

Supporting Information

Facile Synthesis of AgAuPd/Graphene with High Performance for Hydrogen Generation from Formic Acid

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Chemicals

Formic acid (HCOOH, FA, Sigma-Aldrich), graphite flake (C, Alfa Aesar, 325 mesh, 99.8%), potassium permanganate (KMnO₄, Sinopharm Chemical Reagent Co., Ltd, >99%), sulfuric acid (H₂SO₄, Beijing Chemical Works, 98%), phosphoric acid (H₃PO₄, Sinopharm Chemical Reagent Co., Ltd, >85%), hydrochloric acid (HCl, Beijing Chemical Works, 36%~37%), hydrogenperoxide (H₂O₂, Beijing Chemical Works, 30%), tetrachloroauric (III) acid (HAuCl₄·4H₂O, Sinopharm Chemical Reagent Co., Ltd, Au > 47.8%), silver nitrate (AgNO₃, Beijing Chemical Works, 99.8%), palladium (II) chloride (PdCl₂, Sinopharm Chemical Reagent Co., Ltd, Pd >59%), sodium chloride (NaCl, Sinopharm Chemical Reagent Co., >99.5%), ethanol (C₂H₅OH, Beijing Chemical Works, >99.7%) 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 according to a modified Hummers method.^[13] Briefly, a mixture of graphite powder (3.0 g) and KMnO₄ (18.0 g) was put into the H₂SO₄/H₃PO₄ (360/40 mL) solution little by little. Then, the above graphite suspension was heated to 323 K and stirred for 12 h. After the graphite suspension was cooled to room temperature, it was poured onto ice to control the temperature

below 323 K, and followed by addition of H₂O₂ (30~40 mL) and de-ionized water. The mixture was centrifuged (12000 r/min for 3 min), and then water and HCl (100 mL) was added to the remaining solid material and stirred for 12 h. The above suspension was centrifuged (12000 r/min) for 10 times with de-ionized water. Finally, GO (0.2 wt%) was achieved by ultrasonication of the washed suspension for 40 min.

Synthesis of catalysts

Typically, for preparation of Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO, 5.0 mL of aqueous solution containing AgNO₃ (0.02 mmol), Na₂PdCl₄ (0.04 mmol) and HAuCl₄ (0.04 mmol) was added into the well dispersed GO and then 40 ml of ethanol was added into above solution. The pH of the solution was adjusted to be 9-10 by adding KOH (1.0 M) aqueous solution. The solution was refluxed in a water bath at 353 K for 3 h with stirring. After 3 h, the obtained product is washed with water for several times and re-dispersed in 10 ml of water for the catalytic H₂ generation from the FA aqueous solution at 298 K. The obtained sample is denoted as AgAuPd/rGO. For comparison, pure rGO, PdAu/rGO, PdAg/rGO, AgAu/rGO, Ag/rGO, Au/rGO and Pd/rGO were also prepared under identical conditions. In order to show the effect of ethanol as the reducing agent, AgAuPd/rGO was synthesized by the similar method except the reducing agent is NaBH₄, and the reducing temperature is 298 K and 353 K, respectively.

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) was applied for the detailed microstructure and composition analyses, and the amorphous carbon coated copper grids were used as the sample supporters. X-ray photoelectron (XPS) was carried out on an ESCALABMKLL X-ray photoelectron spectrometer using an Al K α source. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurement was performed on a Thermo Jarrell Ash (TJA) Atomscan Advantage instrument. Mass spectrometry (MS) analysis for the generated

gas were 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 CO₂, N₂, and O₂ 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: ~10 ppm). Raman spectrum was collected using 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.

Catalytic dehydrogenation of FA

Typically, the as-prepared Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO (113 mg) composite 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 formic acid (FA) aqueous solution (1 M, 5 mL). The catalytic reaction was begun after the FA solution was added into the flask with magnetic stirring (600 r/min). The evolution of gas was monitored using the gas burette. The reaction was carried out at 353 K under ambient atmosphere.

