

Supporting Information

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**An Aqueous Rechargeable Formate-Based Hydrogen Battery Driven  
by Heterogeneous Pd Catalysis\*\***

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# Supporting Information

## 1. Chemicals and materials

Lithium formate (HCOOLi, 99.5 wt %), sodium formate (HCOONa, 99.5 wt %), potassium formate (HCOOK, 99.0 wt %), ammonium formate (HCOONH<sub>4</sub>, 98.0 wt %), lithium bicarbonate (LiHCO<sub>3</sub>, 99.5 wt %), sodium bicarbonate (NaHCO<sub>3</sub>, 99.5 wt %), potassium bicarbonate (KHCO<sub>3</sub>, 99.5 wt %), ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>, 99.0 wt %), palladium chloride (PdCl<sub>2</sub>, Pd ≥ 60.0 wt %), rhodium chloride hydrate (RhCl<sub>3</sub> xH<sub>2</sub>O, Rh ≥ 38.5 wt %), chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub> 6H<sub>2</sub>O, Pt ≥ 37.5 wt %), chloroauric acid tetrahydrate (HAuCl<sub>4</sub> 4H<sub>2</sub>O, Au ≥ 48.5 wt %), ruthenium chloride hydrate (RuCl<sub>3</sub> xH<sub>2</sub>O, Ru ≥ 37.5 wt %), iridium chloride (H<sub>2</sub>IrCl<sub>6</sub>, Ir ≥ 35.0 wt %), and D<sub>2</sub>O (99.0 wt %) were supplied by Alfa Aesar and used without further purification.

5.0 wt % Pd/C (stock # 38300), 5.0 wt % Ir/CaCO<sub>3</sub> (stock # 38306), 1.0 wt % Ir/C (stock # 38330), 5.0 wt % Pt/C (stock # 38325), 5.0 wt % Ru/C (stock # 11748), 5.0 wt % Ru/Al<sub>2</sub>O<sub>3</sub> (stock # 11749), and 5.0 wt % Pd/Al<sub>2</sub>O<sub>3</sub> (stock # 11752) were purchased from Alfa Aesar. 1.0 wt % Au/TiO<sub>2</sub> (stock # 79-0165) was supplied by Mintek. TiO<sub>2</sub> (P25) and CeO<sub>2</sub> (Adnano 90) were supplied by Evonik. Graphite powder, H<sub>2</sub>SO<sub>4</sub> (98 wt %), NaOH (99 wt %), NaBH<sub>4</sub> (99.5 wt %), NaNO<sub>3</sub> (99 wt %), KMnO<sub>4</sub> (98 wt %), H<sub>2</sub>O<sub>2</sub> (30 wt %), HCl (38 wt %), NH<sub>3</sub> H<sub>2</sub>O (28 wt %), MgSO<sub>4</sub>, PVP (K29-32, Mw = 58000), and PVA (1788) were purchased from Aladdin.

## 2. Catalyst preparation

**2.1 Preparation of graphite oxide (GO):** GO was prepared by a modified Hummers method.<sup>[S1]</sup> Briefly, 2.0 g as-received graphite powders was stirred in concentrated H<sub>2</sub>SO<sub>4</sub> (46 mL) at 25 °C, and NaNO<sub>3</sub> (1.0 g) was added. After over continuous stirring for over 2 h, the mixture was cooled to 0 °C and KMnO<sub>4</sub> (6.0 g) was slowly added to the suspension under vigorous stirring. The rate of addition was controlled to prevent the rapid rise in the temperature of the suspension (should be < 10 °C). After that, the mixture was stirred at 25 °C for 1 h, followed by further stirring at 35 °C for 3 h. Then distilled water (92 mL) was slowly added to the reaction vessel. The diluted suspension was stirred for an additional 15 min and further diluted with distilled H<sub>2</sub>O (280 mL) and then H<sub>2</sub>O<sub>2</sub> (20 mL, 30 wt %) was added. After filtered and washed with 5 % HCl aqueous solution, the resulting gel-like material was dried in air at 65 °C to give a fine dark brown GO powder.

**2.2 Preparation of Pd/r-GO catalyst:** A series of Pd/r-GO catalysts with the actual Pd loading of 1–5 wt % (based on ICP bulk chemical analysis) were prepared via a facile wet chemical reduction method. Briefly, 0.5 g GO was introduced into 200 mL distilled H<sub>2</sub>O at 25 °C under stirring. Then 0.1 M NaOH was slowly added into the GO solution for adjusting the pH at the constant value of 9.5. After stirring at 25 °C for 24 h, an appropriate amount of PdCl<sub>2</sub> solution (6 g L<sup>-1</sup>) was added into the solution at a fixed pH (9.5). After stirring for 1 h, the calculated amount of NaBH<sub>4</sub> solution (freshly prepared, n<sub>NaBH<sub>4</sub></sub>/n<sub>Pd</sub> = 15/1) was rapidly injected into the GO-PdCl<sub>2</sub> solution. After stirring the resultant mixture for 2 h at 25 °C, the suspension was filtered and extensively washed with distilled water until it was chloride-free. The sample was dried in air at 100 °C for 12 h to give a black Pd/r-GO sample.

**2.3 Preparation of 5 wt % Pd/XC-72, 5 wt % Pd/CNTs, 5 wt % Ir/r-GO, 5 wt % Pt/r-GO, 5 wt % Ru/r-GO, and 5 wt % Rh/r-GO catalysts:** In analogy to the case of Pd/r-GO, these catalysts were

prepared by the procedure of wet chemical reduction.

**2.4 Preparation of 5 wt % Pd/TiO<sub>2</sub> catalyst:** The catalyst was prepared using the routine incipient wetness technique. Appropriate amount of TiO<sub>2</sub> (P25) was added to the aqueous solution of PdCl<sub>2</sub>. After a perfect mixing of the corresponding slurries and static standing for 12 h, the sample was dried at 100 °C for 12 h, followed by reduction in 5 vol % H<sub>2</sub>/Ar at 400 °C for 2 h.

**2.5 Preparation of 5 wt % Au/r-GO catalyst:** The catalyst was prepared following a procedure as described elsewhere.<sup>[S2]</sup> Typically, the PVA was added (Au/PVA = 1.5/1, wt/wt) to an aqueous solution containing 0.5 mM HAuCl<sub>4</sub> at 25 °C under vigorous stirring. The obtained solution was then left under stirring for 10 min. Following the rapid injection of an aqueous solution of 0.1 M NaBH<sub>4</sub> (Au/NaBH<sub>4</sub> = 1/5, mol/mol), the color of the solution turns orange/brown indicating the formation of Au NPs. The r-GO solution (prepared via the method mentioned above) was then added to the colloidal Au solution under stirring and kept in contact until total adsorption (5 wt % of gold on the support) occurred. After 2 h, the slurry was filtered and the resulting sample was dried at 25 °C in vacuum for 12 h.

**2.6 Preparation of 0.8 wt % Au/ZrO<sub>2</sub> catalyst:** A modified deposition–precipitation (DP) procedure has been employed to prepare the Au/ZrO<sub>2</sub> sample.<sup>[S2]</sup> Briefly, 2.0 g ZrO<sub>2</sub> powder was dissolved with desired amounts of aqueous solution of HAuCl<sub>4</sub> (100 mL, 1 mM), and the pH was adjusted to 9.0 by dropwise addition of 0.25 M NH<sub>4</sub>OH (CAUTION: the addition of NH<sub>4</sub>OH to HAuCl<sub>4</sub> solution could give rise to highly explosive fulminating gold). After 6 h of stirring at 25 °C, the catalyst was washed five times with distilled water and separated by filtration. The samples were dried at 100 °C in air for 1 h, followed by a careful reduction with a stream of 5 vol % H<sub>2</sub>/Ar at 350 °C for 2 h.

**2.7 Preparation of 1 wt % Au/CeO<sub>2</sub> catalyst:** Au/CeO<sub>2</sub> catalysts were prepared by a routine DP method.<sup>[S3]</sup> An appropriate amount of aqueous solution of chloroauric acid (HAuCl<sub>4</sub>) was heated to 70 °C under vigorous stirring. The pH was adjusted to 9 by dropwise addition of NaOH (0.2 M), and then 1.0 g of CeO<sub>2</sub> powders was dispersed in the solution. The mixture was aged for 1 h, followed by filtering and washing several times with distilled water to remove Cl<sup>-</sup>. The resulting solid product was dried overnight before reduction at 300 °C for 2 h in 5 vol % H<sub>2</sub>/Ar.

**2.8 Preparation of PVP-stabilized 1 wt % Pd/r-GO catalyst:** This catalyst was prepared following a procedure as described elsewhere.<sup>[S4]</sup> Typically, the PVP (PVP/Pd = 10/1, mol/mol) was added to an aqueous solution containing 2 mM PdCl<sub>2</sub> at 25 °C under vigorous stirring. The obtained solution was then left under stirring for 10 min. A following rapid injection of an aqueous solution of 0.1 M NaBH<sub>4</sub> (freshly prepared,  $n_{\text{NaBH}_4}/n_{\text{Pd}} = 15/1$ ), led to formation of a dark orange-brown solution, indicating the formation of the palladium sol. The r-GO solution (prepared via the method mentioned above) was then added to the colloidal palladium solution under stirring and kept in contact until total adsorption (1 wt % of palladium on the support) occurred. After 2 h stirring, the slurry was filtered and the resulting sample was dried at 100 °C in air for 4 h.

### 3. Catalyst characterization

**3.1 Elemental analysis:** The Pd loading of the catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer.

**3.2 BET analysis:** The BET specific surface areas of the prepared catalysts were determined by adsorption–desorption of nitrogen at liquid nitrogen temperature, using a Micromeritics TriStar 3000

equipment. Sample degassing was carried out at 300 °C prior to acquiring the adsorption isotherm.

**3.3 X-ray diffraction (XRD) analysis:** The crystal structures were characterized with XRD on a Bruker D8 Advance X-ray diffractometer using the Ni-filtered Cu K $\alpha$  radiation source at 40 kV and 40 mA.

