Supporting Information for

Highly active and durable hydrogen production by room-temperature formaldehyde oxidation on Fe_2O_3/Pd

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Synthesis of α-Fe_2O_3 hexagonal nanoplates

The α-Fe_2O_3 hexagonal nanosheets are prepared based on previous reports. Under vigorous magnetic stirring, 0.5406 g of $FeCl_3 \cdot 6H_2O$ was dissolved into a mixture solvent containing 20 mL of ethanol and 1.4 mL of deionized water. After complete dissolution of the $FeCl_3 \cdot 6H_2O$, 1.6 g of sodium acetate was added under continuous stirring. Thereafter, the mixed solution was transferred into a Teflon autoclave with a capacity of 50 mL, and then the mixture was subjected to a hydrothermal treatment at 180 °C for 12 h. The prepared sample was named α-Fe_2O_3.

Synthesis of α-Fe_2O_3/Pd catalysts

The α-Fe_2O_3/Pd catalysts were prepared by impregnation reduction of the above-prepared α-Fe_2O_3 powders (0.1 g) into a clean beaker, which contained 40 mL of deionized water and 10 mL of ethanol were mixed with 0.5, 1, 3 and 5 wt % of H_2PdCl_4 solution. Then 10 mL of 0.5 M $NaBH_4$ (freshly prepared) were added drop-wise into the solution with continuous magnetics stirring, the color of the solutions has changed from brick red to gray black at last, the reaction solution kept on stirring for 24 h to complete the reduction reaction. The black granules washed with ethanol and deionized water for four times, and then dried in an oven at 60 °C for 8 h. The prepared samples were denoted as α-Fe_2O_3/Pd-0.5%, α-Fe_2O_3/Pd-1%, α-Fe_2O_3/Pd-3% and α-Fe_2O_3/Pd-5%, corresponding to the mass fraction of H_2PdCl_4 solution added.

Material characterizations

Scanning electron microscope (SEM) images were taken using a field-emission scanning electron microscope (Hitachi, S 4800) operated at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) images were obtained on a transmission electron microscope (FEI, Tecnai G2 F 20) at an acceleration voltage of 200 kV. The Benchtop X-ray diffractometer (Rigaku Mini Flex 600), operating at 40 kV and 15 mA with Cu Kα radiation, was used to collect the X-ray powder diffraction (XRD) patterns. X-ray photoelectron spectrometry (XPS) was carried out on the K-ALPHA 0.5EV X-ray photoelectron spectrometer using an Al Kα source.

Activity tests

In the catalytic activity of experiments, amount of catalysts (15 mg) was added into the sealed flask containing HCHO and NaOH solution. Then, the hydrogen production reaction started while the solution was stirred vigorously. The amounts of hydrogen produced were measured by a GC (gas chromatograph) equipped with a TCD detector and argon as carrier gas. The amounts of the hydrogen produced were measured every five minutes, each experiment was measured at least 3 times to make sure accuracy. Due to the deficiencies and limitations of our current detection method, no carbon monoxide or other gaseous have been detected in all these catalytic processes

To be more specific, the amounts of the hydrogen produced were measured every 5 minutes by manually extracting 150 μL of produced gas form the upper part of the flask (the remained volume was 500 ml) using a gas injector and injected into the chromatogram injector to analyze the evolved gases. Moreover, the chromatogram was calibrated with pure hydrogen (99.999%) by external standard method, the standard curves of hydrogen production (V, mL) versus chromatographic peak area (S) is as following:

$$V\ (mL) = 3.6021\times10^{-5}S+12.51 \qquad (1)$$

Thus, once the value of S is obtained, the produced volume of hydrogen can be calculated accordingly.

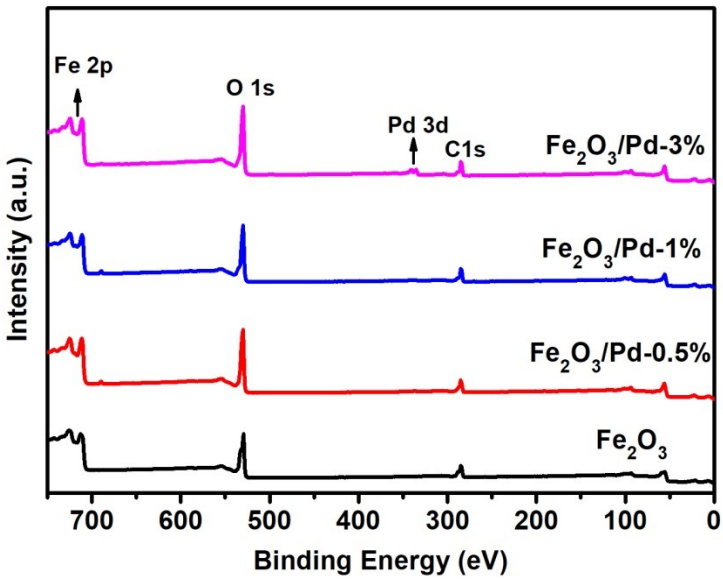

Figure S1. Survey XPS of Fe_2O_3 and Fe_2O_3/Pd-0.5%, Fe_2O_3/Pd-1%1% and Fe_2O_3/Pd-3%.

