Electronic Supplementary Information

Catalytic CO_2 Hydrogenation to Formic Acid over Carbon Nanotube–Graphene Supported PdNi Alloy Catalysts

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S1. Synthesis of graphene oxide

Graphene oxide was synthesized by Hummers method using graphite flake. Briefly, 2g of graphite flake was added into a mixture solution of H_2SO_4 (50 mL) and $NaNO_3$ (1 g) in a 3 neck round bottom flask (500 mL). The mixture was vigorous stirred with magnetic bar in 10 min, then put in an ice-bath (0 – 5^oC) and further stirring 20 min to obtain green solution. $KMnO_4$ (6 g) was slowly added to flask under continuous stirring in ice-bath (0 – 5^oC). After 20 min, ice-bath was removed and temperature increased to 35^oC. The solution was further stirred at 35^oC for 2 h and then 100 mL DI H_2O was added dropwise to the mixture. The solution temperature increased up to 98^oC and kept for 30 min until no bubble appeared and dark brown solution turned to light brown solution. After that, the reaction was terminated by addition of 300 mL DI H_2O (40^oC) and mixture of 4 mL H_2O_2 35% solution in 40 mL DI H_2O. The product was filtered using mixed-cellulose ester membrane filter (pore size: 0.45µm) and washed 2 times with DI H_2O. The resulting mixture was then re-dispersed in 350 mL DI H_2O (40^oC) to remove residual metal ions and acid and kept stirring for 1 h at 40^oC. After the second filtering, graphite oxide was washed with liquid N_2 and transferred to Freeze drying in 4 days. Finally, we obtained around 3.3 g of graphite oxide after grinding (Fig. S1).

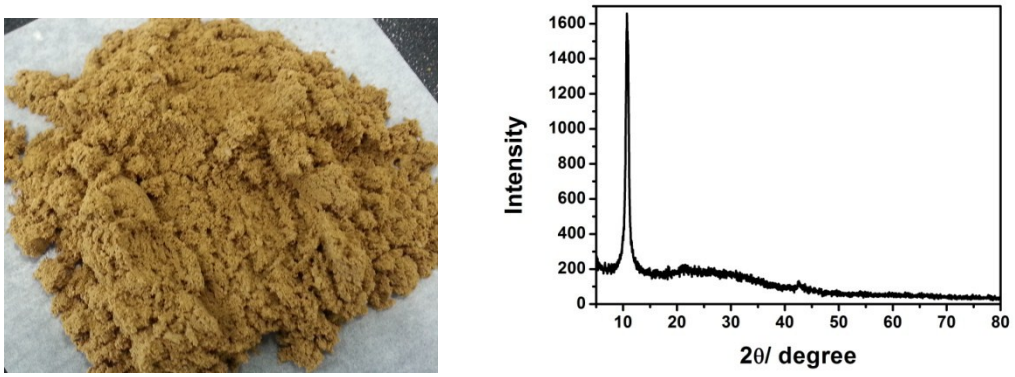

Fig. S1 (a) Photograph of GO and (b) XRD pattern of GO

1. Catalyst characterization

1.1. Energy dispersive spectrum (EDS) - High angle annular dark field (HAADF) TEM image

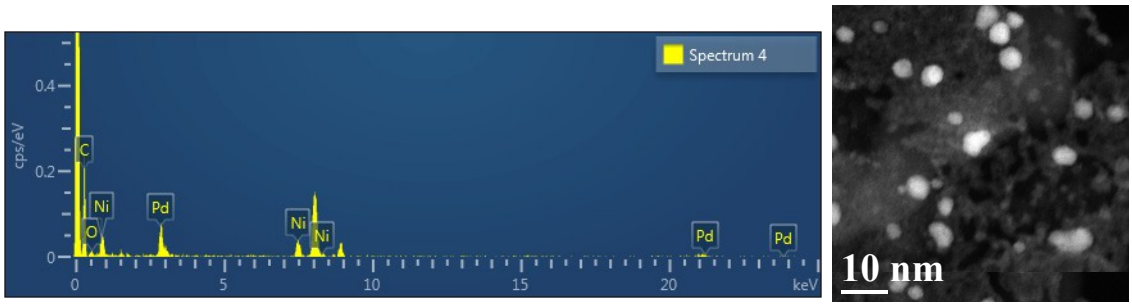

Fig. S2 (a) EDS spectrum and (b) HAADF TEM image of Pd_3Ni_7/CNT-GR.

