

# **Solvent-Switched *In Situ* Confinement Approach for Immobilizing Highly-Active Ultrafine Palladium Nanoparticles: Boosting Catalytic Hydrogen Evolution**

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## 1. Chemicals and Materials

All chemicals were commercial and used without further purification. Palladium(II) acetate ( $\text{Pd}(\text{OAc})_2$ , Wako Pure Chemical Industries, Ltd., >98%), potassium tetrachloropalladate ( $\text{K}_2\text{PdCl}_4$ , Wako Pure Chemical Industries, Ltd., >97%), sodium borohydride (SB,  $\text{NaBH}_4$ , Sigma-Aldrich, 99%), Maxsorb MSC-30 (Nanoporous Carbon, Kansai Coke and Chemicals Co. Ltd.), formic acid (FA,  $\text{HCOOH}$ , Kishida Chemicals Co. Ltd., >98%), sodium formate dehydrate (SF,  $\text{HCOONa}$ , Sigma-Aldrich, 99.5%), acetone (Kishida Chem. Co., >99.5%) were used as received. De-ionized water was obtained by reverse osmosis followed by ion-exchange and filtration (RFD 250NB, Toyo Seisakusho Kaisha, Ltd., Japan).

## 2. Instrumentation

Laboratory powder X-ray diffraction patterns were collected for samples on Rigaku Ultima IV X-ray diffractometer using  $\text{Cu K}_\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ) (40 kV, 40 mA). The surface area measurements were performed with  $\text{N}_2$  adsorption/desorption isotherms at liquid nitrogen temperature (77 K) using automatic volumetric adsorption equipment (Belsorp-max) after dehydration under vacuum at 120 °C for 12 h. The metal content of the catalyst was analyzed using ICP-OES on Thermo Scientific iCAP6300. X-ray photoelectron spectroscopic (XPS) measurements were conducted on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer using a  $\text{Mg K}_\alpha$  source (10 kV, 10 mA). The charging potentials of the catalyst samples were corrected by setting the binding energy of the adventitious carbon (C 1s) at 284.6 eV. The TEM and HAADF-STEM images and energy-dispersive X-ray (EDX) spectra were recorded on Transmission electron microscope (TEM, TECNAI G<sup>2</sup> F20) with operating voltage at 200 kV equipped with EDX detector. The gas generated from the dehydrogenation of formic acid was analyzed by GC-8A TCD (molecular sieve 5A, Ar as carrier gas) and GC-8A TCD (Porapak N, He as carrier gas) analyzers (Shimadzu), which was collected after purging the reactor with nitrogen three times. The detection limit was below 10 ppm for CO.

## 3. Synthesis of Catalysts

**3.1 Synthesis of the  $\text{Pd}^{2+}@\text{MSC}$  pre-catalyst:** Typically, 120 mg of  $\text{Pd}(\text{OAc})_2$  was dissolved in 120 mL of acetone in a beaker under vigorous stirring at room temperature. After stirring for 10 min, 500 mg of porous carbon MSC was added and mixed for another 1 hour for sufficiently absorbing the metal precursor into the carbon pores. Subsequently, the solvent and residual metal precursor were removed by centrifugation. The collected solid was washed with anhydrous acetone twice only to avoid serious loss of the metal precursor in the pores of MSC, while the metal precursor absorbed on the external surface can be easily removed. The sample was finally dried under vacuum at room temperature to give the  $\text{Pd}^{2+}@\text{MSC}$  pre-catalyst.

**3.2 Synthesis of *in situ*- $\text{Pd}@\text{MSC}$  and *in situ*- $\text{Pd}/\text{MSC}$ :** The *in situ*- $\text{Pd}@\text{MSC}$  and *in situ*- $\text{Pd}/\text{MSC}$  were *in situ* reduced from the  $\text{Pd}^{2+}@\text{MSC}$  pre-catalyst and the physical mixture of MSC and  $\text{K}_2\text{PdCl}_4$ , respectively, in the FA dehydrogenation system. The detailed procedures are described in the section of catalytic activity characterization.