Table S1. The overview of Fe 2p and Pd 3d over pure Fe_2O_3, Fe_2O_3/Pd-0.5%, Fe_2O_3/Pd-1% and Fe_2O_3/Pd-3%.

Samples	BE (eV) of Fe 2p				BE (eV) of Pd 3d			
	Fe^{2+}, 3/2	Fe^{3+}, 3/2	Fe^{2+}, 1/2	Fe^{3+}, 1/2	Pd^0, 5/2	Pd^{3+}, 5/2	Pd^0, 3/2	Pd^{3+}, 3/2
Fe_2O_3	710.62	713.21	724.54	727.71	-	-	-	-
Fe_2O_3/Pd-0.5%	710.82	713.21	724.56	727.47	335.67	337.49	340.84	343.33
Fe_2O_3/Pd-1%	710.82	713.52	724.54	727.61	335.73	337.70	340.67	342.84
Fe_2O_3/Pd-3%	710.77	713.47	724.48	727.51	335.15	337.51	340.46	342.86

Table S2. ICP-AES results of HPC-Pd catalysts.

Sample	Fe content (wt.%)	Pd content (wt.%)
Fe_2O_3/Pd-0.5%	68.5925	0.4157
Fe_2O_3/Pd-1%	68.2433	0.7635
Fe_2O_3/Pd-3%	66.3549	2.8512

Table S3. Structural characteristics of Fe_2O_3, Fe_2O_3/Pd-0.5%, Fe_2O_3/Pd-1%1% and Fe_2O_3/Pd-3%.

Samples	S_{BET} /($m^2 \cdot g^{-1}$)	Pore diameter /nm	Pore volume V /($cm^3 \cdot g^{-1}$)
Fe_2O_3	21.4003	9.0926	0.1708
Fe_2O_3/Pd-0.5%	63.5684	8.1260	0.2753
Fe_2O_3/Pd-1%	75.4554	7.6484	0.2769
Fe_2O_3/Pd-3%	86.0204	7.0918	0.2851

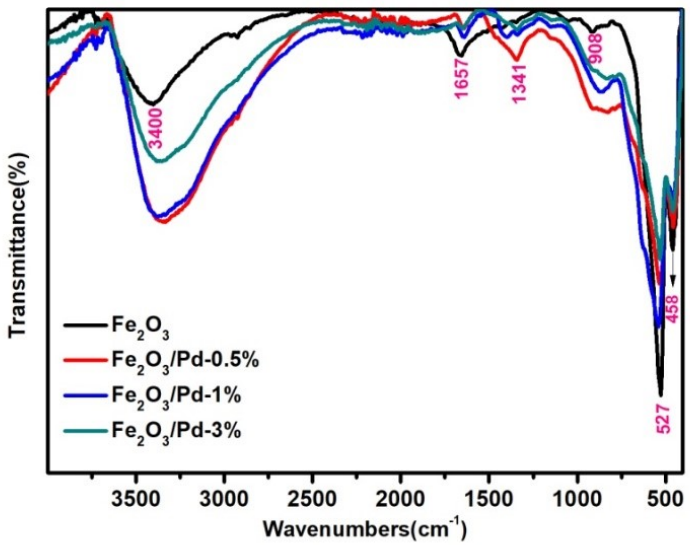

Figure S2. FTIR spectra of Fe_2O_3 and Fe_2O_3/Pd-0.5%, Fe_2O_3/Pd-1%1% and Fe_2O_3/Pd-3%.

