Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Efficient PdNi and PdNi@Pd-Catalyzed Hydrogen Generation via Formic Acid Decomposition at Room Temperature

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Experimental section

Synthesis of Pd-based NCs

Palladium chloride ($PdCl_2$, 60%), nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, 99%), sodium borohydride ($NaBH_4$, 98%), formic acid (HCOOH, ≥ 98%), sodium formate (HCOONa, AR) were purchased from Aladdin Reagent. All the chemicals were used without any further purification. GO was made by a modified Hummers method.[S1,S2].

PdNi/GNs-CB: For the first step, 120 mg of XC-72 carbon powder was ultrasonically dispersed in 15 mL of water and subsequently mixed with 10 mL GO solution (3 mg mL^{-1}), then the mixture was stirred for 6 h. Na_2PdCl_4 (0.0439 M, 1 mL) and specific atom proportion of $NiCl_2$ aqueous solution were added into the mixture, followed by adding 10 mL of $NaBH_4$ (22 mg mL^{-1}) solution under Ar atmosphere. The mixture was stirred for another 8 h at room temperature. Finally, the desired catalyst from the suspension was centrifuged and washed with the distilled water and then dried under vacuum at 80 °C overnight.

PdNi@Pd/GNs-CB: As-synthesized PdNi/GNs-CB (Pd:Ni = 1:2) was washed with distilled water and then diluted with 30 mL of water. 3 mL of Na_2PdCl_4 (0.0438 M) was added into the mixture with stirring slowly under Ar atmosphere. After 12 h, the resultant production was centrifuged, washed and then dried under vacuum at 80 °C overnight.

Characterization methods

Transmission electron microscope (TEM) was performed using a FEI Tecnai G2 S-Twin instrument with a field emission gun operating at 200 kV. Mass analysis of the generated gases was performed using a ThermoStar^{TM} gas analysis system. XPS spectra were obtained with an

ESCALABMKLL X-ray photoelectron spectrometer using an Al Kα source. The liquid chromatogram (LC) was obtained by Shimadzu LC-20AB. Powder X-ray diffraction (XRD) patterns were collected on Bruker D8 Focus Powder X-ray diffractometer using Cu Kα radiation. The electrochemical tests were carried out with a BioLogic VMP3 electrochemical workstation. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were performed on a TJA (Thermo Jarrell Ash) Atomscan Advantage instrument.

Electrochemical Characterizations for the Catalysts

For preparation of the thin-film working electrode, the GC electrode was polished with 3 and 0.5 μm Al_2O_3 paste (mixed with Al_2O_3 powder and ultrapure water). After the mechanical pretreatment, the electrode was cleaned by sonication in ultrapure water. To prepare the working electrode, 5 mg of the catalysts was dispersed in diluted Nafion alcohol solution and was sonicated for 1 h to obtain a uniform suspension and then the suspension was pipetted onto the flat glassy carbon electrode. The coated electrode was then dried at room temperature for 10 min. Electrochemical experiments were carried out in a standard three-electrode cell at room temperature. The working electrode was the obtained thin-film electrode with catalysts. Pt foil and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. All potentials in this report referred to Ag/AgCl electrode. All electrolyte solutions were deaerated with high-purity nitrogen for at least 30 min prior to any measurement. For CO stripping voltammetry, the 0.5 M H_2SO_4 solution was first bubbled with pure nitrogen for 30 min in order to remove the dissolved oxygen. CO was then purged into solution for 20 min to allow complete adsorption of CO onto the electrocatalyst, while maintaining a constant potential at 0 V. Excess CO was then purged with nitrogen for 30 min.