The catalytic activities of other catalysts for FA decomposition were also applied as the above method. The molar ratio of metal: FA (n_{metal}/n_{FA}) for all the catalytic reactions was kept as a constant of 0.02. All experiments were repeated at least two times. The experiments showed repeatable results.

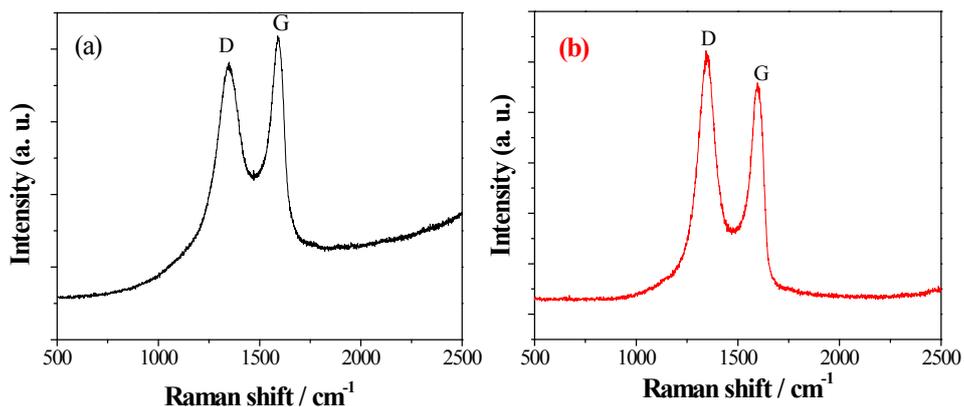


Figure S1. Raman spectra of (a) GO and (b) Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO.

Figure S1 shows the Raman spectra of the GO and Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO hybrid. A typical D and G band can be observed at 1350 cm⁻¹ and 1580 cm⁻¹, respectively. It is clear that, before reduction (Figure S1a), the intensity of G band of GO is higher than that of the D band, while after reduction (Figure S1b), the intensity of D band is higher than that of G band, which indicates that GO is successfully reduced to rGO.^[23c]

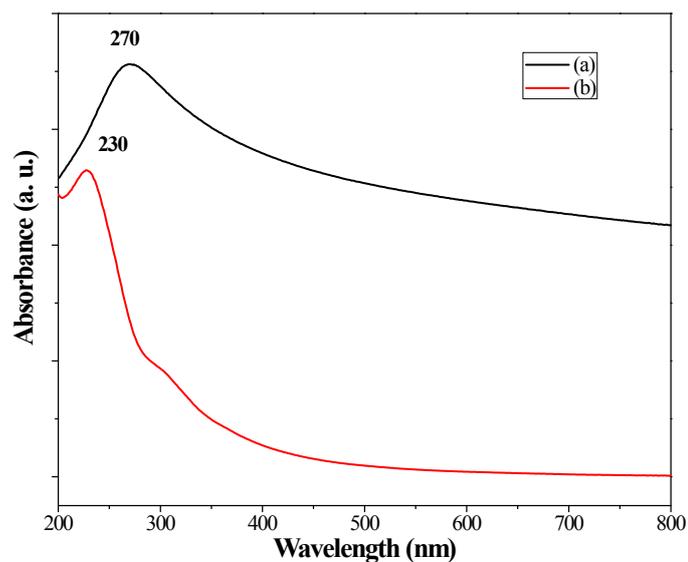


Figure S2. UV-vis spectra of (a) $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$ and (b) GO.

