

Electronic Supporting Information

Au@Pd Core-shell Nanoclusters Growing on Nitrogen-Doped Mildly Reduced Graphene Oxide with Enhanced Catalytic Performance for Hydrogen Generation from Formic Acid

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Chemicals

Formic acid (HCOOH, FA, Sigma-Aldrich, 96%), graphite flake (C, Alfa Aesar, 325 mesh, 99.8%), sodium tetrachloropalladate (II) (Na_2PdCl_4 , Sinopharm Chemical Reagent Co., Ltd, Pd >36.4%), tetrachloroauric (III) acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co. Ltd, Au >47.8%), 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%), aqueous ammonia (NH_4OH , Beijing Chemical Works, 25%), hydrochloric acid (HCl, Beijing Chemical Works, 36%~37%), phosphoric acid (H_3PO_4 , Sinopharm Chemical Reagent Co. Ltd, >85%) were used without further purification. De-ionized water with the specific resistance of $18.2 \text{ M}\Omega \cdot \text{cm}$ was obtained by reversed osmosis followed by ion-exchange and filtration.

Synthesis of graphene oxide (GO)

GO was synthesized from graphite by a modified Hummers' method.³⁴ Briefly, a mixture of graphite powder (3.0 g) and KMnO_4 (18.0 g) was put into the $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (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 Au@Pd/N-mrGO hybrid

Firstly, NH_4OH (25.0 wt%, 0.5 mL) is added into the GO aqueous solution (0.2 wt%, 20.0 mL) with magnetic stirring for 8 h at 353 K to get the N-mrGO. For Au@Pd/N-mrGO hybrid with the atomic ratio of Au:Pd = 1:1, HAuCl_4 aqueous solution (20.0 mM, 2.5 mL) is dissolved into the above N-mrGO suspension with magnetic stirring for 30 min at 298 K. And then, Na_2PdCl_4 aqueous solution (20.0 mM, 2.5 mL) is dissolved into the above mixture with magnetic stirring for 30 min. The black product is separated by centrifugation, washed with water, and re-dispersed into 10.0 mL of water for the following catalytic reaction. In addition, Au@Pd/mrGO and Au@Pd/N-mrGO with different doping level of N were prepared by the same preparation method as Au@Pd/N-mrGO expect that without ammonia solution and the usage of various amount of ammonia solution (0.20 and 0.35 mL), respectively.

For comparison, Au@Pd/N-mrGO hybrid with different atomic ratio of Au:Pd, Au/N-mrGO and Pd/N-mrGO hybrid were also prepared as the same method mentioned above. All catalysts were prepared under same experimental conditions, including the amount of GO, ammonia solution, and metal precursors and the reaction temperature, reaction time, and stirring speed.

Synthesis of AuPd/N-mrGO hybrid

For AuPd/N-mrGO hybrid with the atomic ratio of Au:Pd = 1:1, HAuCl_4 aqueous solution (20.0 mM, 2.5 mL) and Na_2PdCl_4 aqueous solution (20.0 mM, 2.5 mL) are simultaneous dissolved into the N-mrGO suspension with magnetic stirring

for 30 min at 298 K. The black product is separated by centrifugation, washed with water, and re-dispersed into 10.0 mL of water for the following catalytic reaction.

Characterizations

Powder X-ray diffraction (XRD) was performed on a Rigaku RINT-2000 X-ray diffractometer with Cu K α . 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 K α source. Raman spectrum was collected on a micro-Raman spectrometer (Renishaw) with a laser of 532 nm wavelength. UV-Vis absorption spectra were recorded on an Agilent Cary 50 spectrophotometer in the wavelength range of 200-800 nm. Mass spectrometry (MS) analysis for the generated gas was performed on an OmniStar GSD320 mass spectrometer, and the reaction flask was kept under vacuum for 30 min and purged with argon for 30 min to remove any trace of CO, N₂, O₂, and CO₂ from air before the catalytic reaction. Detailed analyses for CO₂, H₂ 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 H₂ generation from FA decomposition

Typically, the aqueous solution (5.0 mL) containing Au@Pd/N-mrGO hybrid (theoretical value: $n_{Au+Pd} = 0.10$ 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 was begun once the FA solution was added into the flask with magnetic stirring. The evolution of gas was monitored using the gas burette. The reaction was carried out at 298 K under ambient atmosphere.