Formic acid decomposition reaction

Catalytic reactions were carried out at room temperature using a two-necked round bottom flask with one of the flask openings connected to a gas burette and the other for the introduction of formic acid. Catalytic decomposition reaction of formic acid for the release of hydrogen (along with carbon dioxide) was initiated by stirring the mixture of formic acid solution introduced via a pressure-equalization funnel and the aqueous suspension of the catalyst prepared as described above. Repeated testing was obtained by adding pure formic acid into the reaction vessel after the completion of the previous run. Turnover frequency (TOF) = mole of hydrogen gas production per hour/mole of active site.[S3] The number of active sites were estimated from hydrogen desorption in H_2SO_4 electrolyte using an electrocatalytic surface area technique. Before the reaction, the gas burette system was cleaned by Ar. The generated gas was detected by mass spectrometer to determine the component.

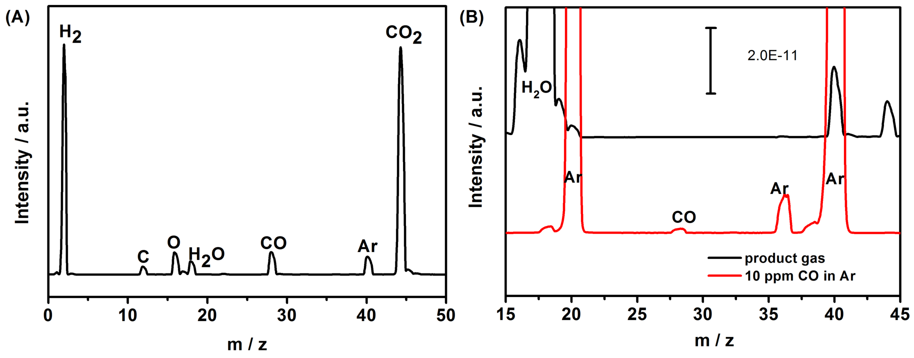

Figure S1. Mass spectral profiles of generated gas: (A) Faraday, (B) C-SEM.

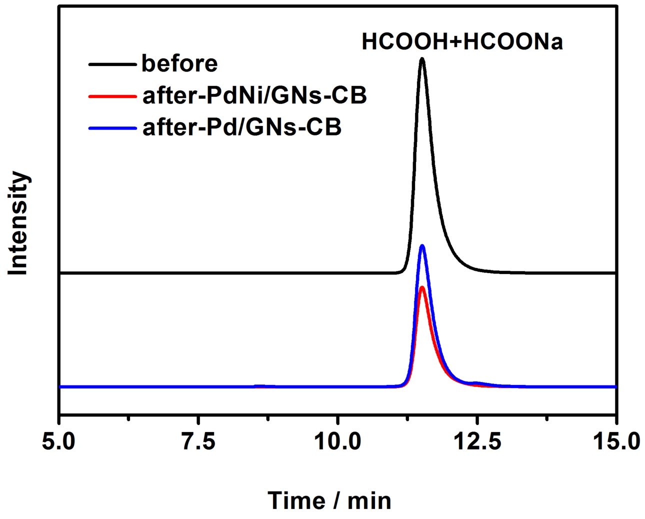

Figure S2. Liquid chromatogram of formic acid solution (1 M HCOOH and 1 M HCOONa) over PdNi/GNs-CB and Pd/GNs-CB catalysts before and after reaction.

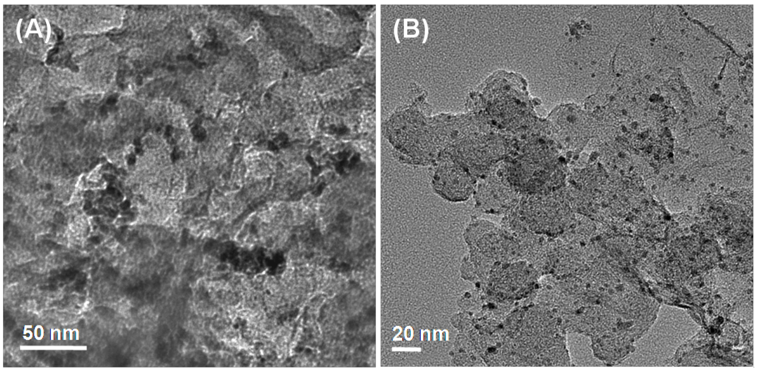

Figure S3. TEM images of (A) PdNi/GNs-CB and (B) PdNi@Pd/GNs-CB catalysts after reaction.