**3.3 Synthesis of *pre*-Pd@MSC:** 20 mg of NaBH<sub>4</sub> was dissolved in 2.0 mL of water, to which 100 mg of the Pd<sup>2+</sup>@MSC pre-catalyst was added under vigorous stirring. After stirring for 10 min, the solid was collected by centrifugation, washed with de-ionized water three times and dried under vacuum at room temperature.

## 4. Catalytic Activity Characterization

**4.1 Procedure for hydrogen evolution from formic acid:** The Pd<sup>2+</sup>@MSC pre-catalyst (100 mg) was placed in a two-necked round-bottomed flask (30 mL), which was placed in a water bath at a preset temperature (30-60 °C) under ambient atmosphere. A gas burette filled with water was connected to the reaction flask to measure the volume of released gas (lab temperature kept constant at 25 °C during measurements). The Pd<sup>2+</sup>@MSC pre-catalyst was firstly reduced when 2.5 mL of the mixed aqueous solution containing 9 mmol FA and 9 mmol SF was injected into the mixture, which is followed by gas evolution catalyzed by the *in-situ*-generated catalyst denoted as *in situ*-Pd@MSC. The volume of the released gas was monitored by recording the displacement of water in the gas burette.

The activity evaluation of the *in situ*-Pd/MSC catalyst for hydrogen evolution from FA was performed using the similar procedure as described for *in situ*-Pd@MSC. 200 mg of MSC was ultrasonically dispersed in 1.0 mL of water in a two-necked round-bottomed flask (30 mL) and subsequently mixed with 29.5 mg of K<sub>2</sub>PdCl<sub>4</sub>. The resulted aqueous suspension was further homogenized under sonication conditions for half hour. The *in situ*-Pd/MSC catalyst was generated when 1.5 mL of the mixed aqueous solution containing 9 mmol FA and 9 mmol SF was injected, which is followed by catalytic gas evolution.

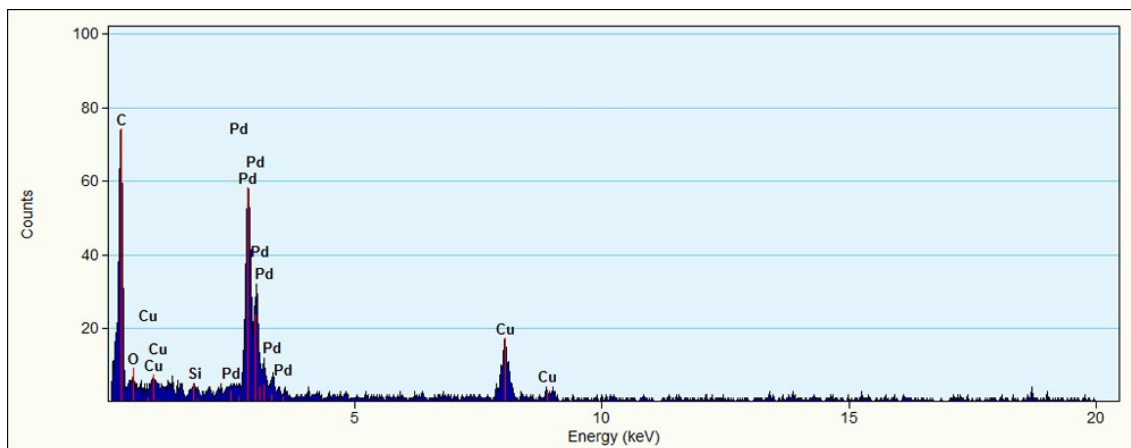
After the reaction, the catalysts were separated from the reaction solution by centrifugation, washed with water, and dried under vacuum at room temperature for the XPS, PXRD and TEM analyses.

**4.2 Durability testing of the catalysts:** For testing the durability of the catalyst, a new batch of pure FA (0.34 mL, 9.0 mmol) was subsequently added into the reaction flask after the completion of the first-run dehydrogenation of FA. Such test cycles of the catalyst for the dehydrogenation of FA were carried out for 5 runs at 60 °C by adding aliquots of pure FA.

