Supporting Information

High-quality hydrogen generated from formic acidtriggered by in situ prepared Pd/C catalyst for fuel cells

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Materials and Methods

Materials

Formic acid (HCOOH, Alfa Aesar, 97%), $PdCl_2$ (Aldrich Chemical Co., USA), sodium hydroxide (NaOH, Beijing Chemical Co., China), Vulcan carbon powder XC-72 (Cabot Co., USA), sulfuric acid (H_2SO_4, 98%, Beijing Chemical Co.), ethanol (CH_3CH_2OH, Beijing Chemical Co.), methanol (CH_3OH,Tedia Co.) and Nafion solution (5%, Dupont Co., USA) were all used as received. Commercial Pd/C (20wt.%Pd loading)used for formic acid electrooxidation was purchased from Johnson Matthey Corp..Ultrapure Millipore water (18.2 MΩ) was used to prepare the solutions.Highly purified nitrogen (≥ 99.99%), oxygen (≥ 99.99%)and carbon monoxide (≥ 99.99%) were supplied by Changchun Juyang Co Ltd. Reference gasfor GC was supplied by Dalian Special Gas Co., Ltd..

Experiment

40mg of Vulcan XC-72 carbon black was dispersed into deionized water in a 100 mL round-bottom flask under ultrasonic treatment toform a uniform ink. Under stirring, 1061 μL 9.425 mg_{Pd} / mL H_2PdCl_4 aqueous solution (containing 10 mg Pd) was added into the flask and then 0.955 g of NaOH was added was added; finally1.5 ml of formic acid; thus, the final formate ratio is expected to be 60%. The whole volume of the obtained suspension was 50 mL.

The above is an specified example; in the present work, firstly, the initial amount for formic acid of 1.5 ml was studied, in which the formate molar ratio in the mixture was adjusted by NaOH and different molar percent of formate to the whole formate and formic acid (0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100%) was investigated.

And the effect of formic acid amount was further studied by fixing the formate percent of 60%; different initial amount of formic acid (0.5 mL, 1.0 mL, 1.5 mL, 2.0 mL and 2.5 mL) in the study was performed. The composition of different mixtures of formic acid and formate are listed in table S1. Gas is collected by graduation injector. When gas generation stopped, the suspension was filtered, washed and dried overnight at 80℃ in a vacuum oven to obtain Pd/C catalyst.

Physical characterizations

The X-raydiffraction (XRD) patterns were obtained using a Rigaku-D/MAX-PC 2500 X-ray diffraction meter with theCu Kα (λ=1.5405 Å)as a radiation source operating at 40 kV and200 mA. The transmission electron microscope (TEM) images were obtained by using a TECNAI G2 operating at 200 kV. H_2, O_2, N_2, CO, and CO_2were analyzed by a gas chromatography (GC, Kechuang, GC9800) equipped with a thermal conductivity detector (TCD), using a packed TDX-01 (1 m) and molecular sieve5A column (1.5 m). The carrier gas for TCD is Ar (puity≥99.999%), and the detection limit is ca. 50 ppm. The evolution gas was firstly collected in a gasbag and then sampled into the GC through a six-way valve. The relative correction factors for H_2, O_2, N_2, CO,$CH_4$and CO_2 are 0.293, 3.19, 2.50, 2.50, 1 and 3.8, respectively, corrected according to the reference gas and pure CO_2.

Electrochemical measurement

Electrochemical measurements were carried out with an EG&G mode 273 potentiostat/galvanostat and a conventional three-electrode test cell. The catalyst ink was prepared by ultrasonically dispersing a mixture containing 5 mg of catalyst, 1000 μL of ethanol and 50 μL of a 5 wt% Nafion solution (Aldrich, 5% w/oNafion). Next, 10 μL of the catalyst ink was pipetted onto a pre-cleaned glassy carbon disk (diameter = 5 mm) as the working electrode. A Pt foil and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively. All of thepotentials were relative to SCE. The cyclic voltammetry measurements were carried out at room temperature in 0.5 M H_2SO_4 and 1.0 M solution of formic acid at potential range between -0.2 and 0.8 V vs SCE and at a potential sweep rate of 50 mV s^{-1}.