**3.4 Synchrotron radiation X-ray diffraction (SRXRD) analysis:** The diffraction data of Pd(111) plane for 1 wt % Pd/r-GO and 2 wt % Pd/r-GO catalysts with low metal loading and highly dispersed Pd NPs can be obtained by SRXRD. The SRXRD was carried out at room temperature using the Fe radiation source at beam line BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. During the measurement, the synchrotron was operated at energy of 3.5 GeV and a current of 300 mA. Batch refinements of the SRXRD patterns were performed using the GSAS/EXPGUI suite of programs.

The peak position  $\theta'$  in SRXRD patterns with Fe radiation source can be transformed to the peak position  $\theta$  in XRD patterns with CuK $\alpha$  radiation source following Equation S1.

$$\theta = 1.26 \theta' \quad (\text{S1})$$

Size-strain broadening was evaluated through Equation S2 as, the instrumental XRD broadening determined from a LaB<sub>6</sub> standard sample was subtracted from the total broadening.  $d$ , as the grain diameter, and  $\varepsilon$ , as the lattice strain, can be calculated with  $B$  as measured full width at half maximum intensity of the considered diffraction peak at  $\theta$  Bragg angle and  $\lambda$  as the X-ray wavelength (CuK $\alpha$ ).<sup>[S5]</sup>

$$B \cos \theta = \frac{0.9\lambda}{d} + \varepsilon \sin \theta \quad (\text{S2})$$

**3.5 X-ray photoelectron spectroscopy (XPS):** XPS data were recorded with a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The spectrometer was operated at 15 kV and 20 mA, and a magnesium anode (Mg K $\alpha$ ,  $h\nu = 1253.6$  eV) was used. The C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (BE).

**3.6 Transmission electron microscopy (TEM):** A JEOL 2011 microscope operating at 200 kV equipped with an EDX unit (Si(Li) detector) was used for the TEM investigations. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids. The size distribution of the metal nanoparticles was determined by measuring about 200 random particles on the images.

**3.7 High-resolution transmission electron microscopy (HRTEM):** A JEM 2100F electron microscope operating at 200 kV equipped with an EDX unit (Si(Li) detector) was used for the HRTEM investigations. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids. The size distribution of the metal nanoparticles was determined by measuring about 200 random particles on the images.

**3.8 Quantitative analysis of trace CO in the H<sub>2</sub>-containing stream:** CO concentration with very low levels can be reliably measured by using a gas chromatograph (Agilent 6890 GC) analysis system equipped with a methanizer and a flame ionization detector (FID, detection limit ~ 1.0 ppmv). Prior to the analysis, the catalyst in methanizer was reduced *in situ* by 5 vol % H<sub>2</sub>/Ar at 400 °C for 1 h. The

evolved gas was first cleaned by concentrated NaOH solution for potential CO<sub>2</sub>-trapping and MgSO<sub>4</sub> powder for moisture-trapping, then flowing the methanizer at 300 °C under atmospheric pressure. The effluent from methanizer was again cleaned by MgSO<sub>4</sub> powder and later analyzed by the FID. For calibration purpose, the methanation data of a series of premixed reference gases containing different concentrations CO in H<sub>2</sub> were also collected using the similar method.

**3.9 Diffuse Reflectance Infrared Fourier Transform (DRIFT) measurements:** The DRIFT experiments were carried out on a Bruker Vector 22 FTIR spectrometer equipped with a MCT detector and Harrick diffuse reflectance accessory. Spectra were obtained on a homemade apparatus loaded with 50 mg of catalyst. All spectra were collected in He atmosphere at room temperature.

**3.10 Raman spectroscopy:** Raman spectra were obtained on a LabRAM-1B confocal microscope with exciting wavelength of 514.5 nm under ambient conditions.

## 4. Catalyst test

**4.1 Dehydrogenation of aqueous formate in an open system:** All catalytic experiments were carried out under ambient atmosphere of air. It should be noted that the use of oxygen atmosphere (O<sub>2</sub>) gave essentially the same rate of H<sub>2</sub> evolution as air in this reaction. All reactions, unless otherwise stated, were performed in a reaction vessel (10 mL) using oil bath under steady magnetic stirring (800 rpm) at given temperature (40–90 °C) with a reflux condenser, which is connected to an automatic gas burette, where the gases are collected. In addition, evolved gas was qualitatively and quantitatively analyzed by GC (Agilent 6820 equipped with a TDX-01 column connected to a thermal conductivity detector). Average values of two or three measurements were reported with a reproducibility of ± 5 %. For the dehydrogenation of HCOOK in D<sub>2</sub>O instead of H<sub>2</sub>O media, the isotope distribution for evolved hydrogen gas was carried out by dividing the reactor effluent into two parallel streams: one was analyzed with a mass spectrometer (Balzers OmniStar) and the other with a gas chromatograph Agilent 6820 equipped with a TDX-01 column connected to a thermal conductivity detector.

**4.2 Large-scale durability of 1 wt % Pd/r-GO catalyst for dehydrogenation of aqueous HCOOK:** For the large-scale durability experiment, 20 mL scale of 4.8 M aqueous HCOOK and 3.2 μmol Pd catalyst were placed in a reaction vessel (50 mL) using oil bath under steady magnetic stirring (800 rpm) at 80 °C with a reflux condenser, which is connected to an automatic gas burette, where the gases are collected. In addition, the evolved gas was qualitatively and quantitatively analyzed by GC (Agilent 6820 equipped with a TDX-01 column connected to a thermal conductivity detector). After reaction of 8 h, the centrifuged catalysts from parallel activity tests were collected and washed with distilled water, followed by drying in air at 100 °C for 12 h. All catalytic activity tests were repeatedly carried out by following the same procedure as described above.

**4.3 Temperature dependence of 1 wt % Pd/r-GO for dehydrogenation of aqueous HCOOK:** 10 mL scale of 4.8 M aqueous HCOOK and 6.4 μmol Pd catalyst were placed in a reaction vessel (25 mL) using oil bath under steady magnetic stirring (800 rpm) with a reflux condenser, which is connected to an automatic gas burette, where the gases are collected. The reaction was first performed at 40 °C for 1 h, then at 80 °C (rapidly increased) for 0.5 h and 40 °C for 1 h, last at 25 °C for 1 h. Average values of two or three measurements were reported with a reproducibility of ± 5 %.

**4.4 Pressurized H<sub>2</sub> generation in a closed system:** The catalytic experiment was carried out in a Hastelloy-C high-pressure Parr autoclave (50 mL). Typically, 5.0 mL scale of 4.8 M aqueous HCOOK

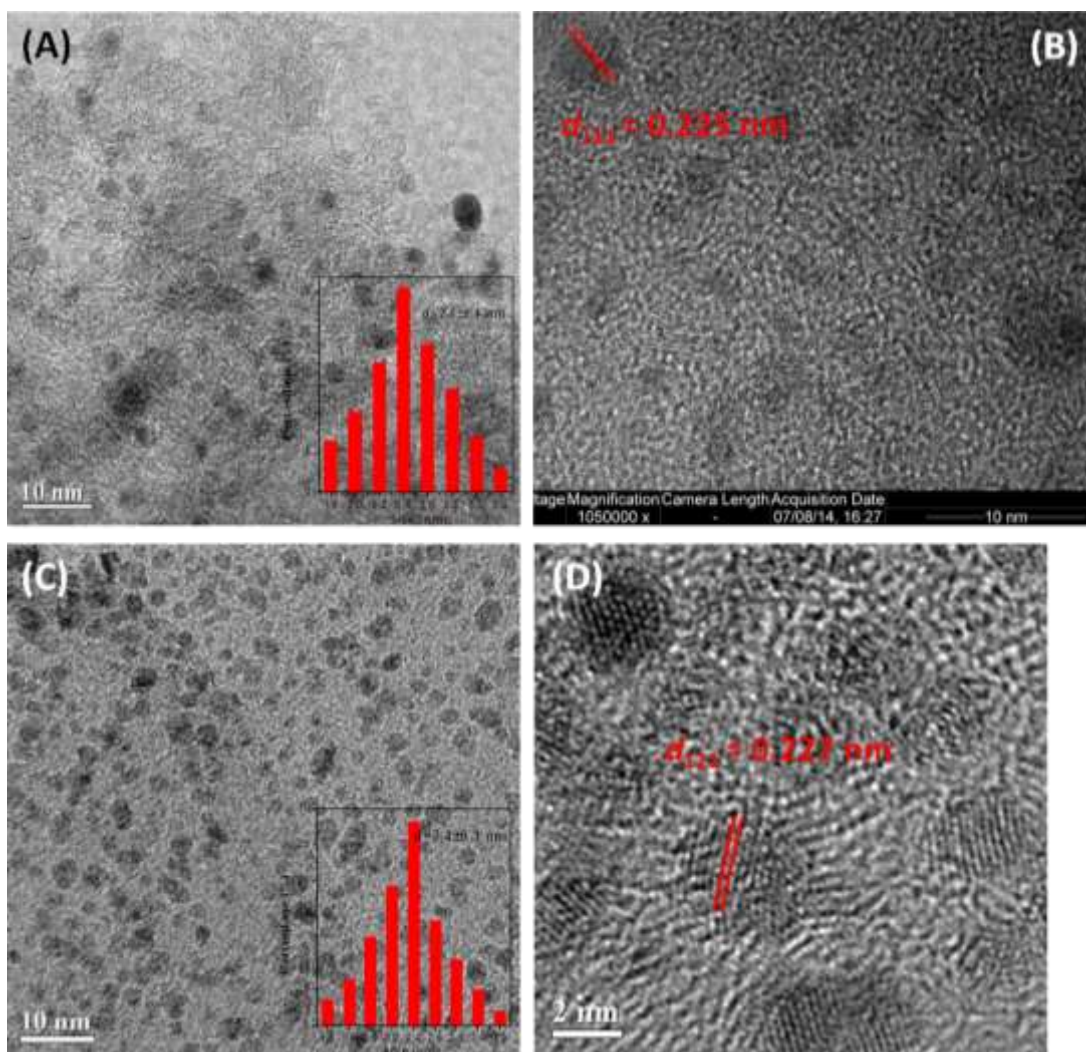
and 3.2  $\mu\text{mol}$  Pd (1 wt % Pd/r-GO) were placed in the autoclave. Then the autoclave was sealed and the internal air was degassed quickly and completely using  $\text{N}_2$  at room temperature. The stirrer was started (800 rpm) when the desired temperature of 80  $^\circ\text{C}$  was reached.

