Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information for

An Efficient Room Temperature Core-Shell AgPd@MOF Catalyst for Hydrogen Production from Formic Acid

Fei Ke,[a,b] Luhuan Wang[a] and Junfa Zhu*[a,b]

[a]*National Synchrotron Radiation Laboratory and Collaborative Innovation Center of Suzhou Nano Science and Technology, University of Science and Technology of China, Hefei 230029, P. R. China.*

E-mail: jfzhu@ustc.edu.cn

[b]*Department of Applied Chemistry, Anhui Agricultural University, Hefei 230036 (P.R. China).*

Materials and Characterization

Benzene-1,3,5-tricarboxylic acid (H_3BTC) was purchased from Sigma-Aldrich Co. LLC. Formic acid (HCOOH, FA), Palladium nitrate ($Pd(NO_3)_2$), Silver nitrate ($AgNO_3$), Ferric trichloride hexahydrate ($FeCl_3$ $6H_2O$), Poly-vinylpyrrolidone (PVP, M.W. 30000), N,N-dimethylformamide (DMF) and Ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All chemicals used in this work were purchased from commercial suppliers and used without further purification unless of otherwise noted.

The PXRD patterns of the samples were collected using an X-ray diffractometer with Cu target (36 kV, 25 mA) from 2 to 60°. SEM measurement was performed by a JSM-6700F field emission scanning electron microscope. TEM images, HAADF-STEM imaging and EDX elemental mapping were characterized by a JEM-2100F transmission electron microscope at 200 kV. The UV-vis absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Nitrogen sorption-desorption isotherms were obtained at 77 K on a Micromeritics Tristar II 3020 M analyzer. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurement was performed on an XSP Intrepid II spectrometer instrument.

Experimental Section

Synthesis of AgPd NPs:

1.46 g PVP was dissolved in 24 mL DMF-ethanol (v/v = 5:3) mixed solution. After dissolved thoroughly, 160 μL $Pd(NO_3)_2$ (0.141 M) and 153 μL $AgNO_3$ (0.147 M) were added while stirring. Then the mixture was transferred into a Teflon-lined stainless steel autoclave (50 mL) and heated at 140 ^{o}C for 12 h. After cooling, the obtained products were collected by centrifugation, washed with DMF and ethanol, and finally dried overnight at 120 ℃ under vacuum.

One-pot synthesis of core-shell AgPd@MIL-100(Fe)_A:

22.2 mg $FeCl_3$•$6H_2O$, 11.4 mg H_3BTC and 2.187 g PVP were dissolved in 24 mL DMF-ethanol (v/v = 5:3) mixed solution. After dissolved thoroughly, 460 μL $Pd(NO_3)_2$ (0.141 M) and 440 μL $AgNO_3$ (0.147 M) were added while stirring. Then the mixture was transferred into a Teflon-lined stainless steel autoclave (50 mL) and heated at 140 ^{o}C for 12 h. After cooling, the obtained products were collected by centrifugation, washed with DMF and ethanol, and finally dried overnight at 120 ℃ under vacuum.

One-pot synthesis of core-shell AgPd@MIL-100(Fe)_B:

22.2 mg $FeCl_3$•$6H_2O$, 11.4 mg H_3BTC and 1.46 g PVP were dissolved in 24 mL DMF-ethanol (v/v = 5:3) mixed solution. After dissolved thoroughly, 160 μL $Pd(NO_3)_2$ (0.141 M) and 153 μL $AgNO_3$ (0.147 M) were added while stirring. Then the mixture was transferred into a Teflon-lined stainless steel autoclave

(50 mL) and heated at 140 °C for 12 h. After cooling, the obtained products were collected by centrifugation, washed with DMF and ethanol, and finally dried overnight at 120 ℃ under vacuum.

One-pot synthesis of core-shell AgPd@MIL-100(Fe)_C:

22.2 mg $FeCl_3•6H_2O$, 11.4 mg H_3BTC and 0.367 g PVP were dissolved in 24 mL DMF-ethanol (v/v = 5:3) mixed solution. After dissolved thoroughly, 32 μL $Pd(NO_3)_2$ (0.141 M) and 30.6 μL $AgNO_3$ (0.147 M) were added while stirring. Then the mixture was transferred into a Teflon-lined stainless steel autoclave (50 mL) and heated at 140 °C for 12 h. After cooling, the obtained products were collected by centrifugation, washed with DMF and ethanol, and finally dried overnight at 120 ℃ under vacuum.

