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Electronic Supporting Information

DNA-Directed Growth of Ultrafine CoAuPd Nanoparticles on Graphene as Efficient Catalysts for Formic Acid Dehydrogenation

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Chemicals

Formic acid (HCOOH, FA, Sigma-Aldrich, 96%), graphite flake (C, Alfa Aesar, 325 mesh, 99.8%), deoxyribonucleic acid (DNA, Sinopharm Chemical Reagent Co., Ltd, >85%), sodium tetrachloropalladate (II) (Na_2PdCl_4, Sinopharm Chemical Reagent Co., Ltd, Pd >36.4%), tetrachloroauric (III) acid ($HAuCl_4 \cdot 4H_2O$, Sinopharm Chemical Reagent Co. Ltd, Au >47.8%), cobalt (II) chloride hexahydrate ($CoCl_26 \cdot H_2O$, Sinopharm Chemical Reagent Co., Ltd, >99%), sulfuric acid (H_2SO_4, Beijing Chemical Works, 98%), potassium permanganate ($KMnO_4$, Sinopharm Chemical Reagent Co. Ltd, >99%), hydrogenperoxide (H_2O_2, Beijing Chemical Works, 30%), hydrochloric acid (HCl, Beijing Chemical Works, 36%~37%), phosphoric acid (H_3PO_4, Sinopharm Chemical Reagent Co. Ltd, >85%), polyvinylpyrrolidone K30 (PVP, $(C_6H_9NO)_n$, Mw: av. 58000 g/mol, Beijing Chemical Works), and hexadecyltrimethyl ammonium bromide (CTAB, Aladdin Chemistry Co., Ltd, >99%) were used without further purification. De-ionized water with the specific resistance of 18.2 MΩ·cm was obtained by reversed osmosis followed by ion-exchange and filtration.

Synthesis of graphene oxide (GO)

GO was synthesized from graphite by a modified Hunmers' method.[S1] Briefly, a mixture of graphite powder (3.0 g) and $KMnO_4$ (18.0 g) was put into the H_2SO_4/H_3PO_4 (360/40 mL) solution. Then, the above graphite suspension was stirred and heated to 323 K for 12 h. After the graphite suspension was cooled to room temperature, it was poured onto ice (600 mL) and followed by addition of H_2O_2 (4.0

mL). The suspension was then filtered by using a 0.2 micron Nylon Millipore filter, and washed with 5% HCl solution and water. Finally, GO (0.2 wt%) was achieved by ultrasonication of the washed suspension for 40 min.

Synthesis of CoAuPd/DNA-rGO composite

A facile two-step method is employed for preparing CoAuPd/DNA-rGO composite. In the first step, 10.0 mg of DNA is added into 30.0 mL of homogeneous GO aqueous dispersion (1.5 mg mL^{-1}) and sonicated for 2 h, followed by heating at 368 K for 10 min. In the second step, 5.0 mL of aqueous solution containing $CoCl_2$ (5.0 mM), $HAuCl_4$ (5.0 mM), and Na_2PdCl_4 (5.0 mM) is mixed with the above DNA-GO suspension, and then an aqueous $NaBH_4$ solution (5.0 mL, 300.0 mM) is added into the above mixture under magnetic stirring for 90 min. The product was separated by centrifugation, washed with water for several times, and re-dispersed into 5.0 mL of water for the following catalytic reaction.

For comparison, CoAuPd/rGO composite, CoAuPd NPs, CoAuPd/C, CoAuPd/PVP-rGO (PVP: 10.0 mg), and CoAuPd/CTAB-rGO (CTAB: 10.0 mg) catalyst are also prepared as the same method mentioned above. All catalysts are prepared under same experimental conditions, including the amount of GO, metal precursors, the reaction temperature, reaction time, and stirring speed.

Characterizations

Powder X-ray diffraction (XRD) was performed on a Rigaku RINT-2000 X-ray diffractometer with Cu Kα. Transmission electron microscope (TEM, Tecnai F20,

Philips) and corresponding energy-dispersive X-ray (EDX) spectrometry were applied for the detailed microstructure and composition analyses, and the amorphous carbon coated copper grids were used as the sample supporter. X-ray photoelectron spectrometry (XPS) was carried out on an ESCALABMKLL X-ray photoelectron spectrometer by using an Al Kα source. Raman spectrum was collected on a micro-Raman spectrometer (Renishaw) with a laser of 532 nm wavelength. Ultraviolet-visible (UV-Vis) absorption spectra were recorded on an Agilent Cary 50 spectrophotometer in the wavelength range of 200-700 nm. Detailed analyses for CO_2, H_2 and CO were performed on GC-7900 with thermal conductivity detector (TCD) and flame ionization detector (FID)-Methanator (detection limit for CO: ~10 ppm).