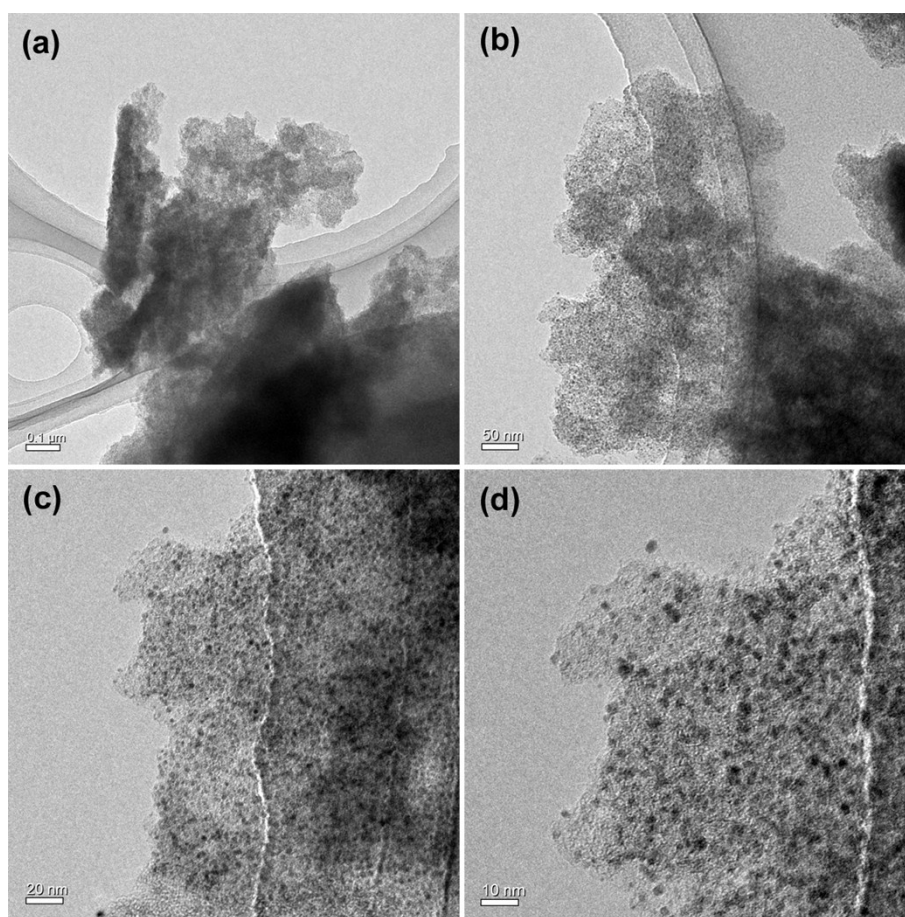
**4.4 Calculation Methods:** The turnover frequency (TOF) reported here is an apparent TOF value based on the number of Pd atoms in catalyst, which is calculated from the time of half-completion of gas generation, and the equation as follows:

