# **Supporting Information**

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## I. Reagents.

Tetrachloroauric (III) acid (Aladdin, 99.99%, Shanghai) Sodium tetrachloropalladate (II) (Aladdin, 98%, Shanghai) Magnesium nitrate hexahydrate (Aladdin, 99%, Shanghai) sodium borohydride (NaBH<sub>4</sub>, Aladdin, 98%, Shanghai) Formic acid (HCOOH, FA, Aladdin, 98%, Shanghai) Sodium formate (Aladdin, 96%, Shanghai) Ethanol (Tianjin Chemical Reagents, >98%, China) De-ionized water All the chemicals were used as received without further purification.

#### **II.** Preparation of Catalyst.

The synthesis of Au<sub>6</sub>Pd<sub>4</sub>-L-Mg is carried out in ethanol-water bath (the whole process of reduction was performed at -3 °C, the temperature was controlled and maintained through circulating cold pump). Typically, 167 mg carbon (VXC-72) and 100 mg Mg(NO<sub>3</sub>)<sub>2</sub> is dispersed into a mixture of 10 ml distilled water and 5 ml ethanol, sonicated for 1 h. Add 5 ml aqueous solution (containing 0.018 mmol HAuCl<sub>4</sub> and 0.012 mmol Na<sub>2</sub>PdCl<sub>4</sub>) as precursor and stir for 30 min. Then, 10 ml fresh NaBH<sub>4</sub> aqueous solution (containing 0.1 g NaBH<sub>4</sub>) is added into above mixture with magnetic stirring (800 r/min). After reduction for 5 h, the catalyst is separated by centrifugation, washed with distilled water and ethanol for several times respectively and dried in vacuum oven for 24 h at 25 °C. At last, the catalyst is triturated to be ready for characterization and H<sub>2</sub> generation.

Catalysts with different Au-Pd ratio is synthesized by replacing precursor with solution of different concentration of HAuCl<sub>4</sub> and Na<sub>2</sub>PdCl<sub>4</sub>.

The synthesis of Au<sub>6</sub>Pd<sub>4</sub>-L is carried out in ethanol-water bath (-3  $^{\circ}$ C) in the same condition except for adding magnesium ion.

The synthesis of Au<sub>6</sub>Pd<sub>4</sub>-R is carried out in water bath (25 °C) in the same condition as Au<sub>6</sub>Pd<sub>4</sub>-L.

For UV-Vis characterization needs, Au, Pd and AuPd nano-catalysts were prepared in the same condition with aluminum oxide as carrier, (separately labeled as Au-Al<sub>2</sub>O<sub>3</sub>, Pd-Al<sub>2</sub>O<sub>3</sub> and Au<sub>6</sub>Pd<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub>)

#### **III.** Characterization of Catalysts.

Powder X-ray diffraction (XRD) patterns were recorded using a Bruker diffractometer with Cu K a radiation (D8 Advance X-ray diffractometer, Cu K a,  $\lambda$ =1.5406 Å 40 kV and 40 m A). The composition of the catalysts was measured by inductively coupled plasma-atomic emission spectrometer (ICP-AES, USA Thermo Jarrell-Ash Corp. ICP-9000 (N+M)). Field-emission electron microscopy (TEM), energy-dispersive X-ray spectrometry (EDS), Oxford EDXS system and Inca software were used to collect and process STEM-EDX data and EELS elemental mapping observations were performed on a Philips Tecnai F20 microscope, working at 200 kV. All samples subjected to TEM measurements were dispersed in ethanol ultrasonically and were dropped on copper grids. Concentration of H<sub>2</sub>, CO<sub>2</sub> and CO is measured on SP-2100A with thermal conductivity detector (TCD) and flame ionization detector (FID)-Methanator (Detailed gas analysis for H<sub>2</sub> was conducted by GC-TCD. The CO<sub>2</sub> and CO compositions were determined by GC-FID-Methanator using calibrating gas containing 100 ppm CO. Normalization method was adopted to quantify the CO concentration). The UV-Vis spectra of solid catalyst were recorded with a Shimadzu UV-2450 dual beam spectrometer in the 190-900 nm regions with 0.1 nm resolution, barium sulfate was as reference substance.