From Figure S2, it can be seen that the characteristic peak of GO at 230 nm is red shifted to 270 nm, which also indicates the successful reduction of GO to rGO.^[9b]

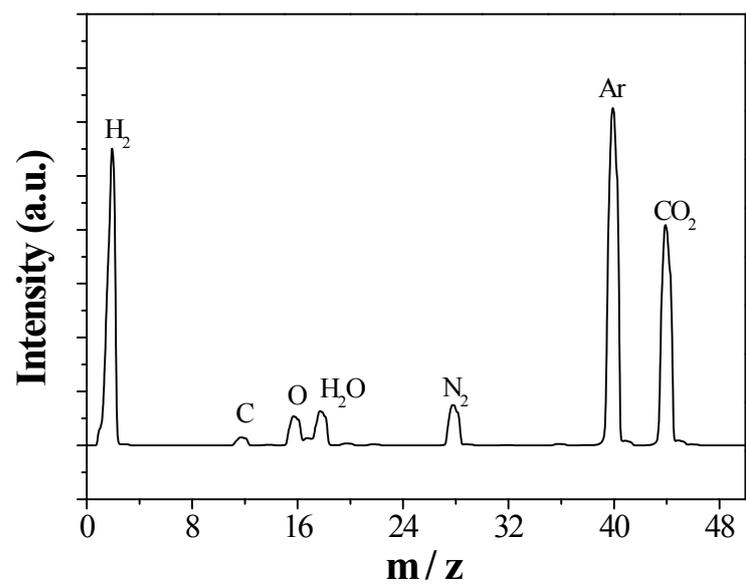


Figure S3. MS spectrum for the evolved gas from FA aqueous solution (1 M, 5.0 mL) over Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO hybrid at 298 K under Ar atmosphere. ($n_{metal}/n_{FA} = 0.02$)

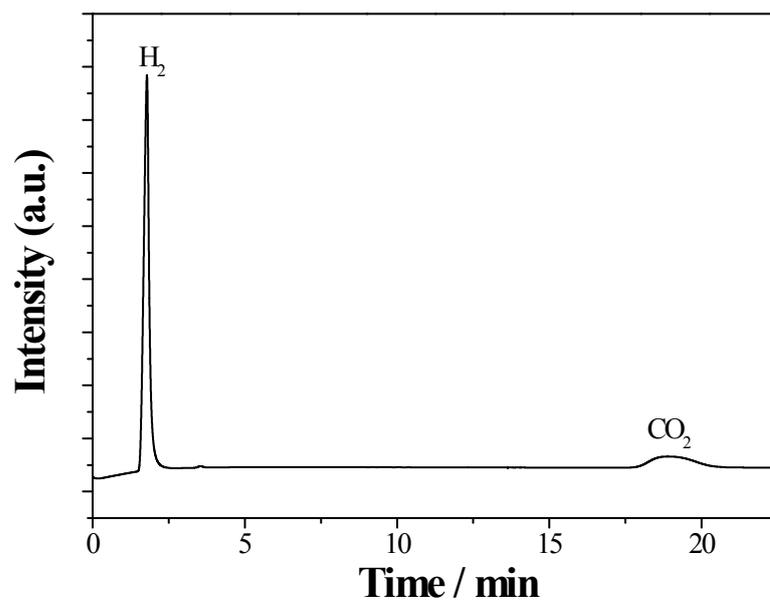


Figure S4. GC spectrum using TCD for the evolved gas from FA aqueous solution (1M, 5 mL) over Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO hybrid at 298 K. ($n_{metal}/n_{FA} = 0.02$)

