Supporting information

Exceptional size-dependent catalytic activity enhancement in the room-temperature hydrogen generation from formic acid over bimetallic nanoparticles supported by porous carbon

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1. Syntheses of catalysts

1.1 Synthesis of Au_{0.5}Pd_{0.5}/C-L-7.5

 $HAuCl_4 \cdot 4H_2O$ (0.0814 g, 0.197 mmol) and $PdCl_2$ (0.0349 g, 0.197 mmol) were dispersed in 40 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.24 g) was added into the above mixture. Two hours later, lysine (0.433 g, 2.96 mmol) in 150 mL of deionized H₂O was added into the suspension. After 2 hours, 30 mL of methanol containing 0.26 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H₂O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst Au_{0.5}Pd_{0.5}/C-L-7.5.

1.2 Synthesis of Au_{0.5}Pd_{0.5}/C-L-7.5 with 10 wt % of metal loading

 $HAuCl_4 \cdot 4H_2O$ (0.0407 g, 0.099 mmol) and $PdCl_2$ (0.0175 g, 0.099 mmol) were dispersed in 40 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.27 g) was added into the above mixture. Two hours later, lysine (0.217 g, 1.48 mmol) in 150 mL of deionized H_2O was added into the suspension. After 2 hours, 30 mL of methanol solution containing 0.13 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H_2O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst $Au_{0.5}Pd_{0.5}/C-L$ with 10 wt % of metal loading.

1.3 Synthesis of Au_{0.67}Pd_{0.33}/C-L-7.5

 $HAuCl_4 \cdot 4H_2O$ (0.0988 g, 0.24 mmol) and $PdCl_2$ (0.0213 g, 0.12 mmol) were dispersed in 40 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.24 g) was added into the above mixture. Two hours later, lysine (0.395 g, 2.7 mmol) in 150 mL of deionized H_2O was added into the suspension. After 2 hours, 30 mL of methanol containing 0.27 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H_2O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst $Au_{0.67}Pd_{0.33}/C-L-$ 7.5.

1.4 Synthesis of Au_{0.67}Pd_{0.33}/C-L-7.5 with 10 wt % of metal loading

 $HAuCl_4 \cdot 4H_2O$ (0.0494 g, 0.12 mmol) and $PdCl_2$ (0.01 g, 0.06 mmol) were dispersed in 40 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.27 g) was added into the above mixture. Two hours later, lysine (0.197 g, 1.35 mmol) in 150 mL of deionized H_2O was added into the suspension. After 2 hours, 30 mL of methanol solution containing 0.136 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H_2O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst $Au_{0.67}Pd_{0.33}/C-L$ with 10 wt % of metal loading.

1.5 Synthesis of Au_{0.33}Pd_{0.67}/C-L-7.5

 $HAuCl_4 \cdot 4H_2O$ (0.06 g, 0.146 mmol) and $PdCl_2$ (0.052 g, 0.293 mmol) were dispersed in 40 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.24 g) was added into the above mixture. Two hours later, lysine (0.48 g, 3.29 mmol) in 150 mL of deionized H_2O was added into the suspension. After 2 hours, 30 mL of methanol containing 0.332 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H_2O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst $Au_{0.33}Pd_{0.67}/C-L-7.5$.

1.6 Synthesis of Au_{0.33}Pd_{0.67}/C-L-7.5 with 10 wt % of metal loading

 $HAuCl_4 \cdot 4H_2O$ (0.03 g, 0.073 mmol) and $PdCl_2$ (0.026 g, 0.147 mmol) were dispersed in 40 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.27 g) was added into the above mixture. Two hours later, lysine (0.24 g, 1.65 mmol) in 150 mL of deionized H_2O was added into the suspension. After 2 hours, 30 mL of methanol solution containing 0.166 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H_2O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst $Au_{0.33}Pd_{0.67}/C-L$ with 10 wt % of metal loading

1.7 Synthesis of Au_{0.25}Pd_{0.75}/C-L-7.5

 $HAuCl_4 \cdot 4H_2O$ (0.0478 g, 0.116 mmol) and $PdCl_2$ (0.0617 g, 0.348 mmol) were dispersed in 40 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.24 g) was added into the above mixture. Two hours later, lysine (0.51 g, 3.48 mmol) in 150 mL of deionized H_2O was added into the suspension. After 2 hours, 30 mL of methanol containing 0.35 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H_2O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst $Au_{0.25}Pd_{0.75}/C-L-$ 7.5.