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

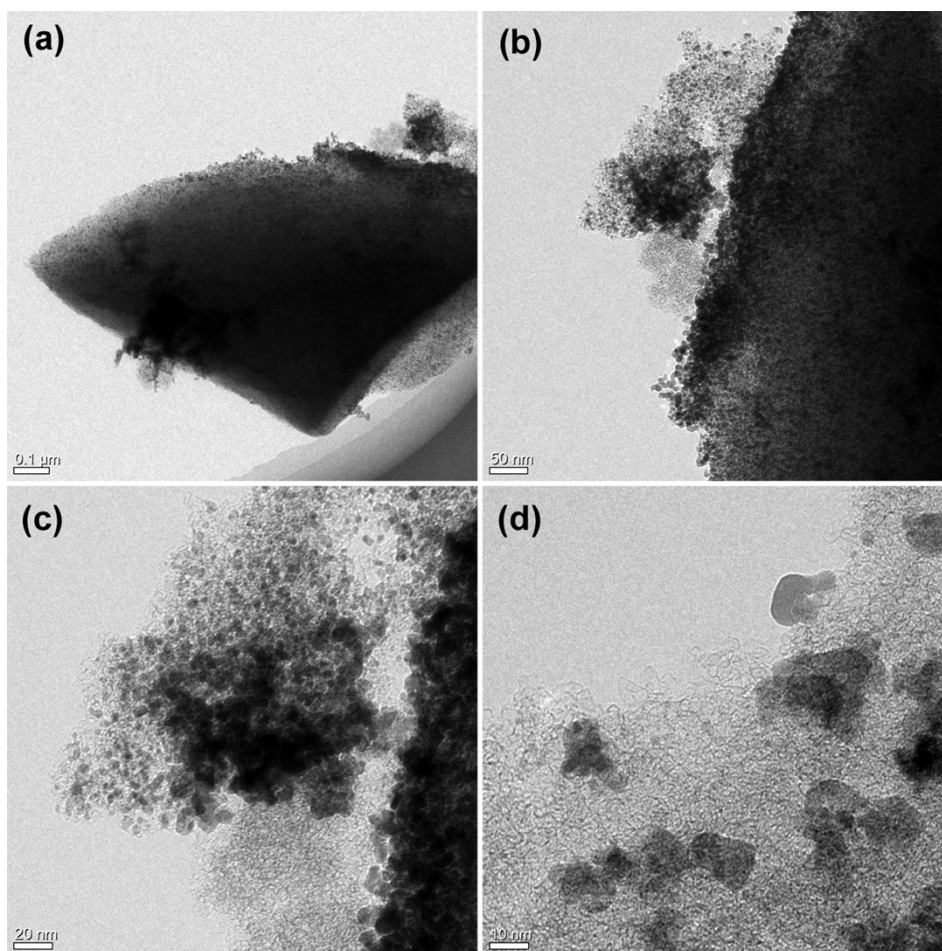
Where  $P_{atm}$  is the atmospheric pressure (101325 Pa),  $V_{gas}$  is the generated volume of H<sub>2</sub>/CO<sub>2</sub> gas at the time of half-completion of gas generation,  $R$  is the universal gas constant (8.3145 m<sup>3</sup> Pa mol<sup>-1</sup> K<sup>-1</sup>),  $T$  is the room temperature (298 K),  $n_{Pd}$  is the total mole number of Pd atoms in catalyst, and  $t$  is the time of half-completion of gas generation.



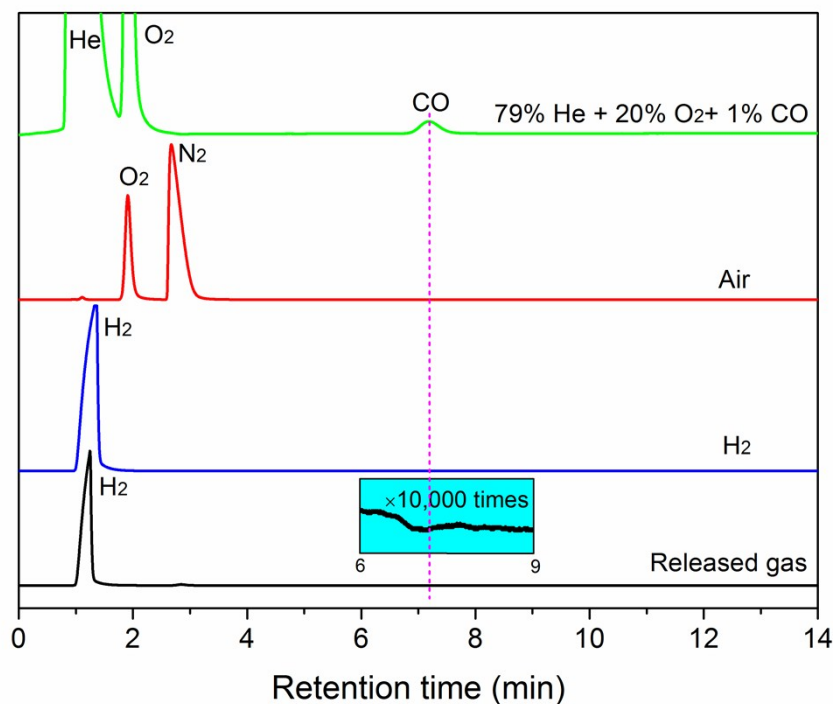
**Fig. S1** EDX spectrum of the bulk solid of *in situ*-Pd@MSC from TEM measurement. The copper signal originates from Cu grid.