Preparation of MEA

Nafion 117 was used as proton exchange membranes and the pre-treatment of the Nafion membrane wasaccomplished by successively treated in 5 wt.%H_2O_2 solution at 80℃, distilled water at 80℃, 8 wt.% H_2SO_4solution at 80℃ and then in distilled water at 80℃ again,each step for 30 min. Prior to the fabrication of hot-pressedMembrane electrode assemblies (MEAs) and catalyst-coated membrane (CCM), a carbon cloth was used as Gas diffusion layer (GDL) for current collector.

Membrane electrode assemblies (MEAs) with 3×3 cm^2 active cell area were fabricated using a 'direct paint' technique applied to the catalyst layer. The 'catalyst inks' were prepared by dispersing a certain amount of 20% commercial Pt/C(Johnson Matthey) into appropriate amounts of Millipore® water and a 5% recast Nafion®solution. Anode and cathode 'catalyst inks' were directly painted onto either side of a Nafion®117 membrane. The catalyst loading in both the anode and cathode was 1 mg cm^{-2}. Hot-pressing was conducted at 140°C and 10 MPa for90 s.

Fuel cell performance test

The MEA was fitted between two stainless steel plates with a punctual flow bed in machined graphite. The polarization curves were obtained using a Fuel Cell Test System (Arbin Instrument Corp.)at room temperature. The reforming gas was directly fed into the anode of fuel cells or after it flowed through NaOH solution to remove CO_2 and a small quantity of HCOOH as shown in scheme S1. Oxygen with a flow rate of 15 mL min^{-1} was fed into the cathode of fuel cells. Both sides are under ambient pressure.

TOF calculation

The turnover frequency (TOF) was calculated according to the formula below.

$$TOF = \frac{moles\ of\ the\ generated\ hydrogen\ molecules}{reaction\ time\ \times\ moles\ of\ the\ total\ Pd\ atoms\ in\ Pd/C\ catalyst}$$

Theoretical generation of hydrogen from formic acid

$$V_{H_2} = \frac{n_{HCOOH}RT}{P}$$

Where $V_{H_2}$is the theoretical generated volume of hydrogen, n_{HCOOH} the moles of formic acid, R is the universal gas constant, T is the room temperature and P is the atmospheric pressure.

Table S1. The compositions of different formic acid and formate mixtures.

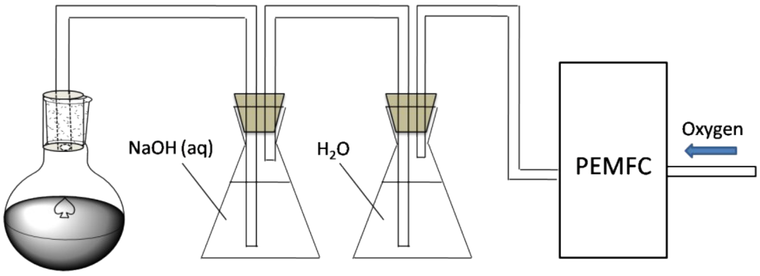
V (HCOOH) / mL	m (NaOH) / g	c (HCOOH) / mol L^{-1}	c ($HCOO^-$) / mol L^{-1}	Formate molar percent / %
1.5	0	0.796	0	0
1.5	0.159	0.716	0.080	10
1.5	0.318	0.637	0.159	20
1.5	0.477	0.557	0.239	30
1.5	0.637	0.478	0.318	40
1.5	0.797	0.398	0.398	50
1.5	0.955	0.318	0.478	60
1.5	1.114	0.239	0.557	70
1.5	1.273	0.159	0.637	80
1.5	1.432	0.080	0.716	90
1.5	1.591	0	0.796	100
0.5	0.318	0.103	0.155	60
1.0	0.637	0.212	0.318	60
2.0	1.273	0.425	0.637	60
2.5	1.591	0.531	0.796	60

Table S2. Thegas evolution rate of different formic acid and formate mixtures catalyzed by *in situ* prepared Pd/C within the initial 15minutesat 313 K.The volume of initial added formic acid is 1.5 ml and the formate molar percentages were varied from 0% to 100% adjusted by NaOH.

