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Supporting Information

Ag_{0.1}Pd_{0.9}/rGO: An Efficient Catalyst for Hydrogen Generation from Formic Acid/Sodium Formate

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Chemicals

Vulcan XC-72 carbon (C, 500m²/g, Sinopharm Chemical Reagent Co., Ltd), sulfuric acid (H₂SO₄, Beijing Chemical Works, 98%), potassium permanganate (KMnO₄, Sinopharm Chemical Reagent Co., Ltd, ≥99%), potassium peroxodisulfate (K₂S₂O₈, Beijing Chemical Works, ≥99%), phosphorus pentoxide (P₂O₅, Beijing Chemical Works, ≥99.99%) hydrogenperoxide (H₂O₂, Beijing Chemical Works, 30%), hydrochloric acid (HCl, Beijing Chemical Works, 36%~37%), 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., Ltd, >99.5%), sodium borohydride (NaBH₄, Sinopharm Chemical Reagent Co., Ltd, 96%), formic acid (HCOOH, FA, Sigma-Aldrich, 96%), and sodium formate dehydrate (HCOONa·2H₂O, Sinopharm Chemical Reagent Co., Ltd, 99.5%) were used without purification. De-ionized water with the specific resistance of 18.2 MΩ·cm was obtained by reversed osmosis followed by ion-exchange and filtration.

Physical 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 spectrometry (XPS) was carried out on an ESCALABMKLL X-ray photoelectron spectrometer using an Al K α source. 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). UV-vis absorption spectra were recorded on an Agilent Cary 50 spectrophotometer in the wavelength range of 200–800 nm.

Synthesis of graphene oxide (GO)

Graphene oxide was prepared according to a modified Hummer's method.^{S1, S2} Briefly, graphite powder (3 g, 325 mesh) was put into a 323 K solution of concentrated H₂SO₄ (12 mL), K₂S₂O₈ (2.5 g), and P₂O₅ (2.5 g). After keeping at 323 K for 4.5 h using a hotplate, the mixture was cooled to room temperature and diluted with 0.5 L of de-ionized water. Then, the mixture was filtered and washed with water using a 0.2 micron Nylon Millipore filter to remove the residual acid. Next, the pretreated graphite powder was put into cold (273 K) concentrated H₂SO₄ (120 mL) in a 250 mL round-bottom flask equipped with a magnetic stir bar. 15 g KMnO₄ was added gradually under stirring while the temperature of the mixture was kept below 293 K. The solution was then stirred at 308 K for 2 h. Afterwards, 250 mL of de-ionized water was added and the suspension was stirred for another 2 h. Subsequently, additional 0.7 L of de-ionized water was added. Shortly after that, 20 mL of 30% H₂O₂ was added to the mixture to destroy the excess of permanganate. The suspension was then repeatedly centrifuged and washed firstly with 5% HCl solution and then with water. Exfoliation of graphite oxide to GO was achieved by ultrasonication of the dispersion for 40 min.

Syntheses of catalysts

Firstly, Na_2PdCl_4 aqueous solution was prepared by dissolving the salts of PdCl_2 (1.0 g) and NaCl (0.65 g) into 50 mL of water with magnetic stirring for 10 h at room temperature (298 K).

Catalysts of AgPd/rGO with different molar ratio of $\text{Ag}:\text{Pd}$ were synthesized through a surfactant-free coreduction method at 298 K. Typically, for preparation of $\text{Ag}_{0.1}\text{Pd}_{0.9}/\text{rGO}$, 3 mL of GO is firstly dispersed in 10.0 mL of water with sonication for 40 min to get the well dispersed GO suspension. And then, 5.0 mL of aqueous solution containing AgNO_3 (0.01 mmol) and Na_2PdCl_4 (0.09 mmol) is mixed with the 10.0 mL of aqueous solution containing the well-dispersed GO under stirring to mix uniformity for 30 min. The fresh NaBH_4 aqueous solution (1.05 M, 1.0 mL) was added into the above mixture with magnetic stirring (600 r/min). After 2 h, the product was separated by centrifugation, washed with de-ionized water for several times to remove the unreacted NaBH_4 . Then, the product of $\text{Ag}_{0.1}\text{Pd}_{0.9}/\text{rGO}$ is obtained and ready for the catalytic H_2 generation from FA aqueous solution at 298 K.