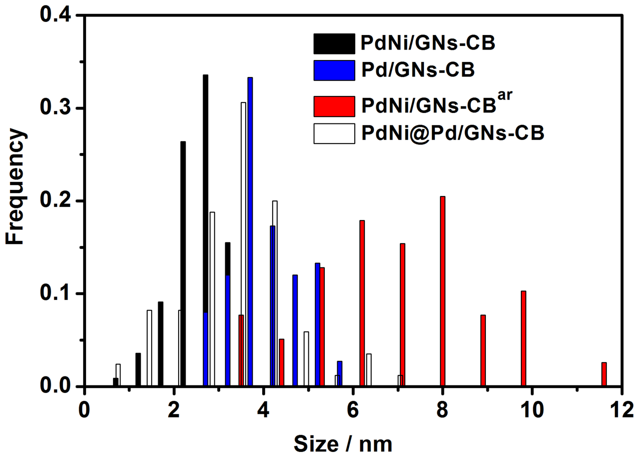

Figure S4. Particle size distribution derived from TEM images. (ar: after reaction)

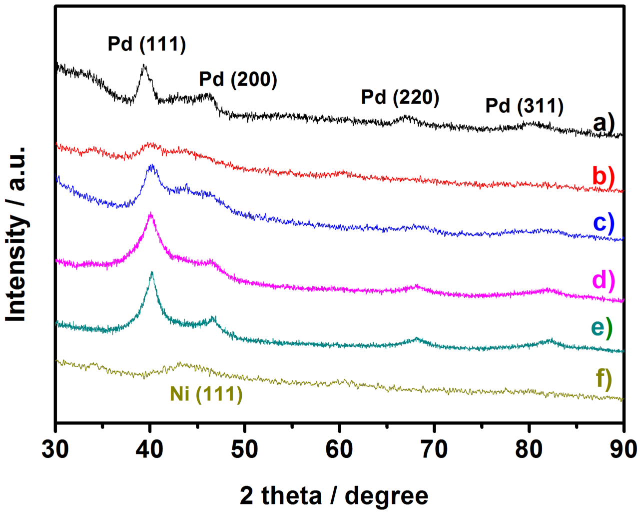

Figure S5. XRD patterns of the prepared nanocatalyst. a) Pd/GNs-CB, b) PdNi/GNs-CB, c) PdNi/GNs-CB after reaction, d) PdNi@Pd/GNs-CB, e) PdNi@Pd/GNs-CB after reaction, f) Ni/GNs-CB.

Table S1. ICP analyses for the catalysts before or after FA decomposition reaction.

Sample	**Metal content (%)**	**Pd-Ni atom ratio**
Pd/GNs-CB	Pd, 3.52	--
$Pd_1Ni_{0.5}$/GNs-CB	Pd, 3.49; Ni, 0.92	1/0.48
Pd_1Ni_1/GNs-CB	Pd, 3.48; Ni, 2.11	1/1.12
Pd_1Ni_2/GNs-CB	Pd, 3.46; Ni, 4.13	1/2.17
Pd_1Ni_2/GNs-CB (after reaction)	Pd, 3.45; Ni, 0.10	19.02/1
PdNi@Pd/GNs-CB	Pd, 9.27; Ni, 0.89	5.73/1
PdNi@Pd/GNs-CB (after reaction)	Pd, 8.97; Ni, 0.87	5.67/1

References:

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S3 K. Tedsree, T. Li, S. Jones, C. W. A. Chan, K. M. K. Yu, P. A. Bagot, E. A. Marquis, G. D. W. Smith and S. C. E. Tsang, *Nat. Nanotechnol.*, 2011, **6**, 302.