs.
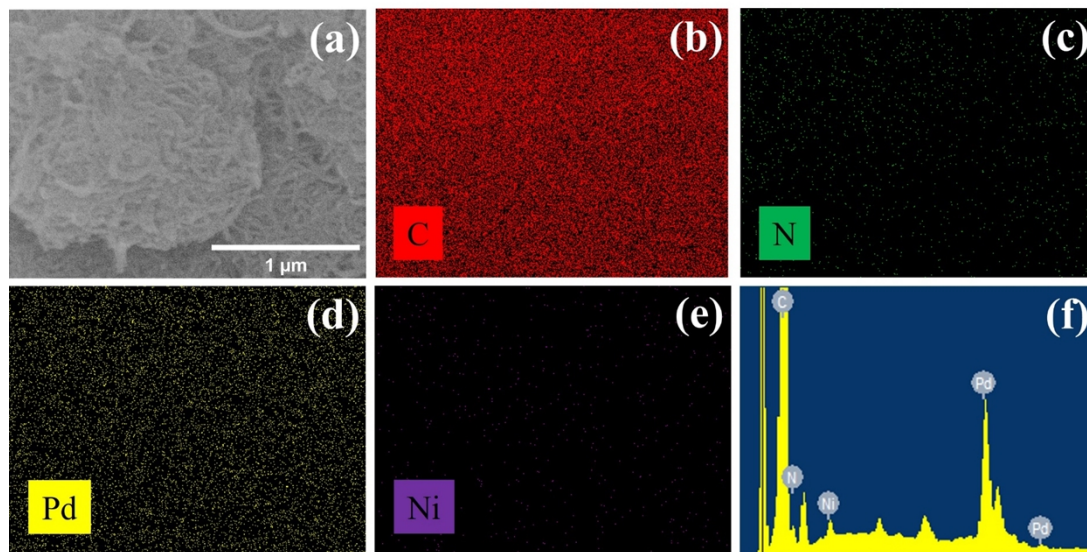
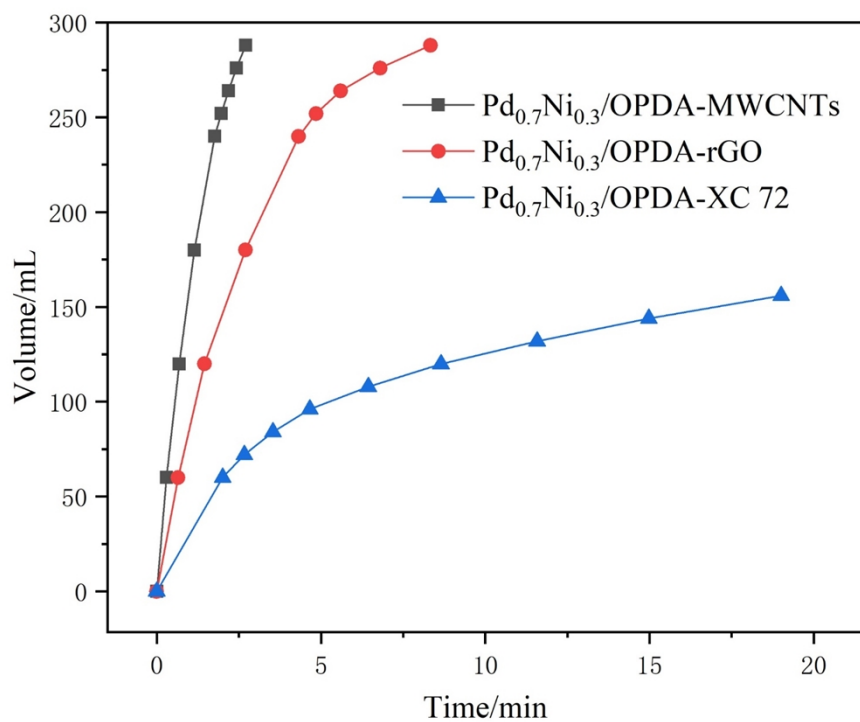**Fig. S4.** Elemental mappings of C, N, Pd and Ni.

Fig. S5 Volume of the generated gas versus time for the dehydrogenation of FA over $Pd_{0.7}Ni_{0.3}$/OPDA-MWCNTs, $Pd_{0.7}Ni_{0.3}$/OPDA-rGO, $Pd_{0.7}Ni_{0.3}$/OPDA-XC 72.