H_2 generation from FA aqueous solution:

Typically, the reactions were carried out in a closed circulation system consisting of a gas circulation pump, a pressure sensor, and gas sampling valves.[S1] The as-synthesized catalysts (20 mg) were dispersed with constant stirring in a quartz reaction cell filled with 9.6 mL distilled water. Then 0.4 mL of FA was injected into the catalyst solution at room temperature. The catalytic reaction was begun once the FA was added into the solution. Generated gases were analyzed through an on-line gas chromatograph with a TCD detector (GC-2014C, Shimadzu). The reaction system was stabilized at ambient temperature through cooling water.

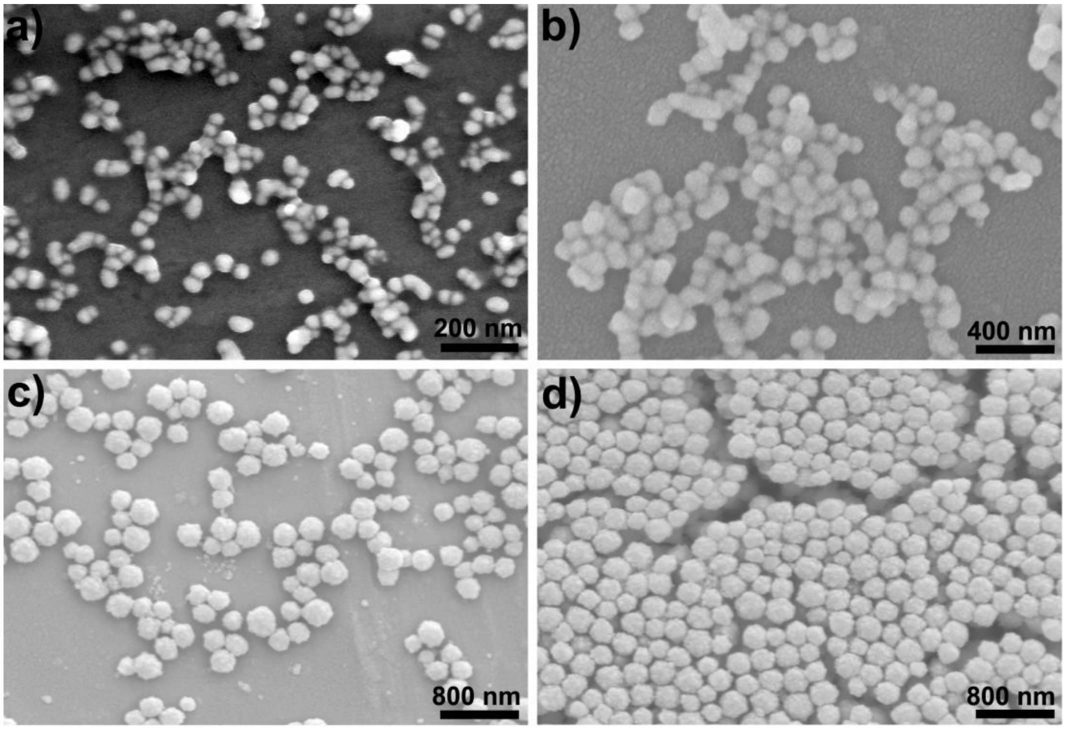


Fig. S1 SEM images of (a) AgPd NPs, (b) AgPd@MIL-100(Fe)_**A**, (c) AgPd@MIL-100(Fe)_**B**, and (d) AgPd@MIL-100(Fe)_**C**. The average diameters were (a) 40 nm for the AgPd NPs and (b) 100 nm, (c) 200 nm, and (d) 250 nm for AgPd@MIL-100(Fe) core-shell NPs (obtained from the SEM investigations by averaging over 100 NPs).