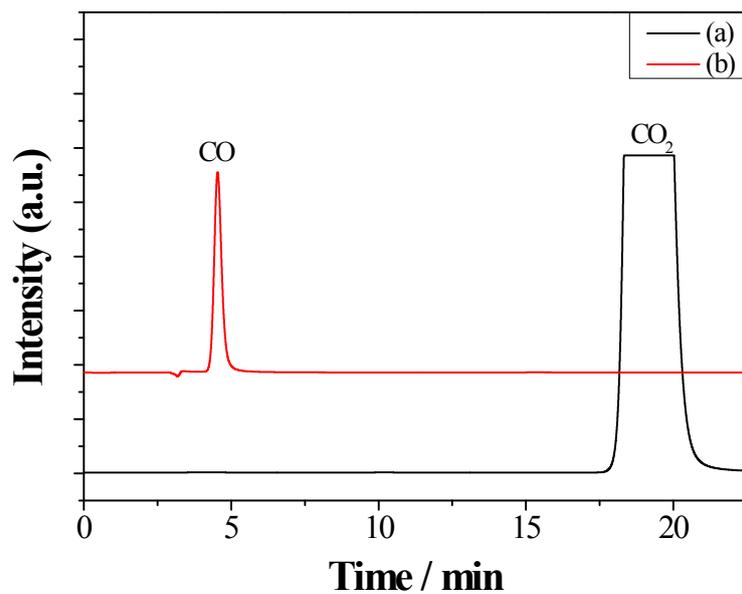


Figure S5. GC spectrum using FID-Methanator for the (a) commercial pure CO, and (b) evolved gas from FA aqueous solution (1M, 5 mL) over Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO hybrid at 298 K. ($n_{\text{metal}}/n_{\text{FA}} = 0.02$)

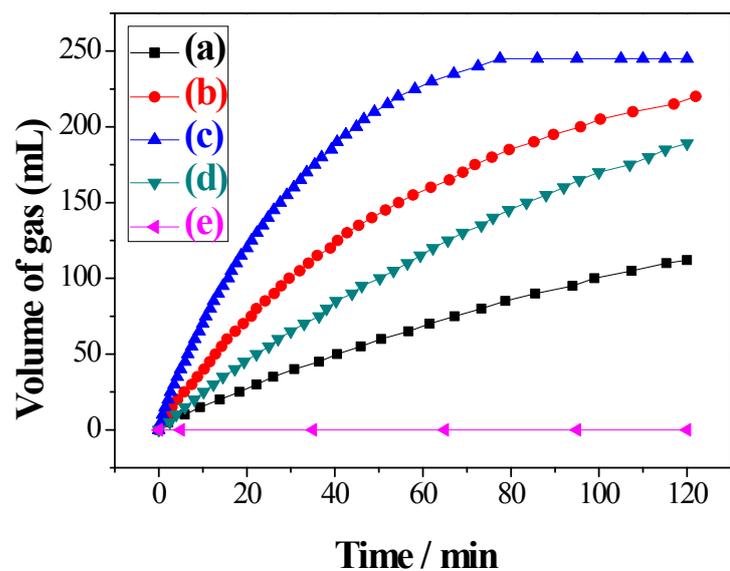


Figure S6. Gas generation by decomposition of FA (1M, 5mL) over catalyst of $\text{Ag}_{0.2}\text{Au}_{0.8-x}\text{Pd}_x/\text{rGO}$ when x value is (a) 0.8, (b) 0.6, (c) 0.4, (d) 0.2, and (e) 0. ($n_{\text{Ag}}/n_{\text{metal}}=0.2$, $n_{\text{metal}}/n_{\text{FA}} = 0.02$)