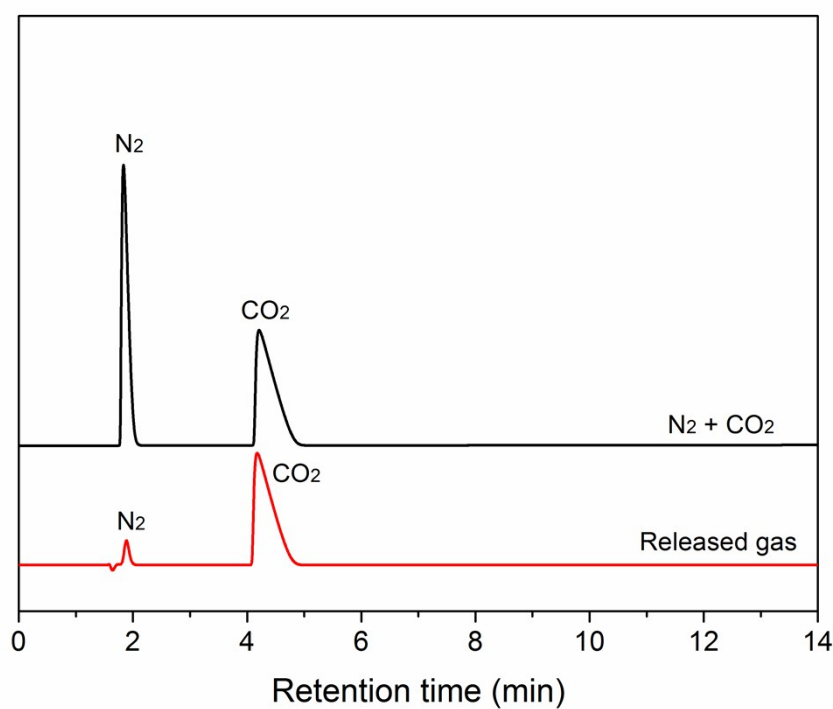
**Fig. S2** TEM images of *pre*-Pd@MSC.



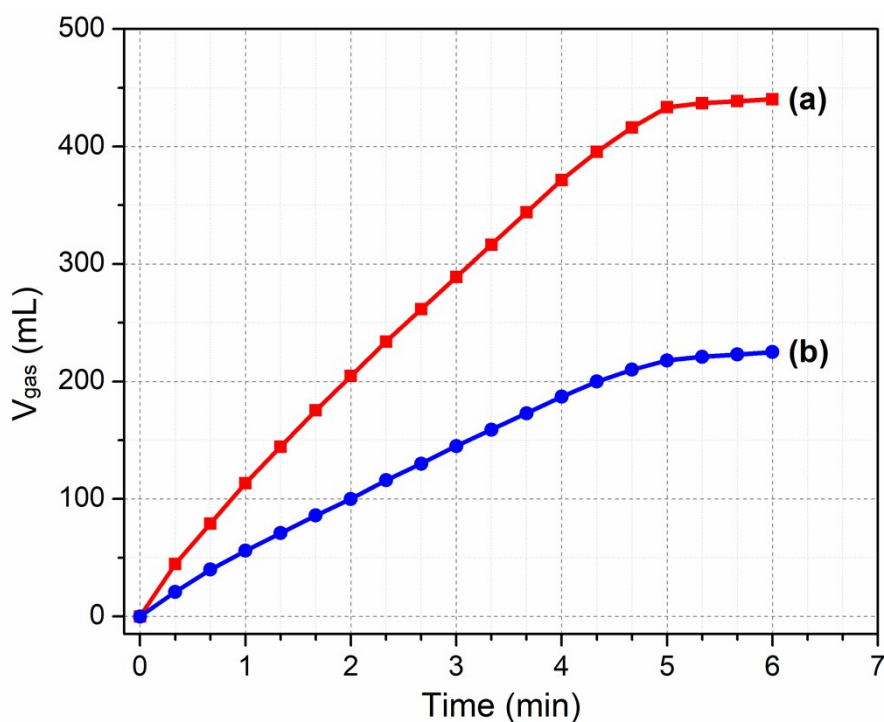
**Fig. S3** TEM images of *in situ*-Pd/MSC.