1.8 Synthesis of Au_{0.25}Pd_{0.75}/C-L-7.5 with 10 wt % of metal loading

HAuCl₄·4H₂O (0.024 g, 0.058 mmol) and PdCl₂ (0.031 g, 0.174 mmol) were dispersed in 40 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.27 g) was added into the above mixture. Two hours later, lysine (0.254 g, 1.74 mmol) in 150 mL of deionized H₂O was added into the suspension. After 2 hours, 30 mL of methanol solution containing 0.175 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H₂O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst Au_{0.25}Pd_{0.75}/C-L with 10 wt % of metal loading.

1.9 Synthesis of Au_{0.75}Pd_{0.25}/C-L-7.5 with 10 wt % of metal loading

 $HAuCl_4 \cdot 4H_2O$ (0.0532 g, 0.129 mmol) and $PdCl_2$ (0.0076 g, 0.0430 mmol) were dispersed in 40 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.27 g) was added into the above mixture. Two hours later, lysine (0.189 g, 1.29 mmol) in 150 mL of deionized H_2O was added into the suspension. After 2 hours, 30 mL of methanol solution containing 0.13 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H_2O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst $Au_{0.75}Pd_{0.25}/C-L-7.5$ with 10 wt % of metal loading.

1.10 Synthesis of Au_{0.75}Pd_{0.25}/C

HAuCl₄·4H₂O (0.1064 g, 0.258 mmol) and PdCl₂ (0.0152 g, 0.086 mmol) were dispersed in 30 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.24 g) was added into the above mixture. Two hours later, 150 mL of deionized H₂O was added into the suspension. After 2 hours, 15 mL of methanol solution containing 0.26 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H₂O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst Au_{0.75}Pd_{0.25}/C.

1.11 Synthesis of Au_{0.75}Pd_{0.25}/C-L-3.5

 $HAuCl_4 \cdot 4H_2O$ (0.1064 g, 0.258 mmol) and $PdCl_2$ (0.0152 g, 0.086 mmol) were dispersed in 40 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.24 g) was added into the above mixture. Two hours later, lysine (0.177 g, 1.21 mmol) in 150 mL of deionized H_2O was added into the suspension. After 2 hours, 30 mL of methanol solution containing 0.26 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H_2O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst $Au_{0.75}Pd_{0.25}/C-L-3.5$.

1.12 Synthesis of Au_{0.75}Pd_{0.25}/C-L-10

 $HAuCl_4 \cdot 4H_2O$ (0.1064 g, 0.258 mmol) and $PdCl_2$ (0.0152 g, 0.086 mmol) were dispersed in 40 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.24 g) was added into the above mixture. Two hours later, lysine (0.503 g, 3.44 mmol) in 150 mL of deionized H₂O was added into the suspension. After 2 hours, 30 mL of methanol solution containing 0.26 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H₂O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst Au_{0.75}Pd_{0.25}/C-L-10.

1.13 Synthesis of CTAB-directed Au_{0.75}Pd_{0.25}/C

HAuCl₄·4H₂O (0.1064 g, 0.258 mmol) and PdCl₂ (0.0152 g, 0.086 mmol) were dispersed in 30 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.24 g)

was added into the above mixture. Two hours later, CTAB (0.940 g, 2.58 mmol) in 150 mL of deionized H_2O was added into the suspension. After 2 hours, 15 mL of methanol solution containing 0.26 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H_2O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst CTAB-directed Au_{0.75}Pd_{0.25}/C-L.