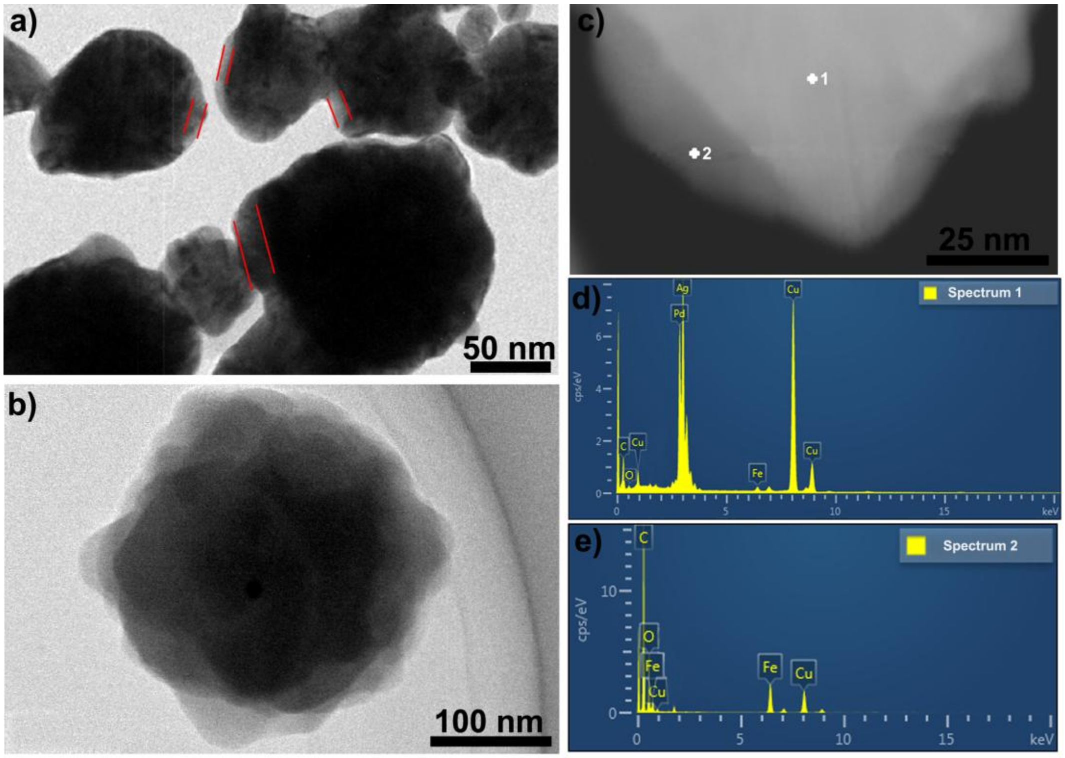


Fig. S2 Representative TEM images for (a) AgPd@MIL-100(Fe)**_A** and (b) AgPd@MIL-100(Fe)**_C.** HAADF-STEM image (c) and the corresponding EDX spectra (d,e) for AgPd@MIL-100(Fe)**_A** NPs (point 1: core; point 2: shell). The Cu signal originates from the Cu grid which was used to support the sample for the measurement.

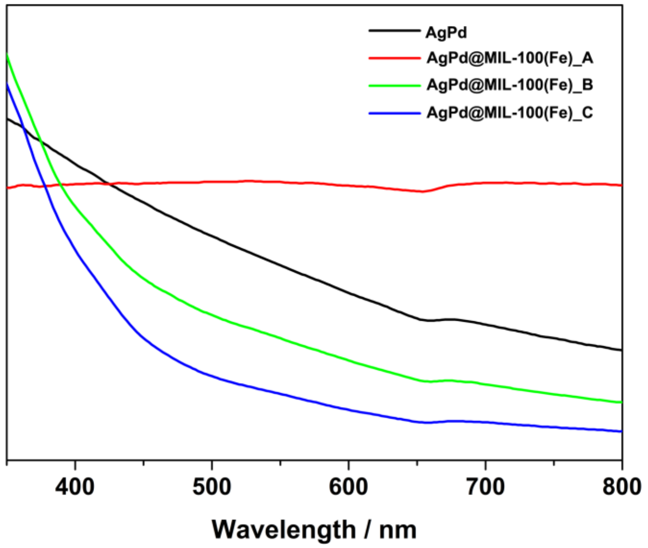


Fig. S3 UV-vis absorption spectra of AgPd NPs and core-shell AgPd@MIL-100(Fe) NPs.