Formate molar percent / %	Gas generation rate / mL min^{-1}
0	0.2
10	2.4
20	2.8
30	4.3
40	5.3
50	7.1
60	9.3
70	12.9
80	13.3
90	15.0
100	0

Table S3. The mass fraction of Pd in Pd/C detected by inductively coupled plasma optical emission spectrometry (ICP-OES).

Volume of initial HCOOH / mL	Molar percent of $HCOO^-$ / %	mass fraction of Pd in Pd/C / %
1.5	0	9.15
1.5	20	18.2
1.5	40	20.1
1.5	60	19.7
1.5	80	20.9
1.5	100	19.3
0.5	60	19.8
1.0	60	19.9
2.0	60	20.2
2.5	60	20.7
Commercial Pd/C		20.1



Scheme S1. Reforming gas supplied to the PEMFC directly. NaOH solution was used to remove CO_2 and a small quantity of HCOOH.

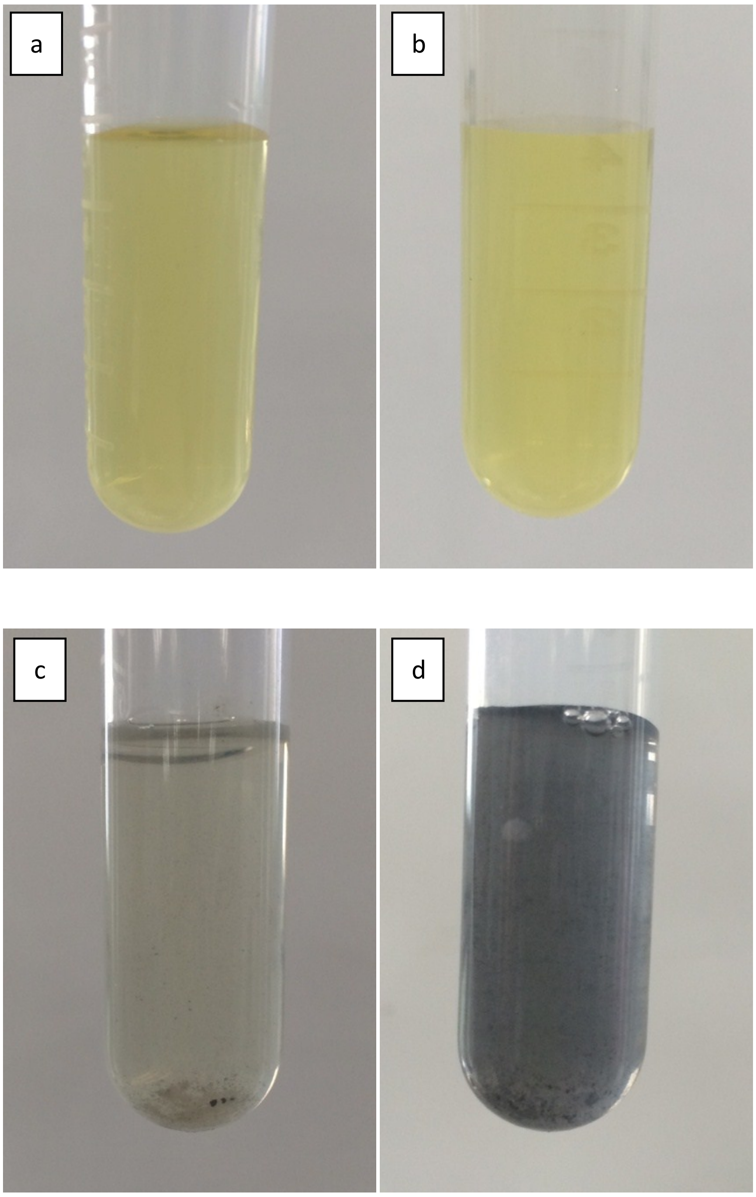


Figure S1. Digital photos of H_2PdCl_4 aqueous solution (5mL) (a);HCOOH was mixed with H_2PdCl_4 solution for 3 hours (b); NaOH and HCOOH were mixed with H_2PdCl_4 solution after 30 seconds(c), after2 minutes (d),molar ratio of HCOOH and NaOH was 1:1(100% formate) at ambient condition.