1.2. Fourier transform infrared (FTIR) and Raman spectroscopy

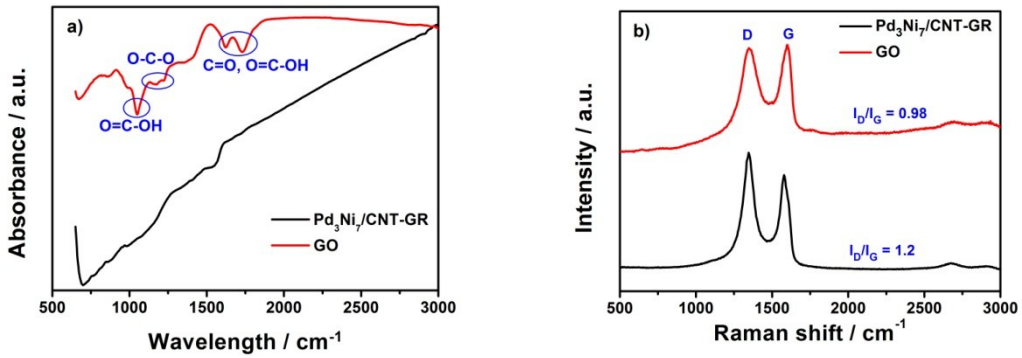

Fig. S3 (a) FTIR spectra and (b) Raman spectra of Pd_3Ni_7/CNT-GR and GO samples

1.3. Ni 2p XPS spectra

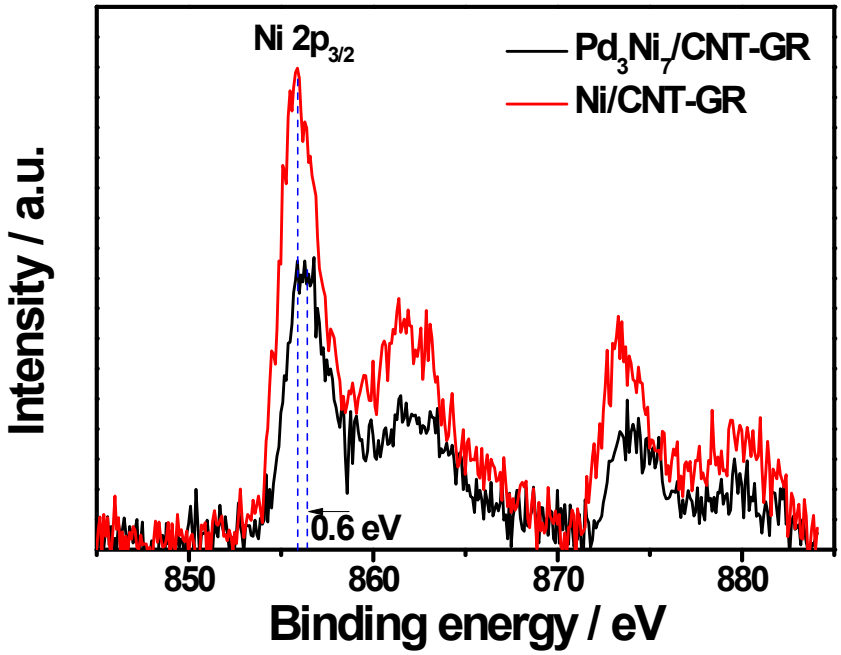

Fig. S4 Ni 2p XPS spectra comparison of Pd_3Ni_7/CNT-GR and Ni/CNT-GR.