H_2 generation from FA/SF aqueous solution

Typically, the as-prepared $\text{Ag}_{0.1}\text{Pd}_{0.9}/\text{rGO}$ re-dispersed in 10 mL of water 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/sodium formate (FA/SF) aqueous solution (1 M/0.67 M, 5 mL). The catalytic reaction was begun once the FA/SF 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 298 K under ambient atmosphere. The catalytic activities of other catalysts for FA decomposition were also applied as the above method. The molar ratios of metal:FA ($n_{\text{AgPd}}/n_{\text{FA}}$) for all the catalytic reactions were kept as a constant of 0.02.

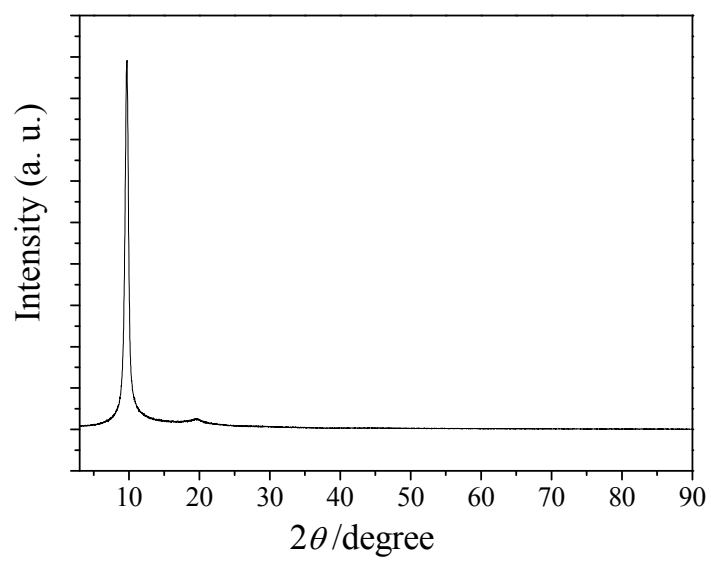


Figure S1. XRD pattern of GO.

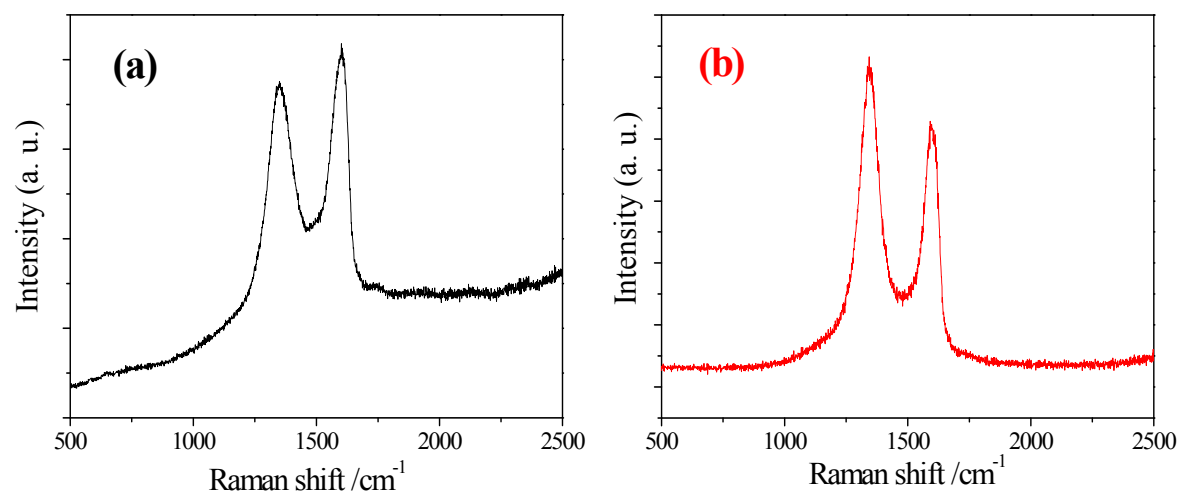


Figure S2. Raman spectral profile of (a) GO and (b) Ag_{0.1}Pd_{0.9}/rGO.