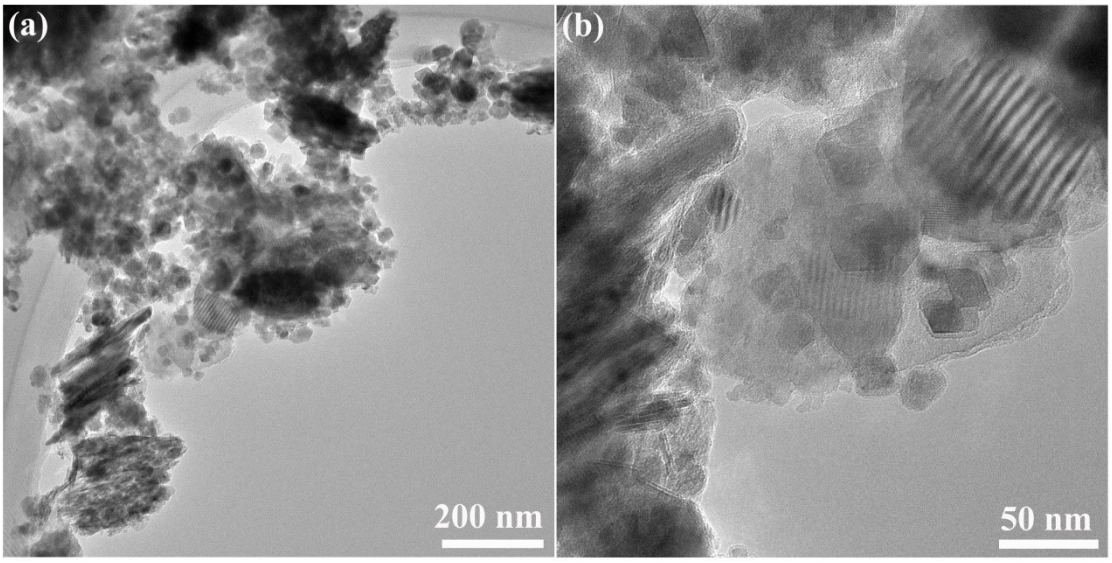

Figure S3. TEM (a) and HRTEM (b) imges of Fe_2O_3/Pd-1%.

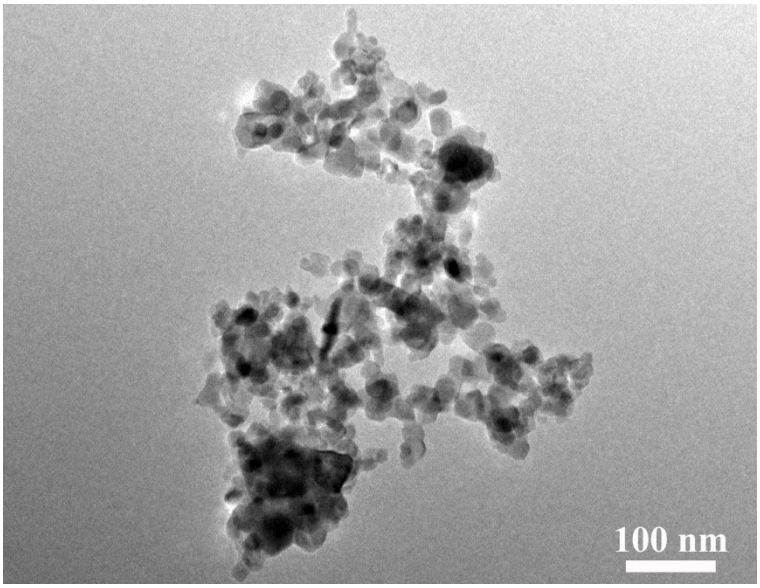

Figure S4. TEM images of as-prepared Pd nanoparticles.

Table S4. Comparison of hydrogen generation rates of the present Fe_2O_3/Pd-1% with the reported Pd based catalysts in the literatures.

Catalysts	Reagents	hydrogen generation rates ($ml \cdot min^{-1}g^{-1}$)	Reaction conditions	Reference
Fe_2O_3/Pd-1%	HCHO	293.98	Fe_2O_3/Pd-1% catalyst：15 mg, NaOH:1 mol/L, HCHO: 0.6 mol/L, reaction temperature: 25°C	This work
Pd/TiO_2	HCHO	250	Pd/TiO_2 catalyst：15 mg, NaOH:1 mol/L, HCHO: 0.6 mol/L, reaction temperature: 25 °C	Journal of Materials Chemistry A, 2016, 4, 796-800.
Pd/BiOCl	HCHO	205	Pd/BiOCl catalyst：15 mg, NaOH: 1 mol/L, HCHO: 0.6 mol/L, reaction temperature: 25 °C	Journal of molecular catalysis, 2015, 5, 441-447.
Pd nanotubes	HCHO	167.6	Pd catalyst：8 mg, NaOH:1 mol/L, reaction temperature: 25°C	Nano Energy, 2014, 8, 103-109.