1.4. Pd concentration on the surface of catalysts

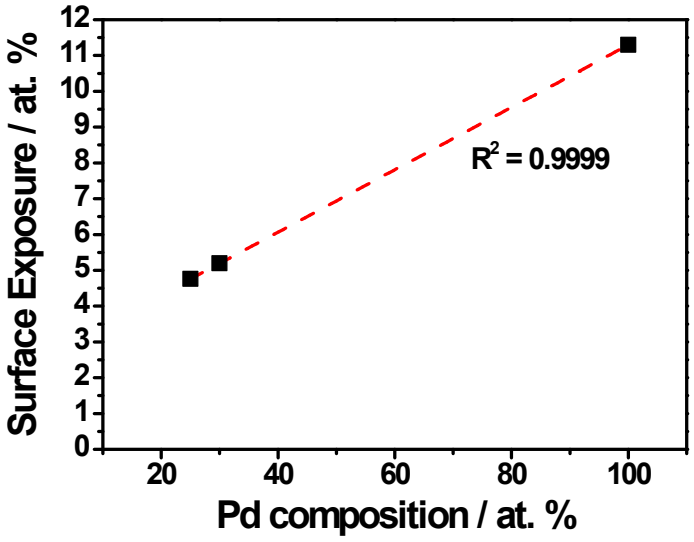

Fig. S5 Linear relation of intended composition of Pd and surface Pd determined by XPS.

1.5. Catalytic activity of Pd, Ni, Pd_3Ni_7 on CNT-GR

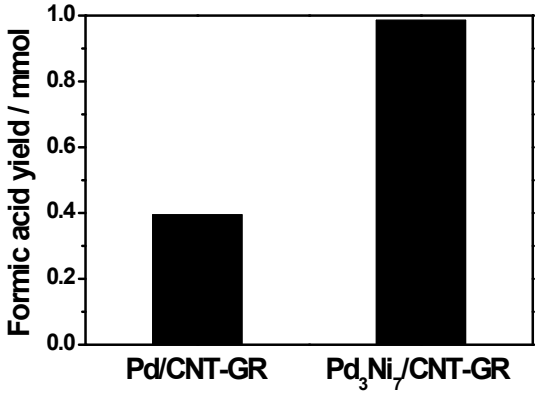

Fig. S6. Formic acid yield as a function of catalyst composition. Reaction conditions: 1 mmol (Pd+Ni) catalysts, 90ml, H_2O, P = 50 bar (H_2/CO_2 = 1), 40 °C, 15 h. No formic acid product was obtained from Ni/CNT-GR catalyst.

1.6. Recycling test of Pd_3Ni_7/CNT-GR catalyst

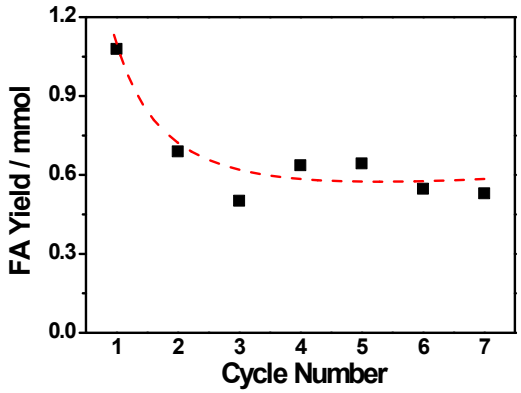

Fig. S7 Formic acid yield as a function of batch cycles. Reaction conditions: 1 mmol (Pd+Ni) catalysts, 90ml, H_2O, P = 50 bar (H2/CO2 = 1), 40 °C, 5 h. Catalyst was regenerated with H_2 treatment (130 °C, 1 h) before each run of catalytic reactions.

2. Catalytic studies

Calculation of turnover number (TON)

$$TON = \frac{Mole\ of\ Formic\ acid\ (mmol)}{Mole\ of\ Pd\ active\ sites\ (mmol)}$$

Calculation of turnover frequency (TOF = TON s^{-1})

$$TOF\ (s^{-1}) = \frac{Mole\ of\ Formic\ acid\ (mmol)}{Mole\ of\ Pd\ active\ sites\ (mmol) \times Reaction\ time\ (s)}$$