**4.5 Catalytic transfer reduction of benzaldehyde:** A mixture of benzaldehyde (1 mmol), metal catalysts (1 mol %), and HCOOK (5 mmol), water (15 mL) was put into a flask (50 mL) fitted with a magnetic stirring bar and a reflux condenser. After the mixture was stirred at 40  $^\circ\text{C}$  for 10 h, the product mixtures were extracted with  $\text{Et}_2\text{O}$  for 3 times and analyzed (the water phase was also analyzed) by using a Shimadzu GC-17 A gas chromatograph equipped with a HP-FFAP column (30 m  $\times$  0.25 mm) and a flame ionization detector (FID). The identification of the products was performed by using a GC-MS spectrometer comparing with commercially pure products.

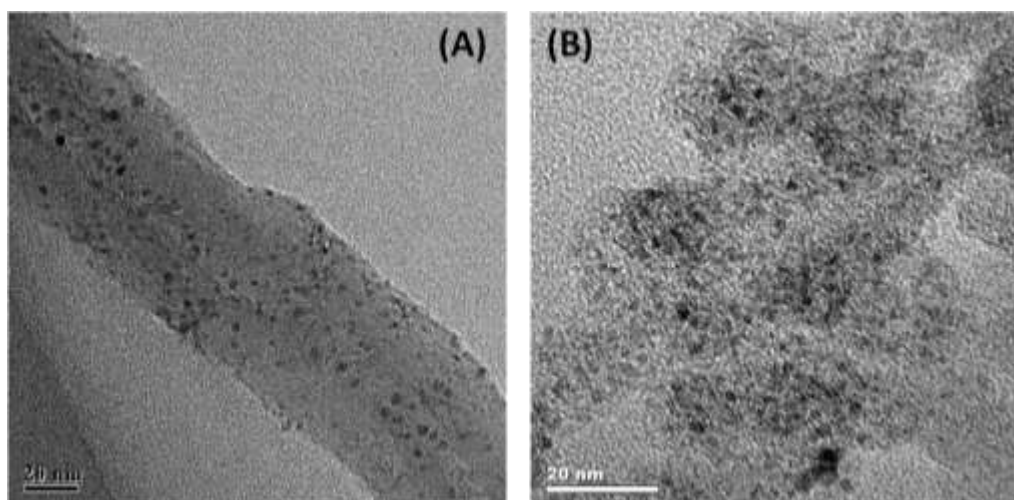
**4.6 Hydrogenation of styrene in aqueous media:** Typically, 10 mL heptane (solvent), 2 mmol styrene and 1 mol % commercial Pd/C (5 wt %) were placed in a reaction vessel (50 mL) using water bath under steady magnetic stirring (800 rpm) at 40  $^\circ\text{C}$ . The inlet of this reaction vessel is connected to the outlet of setup of HCOOK dehydrogenation. After 4 h, the reaction vessel was cooled to 25  $^\circ\text{C}$ . A known amount of octane as internal standard was added into the aqueous product in reactor. The reaction mixture was transferred into a centrifuge tube and the solid was separated by centrifugation. The product solution was quantitatively analyzed using a Agilent 7820 GC equipped with a HP-5 capillary column. Identification of the products was performed by using a GC-MS spectrometer.

**4.7 Hydrogenation of bicarbonate in aqueous media:** The catalytic hydrogenation experiments were carried out in a Hastelloy-C high-pressure Parr autoclave (100 mL). Typically, 5.0 mL scale of 4.8 M aqueous bicarbonate and a known amount of Pd catalyst were placed in the autoclave. Then the autoclave was sealed, and  $\text{H}_2$  gas was charged into it after internal air being degassed completely using  $\text{N}_2$  at 25  $^\circ\text{C}$ . The stirrer (800 rpm) was started until the desired temperature (80–130  $^\circ\text{C}$ ) was reached. After a certain time, the autoclave was placed in cool water and the gas was carefully released. The gaseous mixture was analyzed using a Agilent 6820 GC equipped with a TDX-01 column connected to a TCD. The reaction mixture was transferred into a centrifuge tube and the solid catalyst was separated by centrifugation. Formate product concentrations were monitored by high-performance liquid chromatography (HPLC) on an anion-exclusion column (Tosoh TSKgel SCX( $\text{H}^+$ )) using aqueous  $\text{H}_2\text{SO}_4$  solution (5 mM) as eluent and a ultraviolet detector ( $\lambda = 210$  nm).

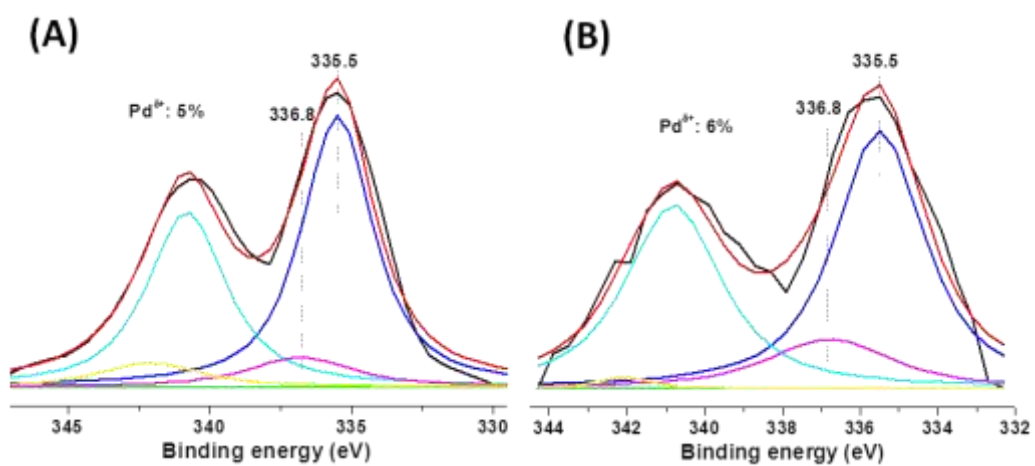
**4.8 Recycling of reversible hydrogen storage over 1 wt % Pd/r-GO catalyst:** The cyclic process was carried out in a Hastelloy-C high-pressure Parr autoclave (100 mL). Typically, 5.0 mL scale of 4.8 M aqueous HCOOK and 9.6  $\mu\text{mol}$  Pd were placed in the autoclave. The dehydrogenation reaction was first performed under magnetic stirring (800 rpm) at 80  $^\circ\text{C}$ . The evolved gas was collected by the automatic gas burette and was qualitatively and quantitatively analyzed by GC (Agilent 6820 equipped with a TDX-01 column connected to a thermal conductivity detector). Then the autoclave was sealed after 40 min for the dehydrogenation reaction, and 40 bar  $\text{H}_2$  gas was charged into it after internal gas being degassed completely using  $\text{N}_2$  at room temperature. The stirrer (800 rpm) was started until the desired temperature of 100  $^\circ\text{C}$  was reached. After 10 h for the hydrogenation reaction, the autoclave was placed in cool water and the gas was carefully released. The gaseous mixture was analyzed using a Agilent 6820 GC equipped with a TDX-01 column connected to a thermal conductivity detector. The regenerated formate can be used as the  $\text{H}_2$  carrier for the next round.



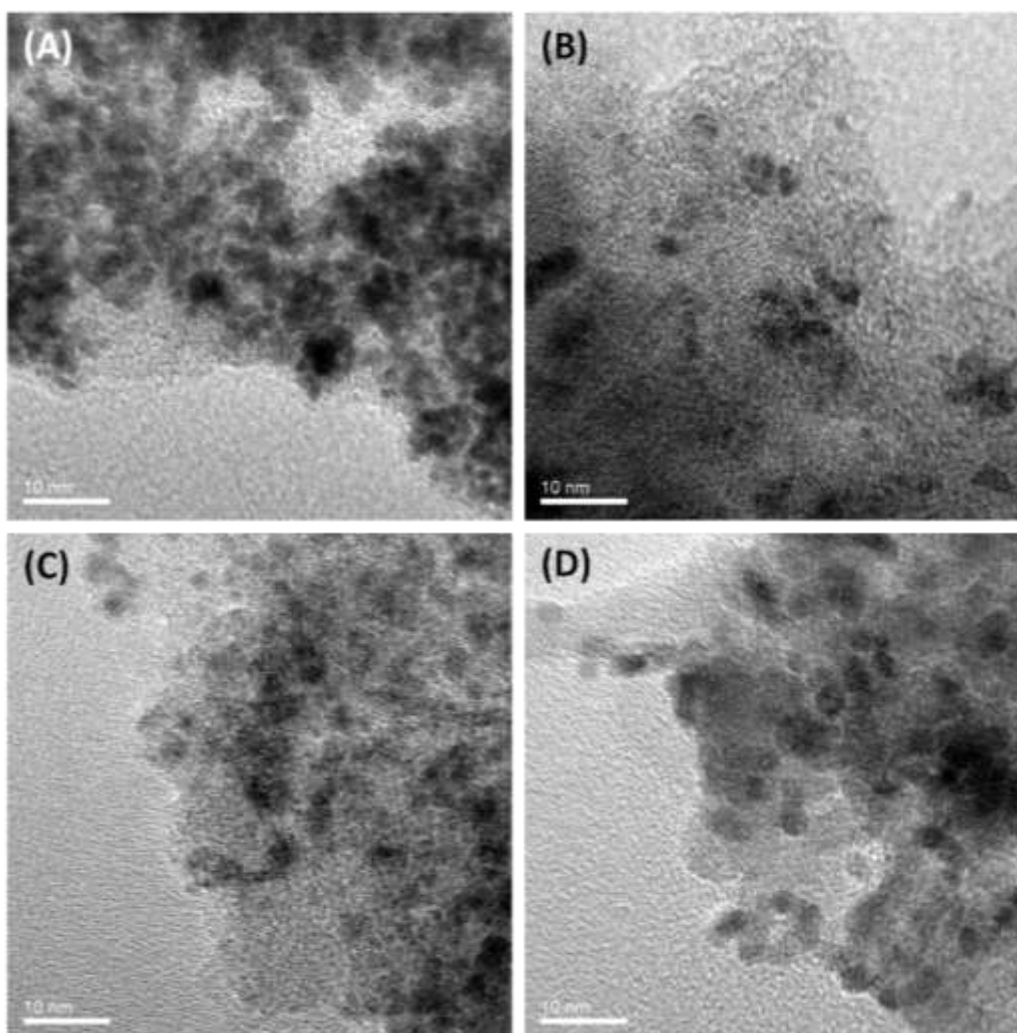
**Figure S1.** HRTEM images of (A, B) 5 wt % Pd/C and (C, D) 5 wt % Pd/r-GO catalysts with the insets of the particle size distribution.