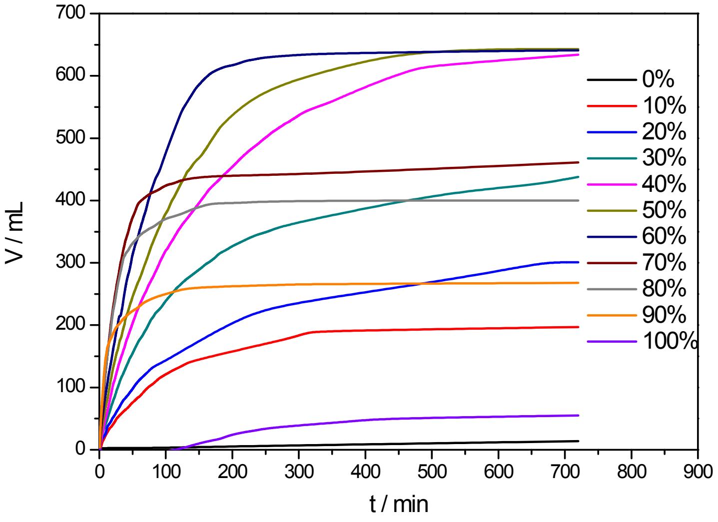


Figure S2.Thegas evolution amount change vs. the time for different formic acid and formate mixtures catalyzed by *in situ* prepared Pd/C at 313 K.The volume of initial added formic acid was 1.5 ml and the formate molar percentages were varied from 0% to 100% adjusted by NaOH.

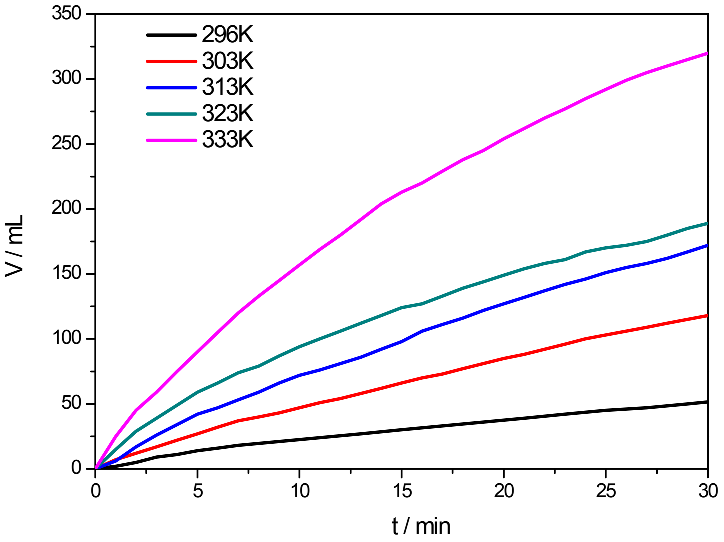


Figure S3. Thegas evolution amount change vs. the time for the formic acid and formate mixtures catalyzed by *in situ* prepared Pd/C at different temperatures. The volume of initial added formic acid was 1.5 mL and the formate molar percentage was 60%.