The catalytic activities of other as-prepared catalysts for the dehydrogenation of FA were also applied at 298 K under ambient atmosphere. The molar ratios of metal:FA (theoretical value: n_{metal}/n_{FA}) for all the catalytic reactions were kept as a constant of 0.02. All experiments were carried out under the same experimental conditions (reaction temperature, stirring speed) and repeated at least three times.

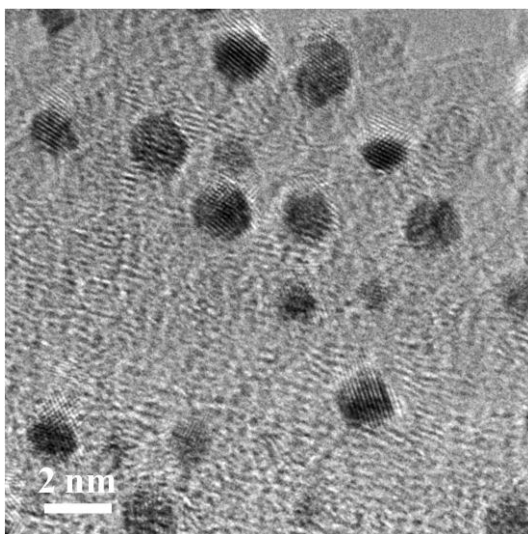


Figure S1. HRTEM image of Au@Pd/N-mrGO hybrid.

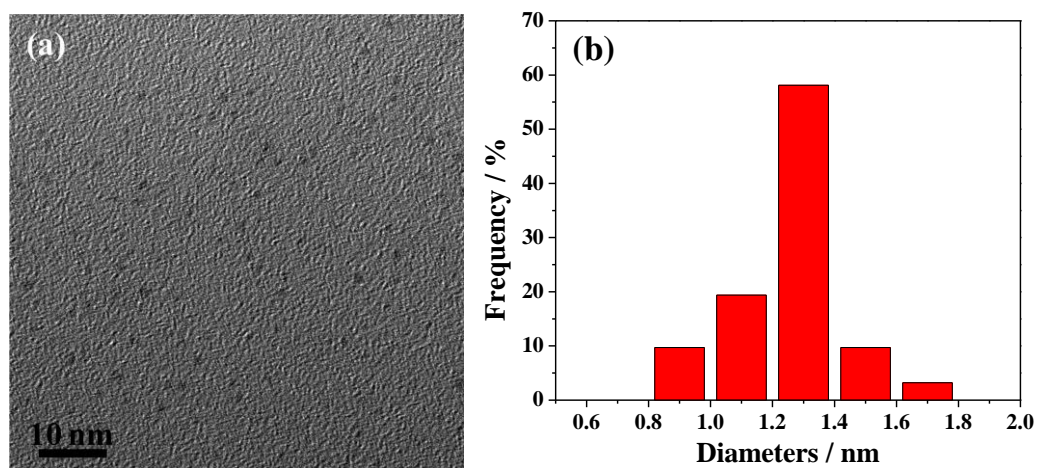


Figure S2. (a) TEM image and (b) size distribution of Au/N-mrGO hybrid.