Catalytic activities for the dehydrogenation of FA

Typically, the aqueous solution (5.0 mL) containing CoAuPd/DNA-rGO composite (n_{metal} = 0.06 mmol) was kept in a two-necked round-bottom flask. One neck was connected to a gas burette, and the other was connected to a pressure-equalization funnel to introduce FA aqueous solution (1.0 M, 5.0 mL). The catalytic reaction begun after the FA solution was added into the flask with magnetic stirring (600 r min^{-1}). A graduated glass tube filled with water was connected to the reaction flask to measure the volume of the gas (absolute volume = observation volume - blank volume) that evolved from the reaction. The reactor was immersed in a water bath to stabilize the temperature at 298 K.

The catalytic activities of other catalysts for FA decomposition were also applied

as the above method. The molar ratios of metal:FA (n_{metal}/n_{FA}) for all the catalytic reactions were kept as a constant of 0.012. All experiments were repeated at least two times. The experiments showed repeatable results.

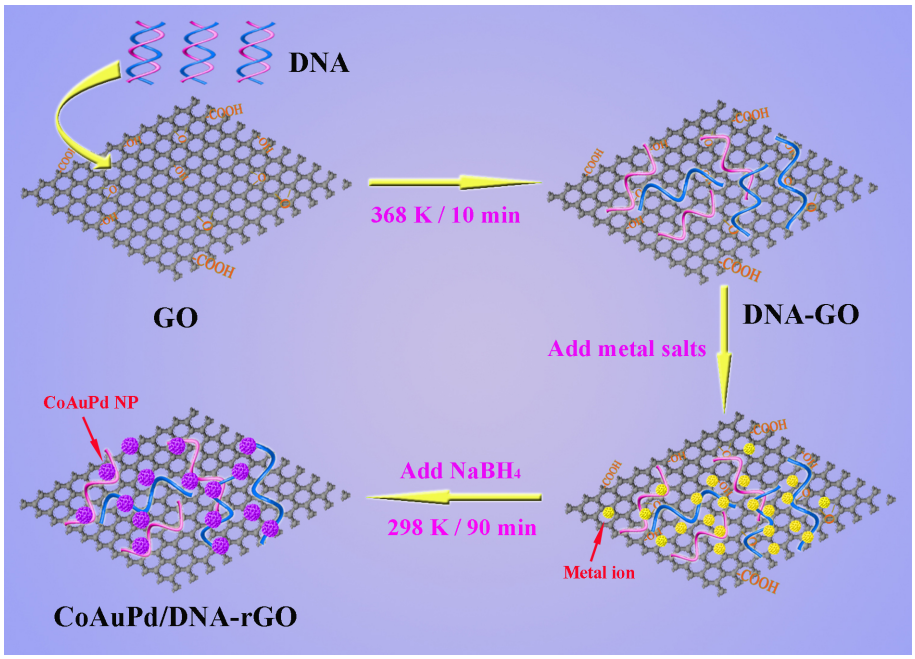
Calculation methods:

$$R_{initial\,H_2} = 1/2\frac{V_{\text{gas}}}{m_{metal}t} \qquad \text{(S1)}$$

Where $R_{initial\,H_2}$ is the initial rate of H_2 generation, m_{metal} is the weight of the metallic catalyst, and t is the reaction time of 20 min.

$$TOF_{initial} = \frac{P_{atm}V'_{H_2}/RT}{n_{metal}t} \qquad \text{(S2)}$$

Where $TOF_{initial}$ is initial turnover frequency, V'_{H_2} is the generated volume of H_2 during the first 20 min of the reaction, n_{metal} is the mole number of the metallic catalyst and t is the reaction time of 20 min.



Scheme S1 Schematic illustration for preparation of CoAuPd/DNA-rGO composite.