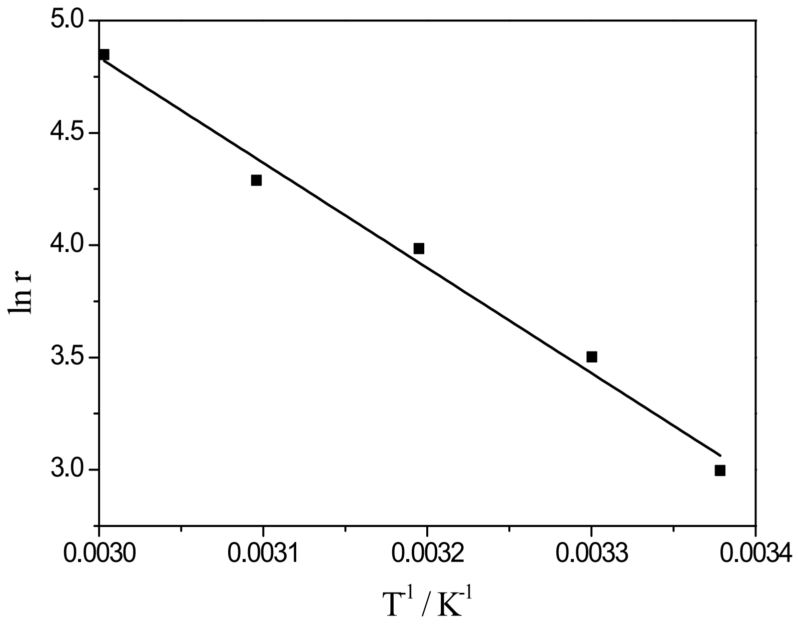


Figure S4. Plots of natural logarithm of reaction rate (lnr) of formic acid decomposition vs. the reciprocal of absolute temperature (T^{-1}) according to Arrhenius equation.

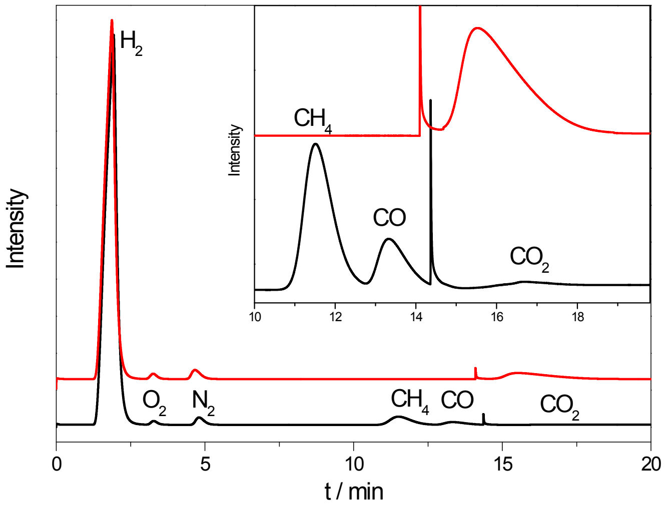


Figure S5.GC spectrum for the reference gas (black) and gas obtained from the experiment (red), the volume of initial added formic acid was 1.5 ml and the formate molar percentage was 60%, inset is an enlarged spectrogram from 10 minutes to 20 minutes. N_2 and O_2 came from the ambient air. Switch peak at around 14.1 minutes resulted from switching the six-channel valve. The molar ratio of H_2 and CO_2 was calculated to be 51:49. Note: The correction factors for CO_2 (3.8) was 13 times than that of H_2 (0.293). Therefore, although the peak areas of H_2 and CO_2 are so different in this figure, the molar ratio of H_2 and CO_2 was almost 1:1.