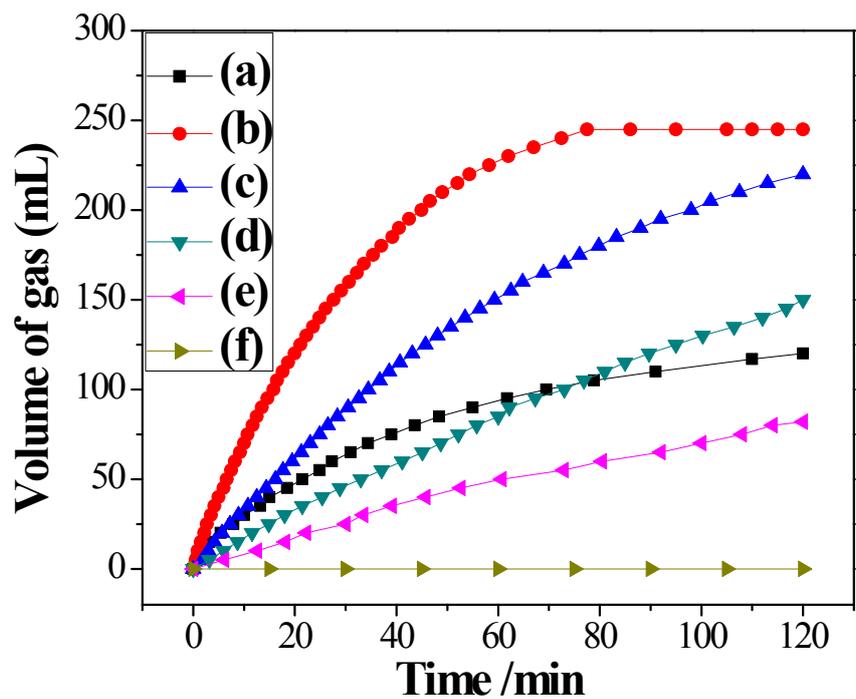


Figure S7. Gas generation by decomposition of FA (1M, 5mL) over catalyst of Ag_{1-2y}Au_yPd_y/rGO when y value is (a) 0.5, (b) 0.4, (c) 0.3, (d) 0.25, (e) 0.2, and (f) 0. ($n_{Au}/n_{Pd} = 1$, $n_{metal}/n_{FA} = 0.02$)