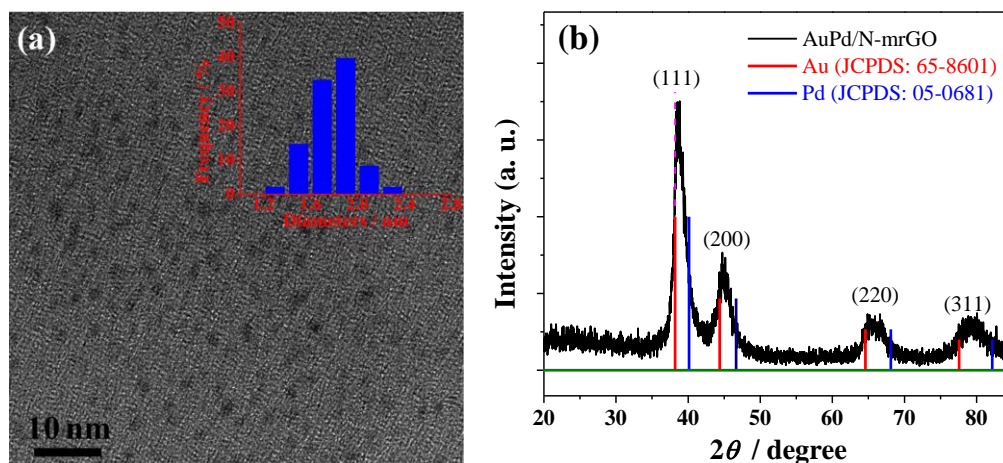


Figure S3. (a) TEM image, (inset) size distribution, and (b) XRD pattern of AuPd/N-mrGO hybrid.

From Figure S3b, it can be seen that the diffraction peaks can be indexed as a fcc crystal structure, and every diffraction peak appeared between the corresponding peak positions of pure fcc Au and Pd, suggesting the successful formation of AuPd alloy NCs.^{S1}

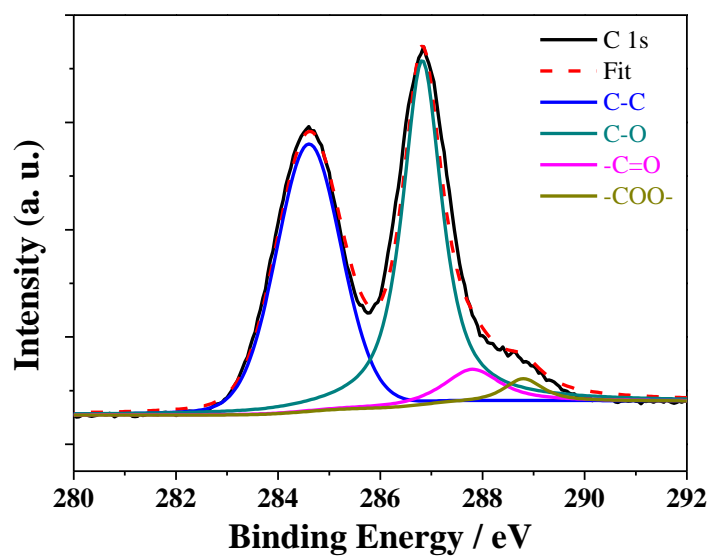


Figure S4. High resolution XPS spectrum of C 1s for GO.

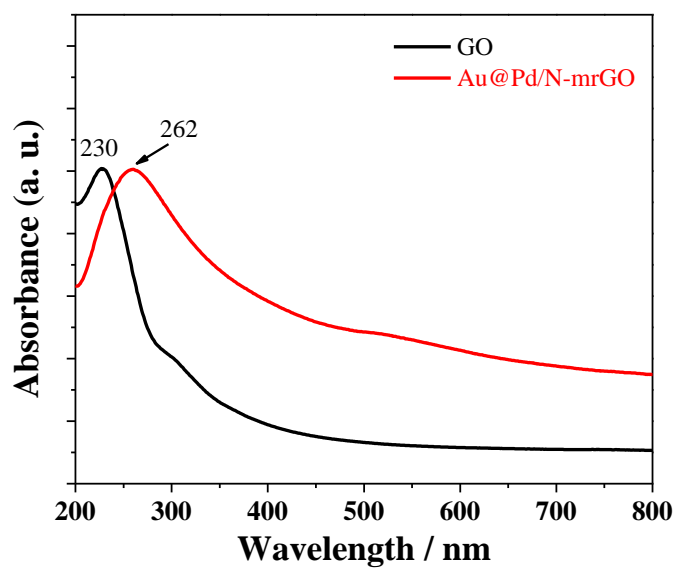


Figure S5. UV-Vis absorption spectra of GO and Au@Pd/N-mrGO hybrid.