1.14 Synthesis of NaOH-directed Au_{0.75}Pd_{0.25}/C

 $HAuCl_4 \cdot 4H_2O$ (0.1064 g, 0.258 mmol) and $PdCl_2$ (0.0152 g, 0.086 mmol) were dispersed in 40 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.24 g) was added into the above mixture. Two hours later, NaOH (0.103 g, 2.58 mmol) in 150 mL of deionized H₂O was added into the suspension. After 2 hours, 30 mL of methanol solution containing 0.26 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H₂O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst NaOH-directed Au_{0.75}Pd_{0.25}/C-L.

1.15 Synthesis of Au/C-L-7.5

HAuCl₄·4H₂O (0.125 g, 0.303 mmol) was dispersed in 40 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.24 g) was added into the above mixture. Two hours later, lysine (0.332 g, 2.27 mmol) in 150 mL of deionized H₂O was added into the suspension. After 2 hours, 30 mL of methanol solution containing 0.23 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H₂O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst Au/C-L-7.5.

1.16 Synthesis of Pd/C-L-7.5

 $PdCl_2$ (0.100 g, 0.565 mmol) was dispersed in 40 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.24 g) was added into the above mixture. Two hours later, lysine (0.62 g, 4.240 mmol) in 150 mL of deionized H₂O was added into the suspension. After 2 hours, 30 mL of methanol solution containing 0.43 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H_2O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst Pd/C-L-7.5.

1.17 Synthesis of Pd/C-S-7.5

PdCl₂ (0.100 g, 0.565 mmol) was dispersed in 40 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.24 g) was added into the above mixture. Two hours later, serine (0.446 g, 4.240 mmol) in 150 mL of deionized H₂O was added into the suspension. After 2 hours, 30 mL of methanol solution containing 0.43 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H₂O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst Pd/C-S-7.5.

1.18 Synthesis of Pd/C-G-7.5

 $PdCl_2$ (0.100 g, 0.565 mmol) was dispersed in 40 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.24 g) was added into the above mixture. Two hours later, glutamic (0.624 g, 4.240 mmol) in 150 mL of deionized H₂O was added into the suspension. After 2 hours, 30 mL of methanol solution containing 0.43 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H₂O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst Pd/C-G-7.5.

1.19 Synthesis of Pd/C

 $PdCl_2$ (0.100 g, 0.565 mmol) was dispersed in 40 mL of methanol with sonication for 3 h. And then activated Vulcan XC-72 carbon (0.24 g) was added into the above mixture. Two hours later, 150 mL of deionized H₂O was added into the suspension. After 2 hours, 30 mL of methanol solution containing 0.43 g of NaBH₄ was added into the above mixture. Keep stirring for 4 hours, and the product was obtained by centrifugation (5000 rpm/min), washed with methanol and deionized H₂O for several times, and finally dried in vacuum oven at 80 °C to yield the catalyst Pd/C.

2. 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:

$$TOF = \frac{P_{\rm atm}V_{\rm gas} / RT}{2n_{\rm metal}t}$$

Where P_{atm} (88.8 kPa) is the atmospheric pressure in Hohhot of Inner Mongolia, V_{gas} is the volume of generated H₂ and CO₂, *R* is the universal gas constant (8.314 m³ Pa mol⁻¹ K⁻¹), *T* is the room temperature (298 K), n_{metal} is the total mole number of metal atoms in catalyst, and *t* is the reaction time.