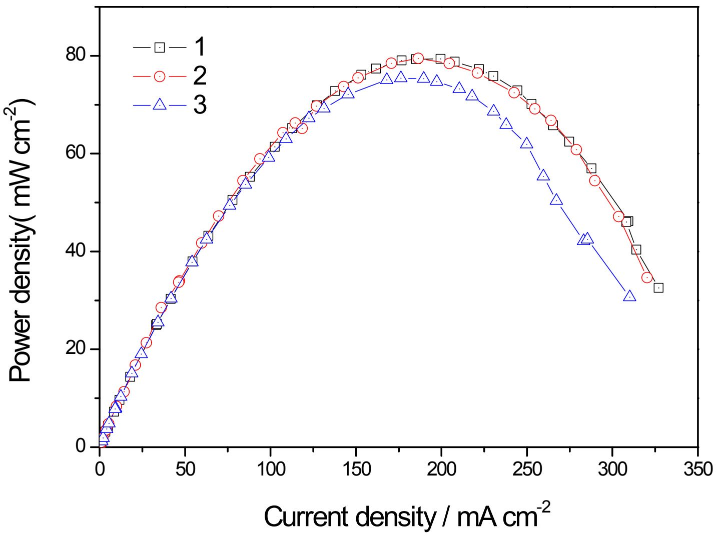
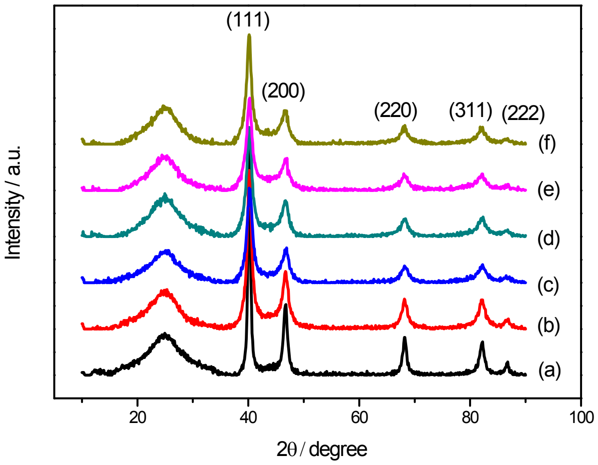
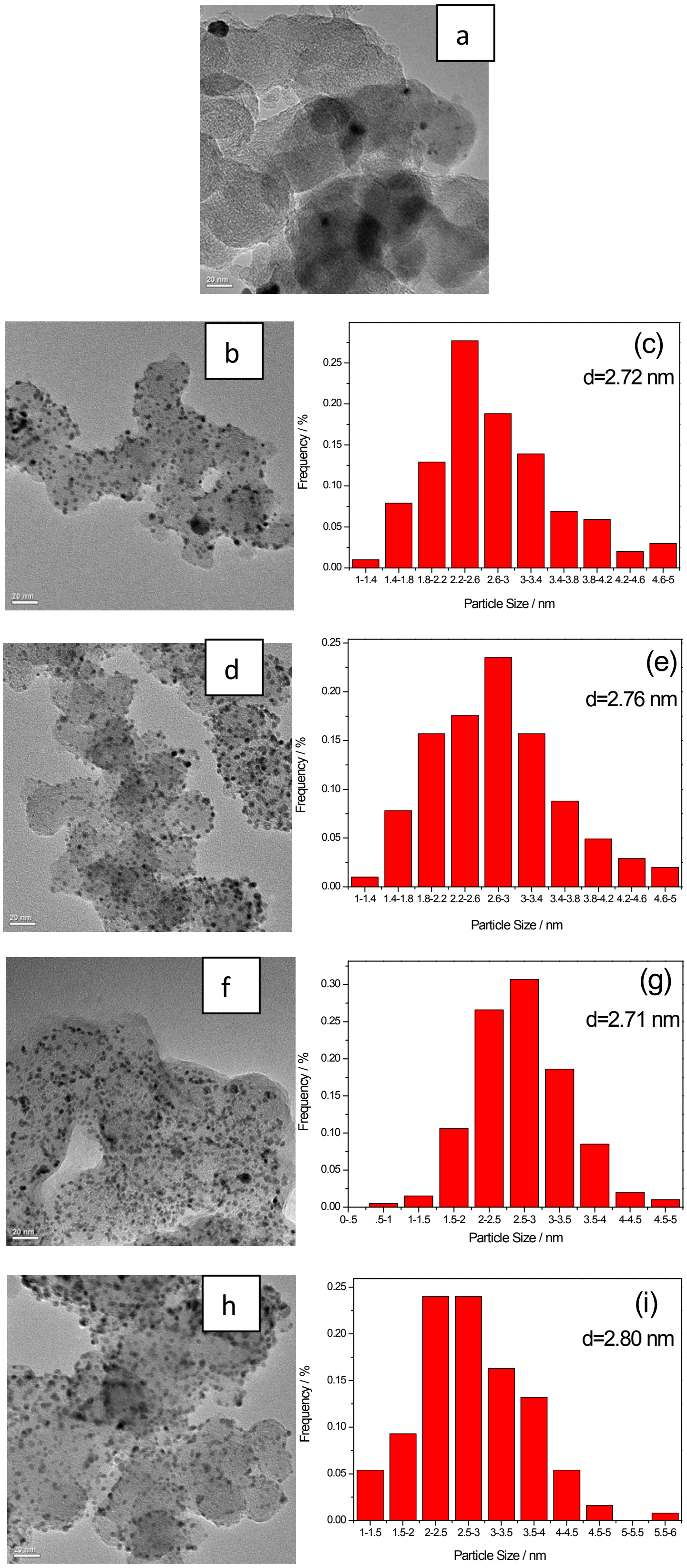