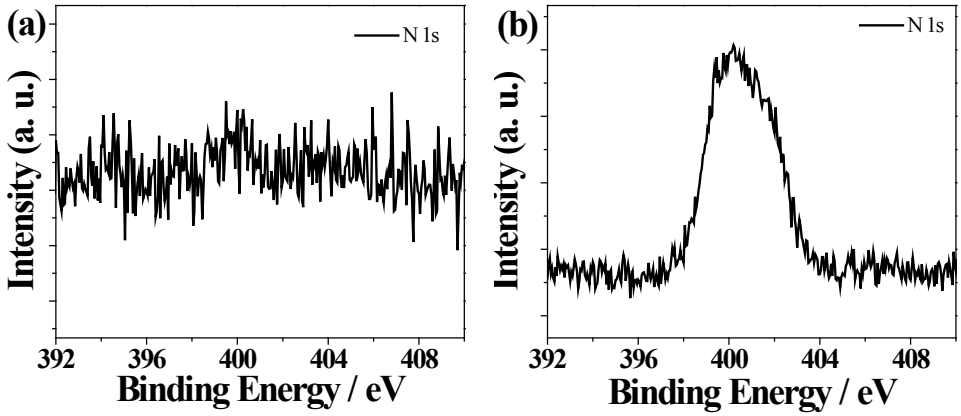


Fig. S1 High resolution XPS spectra of N 1s for (a) GO and (b) DNA-GO composite.

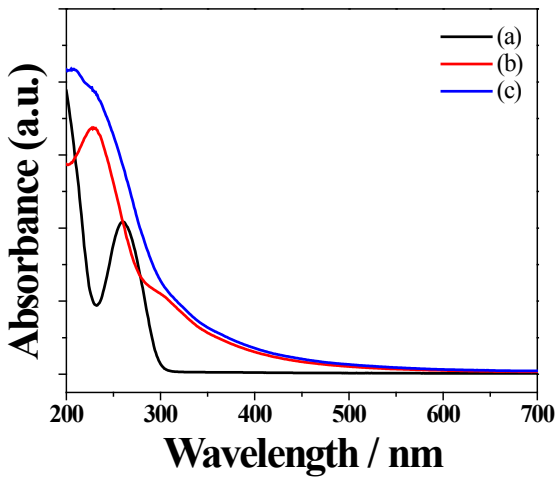


Fig. S2 UV-Vis absorption spectra of (a) DNA, (b) GO and (c) DNA-GO composite dispersed in water.

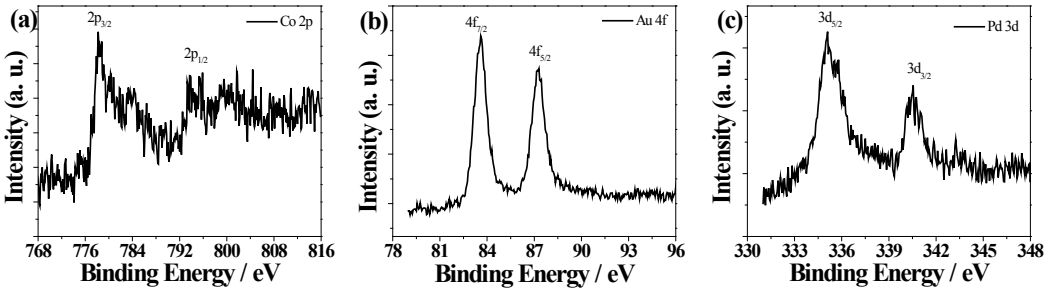


Fig. S3 High resolution XPS spectra of (a) Co 2p, (b) Au 4f, and (c) Pd 3d for CoAuPd/DNA-rGO composite.

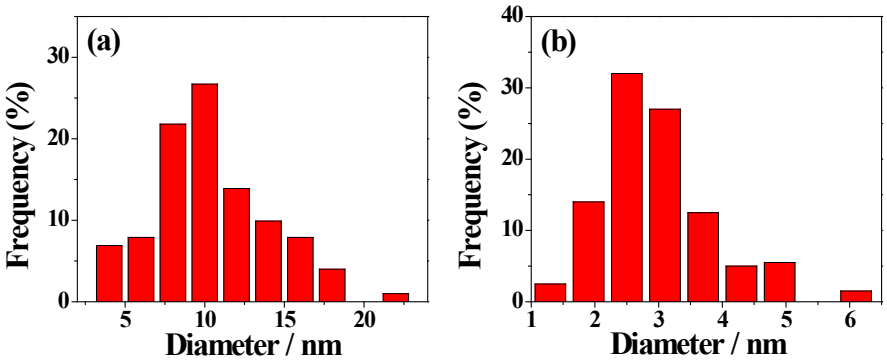


Fig. S4 Size distribution histograms for (a) CoAuPd/rGO and (b) CoAuPd/DNA-rGO composite.