From Figure S5, it can be seen that the characteristic peak of GO at 230 nm is red shifted to 262 nm after the synthetic process, which indicates the successful reduction of GO to N-mrGO.⁵⁵

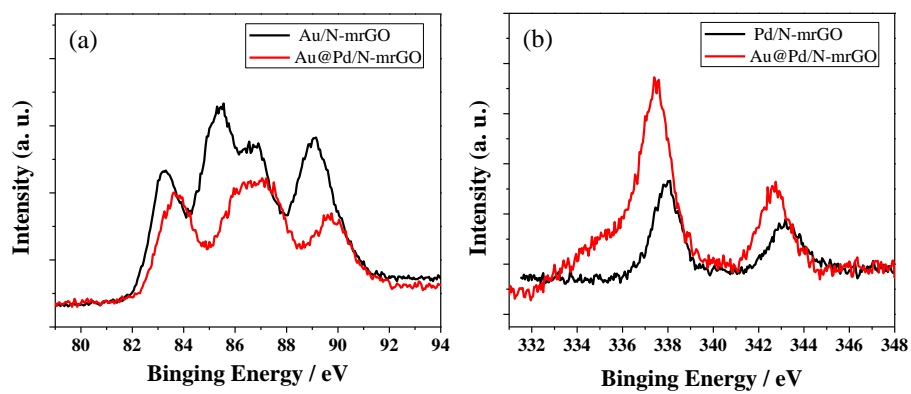


Figure S6. XPS spectra of (a) Au 4f and (b) Pd 3d for Au/N-mrGO, Pd/N-mrGO, and Au@Pd/N-mrGO without Ar etching.

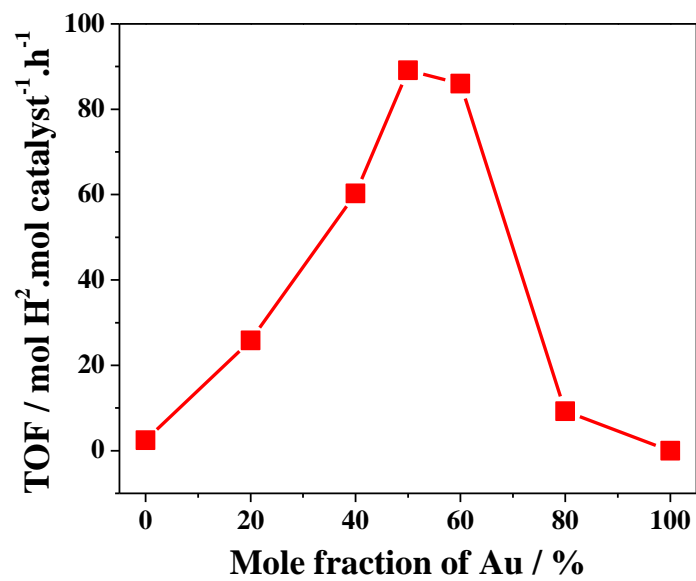


Figure S7. Initial TOFs versus mole fraction of Au in the Au@Pd/N-mrGO system.

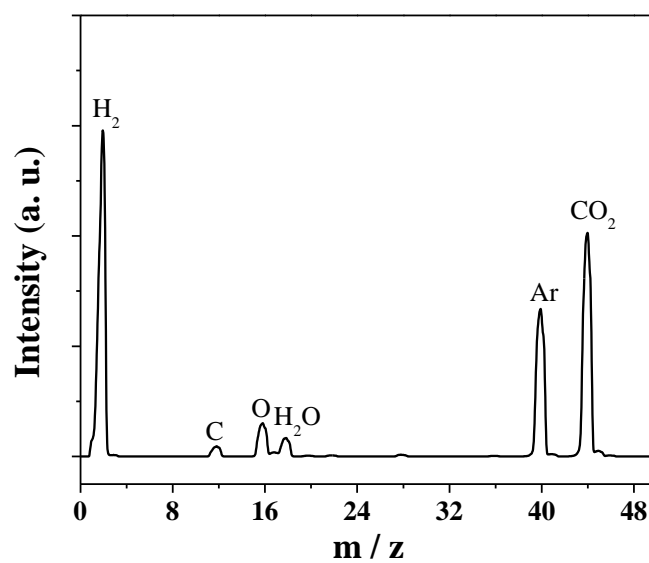


Figure S8. MS spectrum for the evolved gas from FA aqueous solution (0.5 M, 10.0 mL) over Au@Pd/N-mrGO hybrid ($n_{Au+Pd}/n_{FA} = 0.02$) at 298 K under Ar atmosphere.