Sample	Metal content (wt %) Atom ratio (Au/Pd)	
Au _{0.75} Pd _{0.25} /C-L-7.5	Au, 16.72; Pd, 2.99 3.02:1	
Au _{0.67} Pd _{0.33} /C-L-7.5	Au, 15.32; Pd, 4.01	2.06:1
Au _{0.5} Pd _{0.5} /C-L-7.5	Au, 12.79; Pd, 6.89	1:1
Au _{0.33} Pd _{0.67} /C-L-7.5	Au, 9.42; Pd, 10.02	0.51:1
Au _{0.25} Pd _{0.75} /C-L-7.5	Au, 7.38; Pd, 12.01	0.33:1
Au _{0.75} Pd _{0.25} /C-S-7.5	Au, 12.56; Pd, 2.44	2.78:1
Au _{0.75} Pd _{0.25} /C-G-7.5	Au, 12.52; Pd, 2.22	3.05
Au _{0.75} Pd _{0.25} /C-L-7.5 with	Au, 8.11; Pd, 1.48	2.96:1
10wt % of metal loading		
Au _{0.67} Pd _{0.33} /C-L-7.5 with	Au, 7.58; Pd, 1.98	2.07:1
10wt % of metal loading		
Au _{0.5} Pd _{0.5} /C-L-7.5 with 10wt	Au, 6.15; Pd, 3.34	1:1
% of metal loading		
Au _{0.33} Pd _{0.67} /C-L-7.5 with	Au, 4.59; Pd, 4.96	0.5:1
10wt % of metal loading		
Au _{0.25} Pd _{0.75} /C-L-7.5 with	Au, 3.58; Pd, 5.99	0.32:1
10wt % of metal loading		
Au _{0.75} Pd _{0.25} /C	Au, 16.52; Pd, 2.93	3.05:1
Pd/C	Pd, 19.36	/

Table S1. ICP analyses for the samples.



Fig. S1 TEM and SAED images of Au_{0.75}Pd_{0.25}/C-L-7.5.



Fig. S2 XRD patterns of (a) $Au_{0.75}Pd_{0.25}/C-G-7.5$, (b) $Au_{0.75}Pd_{0.25}/C-S-7.5$ and (c) $Au_{0.75}Pd_{0.25}/C-L-7.5$.



Fig. S3 XRD patterns of (a) $Au_{0.75}Pd_{0.25}/C-L-3.5$, (b) $Au_{0.75}Pd_{0.25}/C-L-7.5$ and (c) $Au_{0.75}Pd_{0.25}/C-L-10$.



Fig. S4 XRD patterns of as-synthesized catalysts: (a) $Au_{0.5}Pd_{0.5}/C-L-7.5$ with 10 wt% of metal loading, (b) $Au_{0.75}Pd_{0.25}/C-L-7.5$ with 10 wt% of metal loading, (c) $Au_{0.5}Pd_{0.5}/C-L-7.5$ and (d) $Au_{0.75}Pd_{0.25}/C-L-7.5$.



Fig. S5 N_2 adsorption isotherms of (a) Vulcan XC-72 and (b) $Au_{0.75}Pd_{0.25}/C$ -L-7.5 at 77 K.



Fig. S6 IR spectra of (a) $Au_{0.75}Pd_{0.25}/C-L-7.5$, (b) $Au_{0.75}Pd_{0.25}/C-S-7.5$, (c) $Au_{0.75}Pd_{0.25}/C-G-7.5$ and (d) catalyst support Vulcan XC-72 carbon.



Fig. S7 Plots of time versus volume of generated gas (CO₂ and H₂) from (a) FA-SF aqueous solution (FA/SF = 1:1, FA = 1.0 M, 3.5 mL) and (b) SF (SF = 1 M, 3.5 mL) over 50 mg of $Au_{0.75}Pd_{0.25}/C-L-7.5$ at 298 K.



Fig. S8 Plots of time versus volume of generated gas (CO₂ and H₂) from FA-SF aqueous solution (FA/SF = 1:1, FA = 1.0 M, 3.5 ml) over 50 mg of (a) $Au_{0.75}Pd_{0.25}/C-L-7.5$, (b) Pd/C-L-7.5 and (c) Au/C-L-7.5 at 298 K.



Fig. S9 (a) TEM image of $Au_{0.75}Pd_{0.25}/C$ -L-3.5 and (b) the corresponding size distribution of AuPd NPs.



Fig. S10 (a) TEM image of $Au_{0.75}Pd_{0.25}/C$ -L-10 and (b) the corresponding size distribution of AuPd NPs.