**Figure S2.** TEM images of (A) 5 wt % Pd/CNTs and (B) 5 wt % Pd/XC-72 catalysts.

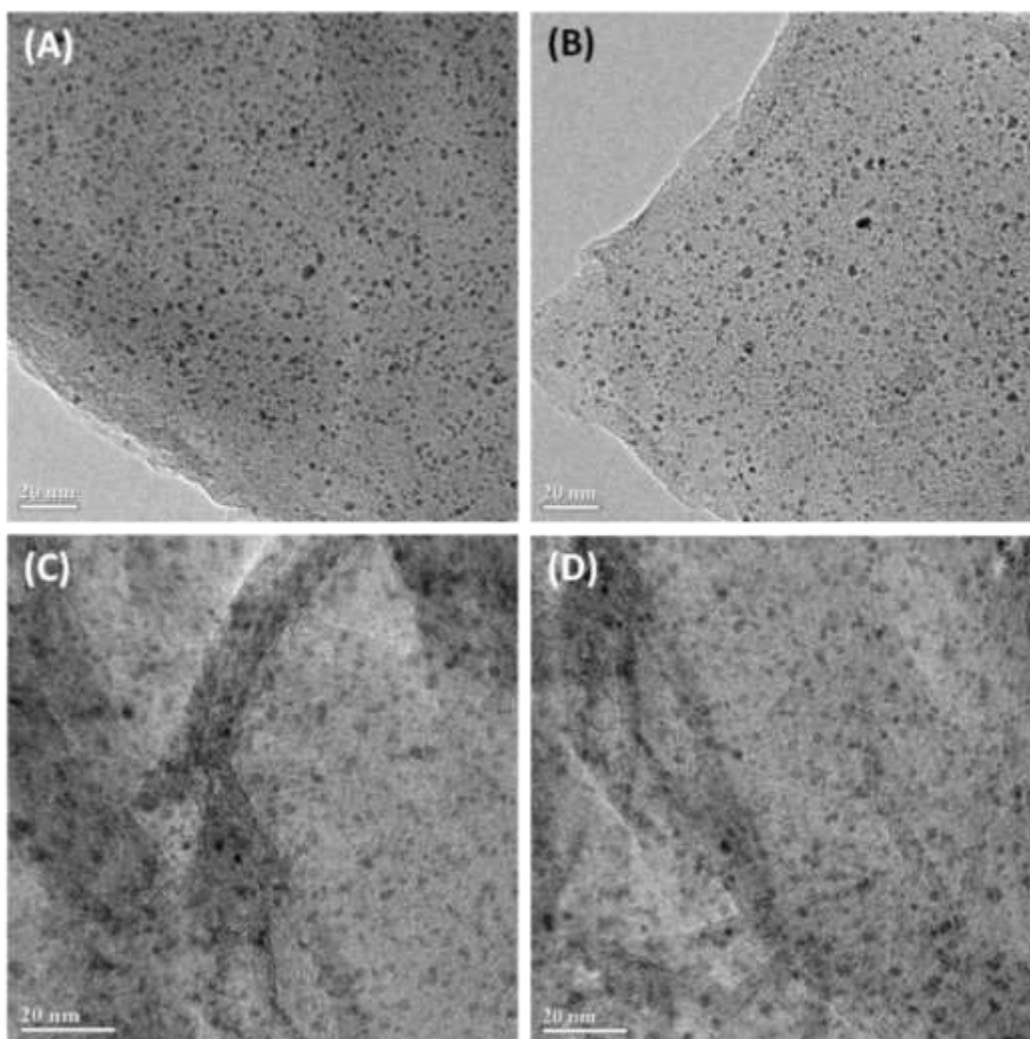


**Figure S3.** XPS data of (A) 5 wt % Pd/C and (B) 5 wt % Pd/r-GO catalysts.

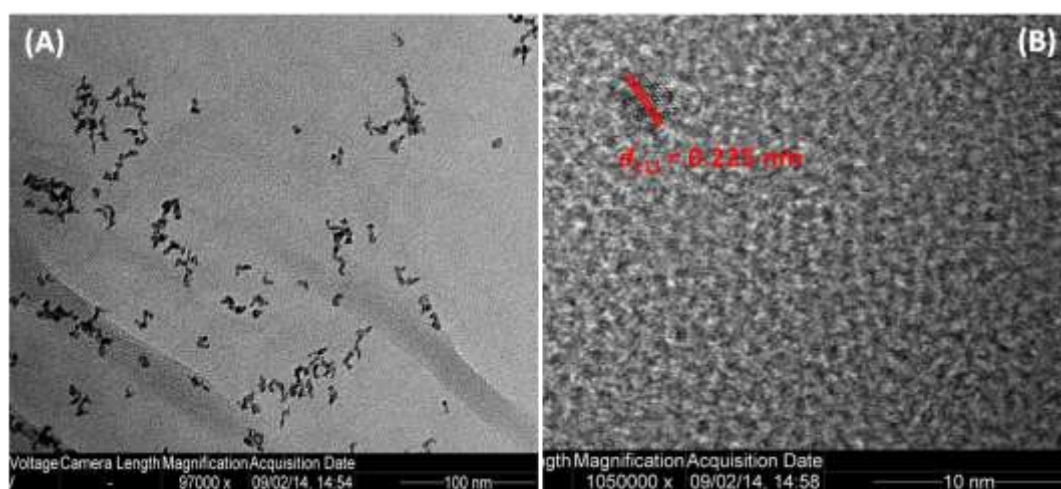


**Figure S4.** TEM images of (A) 1 wt % Ir/C, (B) 5 wt % Pt/C, (C) 5 wt % Ru/C, and (D) 5 wt % Pd/Al<sub>2</sub>O<sub>3</sub> catalysts.





**Figure S5.** TEM images of (A) 5 wt % Ir/r-GO, (B) 5 wt % Pt/r-GO, (C) 5 wt % Ru/r-GO, and (D) 5 wt % Rh/r-GO catalysts.



**Figure S6.** TEM images of PVP-stabilized 1 wt % Pd/r-GO catalyst.

**Table S1:** Catalytic transfer reduction of benzaldehyde with various catalysts.<sup>[a]</sup>

Entry	Catalyst	Metal loading [wt %]	D <sub>NP</sub> [nm]	Yield of benzyl alcohol [%] <sup>[b]</sup>
1	Au/CeO <sub>2</sub>	1	1.9	52
2	Au/TiO <sub>2</sub>	1	2.4	39
3	Au/ZrO <sub>2</sub>	0.8	1.8	48
4	Pd/C	5	2.6	61

[a] Reaction conditions: 1 mmol benzaldehyde, 5 mmol HCOOK, 15 mL water, 10 μmol Metal, 40 °C, 10 h. [b] Yield was determined by GC.

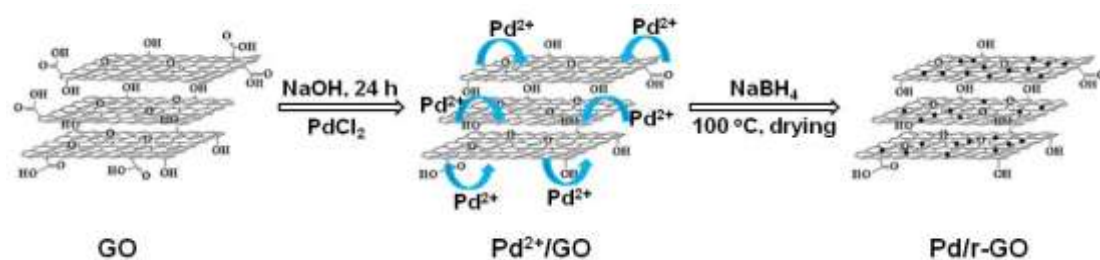
**Table S2:** Comparison of dehydrogenation of aqueous formate salts over various catalysts.