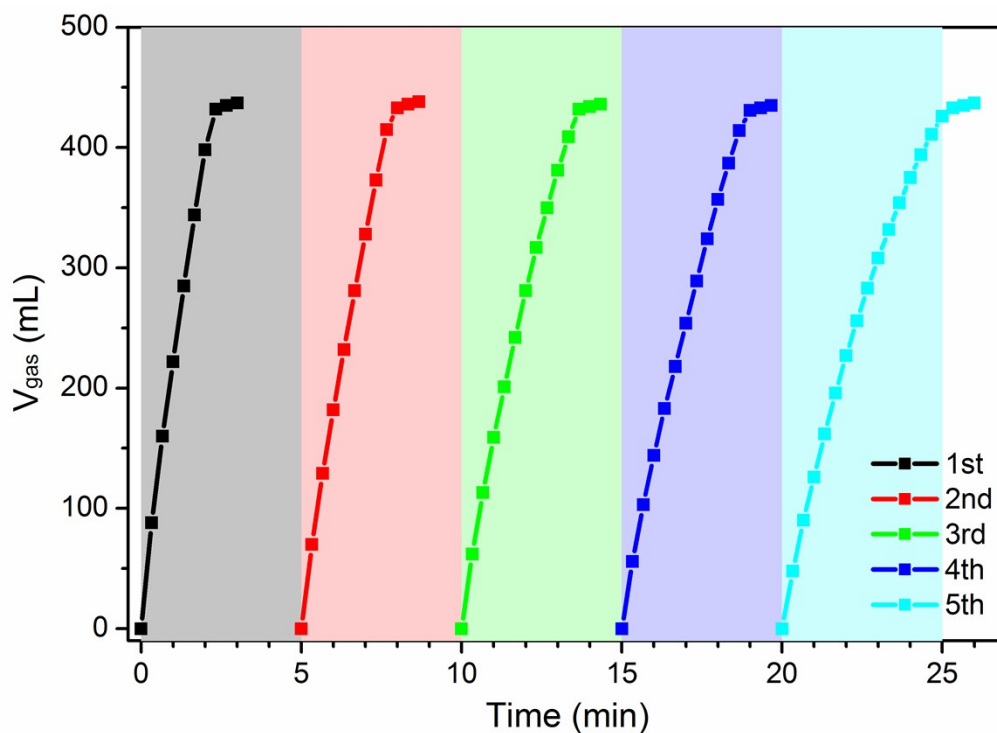
**Fig. S4** Gas chromatograms of CO, air and H<sub>2</sub> as reference gases and the released gas from FA dehydrogenation over *in situ*-Pd@MSC ( $n_{\text{Pd}}/n_{\text{FA}} = 0.0048$ , 60 °C), showing the presence of H<sub>2</sub> and the absence of CO in the released gas.