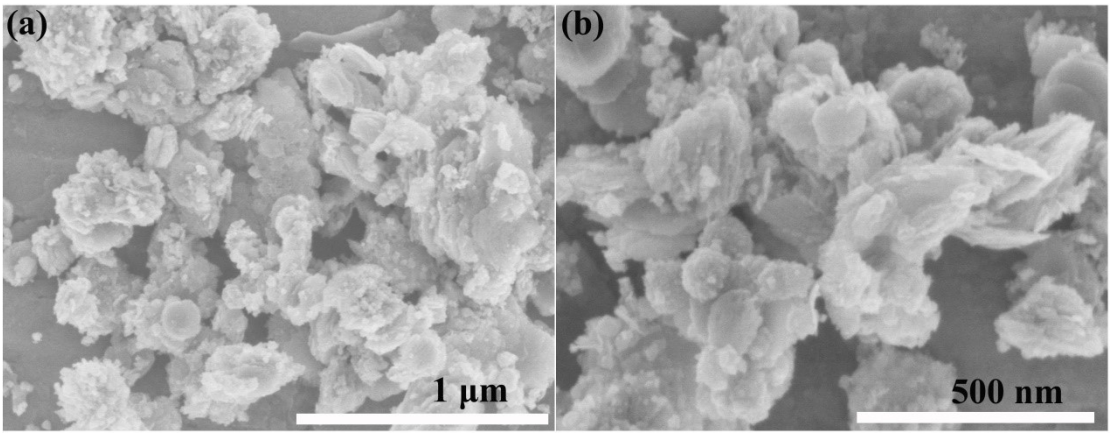

Figure S5. SEM images of Fe_2O_3/Pd-1% after the H_2 production reaction.

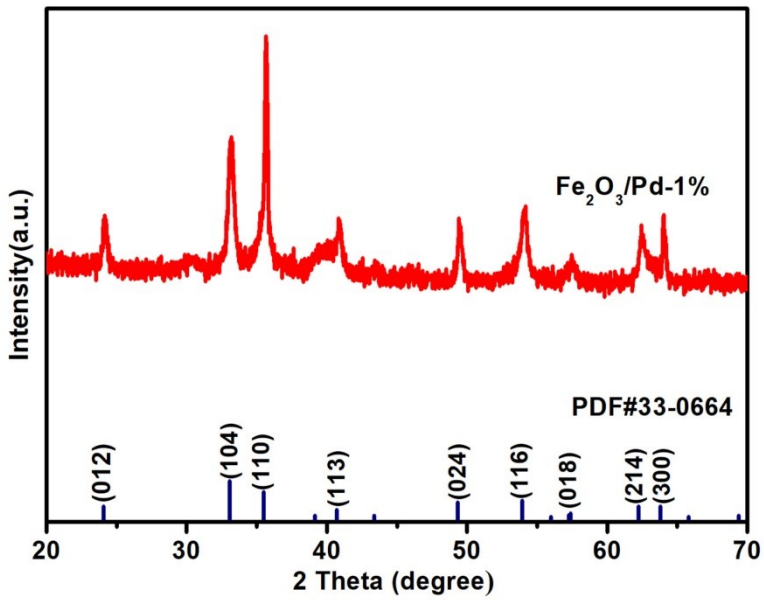

Figure S6. XRD patterns of Fe_2O_3/Pd-1% after the H_2 production reaction.

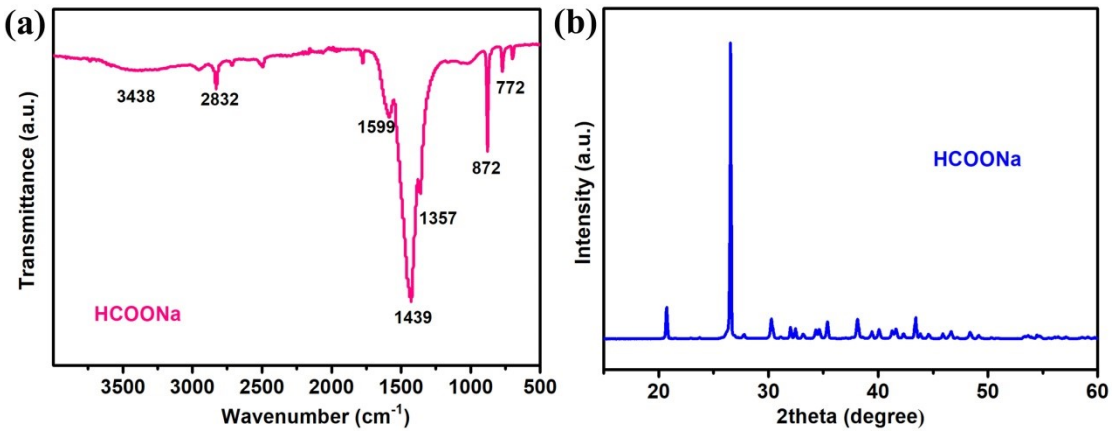

Figure S7. FTIR (a) and XRD pattern of the reation products of formaldehyde over Fe_2O_3/Pd-1% catalyst at 25 °C for 5h, HCHO: 0.6M, NaOH: 1M.