Figure S6.Power density curves after15 minutes (1), 30 minutes (2) and 45minutes (3) during the formic acid decomposition.The experiment was performed at room temperature and atmospheric pressure. Anode: Pt loading (1.0 mg cm^{-2}); cathode: Pt loading (1.0 mg cm^{-2}).



FigureS8. XRD patterns of Pd/C from 1.5 mL HCOOH and different molar percent of $HCOO^-$, a, b, c, d, e and f for 0%, 20%, 40%, 60%, 80% and 100%, respectively.


a
20 nm
b
20 nm
(c)
d=2.72 nm
Frequency / %
0.00
0.05
0.10
0.15
0.20
0.25
1-1.4
1.4-1.8
1.8-2.2
2.2-2.6
2.6-3
3-3.4
3.4-3.8
3.8-4.2
4.2-4.6
4.6-5
Particle Size / nm
d
20 nm
(e)
d=2.76 nm
Frequency / %
0.00
0.05
0.10
0.15
0.20
0.25
1-1.4
1.4-1.8
1.8-2.2
2.2-2.6
2.6-3
3-3.4
3.4-3.8
3.8-4.2
4.2-4.6
4.6-5
Particle Size / nm
f
20 nm
(g)
d=2.71 nm
Frequency / %
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0-.5
.5-1
1-1.5
1.5-2
2-2.5
2.5-3
3-3.5
3.5-4
4-4.5
4.5-5
Particle Size / nm
h
20 nm
(i)
d=2.80 nm
Frequency / %
0.00
0.05
0.10
0.15
0.20
0.25
1-1.5
1.5-2
2-2.5
2.5-3
3-3.5
3.5-4
4-4.5
4.5-5
5-5.5
5.5-6
Particle Size / nm

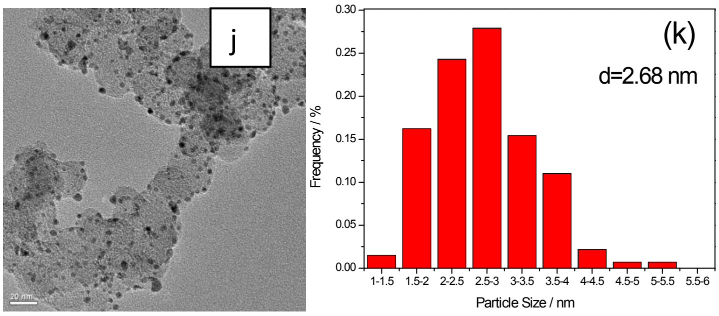


Figure S8.TEM images (a, b, d, f, h, j) and particle size distribution histograms (c, e, g, i, k) of Pd/C from 1.5 mL HCOOH and different molar percent (0%, 20%, 40%, 60%, 80%, 100%) of HCOO$^-$.Note: $PdCl_4^{2-}$was not reduced completely without formate. The mass fraction of Pd was only 9.15% without the addition of NaOH, according to ICP-OES result.The mean particle sizes of Pd were 2.72, 2.76, 2.71, 2.80 and 2.68 nm for 20%, 40%, 60%, 80% and 100% formate molar ratios, respectively, which have been labelled in the distribution histograms. It demonstrates that varied formate molar ratios have little effect on the Pd nanoparticle size.