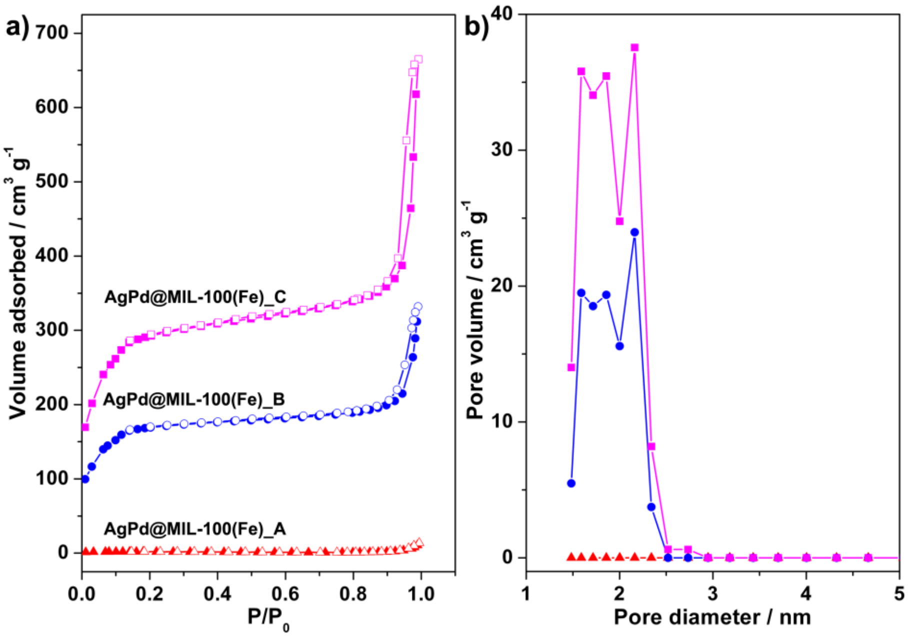
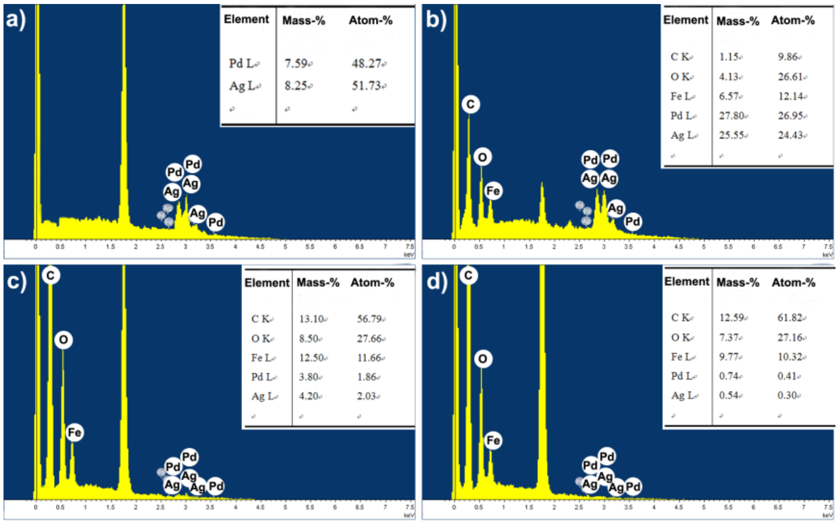


Fig. S4 (a) N_2 adsorption-desorption isotherms of the as-synthesized core-shell AgPd@MIL-100(Fe) NPs at 77 K. Filled and open symbols represent adsorption and desorption branches, respectively. (b) Distributions of pore size obtained using the DFT method.



a)

Element	Mass-%	Atom-%
Pd L	7.59	48.27
Ag L	8.25	51.73

b)

Element	Mass-%	Atom-%
C K	1.15	9.86
O K	4.13	26.61
Fe L	6.57	12.14
Pd L	27.80	26.95
Ag L	25.55	24.43

c)

Element	Mass-%	Atom-%
C K	13.10	56.79
O K	8.50	27.66
Fe L	12.50	11.66
Pd L	3.80	1.86
Ag L	4.20	2.03

d)

Element	Mass-%	Atom-%
C K	12.59	61.82
O K	7.37	27.16
Fe L	9.77	10.32
Pd L	0.74	0.41
Ag L	0.54	0.30

Fig. S5 EDX spectra of (a) AgPd, (b) AgPd@MIL-100(Fe)**_A**, (c) AgPd@MIL-100(Fe)**_B**, and (d) AgPd@MIL-100(Fe)**_C** NPs.