Fig. S11 Plots of time versus volume of generated gas (CO₂ and H₂) from FA-SF aqueous solution (FA/SF = 1:1, FA = 1.0 M, 3.5 mL) over Au_{0.75}Pd_{0.25}/C-L prepared with different molar ratios of lysine/metal at 298 K: (a) 7.5; (b) 3.5; (c) 10.



Fig. S12 Plots of time versus volume of generated gas (CO₂ and H₂) from FA-SF aqueous solution (FA/SF = 1:1, FA = 1.0 M, 3.5 mL) over 50 mg of as-synthesized catalysts at 298 K: (a) $Au_{0.33}Pd_{0.67}/C-L-7.5$; (b) $Au_{0.67}Pd_{0.33}/C-L-7.5$; (c) $Au_{0.75}Pd_{0.25}/C-L-7.5$; (d) $Au_{0.5}Pd_{0.5}/C-L-7.5$; (e) $Au_{0.25}Pd_{0.75}/C-L-7.5$.



Fig. S13 Plots of time versus volume of generated gas (CO₂ and H₂) from FA-SF aqueous solution (FA/SF = 1:1, FA = 1.0 M, 3.5 mL) over 50 mg of as-synthesized catalysts at 298 K: (a) $Au_{0.33}Pd_{0.67}/C$ -L-7.5 with 10 wt% of metal loading; (b) $Au_{0.67}Pd_{0.33}/C$ -L-7.5 with 10 wt% of metal loading; (c) $Au_{0.5}Pd_{0.5}/C$ -L-7.5 with 10 wt% of metal loading; (d) $Au_{0.75}Pd_{0.25}/C$ -L-7.5 with 10 wt% of metal loading.



Fig. S14 XPS spectra for $Au_{0.5}Pd_{0.5}/C$ -L-7.5: (a) Au 4f; (b) Pd 3d.



Fig. S15 XPS spectra for $Au_{0.5}Pd_{0.5}/C$ -L-7.5 with 10 wt% of metal loading: (a) Au 4f; (b) Pd 3d.



Fig. S16 XPS spectra in Pd 3d regions of (a) Au_{0.75}Pd_{0.25}/C-L-7.5, (b) Au_{0.75}Pd_{0.25}/C-S-7.5, (c) Au_{0.75}Pd_{0.25}/C-G-7.5, (d) Au_{0.75}Pd_{0.25}/C, (e) Pd/C-L-7.5, (f) Pd/C-S-7.5, (g) Pd/C-G-7.5 and (h) Pd/C.



Fig. S17 (a) TEM image of $Au_{0.5}Pd_{0.5}/C$ -L-7.5 and (b) the corresponding size distribution of AuPd NPs.



Fig. S18 (a) TEM image of $Au_{0.5}Pd_{0.5}/C-L$ -7.5 with 10 wt% of metal loading and (b) the corresponding size distribution of AuPd NPs.



Fig. S19 (a) TEM images of $Au_{0.75}Pd_{0.25}/C-L-7.5$ with 10 wt% of metal loading and (b) the corresponding size distribution of AuPd NPs.



Fig. S20 Gas generation by decomposition of FA-SF aqueous solution (FA/SF = 1:1, FA = 1.0 M, 3.5 mL) over 50 mg of $Au_{0.75}Pd_{0.25}/C$ -L-7.5 (a) without and (b) with re-addition of 3.5 mmol of FA at 298 K.



Fig. S21 (a) TEM image of $Au_{0.75}Pd_{0.25}/C$ -L-7.5 after catalysis and (b) the corresponding size distribution of AuPd NPs.



Fig. S22 Plots of time versus volume of generated gas (CO₂ and H₂) from FA-SF aqueous solution (FA/SF = 1:1, FA = 1.0 M, 3.5 mL) over 50 mg of $Au_{0.75}Pd_{0.25}/C$ -L-7.5 exposed to CO atmosphere at 298 K.