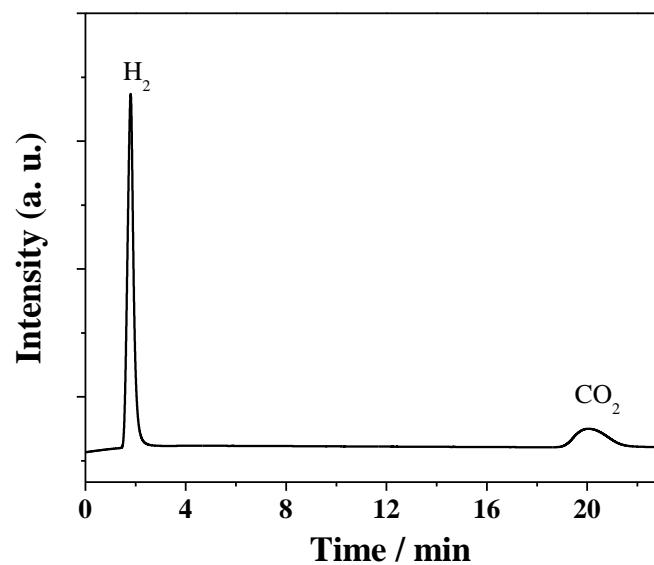


Figure S9. GC spectrum using TCD for the evolved gas from FA aqueous solution (0.5 M, 10.0 mL) over Au@Pd/N-mrGO hybrid ($n_{Au+Pd}/n_{FA} = 0.02$) at 298 K.

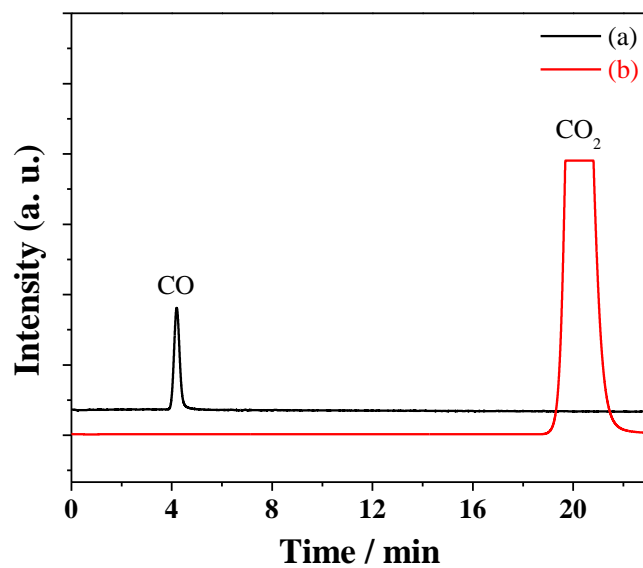


Figure S10. GC spectrum using FID-Methanator for the (a) commercial pure CO, and (b) evolved gas from FA aqueous solution (0.5 M, 10.0 mL) over Au@Pd/N-mrGO hybrid ($n_{Au+Pd}/n_{FA} = 0.02$) at 298 K.