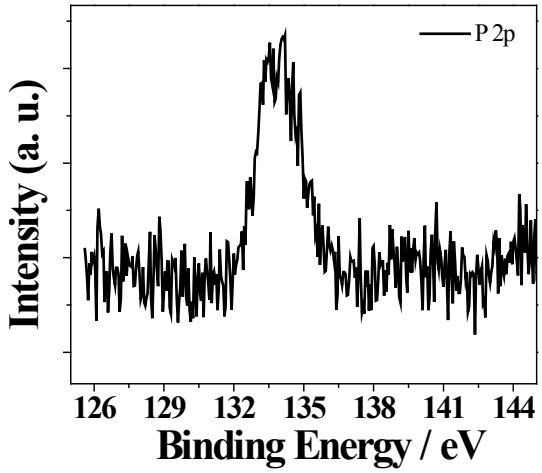


Fig. S5 High resolution XPS spectrum of P 2p for DNA-GO composite.

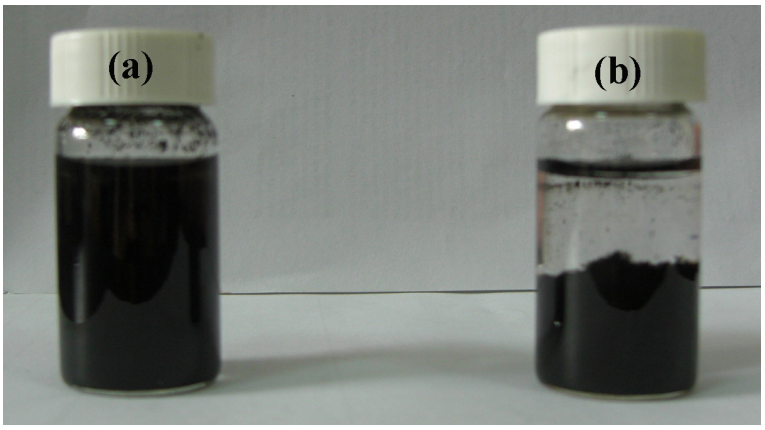


Fig. S6 Photographs of aqueous dispersion of (a) CoAuPd/DNA-rGO and (b) CoAuPd/rGO composite.

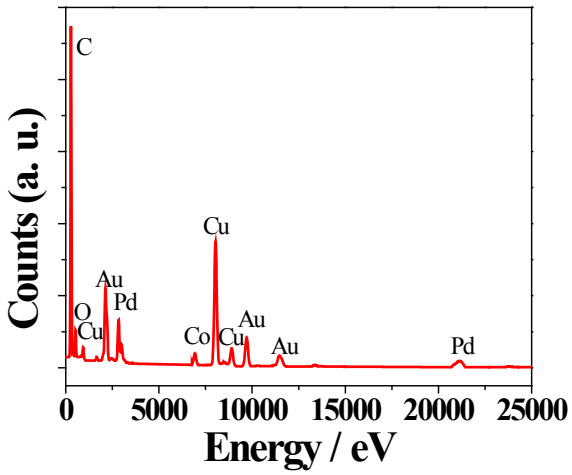


Fig. S7 EDS spectrum of CoAuPd/DNA-rGO composite (Cu signal in EDS are from Cu grids).

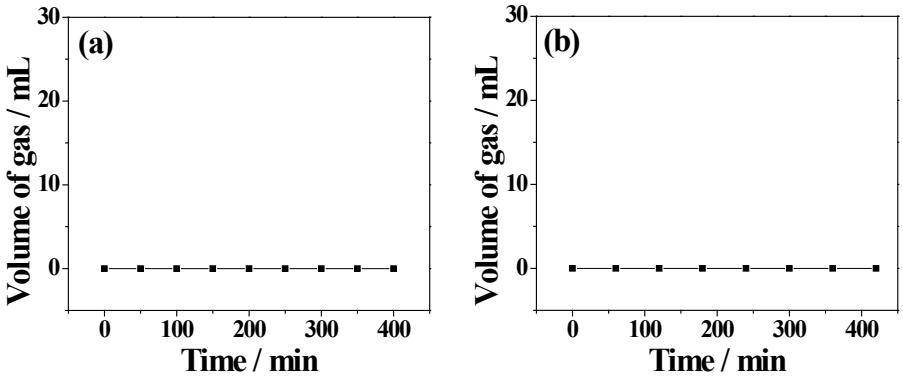


Fig. S8 Gas generation by the decomposition of aqueous FA solution (0.5 M, 10.0 mL) versus time over (a) DNA (10.0 mg) and (b) DNA-GO (10.0 mg DNA + 45.0 mg GO) at 298 K.