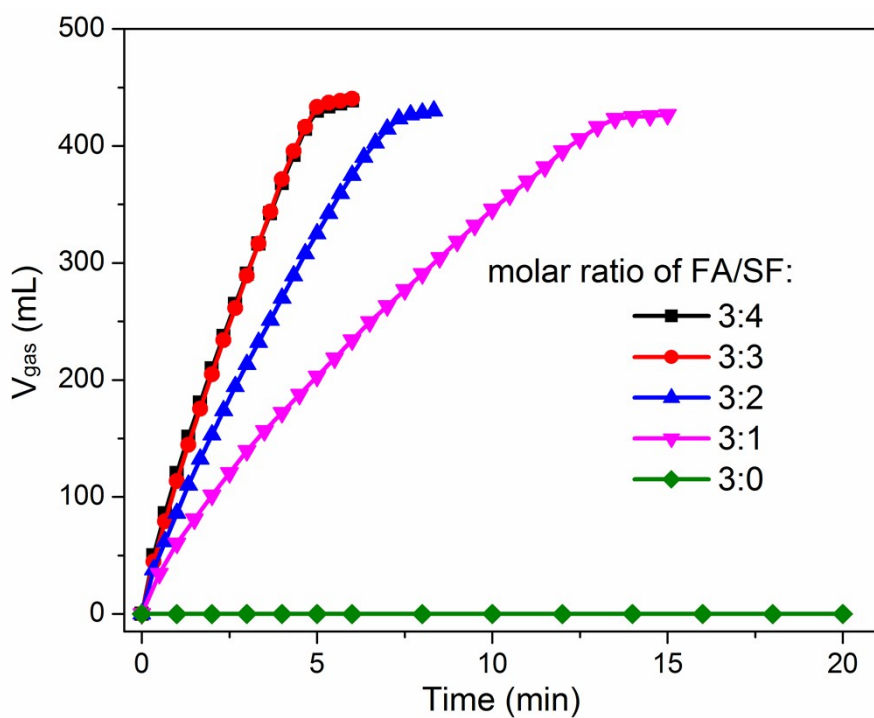
**Fig. S5** Gas chromatograms of CO<sub>2</sub> as reference gas and the released gas from FA dehydrogenation over *in situ*-Pd@MSC ( $n_{\text{Pd}}/n_{\text{FA}} = 0.0048$ , 60 °C), showing the presence of CO<sub>2</sub> in the released gas.



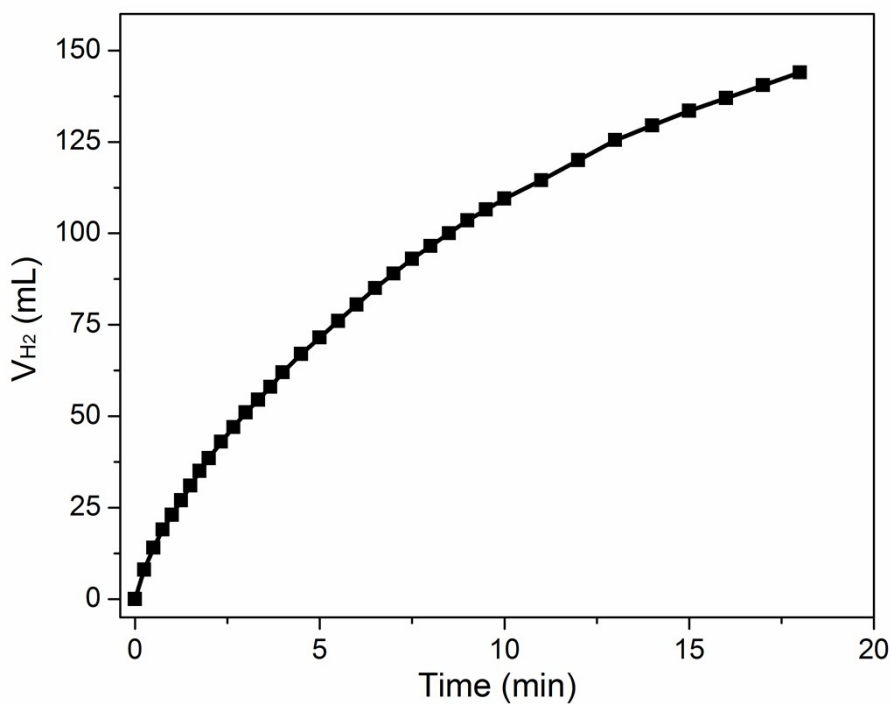
**Fig. S6** The comparison of the volume of the gas released during the *in situ*-Pd@MSC catalyzed dehydrogenation of FA (FA:SF = 1:1,  $n_{\text{Pd}}/n_{\text{FA}} = 0.0048$ ) at 30 °C (a) with and (b) without the trap (10 M NaOH solution).