To clarify the AuPd alloy structure clearly, the catalysts Au<sub>6</sub>Pd<sub>4</sub>-L-Mg, Au-L-Mg and Pd-L-Mg were thermally treated at 300 °C to improve the crystalline structure of

nanoalloy. The thermal treatment was carried out under a 10 %  $H_2$  in He mixture. The samples were heated at 10 °C min<sup>-1</sup> up to 300 °C, kept at final temperature for 1 h and finally cooled in the reducing atmosphere. The annealed samples were denoted as  $Au_6Pd_4-L-Mg-T$ .

## IV. H<sub>2</sub> generation from FA/SF aqueous solution.

Generally, 127 mg as-prepared catalyst is placed in a two-neck round bottom flask with one opening connected to gas burette and the other one connected to a pressure-equalization funnel. Add 10 ml formic acid (1.1 mol•L<sup>-1</sup>) and sodium formate (4.0 mol•L<sup>-1</sup>) aqueous solution into the flask through the funnel with magnetic stirring (800 r•min<sup>-1</sup>). Hydrogen generation starts once the solution is added. The reaction is carried out in water bath (25 °C) and ice-water bath (0 °C) respectively.

### V. The calculation of the initial TOF.

The TOF in this research is calculated by following equation,

$$TOF = \frac{p_{atm}V_{H_2}}{RTn_{Au+Pd}t}$$

Where  $p_{atm}$  is the pressure of atmosphere,  $V_{H_2}$  is the volume of hydrogen generated in certain time, T is the temperature dehydrogenation is carried out,  $n_{Au+Pd}$  is the total mole number of Au and Pd used in the synthesis and t is reaction time.

## VI. Table S1 Activity of catalysts reported.

Catalyst	Solvent/Medium	Temp. (°C)	TOF (h <sup>-1</sup> )	Ref
AuPd-L-Mg	Aqueous HCOONa	25 25 25 25	1530 (5 min) 1120 (10min) 795 (20 min) 250 (overall )	This work
Au-Pd/C	Aqueous HCOONa	25	1075ª	40
Au/ZrO <sub>2</sub> NC <sub>8</sub>	5HCOOH/2NEt <sub>3</sub>	25	292 <sup>b</sup>	13
Ag@Pd/C	Aqueous	20	192°	31
CoAuPd /C	Aqueous	25	80 <sup>b</sup>	30
Pd/C with citric acid	Aqueous HCOONa	25	64 <sup>c</sup>	14
Pd/MSC-30	Aqueous HCOONa	25	750 °	28
$Ag_{0.1}Pd_{0.9}/rGO$	Aqueous HCOONa	25	105.2 <sup>b</sup>	17
Au@Pd-N-mrGO	Aqueous	25	89.1 <sup>b</sup>	39
Pd-poly (allyl-amine)	Aqueous	22	46.1 <sup>b</sup>	27
PdNi@Pd/GNs-CB	Aqueous HCOONa	25	577ª	33
PdNi /GNs-CB	Aqueous HCOONa	25	529ª	33
B-Pd/C	Aqueous HCOONa	30	1184 <sup>a</sup>	34

Activity of catalysts for dehydrogenation of formic acid reported in literature.

<sup>a,b</sup> initial TOF values calculated at the initial stages of the catalytic reactions. (<sup>a</sup> t=10 min, <sup>b</sup> t=20 min), <sup>c</sup> TOF values were calculated according to the amount of released  $H_2$  in overall testing time.

# VII. Table S2 Ea of catalysts reported.

Catalyst	E <sub>a</sub> (kJ/mol)	Ref
AuPd-L-Mg	18.5	This work
L-Au <sub>6</sub> Pd <sub>4</sub>	21.98	40
Au-ZrO <sub>2</sub>	49.3	13
PdAg/C	115	37
PdAu/C	115	37
Pd-Au/C-CeO <sub>2</sub>	84.2±7.4	36
1 wt% Au/TiO <sub>2</sub>	63	15
0.8 wt% Au/C	55	15
1 wt% Pd/C	65	15
1 wt% Pd/C with 2 wt% K	97	26
PtRuBiOx	37	32
Ag@Pd	30	31
AgPd	22	31
Pd-MCM-30	39	28
2 wt% Pt/Norit	70±3	16

Activation energy for dehydrogenation of formic acid reported.