Entry	Catalyst	Salt/Conv. [M]	Temp. [°C]	TOF [h <sup>-1</sup> ]	Ref.
1	10Pd/C	HCOOK/4	70	449	[S6]
2	10Pd/C	HCOOK/4	70	339	[S7]
3	{RuCl <sub>2</sub> (benzene)} <sub>2</sub> + dppm + DMF	HCOONa/0.8	60	2592	[S8]
4	{RuCl <sub>2</sub> (mtppps)} <sub>2</sub>	HCOONa/0.24	80	120	[S9]

**Table S3:** Catalytic activity of various supported catalysts for dehydrogenation of aqueous HCOOK solution.<sup>[a]</sup>

Entry	Catalyst	Metal loading [wt %]	D <sub>NP</sub> [nm]	V <sub>H<sub>2</sub></sub> [mL] (20 min)	TOF [h <sup>-1</sup> ] (20 min)	V <sub>H<sub>2</sub></sub> [mL] (1 h)	TON (1 h)
1	Au/TiO <sub>2</sub>	1	2.4	inactive	–	–	–
2	Ir/CaCO <sub>3</sub>	5	3.2	inactive	–	–	–
3	Ir/C	1	2.5	inactive	–	–	–
4	Pt/C	5	2.3	inactive	–	–	–
5	Ru/C	5	2.1	inactive	–	–	–
6	Ru/Al <sub>2</sub> O <sub>3</sub>	5	2.8	inactive	–	–	–
7	Au/r-GO	5	3.5	inactive	–	–	–
8	Ir/r-GO	5	2.9	inactive	–	–	–
9	Pt/r-GO	5	2.7	inactive	–	–	–
10	Ru/r-GO	5	2.6	inactive	–	–	–
11	Rh/r-GO	5	2.8	inactive	–	–	–
12	PVP-stabilized Pd/r-GO	1	2.5	11	216	–	–
13 <sup>[b]</sup>	r-GO	–	–	inactive	–	–	–
14 <sup>[b]</sup>	GO	–	–	inactive	–	–	–

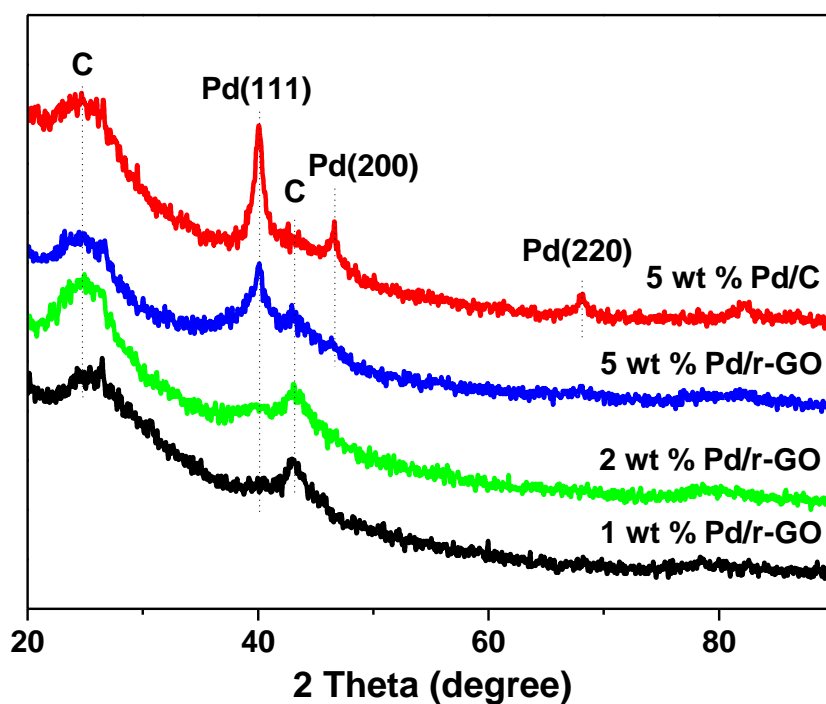
[a] Reaction conditions: 5 mL scale of 4.8 M aqueous HCOOK, 6.4 μmol Metal, 80 °C. [b] 100 mg material.



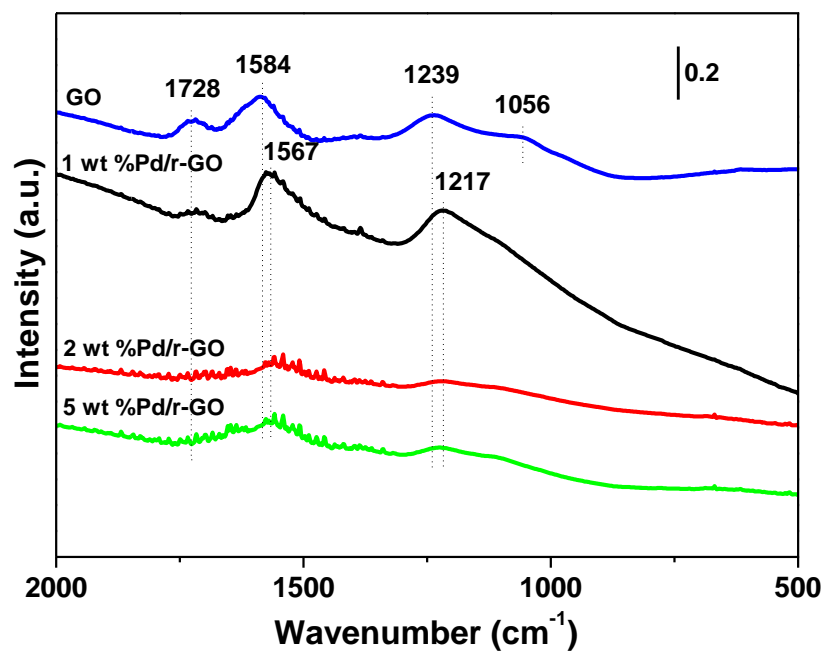
**Scheme S1.** Preparation of Pd/r-GO with uniform Pd nanoparticles using wet chemical reduction method.

**Table S4:** BET surface area of GO and Pd/r-GO samples.

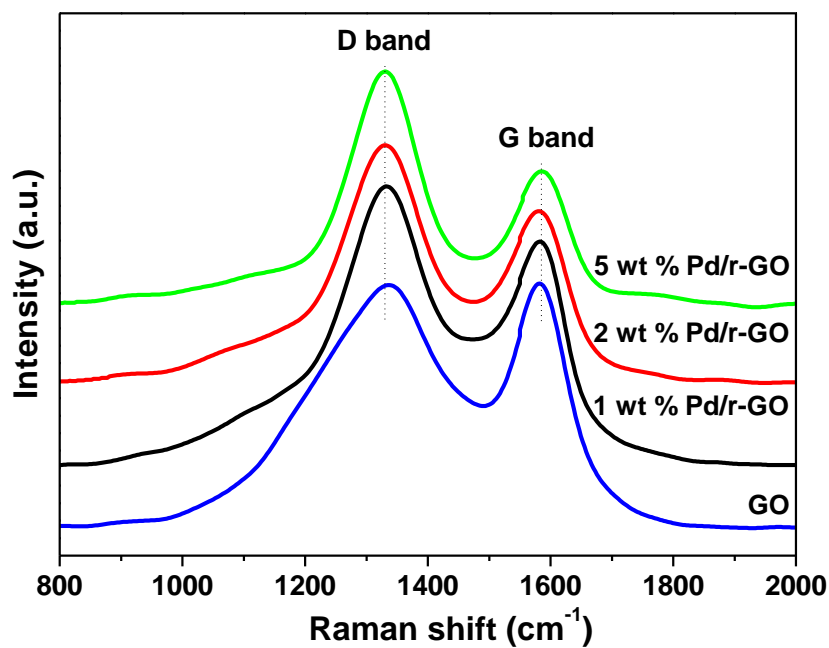
Sample	BET surface area [m <sup>2</sup> g <sup>-1</sup> ]
GO	128
1 wt % Pd/r-GO	116
2 wt % Pd/r-GO	111
5 wt % Pd/r-GO	109



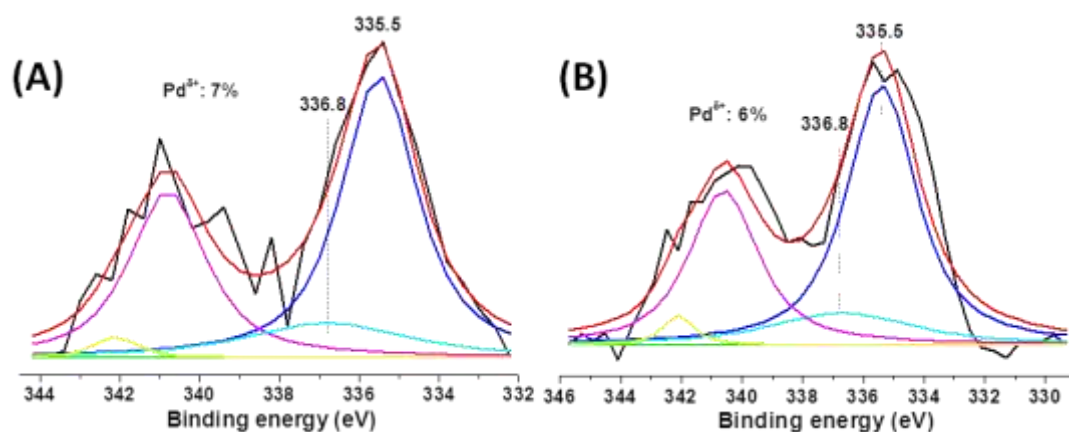
**Figure S7.** XRD patterns of Pd-based catalysts. Note that the diffraction data of Pd(111) plane for 1 wt % Pd/r-GO and 2 wt % Pd/r-GO catalysts cannot be obtained by conventional XRD due to the low metal loading and highly dispersed Pd NPs.