HPLC analysis of liquid product

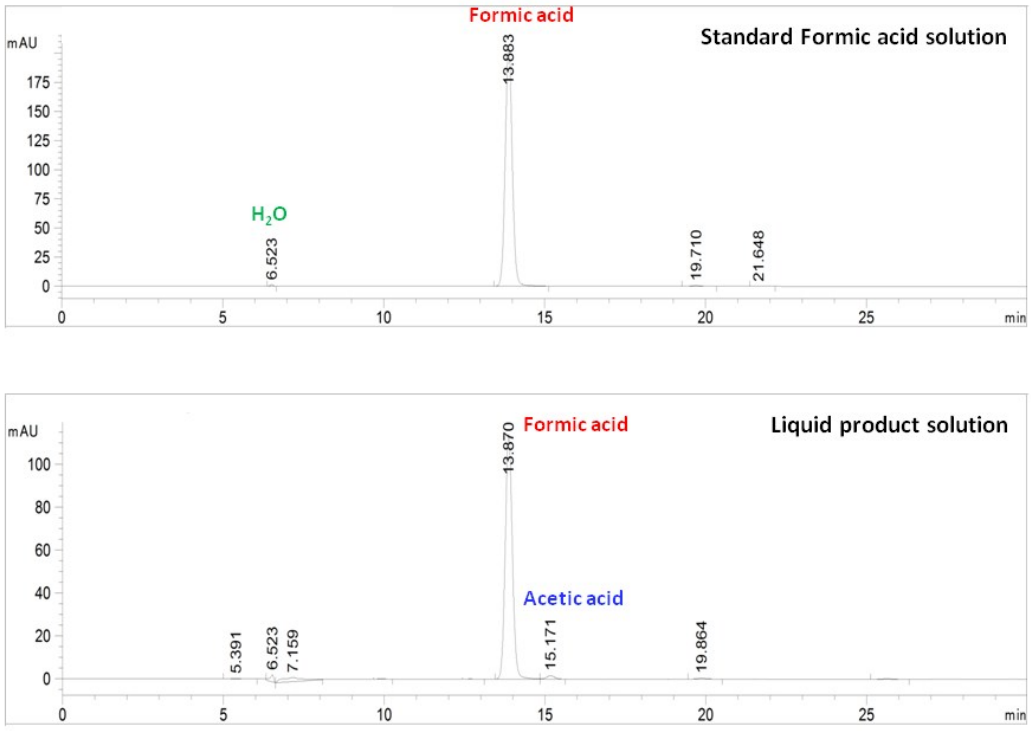

Fig. S8 HPLC analysis of Formic acid (desirable product) and Acetic acid (minor product) after CO_2 hydrogenation reaction.

Table S1. Textural properties of materials.

	Pd_3Ni_7/CNT-GR	CNT-GR	CNT	GR
BET surface area (m^2/g)	266	288	224	33.0
External Surface Area[a] (m^2/g)	213	231	160	30.7
Micropore Area[a] (m^2/g)	52.6	56.9	62.4	2.33
Mesopore Volume[b] (m^3/g)	0.777	0.677	0.636	0.0935
Micropore Volume[a] (cm^3/g)	0.0187	0.0202	0.0249	N.A.[c]

a. Calculated by t-method

b. BJH adsorption pore volume

c. Not available because of too low adsorption amount.

Table S2. Comparison of catalytic performance of pure formic acid formation from CO_2.

Catalyst	Solvent	T (°C)	P (H_2/CO_2) (bar)	Time (h)	FA (M)	TON / TOF (s^{-1})	References
Ru aqua complex	20 ml water (*pH = 2.5 – 5.5*)	40	55 / 25	70	0.035 – 0.055	35 – 55 / 1.4×10^{-4}	Chem. Commun. , **2004**, 2714–2715
Ir aqua complex	20 ml water (*pH = 3*)	40	55 / 25	0.5	0.012	12 / 6.7×10^{-3}	Dalton Trans., **2006**, 4657-4663
Rh aqua complex	5 ml water (*HCOONa 0.5 M*)	50	50 / 50	20	0.13	0.3 / 4.5×10^{-6}	Catal. Commun. **2011**, 14, 74-76
Ru complex	2 ml water	50	50 / 50	120	0.11	0.08 / 1.8×10^{-7}	Nat. Commun. 5:4017, **2014**
	2 ml (DMSO+H_2O)		50 / 50	120	1.31	0.95 / 2.2×10^{-6}	
Pd_3Ni_7/ CNT-GR	45 ml water	40	25 / 25	15	0.036	5.4 / 10^{-4}	**This work**