Catalyst	Т	TOF	Ref.
	(K)	(h^{-1})	
Au _{0.75} Pd _{0.25} /C-L-7.5	298	718	This work
Au _{0.75} Pd _{0.25} /C-S-7.5	298	54	This work
Au _{0.75} Pd _{0.25} /C-G-7.5	298	12	This work
Au _{0.75} Pd _{0.25} /C	298	65	This work
Au _{0.33} Pd _{0.67} /C-L-7.5	298	804	This work
Au _{0.67} Pd _{0.33} /C-L-7.5	298	861	This work
Au _{0.5} Pd _{0.5} /C-L-7.5	298	558	This work
Au _{0.25} Pd _{0.75} /C-L-7.5	298	302	This work
Au _{0.75} Pd _{0.25} /C-L-7.5 with	298	633	This work
10wt% of metal loading			
Au _{0.33} Pd _{0.67} /C-L-7.5 with	298	1086	This work
10wt% of metal loading			
Au _{0.67} Pd _{0.33} /C-L-7.5 with	298	1153	This work
10wt% of metal loading			
Au _{0.5} Pd _{0.5} /C-L-7.5 with	298	822	This work
10wt% of metal loading			
Au _{0.25} Pd _{0.75} /C-L-7.5 with	298	208	This work
10wt% of metal loading			
Pd/MSC-30	298	750	S1
Ag@Pd/C	363	626	S2
Ag@Pd/C	293	125	S2
Ag/Pd alloy	293	144	S2
Pd-B/C	298	1184	S3
Pd/C-NaBH ₄	303	304	S 3
Pd/C	298	64	S4
$Pd/g-C_3N_4$	288	71	S5
Ag _{0.1} Pd _{0.9} /rGO	295	105.2	S6
$Ag_{42}Pd_{58}$	323	382	S7
Au/ZrO ₂	298	252	S8
Pd/NH ₂ -MIL-125	305	214	S9
AuPd-MnO _x /ZIF-8-rGO	298	382.1	S10

Table S2 TOF values for dehydrogenation of FA catalysed by different catalysts at different temperatures.

References

- (S1) Q.-L. Zhu, N. Tsumori and Q. Xu, Chem. Sci., 2014, 5, 195–199.
- (S2) K. Tedsree, T. Li, S. Jones, C. W. A. Chan, K. M. K. Yu, P. A. J. Bagot, E. A. Marquis, G. D. W. Smith and S. C. E Tsang, *Nat. Nanotechnol.*, 2011, 6, 302–307.
- (S3) K. Jiang, K. Xu, S. Zou and W.-B. Cai, J. Am. Chem. Soc., 2014, 136, 4861-4864.
- (S4) Z.-L. Wang, J.-M. Yan, H.-L. Wang, Y. Ping and Q. Jiang, Sci. Rep., 2012, 2, 598-603.
- (S5) Y.-Y. Cai, X.-H. Li, Y.-N. Zhang, X. Wei, K.-X. Wang and J.-S. Chen, *Angew. Chem., Int. Ed.*, 2013, 52, 11822–11825.
- (S6) Y. Ping, J.-M. Yan, Z.-L. Wang, H.-L. Wang and Q. Jiang, J. Mater. Chem. A, 2013, 1, 12188-12191.
- (S7) S. Zhang, Ö. Metin, D. Su and S. Sun, Angew. Chem., Int. Ed., 2013, 52, 3681-3684.
- (S8) Q.-Y. Bi, X.-L. Du, Y.-M. Liu, Y. Cao, H.-Y. He and K.-N. Fan, J. Am. Chem. Soc., 2012, 134, 8926–8933.
- (S9) M. Martis, K. Mori, K. Fujiwara, W.-S. Ahn, and H. Yamashita, J. Phys. Chem. C, 2013, 117, 22805–22810.
- (S10) J. M. Yan, Z. L. Wang, L. Gu, S. J. Li, H. L. Wang, W. T. Zheng and Q. Jiang, Adv. Energy Mater., 2015, 5, 1500107.