# VIII. Table S3 Contents of Au and Pd in Au<sub>6</sub>Pd<sub>4</sub>-L-Mg.

Catalyst	Au	Pd	Mg
ICP- Au <sub>6</sub> Pd <sub>4</sub> - L-Mg EDS-	2.07 (wt, %)	0.69 (wt, %)	0.11 (wt, %)
L-Au <sub>6</sub> Pd <sub>4</sub> -L-Mg	67.2 (mol, %)	32.8 (mol, %)	not detected

ICP-AES results and EDS results of catalysts of content of Au and Pd in catalysts

IX. Figure S1 Arrhenius plot (In TOF vs 1/T).



X. Figure S2 GC spectrum using GC-FID-Methanator and GC-TCD for the gas generated from FA/SF solution (1.1 M FA, 4.0 M SF) and magnified image.



XI. Figure S3 GC spectrum using TCD for H<sub>2</sub> quantitative analysis.

GC spectrum using GC-FID-Methanator and GC-TCD for the gas generated from FA/SF solution (1.1 M FA, 4.0 M SF)







XIII. Figure S5 XRD of catalysts thermally treated.

The catalysts.Au<sub>6</sub>Pd<sub>4</sub>-L-Mg, Au-L-Mg and Pd-L-Mg were thermally treated at 300 °C to improve the crystalline structure of nanoalloy. The annealed samples were denoted as Au<sub>6</sub>Pd<sub>4</sub>-L-Mg-T.

XRD data were collected in the step- scanning mode in the angel interval of 35-43° (2 $\theta$ ) using steps of 0.01° (2 $\theta$ ) and the scanning speed was 1°/min.



XIV. FigureS6 UV-Vis of Au-Al<sub>2</sub>O<sub>3</sub>, Pd-Al<sub>2</sub>O<sub>3</sub> and Au<sub>6</sub>Pd<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub>.

For UV-Vis characterization needs, Au, Pd and AuPd nano-catalysts were prepared in the same condition with aluminum oxide as carrier, (separately labeled as Au-Al<sub>2</sub>O<sub>3</sub>, Pd-Al<sub>2</sub>O<sub>3</sub> and Au<sub>6</sub>Pd<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub>)



XV. FigureS7 EDS (a) and element mapping (b) of Au<sub>6</sub>Pd<sub>4</sub>-L-Mg.



XVI. Figure S8 Gas generation for Au<sub>x</sub>Pd<sub>(1-x)</sub>-L-Mg at room temperature.

Gas generation of the decomposition of FA/SF (1.1 M FA, 4.0 M SF) solution in present of  $Au_xPd_{(1-x)}$ -L- Mg with different x value at room temperature.



XVII. Figure S9 XRD patterns of Au<sub>6</sub>Pd<sub>4</sub>-L-Mg, Au<sub>6</sub>Pd<sub>4</sub>-L and Au<sub>6</sub>Pd<sub>4</sub>-R.

The synthesis of Au<sub>6</sub>Pd<sub>4</sub>-L is carried out in ethanol-water bath (-3 °C) in the same condition except for adding magnesium ion.

The synthesis of Au<sub>6</sub>Pd<sub>4</sub>-R is carried out in water bath (25 °C) in the same condition as Au<sub>6</sub>Pd<sub>4</sub>-L.



XVIII. Figure S10 TEM images of Au<sub>6</sub>Pd<sub>4</sub>-R and Au<sub>6</sub>Pd<sub>4</sub>-L.

1.TEM images of Au<sub>6</sub>Pd<sub>4</sub>-R (a, b). 2.TEM images of Au<sub>6</sub>Pd<sub>4</sub>-L (c, d).



XIX. Figure S11 Catalytic performance of catalysts synthesized in different conditions.

Gas generation of the decomposition of FA/SF (1.1 M FA, 4.0 M SF) solution at room temperature in present of catalysts Au<sub>6</sub>Pd<sub>4</sub>-L-Mg, Au<sub>6</sub>Pd<sub>4</sub>-L, Au<sub>6</sub>Pd<sub>4</sub>-R synthesized in different conditions.



XX. Figure S12 the activity of Pd-L-Mg and Pd-L at room temperature from FA/SF (1.1 M FA, 4.0 M SF).



XXI. Figure S13 TEM images of Pd-L-Mg and Pd-L.

1.TEM images of Pd-L(a, b, c).
2.TEM images of Pd-L-Mg(d, e, f).



XXII. Figure S14 The activity of catalysts (Au $_6$ Pd $_4$ -L-xMg) prepared with different Mg<sup>2+</sup> concentrations.



XXIII. Figure S14 TEM images of Au<sub>6</sub>Pd<sub>4</sub>-L-Mg recycled.