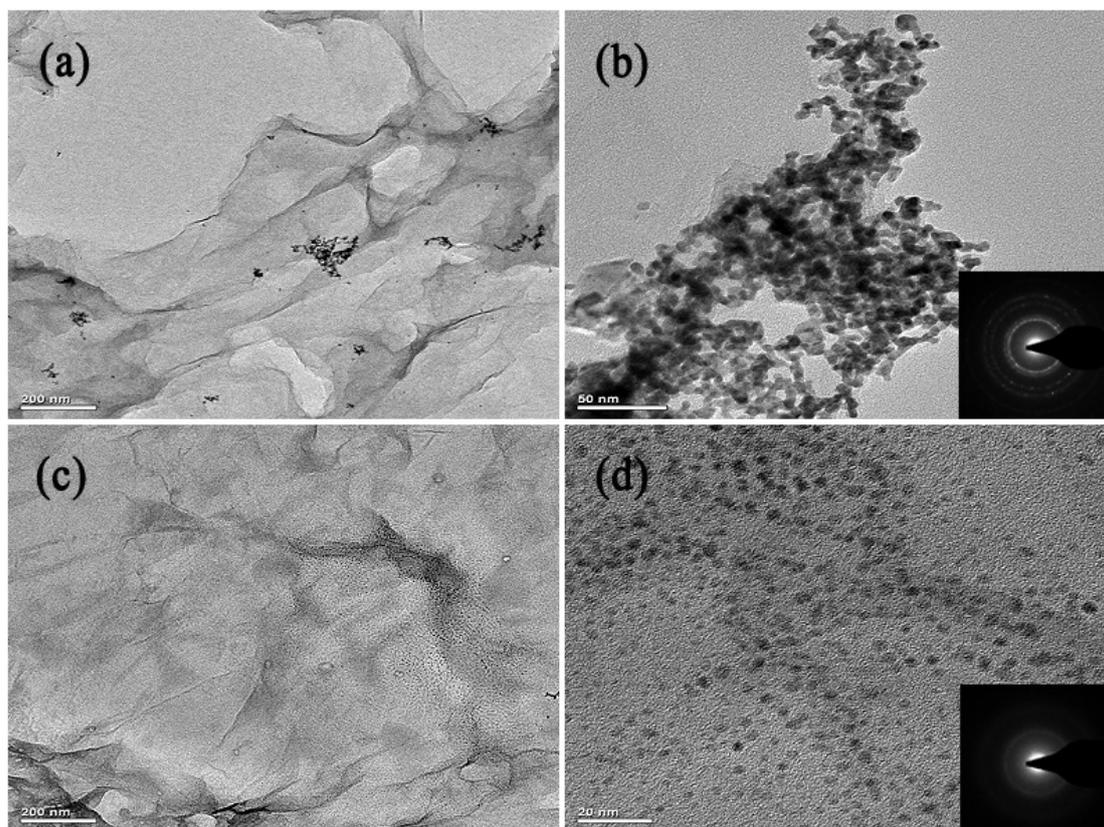


Figure S8. TEM images with the (a) low, and (b) middle resolutions for Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO reduced by NaBH₄ at 353 K; TEM images with the (c) low, and (d) middle resolutions for Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO reduced by NaBH₄ at 298 K. (inset: the corresponding SAED patterns).

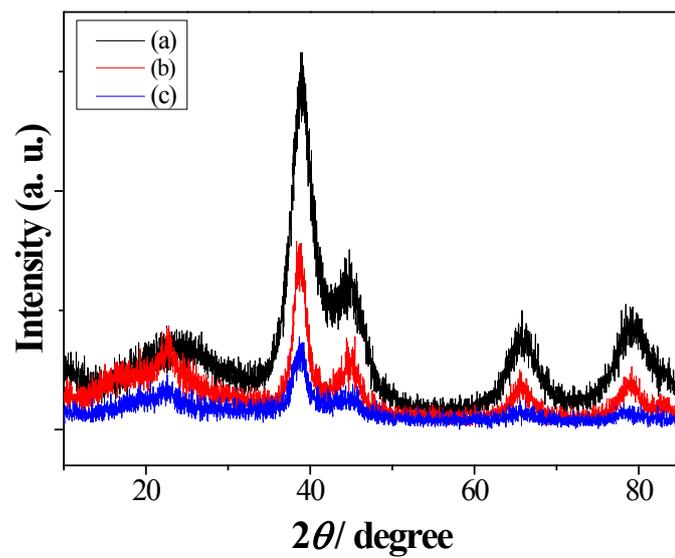


Figure S9. XRD patterns of $\text{Ag}_{0.2}\text{Au}_{0.4}\text{Pd}_{0.4}/\text{rGO}$ reduced by (a) ethanol at 353 K, (b) NaBH_4 at 353 K, and (c) NaBH_4 at 298 K.

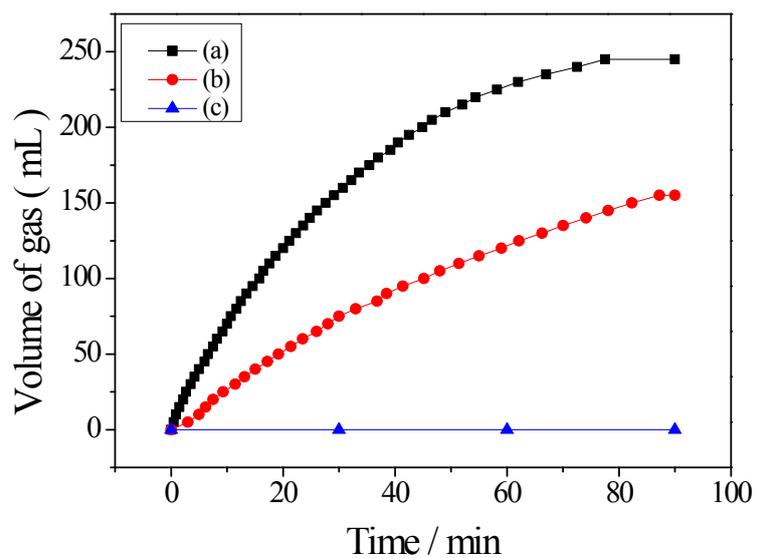


Figure S10. Gas generation by the decomposition of FA (1 M, 5 mL) vs. time at 298 K over Ag_{0.2}Au_{0.4}Pd_{0.4}/rGO reduced by (a) ethanol at 353 K, (b) NaBH₄ at 353 K, and (c) NaBH₄ at 298 K.