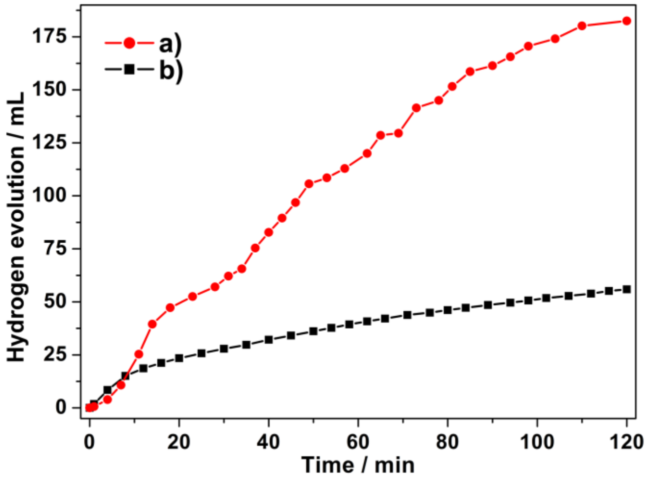


Fig. S6 Hydrogen generation by decomposition of FA (1 M, 10 mL) versus time over a) AgPd@MIL-100(Fe)_**A** and b) physical mixture of AgPd and MIL-100(Fe) (mass ratio of AgPd:MIL-100(Fe) is 75:25) at room temperature.

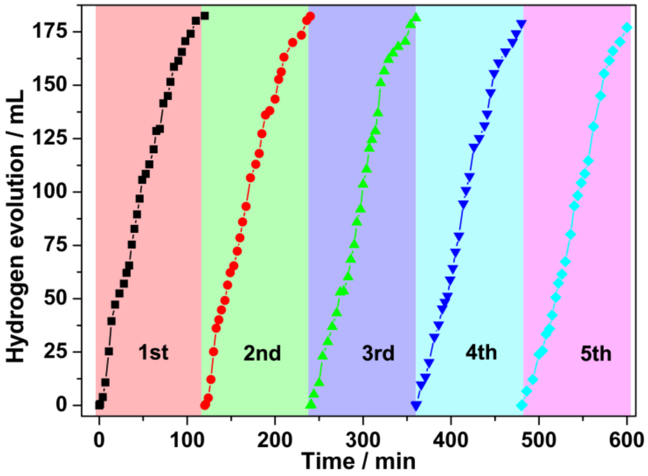


Fig. S7 Durability test for the hydrogen generation from FA catalyzed by core-shell AgPd@MIL-100(Fe)_**A** NPs at room temperature.

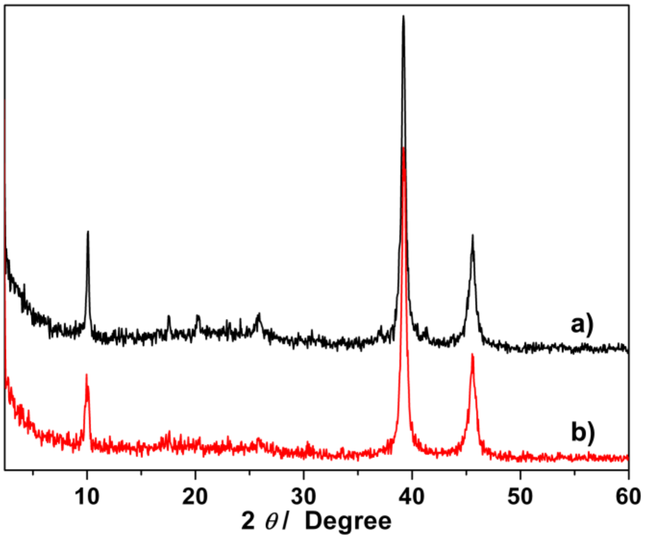


Fig. S8 PXRD patterns of core-shell AgPd@MIL-100(Fe)_**A** NPs before (a) and after (b) five times use, respectively.