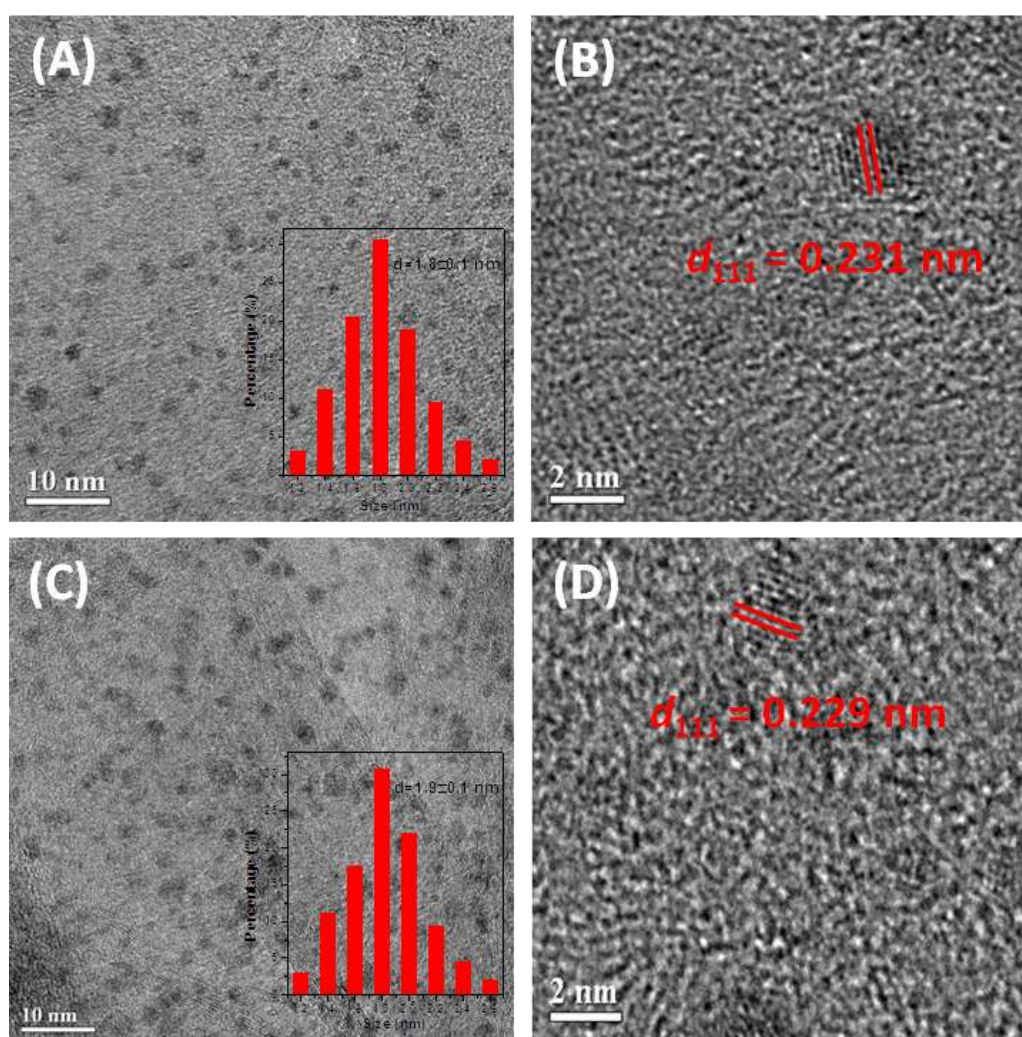
**Figure S8.** IR spectra of GO and Pd/r-GO catalysts.



**Figure S9.** Raman spectra of GO and Pd/r-GO catalysts. Noted that the D band arises from structural defects in the graphitic plane, whereas the G band is related to the  $E_{2g}$  vibrational mode of the  $sp^2$ -bonded graphitic carbons.



**Figure S10.** XPS data of (A) 1 wt % Pd/r-GO and (B) 2 wt % Pd/r-GO catalysts.



**Figure S11.** HRTEM images of (A, B) 1 wt % Pd/r-GO and (C, D) 2 wt % Pd/r-GO catalysts with the insets of the particle size distribution.

In light of a smaller particle size of Pd identified for 1 wt % Pd/r-GO material (Figure S11), one could argue that the enhanced activity of the low loaded Pd/r-GO samples may result from the decreased size

of the anchored Pd NPs. This argument could temper the conclusion that the increases in activity are related to lattice strain as opposed to size-dependent effects. We thus recall that a reference sample comprising 2.5 nm PVP-stabilized Pd NPs immobilized on r-GO (Figure S6) is a poor catalyst (Table S3); that is, identical Pd NPs without strong lattice distortion are inferior to the Pd/r-GO sample prepared via one-step co-reducing method. This points to the lattice strain effect as the primary source of enhanced activity.

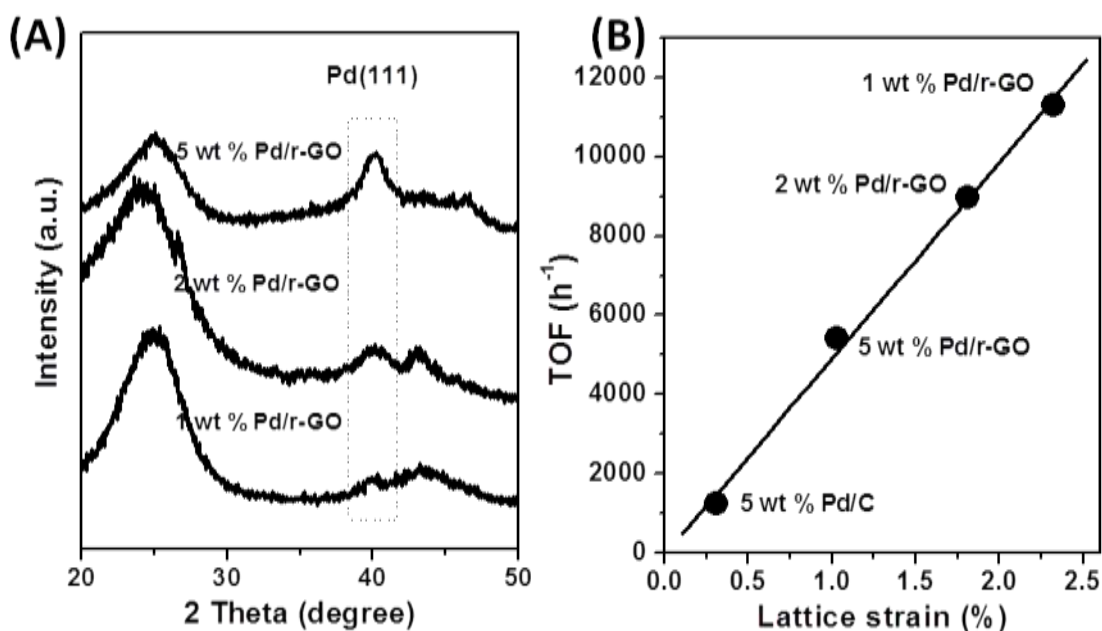
**Table S5:** Lattice strain data of Pd-based catalysts calculated according to Eq. S2.<sup>[a]</sup>

Catalyst	$B$	$d$ [nm] <sup>[b]</sup>	Strain $\varepsilon$ [%]
5 wt % Pd/C	0.0206	6.7344	0.31
5 wt % Pd/r-GO	0.0287	4.8399	1.03
2 wt % Pd/r-GO	0.0353	3.9388	1.81
1 wt % Pd/r-GO	0.0373	3.7301	2.32

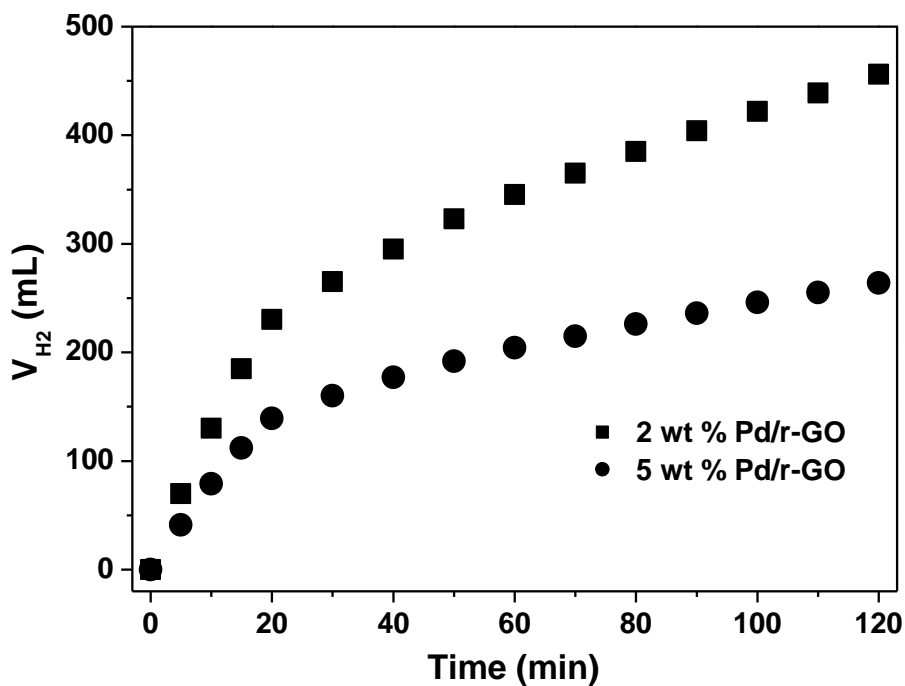
[a] Where  $\theta = 0.35$  ( $2\theta = 40.1^\circ$ ) for Pd(111) plane and  $\lambda = 0.154$  nm in Eq. S2. [b] Crystallite average size.

**Table S6:** Evaluated data of Pd-based catalysts according to lattice expansion of Pd(111).

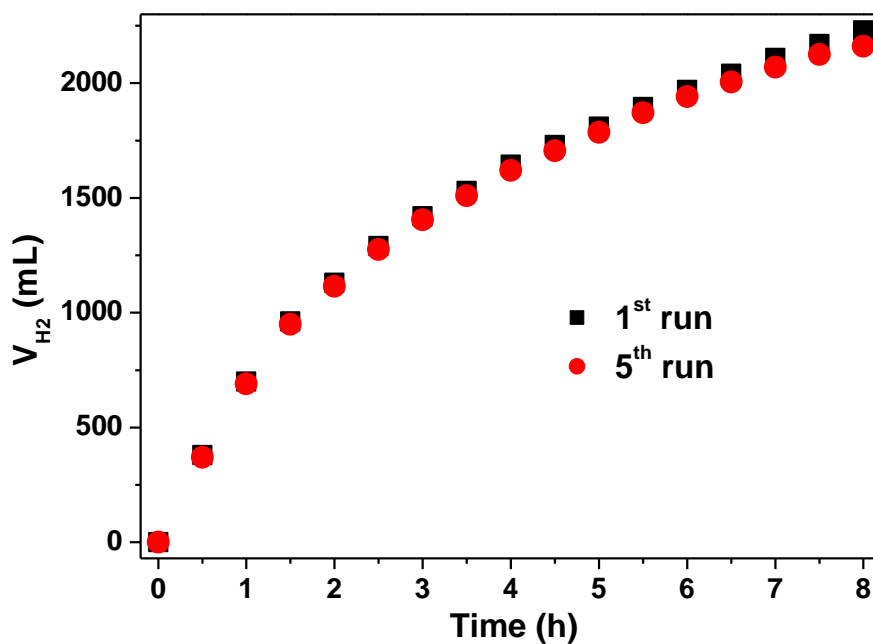
Catalyst	Lattice parameter [nm]	Strain $\varepsilon$ [%]
bulk Pd	0.225	–
5 wt % Pd/C	0.2255	0.22
5 wt % Pd/r-GO	0.227	0.89
2 wt % Pd/r-GO	0.229	1.78
1 wt % Pd/r-GO	0.231	2.67