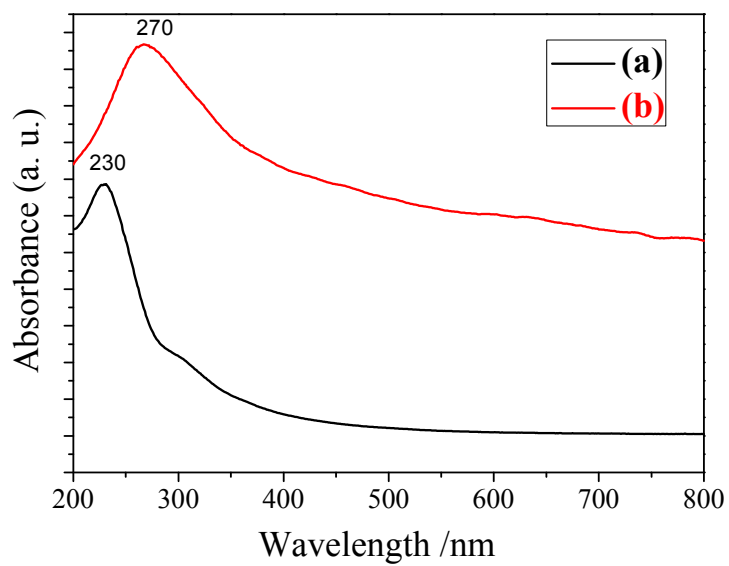


Figure S3. UV-vis spectra of (a) GO and (b) $\text{Ag}_{0.1}\text{Pd}_{0.9}/\text{rGO}$.

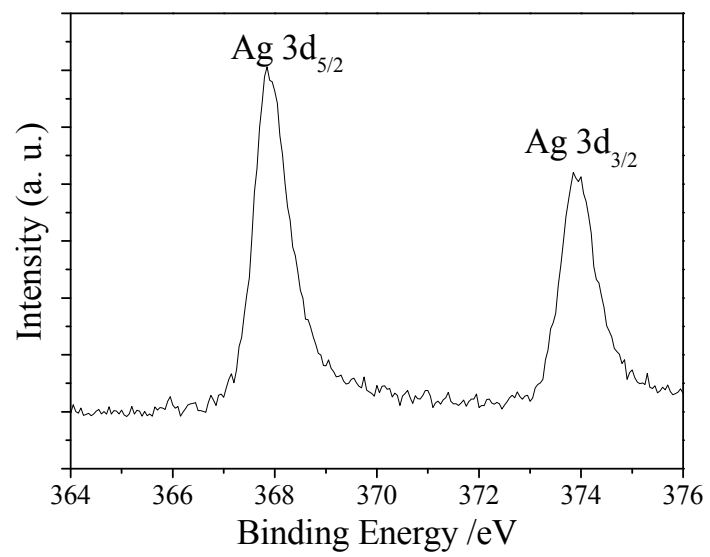


Figure S4. XPS spectra of Ag 3d for Ag_{0.1}Pd_{0.9}/rGO.