**Fig. S7** Recyclability test for hydrogen evolution from FA over the *in situ*-Pd@MSC catalyst (FA:SF=1:1,  $n_{\text{Pd}}/n_{\text{FA}} = 0.0048$ , 60 °C).



**Fig. S8** Volume of the generated gas ( $\text{CO}_2 + \text{H}_2$ ) versus time for hydrogen evolution from FA with different FA/SF molar ratios in the presence of the  $\text{Pd}^{2+}@MSC$  pre-catalyst ( $n_{\text{Pd}}/n_{\text{FA}} = 0.0048$ ,  $60^\circ\text{C}$ ).



**Fig. S9** Volume of  $\text{H}_2$  versus time for hydrogen evolution from aqueous SF over the *in situ*- $\text{Pd}@MSC$  catalyst ( $n_{\text{Pd}}/n_{\text{SF}} = 0.0048$ ,  $60^\circ\text{C}$ ).



**Table S1.** Surface areas and pore volumes of MSC, Pd<sup>2+</sup>@MSC and *in situ*-Pd@MSC

Sample	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )
MSC	2765	1.540
Pd <sup>2+</sup> @MSC	2233	1.231
<i>in situ</i> -Pd@MSC	2392	1.308

**Table S2.** Catalytic activities for dehydrogenation of formic acid catalyzed by selected outstanding heterogeneous catalysts

Catalyst	Medium	Temp. (°C)	CO evolution	TOF (h <sup>-1</sup> )	Ref.
<i>In situ</i> -Pd@MSC	FA-SF	60	No	9110	<b>This work</b>
Pd/C_m	FA-SF	60	No	7256	<i>J. Am. Chem. Soc.</i> , 2015, <b>137</b> , 11743
Pd/PDA-rGO	FA-SF	50	No	3810	<i>ACS Catal.</i> 2015, <b>5</b> , 5141
Pd/S-1-in-K	FA-SF	50	≤10 ppm	3027	<i>J. Am. Chem. Soc.</i> , 2016, <b>138</b> , 7484
(Co <sub>6</sub> )Ag <sub>0.1</sub> Pd <sub>0.9</sub> /RGO	FA-SF	50	No	2739	<i>J. Am. Chem. Soc.</i> , 2015, <b>137</b> , 106
Pd/MSC-30	FA-SF	50	No	2623	<i>Chem. Sci.</i> , 2014, <b>5</b> , 195
Pd-B/C	FA-SF	30	No	1184	<i>J. Am. Chem. Soc.</i> , 2014, <b>136</b> , 4861
Au/ZrO <sub>2</sub> NCs	FA-NEt <sub>3</sub>	50	No	1593	<i>J. Am. Chem. Soc.</i> , 2012, <b>134</b> , 8926
Pd/basic resin	FA-SF	75	≤5 ppm	820	<i>ACS Catal.</i> , 2013, <b>3</b> , 1114
Ag <sub>42</sub> Pd <sub>58</sub>	FA	50	No	382	<i>Angew. Chem. Int. Ed.</i> , 2013, <b>52</b> , 3681
Ag@Pd/C	FA	20	No	192	<i>Nat. Nanotechnol.</i> , 2011, <b>6</b> , 302
PdAu/C-CeO <sub>2</sub>	FA-SF	92	145 ppm	113.5	<i>Chem. Commun.</i> , 2008, 3540
AuPd@ED-MIL-101	FA-SF	90	Yes	106	<i>J. Am. Chem. Soc.</i> 2011, <b>133</b> , 11822
Co <sub>0.30</sub> Au <sub>0.35</sub> Pd <sub>0.35</sub>	FA	25	No	80	<i>Angew. Chem. Int. Ed.</i> , 2013, <b>52</b> , 4406
PdAu@Au/C	FA-SF	92	30 ppm	21.4	<i>Chem. Mater.</i> , 2010, <b>22</b> , 5122