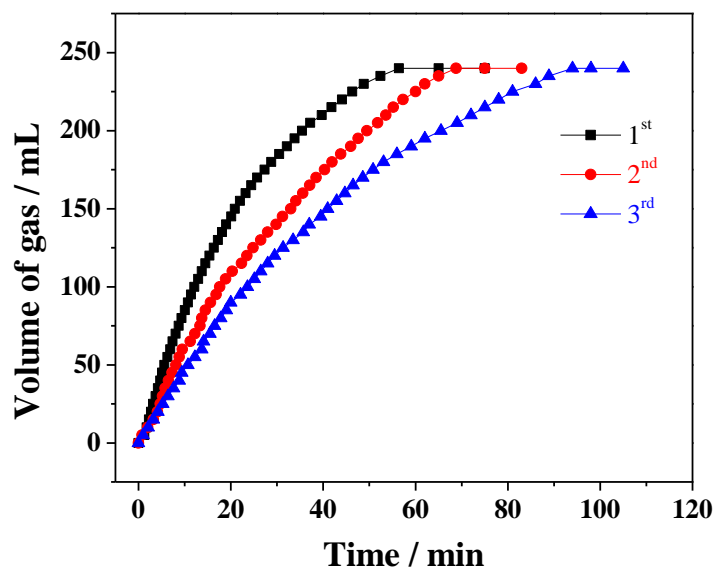


Figure S11. Recycle test of Au@Pd/N-mrGO hybrid toward H₂ generation from FA aqueous solution (0.5 M, 10.0 mL) at 298 K under ambient atmosphere. ($n_{Au+Pd}/n_{FA} = 0.02$).

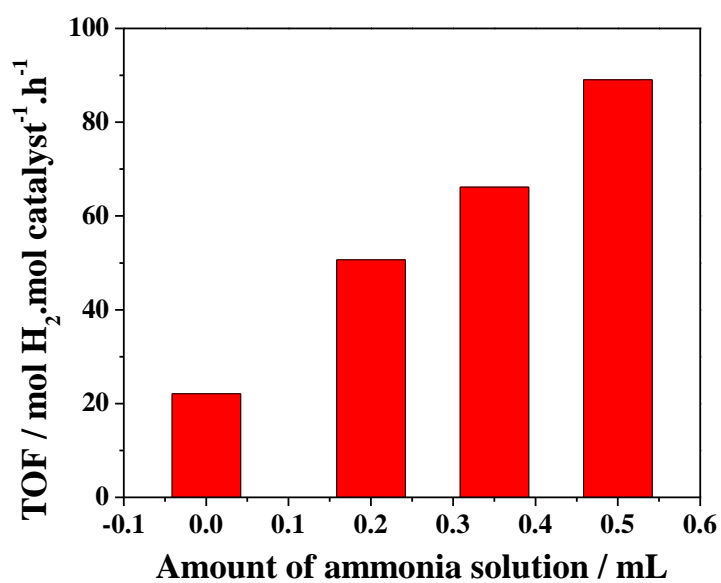


Figure S12. Initial TOFs for the dehydrogenation of FA over Au@Pd/N-mrGO

($n_{Au+Pd}/n_{FA} = 0.02$) prepared with different amounts of ammonia solution.

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

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.
Au@Pd/N-mrGO	5.0	None	298	72.5	0.100	89.1	This work
Pd- poly(allyl-amine)	15.2	None	295	15.0	0.040	46.1	29
Ag@Pd core-shell NPs	10.0	None	293	25.2	0.200	15.5	24
CoAuPd/C	5.0	None	298	30.0	0.100	36.9	28
AgPd/C	10.0	None	323	125.0	0.028	548.8	23
AuPd/C	10.0	None	323	51.0	0.058	108.1	22
PtRuBiOx/C	318.0	None	353	125.0	0.633	24.3	19
Au/ZrO ₂	53.0	NEt ₃ (21.20)	298	61.5	0.030	252.0	21
Citric acid modified Pd/C	5.3	HCOONa (4.20)	298	54.7	0.047	143.1	13
PdAu/ED-MIL-101	3.04	HCOONa (1.02)	363	52.0	0.026	245.9	18
PdAu/C-CeO ₂	49.7	HCOONa (16.65)	365	130.0	0.113	141.4	14
PdAg/C-CeO ₂	49.7	HCOONa (16.65)	365	63.0	0.113	68.5	14
PdAu@Au/C	33.2	HCOONa (33.20)	365	89.3	0.227	48.4	16

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

Calculation methods:

$$x_a = \frac{P_{atm} V_{H_2} / RT}{n_{FA}} \quad S1$$

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

$$TOF_{initial} = \frac{P_{atm} V_{H_2}' / RT}{n_{Au+Pd} t} \quad S2$$

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_{Au+Pd} is the mole number of the Au and Pd, and t is the reaction time of 20 min.

References

S1. L. Zhang, J. Zhang, Q. Kuang, S. Xie, Z. Jiang, Z. Xie, L. Zheng, *J. Am. Chem. Soc.* 2011, **133**, 17114.