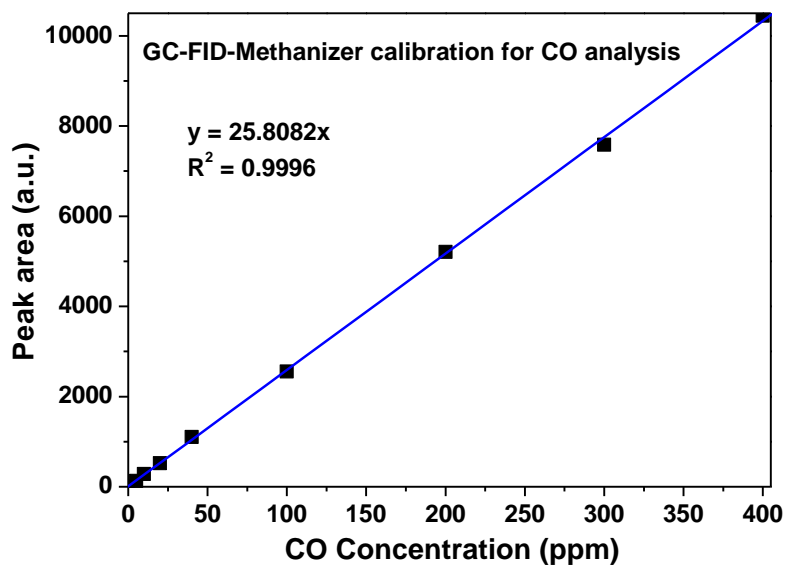
**Figure S12.** (A) Synchrotron radiation XRD patterns of the Pd/r-GO catalysts and (B) Correlation between the lattice strain and the initial TOF value using the Pd-based catalysts.



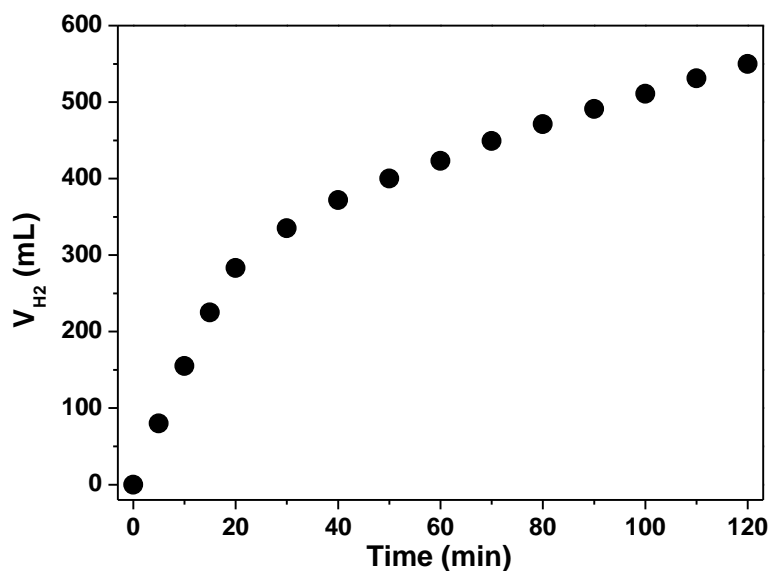
**Figure S13.** Kinetic traces for H<sub>2</sub> evolution via dehydrogenation of aqueous HCOOK catalyzed by 2 wt % Pd/r-GO and 5 wt % Pd/r-GO catalysts. Reaction conditions: 5 mL scale of 4.8 M aqueous HCOOK, 3.2 μmol Pd, 80 °C.



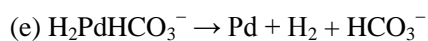
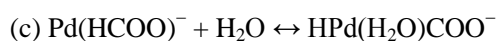
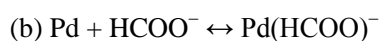
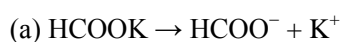
**Figure S14.** Large-scale durability of 1 wt % Pd/r-GO catalyst for H<sub>2</sub> generation. Reaction conditions: 20 mL scale of 4.8 M aqueous HCOOK, 3.2 μmol Pd, reaction time of 8 h in each experiment, 80 °C.



**Figure S15.** Calibration curve for CO quantitative analysis using the GC-FID-Methanizer.



**Figure S16.** Kinetic traces for H<sub>2</sub> evolution via dehydrogenation of aqueous HCOOK catalyzed by 1 wt % Pd/r-GO catalyst under oxygen atmosphere. Reaction conditions: 5 mL scale of 4.8 M aqueous HCOOK, 3.2 μmol Pd, 80 °C.



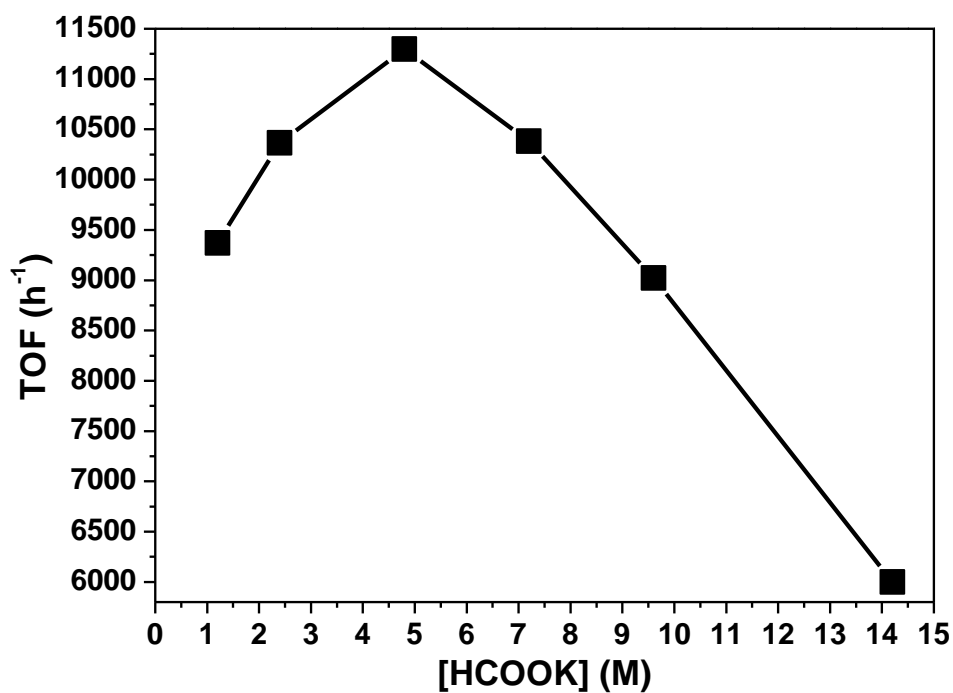
**Scheme S2.** Mechanism of dehydrogenation of aqueous HCOOK over Pd catalyst.



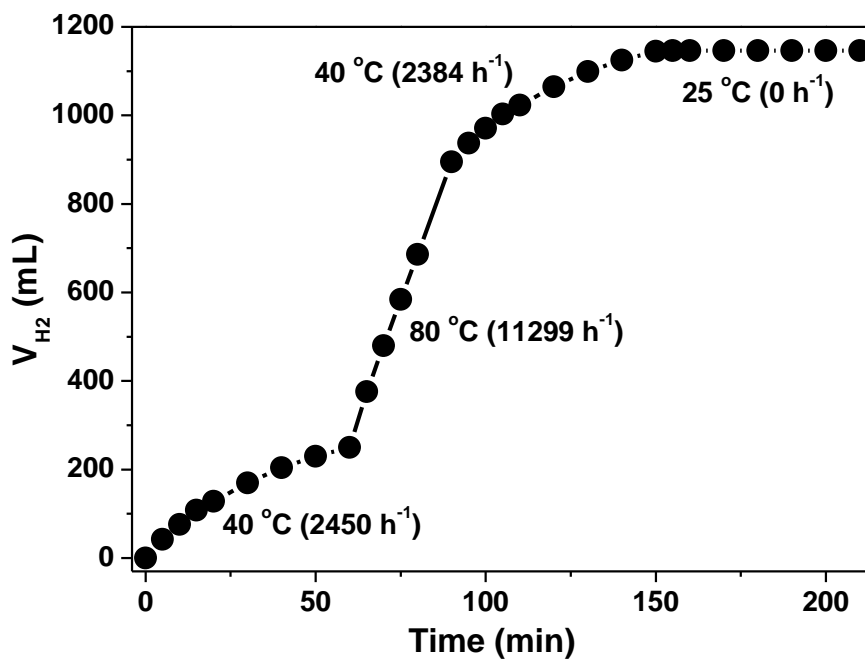
**Table S7:** Comparison of dehydrogenation of aqueous HCOOK catalyzed by 1 wt % Pd/r-GO.<sup>[a]</sup>

Entry	Water	Rate [mmol min <sup>-1</sup> g <sub>Pd</sub> <sup>-1</sup> ]	Fraction [mol %]		
			H <sub>2</sub>	D <sub>2</sub>	HD
1	H <sub>2</sub> O	854.6	100	0	0
2	D <sub>2</sub> O	371.5	11	24	65