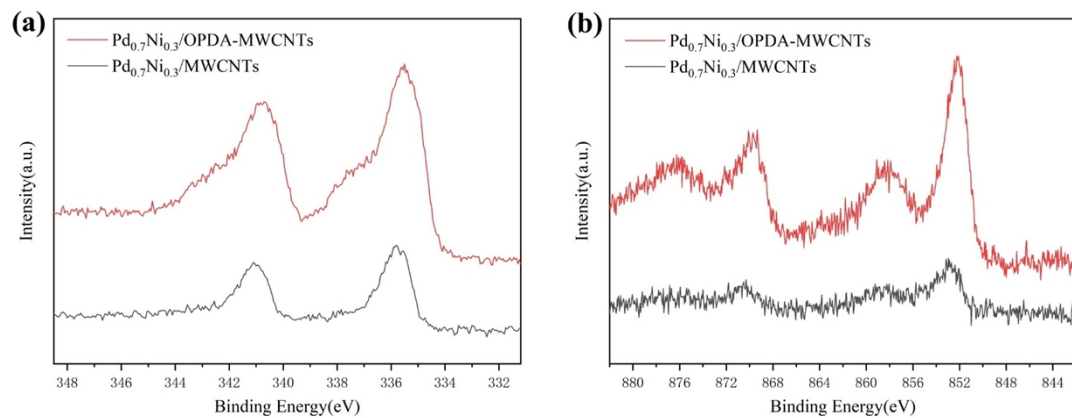
Fig. S6. (a, b) XPS spectra of Pd and Ni for Pd$_{0.7}$Ni$_{0.3}$/OPDA-MWCNTs and Pd$_{0.7}$Ni$_{0.3}$/MWCNTs.
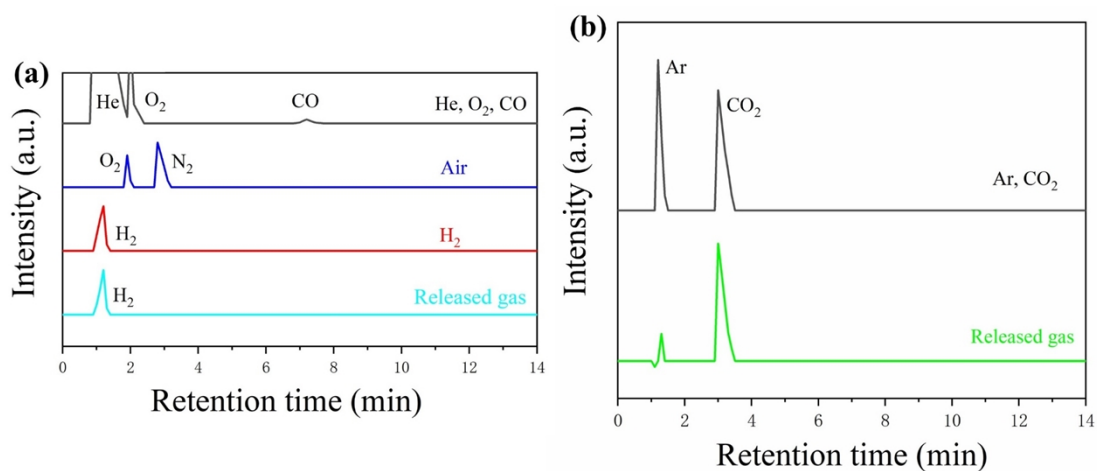
Fig.S7. (a) Gas chromatograms of CO, air and H_2 as reference gases and the released gas from FA decomposition over the as-prepared PdNi/OPDA-MWCNTs catalyst; (b) Gas chromatograms of CO_2 as reference gas and the released gas from FA decomposition over the as-prepared PdNi/OPDA-MWCNTs catalyst.
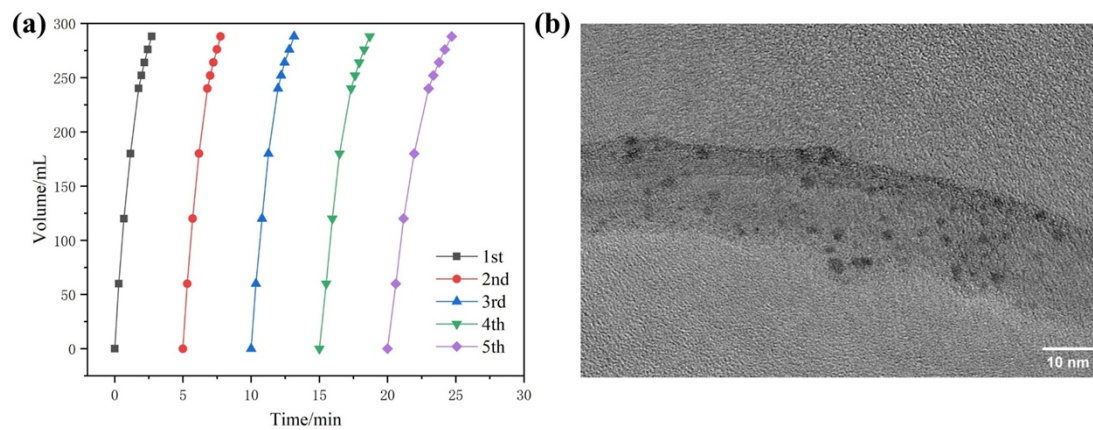
Fig. S8. Durability testing (a) of $Pd_{0.7}Ni_{0.3}$/OPDA-MWCNTs and TEM image (b) after cycling test.