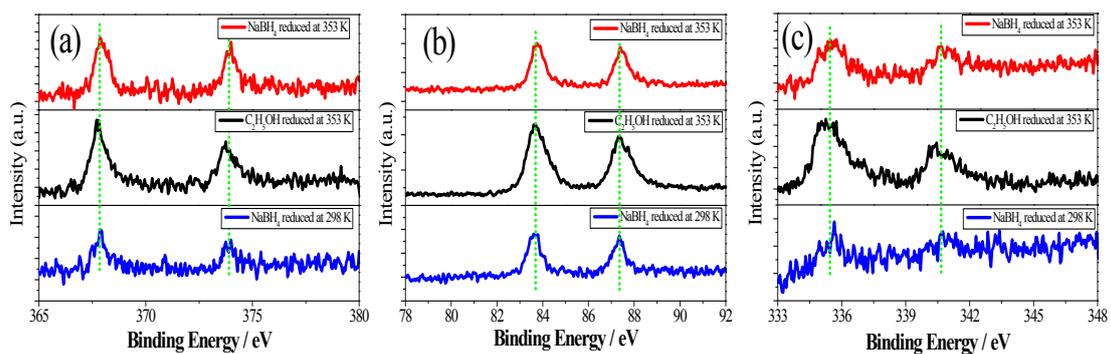


Figure S11. XPS spectra of (a) Ag 3d, (b) Au 4f, and (c) Pd 3d for AgAuPd/rGO prepared at the different reduction condition.

Table S1. The initial TOF and conversions for decomposition of FA catalyzed by various heterogeneous catalysts without any additive at room temperature.

Catalyst	FA (mmol)	Additive (mmol)	Tem (K)	n_{catalyst} (mmol)	Conversion (%)	TOF _{initial} (mol H ₂ mol catalyst ⁻¹ h ⁻¹)	Ref.
AgAuPd/rGO	5.0	None	298	0.100	100	73.6	This work
Pd/mpg-C ₃ N ₄	10.0	None	298	0.0445	46	103.1	20
CoAuPd/DNA-rGO	5.0	None	298	0.060	96	85.0	22
Pd@CN	10.0	None (150 W Xe lamp)	288	0.015	27	53.3	21
AuPd-MnOx/ZIF8-rGO	5.0	None	298	0.065	94	382.1	23a
Ni _{0.4} Au _{0.15} Pd _{0.45} /C	5.0	None	298	0.100	73	12.0	23b
Au@Pd/N-mrGO	5.0	None	298	0.100	98	89.1	9b
Pd-poly(allyl-amine)	15.2	None	295	0.040	18	46.1	25 
Ag@Pd core-shell NPs	10.0	None	293	0.200	41	15.5	6
CoAuPd/C	5.0	None	298	0.100	91	36.9	10h
AuPd-CeO ₂ /N-rGO	5.0	None	298	0.100	98	52.9	23c
Pd/C	93.1	None	294	0.094	6	31.7	24 

Calculation methods:

$$(1) \quad x_a = \frac{P_{\text{atm}} V_{\text{gas}} / RT}{2n_{\text{FA}}} \quad \text{where } x_a = \frac{P_{\text{atm}} V_{\text{gas}} / RT}{2n_{\text{FA}}} \quad \text{and } =$$

Where x_a is the final conversion, P_{atm} is the atmospheric pressure, V_{gas} is the total generated volume of gas (CO₂+H₂), R is the universal gas constant, T is the room temperature (298 K), and n_{FA} is the molar number of FA.

$$TOF_{\text{initial}} = \frac{P_{\text{atm}} V'_{\text{gas}} / RT}{2n_{\text{metal}} t} \quad (2)$$

Where TOF_{initial} is the initial turn over frequency of reaction during the first 20 min, V'_{gas} is the volume of the initial generated gas (CO₂+H₂) within 20 min, n_{metal} is the total molar number of metal in catalyst, and t is the reaction time of 20min (in hour).