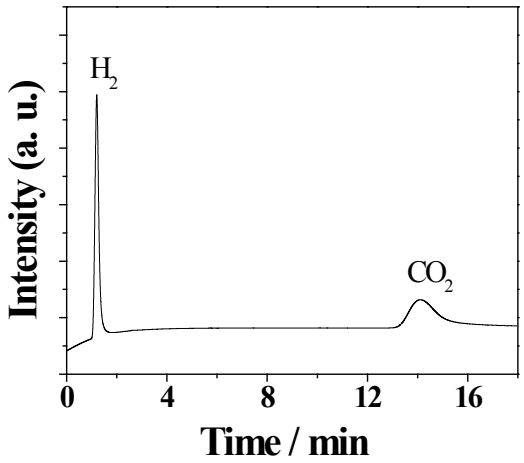


Fig. S9 GC spectrum using TCD for the evolved gas from aqueous FA solution (0.5 M, 10.0 mL) over CoAuPd/DNA-rGO composite at 298 K (n_{metal}/n_{FA} = 0.012).

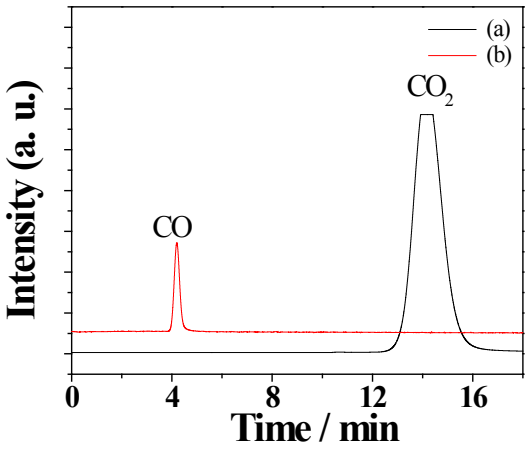


Fig. S10 GC spectrum using FID-Methanator for the (a) commercial pure CO, and (b) evolved gas from aqueous FA solution (0.5 M, 10.0 mL) over CoAuPd/DNA-rGO composite at 298 K (n_{metal}/n_{FA} = 0.012).

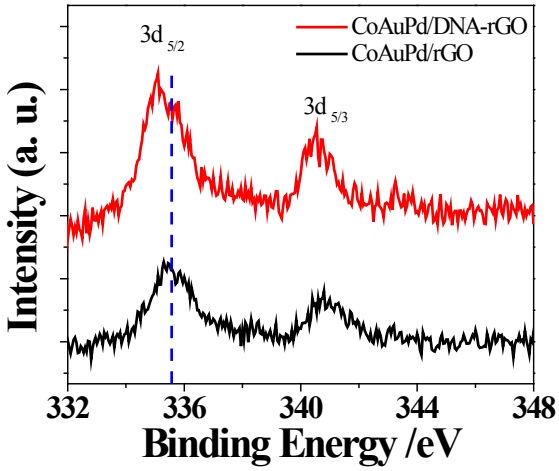


Fig. S11 Pd 3d XPS spectra for CoAuPd/DNA-rGO and CoAuPd/rGO composite.

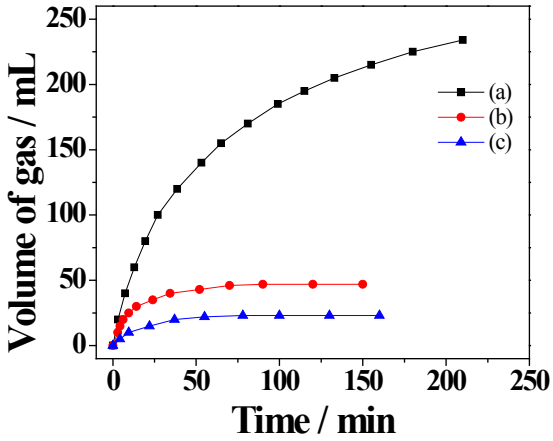


Fig. S12 Gas generation by the decomposition of aqueous FA solution (0.5 M, 10.0 mL) versus time over (a) CoAuPd/DNA-rGO, (b) CoAuPd/PVP-rGO, and (c) CoAuPd/CTAB-rGO at 298 K (n_{metal}/n_{FA}=0.012).