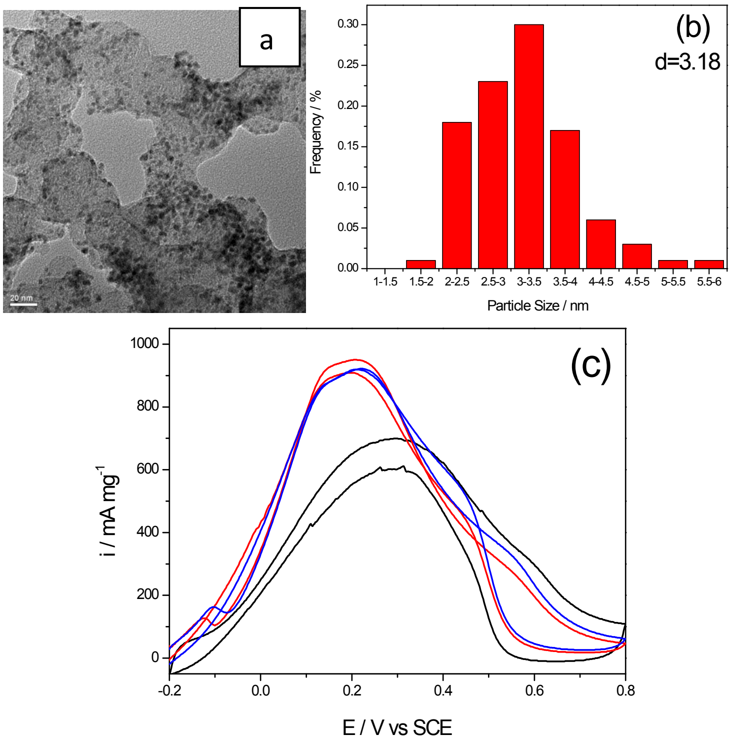


Figure S9.TEM images (a) and particle size distribution histograms (b) of commercial Pd/C, the mean particle size of Pd nanoparticles was 3.18 nm;CyclicvoltammogramsofcommercialPd/C(—), Pd/C obtainedwith 0.5 mL formicacid (—) andPd/C obtainedwith 2.0 mLformicacid(—) measured in 1 mol L^{-1} HCOOH + 0.5 mol L^{-1} H_2SO_4solution at 25 ℃ (c). The formatemolar percent was 60%.

Mechanism Discussion:

From figure S2, it can be seen that the decomposition reaction are related to the concentration of formic acid as well as formate. Reaction rates with only formic or formate are close to 0. It should be noted that the molar ratio changes of formic acid and formate also have influence on the concentration of proton in this system, which may affect the reaction as well. According to literatures reported before[1-7], two plausible pathways for HCOOH dehydrogenation on Pdwere proposed generally.

Mechanism 1:

$HCOOH \leftrightarrow H^+ + HCOO^-$ (Ⅰ)

$HCOO^- + * \rightarrow [HCOO*]^-$ (Ⅱ)

$H^+ + * \rightarrow [H*]^+$ (Ⅲ)

$[HCOO*]^- + [H*]^+ \rightarrow CO_2 + H_2 + 2*$ (Ⅳ)

Mechanism 2:

$HCOOH + 2* \rightarrow HCOO* + H*$ (Ⅴ)

$HCOO* \rightarrow CO_2 + H*$ (Ⅵ)

$H* + H* \rightarrow H_2 + 2*$ (Ⅶ)

In mechanism 1, one of the H atoms in H_2 comes from the breaking C-H and the other from O-H. Generally, the C-H breaking needs high energy. The formation of H-H would have benefit to breaking C-H bond in this mechanism. Although step Ⅳshould be the rate-limiting step in this mechanism, the reaction rate is not the farthest when concentration of $HCOO^-$ multiplied by concentration of H^+ is the largest (the formate molar percents 0%) in our experiments. The reasons may be the space repulsion for the larger sized $HCOO^-$, the different adsorption energy of $HCOO^-$

and H^+ and/or the adsorption orientation of $HCOO^-$. Moreover, Pd^{2+} is difficult to be reduced by pure formic acid. In mechanism 2, Step Ⅵshould be the rate-limiting step.According to this mechanism, hydrogen and CO_2 could also be produced through step Ⅵ and step Ⅶ, if pure formate without formic acid was used, which is inconsistent with our experimental results. The decomposition rate is close to 0 when the formate molar percent was 100% in our experiment.Consequently, mechanism 1 may be the reaction pathway for this system. However, study of calculation and spectroscopy is required to clarify further.

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