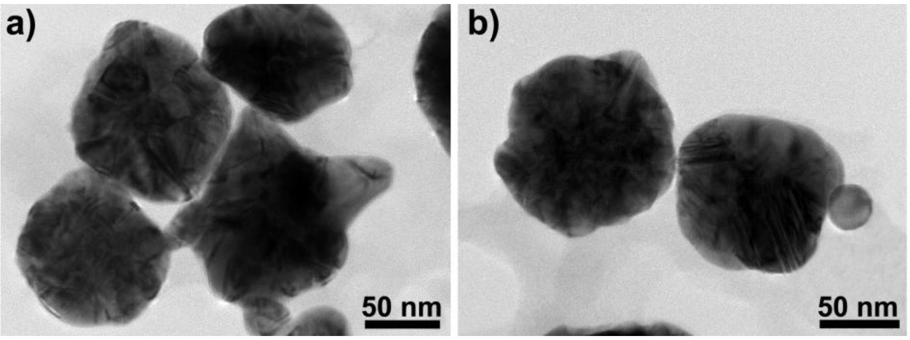


Fig. S9 TEM images of core-shell AgPd@MIL-100(Fe)_**A** NPs (a,b) after five times use.

Table S1 BET surface areas and ICP analyses of the core-shell AgPd@MIL-100(Fe) NPs with different shell thicknesses.

Sample	BET Surface Area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	TOF (h^{-1})	Metal content (%)
AgPd@MIL-100(Fe)_**A**	6.1	0.01	58	Ag, 36.25; Pd, 38.73
AgPd@MIL-100(Fe)_**B**	601.9	0.41	44	Ag, 6.09; Pd, 6.5
AgPd@MIL-100(Fe)_**C**	1036.9	0.72	-	Ag, 1.13; Pd, 1.21
AgPd	-	-	17	Ag, 48.35; Pd, 51.65

Table S2 Initial TOF values for the decomposition of FA over various heterogeneous catalysts.

Catalyst	Additive	Tem. / K	$TOF_{initial}$	Ref.
AgPd@MIL-00(Fe)_**A**	None	298	58	This work
CoAuPd/C	None	298	40	(3)
Ag@Pd	None	293	16	(7)
PtRuBiOx/C	None	353	24	(28b)
PdAg/C-CeO_2	HCOONa	365	44	(8)
PdAu/C-CeO_2	HCOONa	365	101	(8)
PdAu@Au/C	HCOONa	365	44	(28c)
Au@SiO_2_AP	HCOONa	363	59	(27)
Au/ZrO_2	NEt_3	298	252	(28a)
Pd-NH2-MIL-125	HCOONa	305	214	(28d)

Calculation methods:

$$x_a = \frac{P_{atm} V_{H_2} / RT}{n_{FA}} \qquad \text{(S1)}$$

Where x_a is conversion, P_{atm} is the atmospheric pressure, V_{H2} is the generated volume of H_2, R is the universal gas constant, T is room temperature (298 K), and n_{FA} is the mole number of FA.

$$TOF_{initial} = \frac{P_{atm} V_{H_2} / RT}{n_{Ag+Pd} t} \qquad \text{(S2)}$$

Where $TOF_{initial}$ is initial turnover frequency when x_a reaches 20%, n_{Ag+Pd} is the mole number of the Ag and Pd, and t is the reaction time when x_a reaches 20%.

$$R_{initial} = \frac{V_{H_2}}{m_{Ag+Pd} t} \qquad \text{(S3)}$$

Where $R_{initial}$ is the initial rate of H_2 generation when x_a reaches 20%, m_{Ag+Pd} is the weight of the Ag and Pd, and t is the reaction time when xa reaches 20%.

(S1) Y. Yuan, Z. Zhao, J. Zheng, M. Yang, L. Qiu, Z. Li and Z. Zou, *J. Mater. Chem.*, 2010, **20**, 6772.