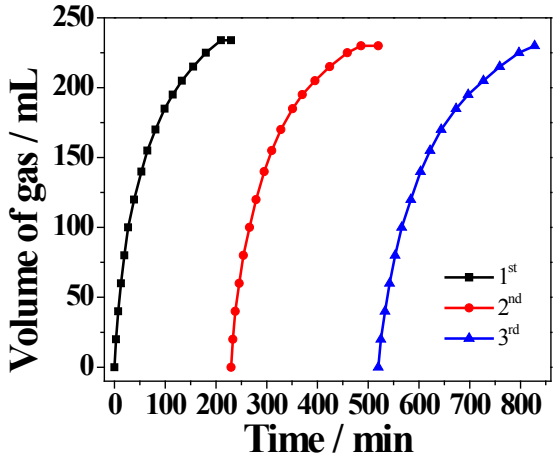


Fig. S13 Recycle test of CoAuPd/DNA-rGO composite toward the dehydrogenation of FA in an aqueous FA solution at 298 K.

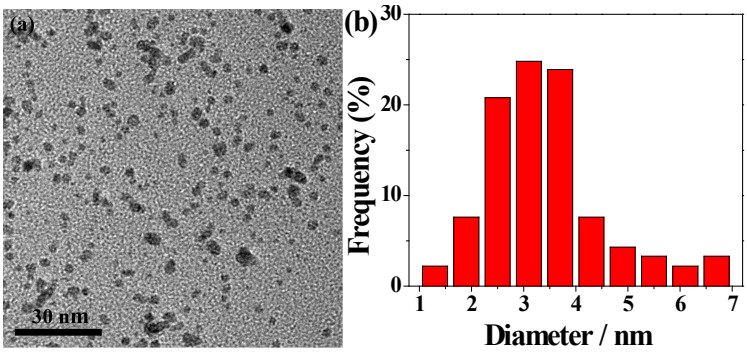


Fig. S14 (a) TEM image and (b) size distribution of CoAuPd/DNA-rGO composite after the catalytic reaction.

Table 1 Initial TOF values for the decomposition of FA over various heterogeneous catalysts.[a]

Catalyst	FA (mmol)	Additive (mmol)	Tem. (K)	H_2 volume (mL)	$n_{catalyst}$ (mmol)	$TOF_{initial}$ (mol H_2 mol catalyst^{-1} h^{-1})[a]	Ref.
Without additive							
CoAuPd/DNA-rGO	**5.0**	**None**	**298**	**41.5**	**0.060**	**85.0**	This work
Pd@CN	10.0	None	288	3.5	0.015	28.7	4d
	10.0	None (150 W Xe lamp)	288	6.5	0.015	53.3	4d
Au@Pd/N-mrGO	5.0	None	298	72.5	0.100	89.1	4e
Pd- poly(allyl-amine)	15.2	None	295	15.0	0.040	46.1	4b
Ag@Pd core-shell NPs	10.0	None	293	25.2	0.200	15.5	4a
CoAuPd/C	5.0	None	298	30.0	0.100	36.9	6a
$Ag_{0.42}Pd_{0.58}$/C	10.0	None	323	125.0	0.028	548.8	5j
$Au_{0.41}Pd_{0.59}$/C	10.0	None	323	51.0	0.058	108.1	5i
PtRuBiOx/C	318.0	None	353	125.0	0.633	24.3	5e
With additive							
Pd/MSC-30	9.0	HCOONa (9.0)	323	225	0.090	2623	5k
Au/ZrO_2	53.0	NEt_3 (21.20)	298	61.5	0.030	252.0	5g
Citric acid modified Pd/C	5.3	HCOONa (4.20)	298	54.7	0.047	143.1	5h
NiPd@Pd/GNs-CB	5.0	HCOONa (5.0)	298	112.5	0.200	138.1	6b
PdAu/ED-MIL-101	3.04	HCOONa (1.02)	363	52.0	0.026	245.9	5d
PdAu/C-CeO_2	49.7	HCOONa (16.65)	365	130.0	0.113	141.4	5a
PdAg/C-CeO_2	49.7	HCOONa (16.65)	365	63.0	0.113	68.5	5a
PdAu@Au/C	33.2	HCOONa (33.20)	365	89.3	0.227	48.4	5c

[a] $TOF_{initial}$ is calculated during the first 20 min of the reactions;

Reference

S1 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80,** 1339.