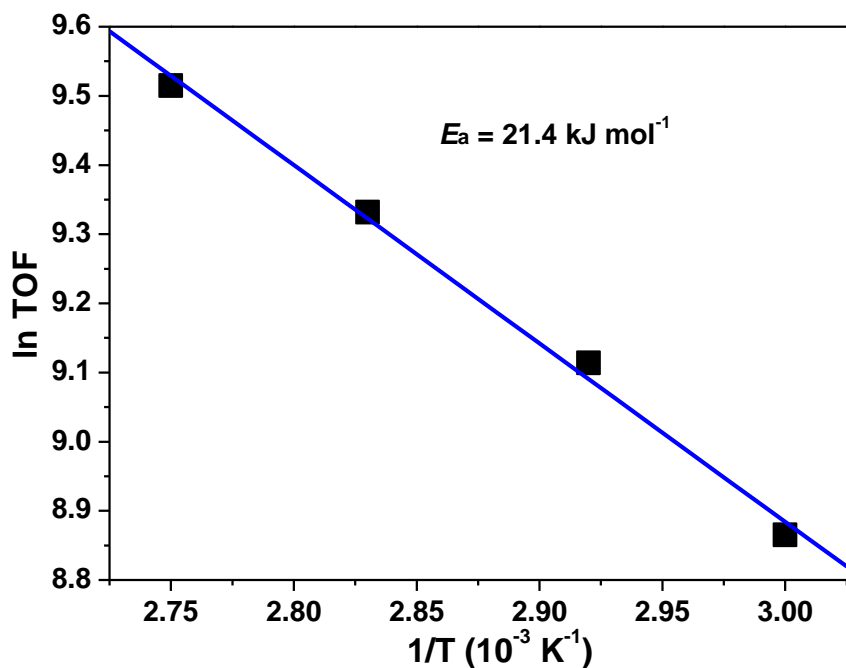
[a] Reaction conditions: 5 mL scale of 4.8 M aqueous HCOOK, 3.2 μmol Pd, 80 °C, 1 h.



**Figure S17.** TOF as a function of the initial concentration of aqueous HCOOK using 1 wt % Pd/r-GO catalyst. Reaction conditions: 5.0 mL scale of aqueous HCOOK,  $n(\text{HCOOK})/n(\text{Pd}) = 7500$ , 80 °C, 1 h.



**Figure S18.** Kinetic traces for H<sub>2</sub> evolution via dehydrogenation of aqueous HCOOK catalyzed by 1 wt % Pd/r-GO catalyst at the indicated temperatures (25–80 °C). Reaction conditions: 10 mL scale of 4.8 M aqueous HCOOK, 6.4 μmol Pd. The values in parenthesis are the initial TOFs.

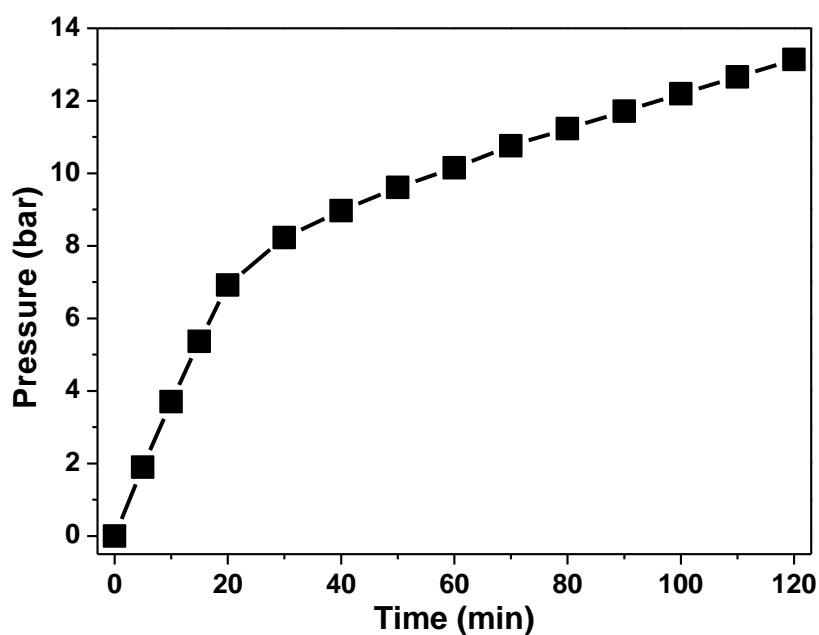


**Figure S19.** Arrhenius plot for 1 wt % Pd/r-GO catalyzed dehydrogenation of aqueous HCOOK. Reaction conditions: 5.0 mL scale of 4.8 M aqueous HCOOK, 3.2 μmol Pd.

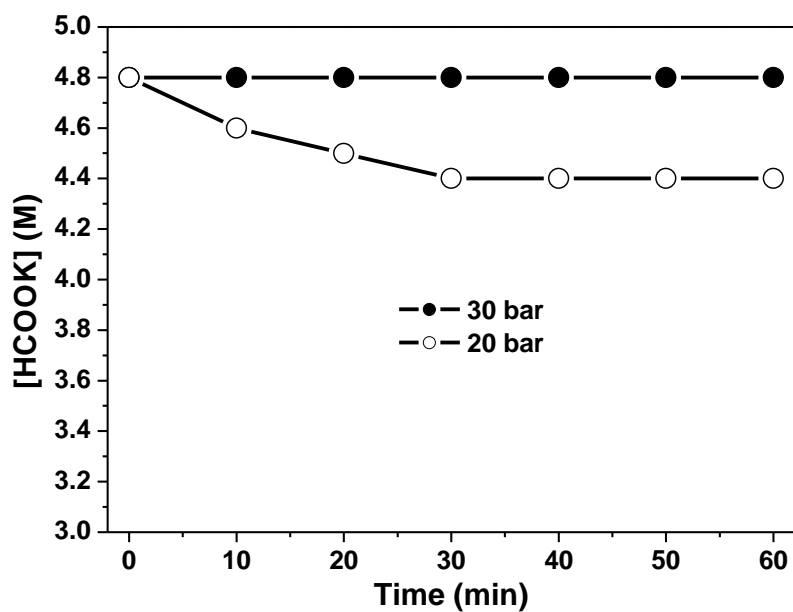
**Table S8:** Comparison of dehydrogenation of aqueous formates using 1 wt % Pd/r-GO catalyst.<sup>[a]</sup>

Entry	Formate	V <sub>H2</sub> [mL] (20 min)	TOF [h <sup>-1</sup> ] (20 min)	V <sub>H2</sub> [mL] (1 h)	TON (1 h)
1	HCOOLi	37.1	1446	53.8	699
2	HCOONa	205.4	8006	286.2	3718
3	HCOOK	289.9	11299	425.5	5527
4	HCOONH <sub>4</sub>	189.2	7374	–	–
5	Ca(HCOO) <sub>2</sub>	72.9	2841	128.3	1667

[a] Reaction conditions: 5 mL scale of 4.8 M aqueous formate, 3.2 μmol Pd, 80 °C.



**Figure S20.** Pressure-time profile for aqueous HCOOK dehydrogenation using 1 wt % Pd/r-GO catalyst in a closed system. Reaction conditions: 5.0 mL scale of 4.8 M aqueous HCOOK and 3.2 μmol Pd in 50 mL Parr autoclave, 80 °C.

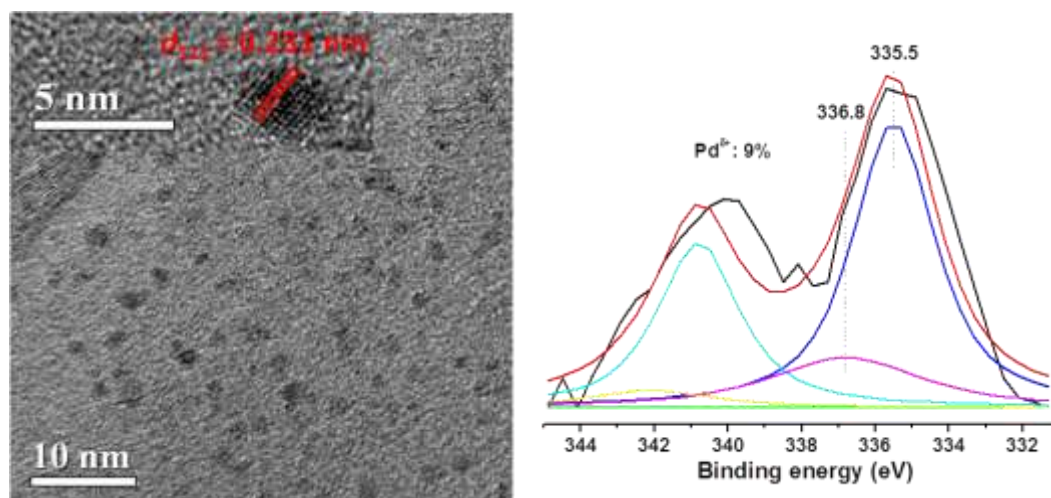


**Figure S21.** Effect of H<sub>2</sub> pressure on dehydrogenation process over 1 wt % Pd/r-GO catalyst in closed system. Reaction conditions: 5.0 mL scale of 4.8 M aqueous HCOOK, 3.2 μmol Pd in 50 mL Parr autoclave, H<sub>2</sub> gas was pre-charged at room temperature, 80 °C.

**Table S9:** Comparison of hydrogenation of aqueous bicarbonates using 1 wt % Pd/r-GO catalyst.<sup>[a]</sup>

Entry	Bicarbonate	Formate yield [%]
1	LiHCO <sub>3</sub>	56.6
2	NaHCO <sub>3</sub>	85.3
3	KHCO <sub>3</sub>	96.8
4	NH <sub>4</sub> HCO <sub>3</sub>	47.5

[a] Reaction conditions: 5 mL scale of 4.8 M aqueous bicarbonate, 40 bar H<sub>2</sub> at room temperature in 100 mL parr autoclave, 9.6 μmol Pd, 100 °C, 10 h.



**Figure S22.** HRTEM images and XPS data of the reused 1 wt % Pd/r-GO after 6 cycles.

TEM and XPS measurements revealed no appreciable changes in the dispersion of the palladium or metallic state of palladium before and after reuse for 1 wt % Pd/r-GO catalyst (see Figures S10, S11 and S22). Moreover, it was confirmed by ICP that there was no leaching of palladium during the reaction (limit of detection: < 7 ppb), verifying the inherent stability of the 1 wt % Pd/r-GO catalyst.

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