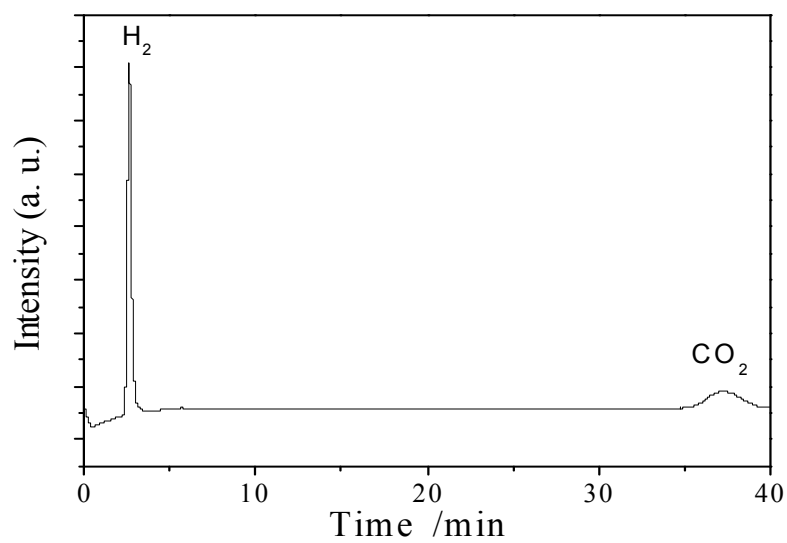


Figure S5. GC spectrum using TCD for the evolved gas from FA/SF system (1 M/0.67 M, 5 mL) over Ag_{0.1}Pd_{0.9}/rGO at 298 K.

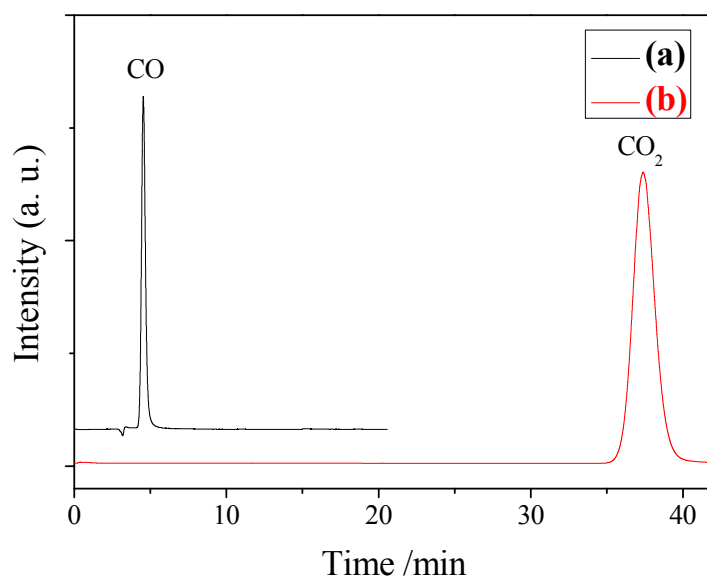


Figure S6. GC spectrum using FID-Methanator for (a) commercial pure CO, and (b) the evolved gas from FA/SF (1 M/0.67 M, 5 ml) over Ag_{0.1}Pd_{0.9}/rGO ($n_{AgPd}/n_{FA} = 0.02$) at 298 K.

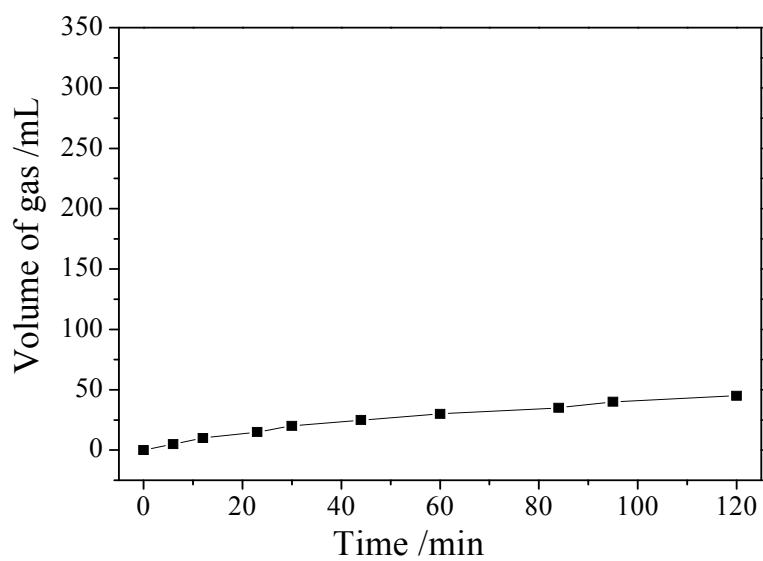


Figure S7. Gas generation by the decomposition of aqueous solution of FA/SF (1 M/0.67 M, 5 ml) vs time in the presence of physical mixture of $\text{Ag}_{0.1}\text{Pd}_{0.9}$ and rGO ($n_{\text{AgPd}}/n_{\text{FA}} = 0.02$) at 298 K under ambient atmosphere.

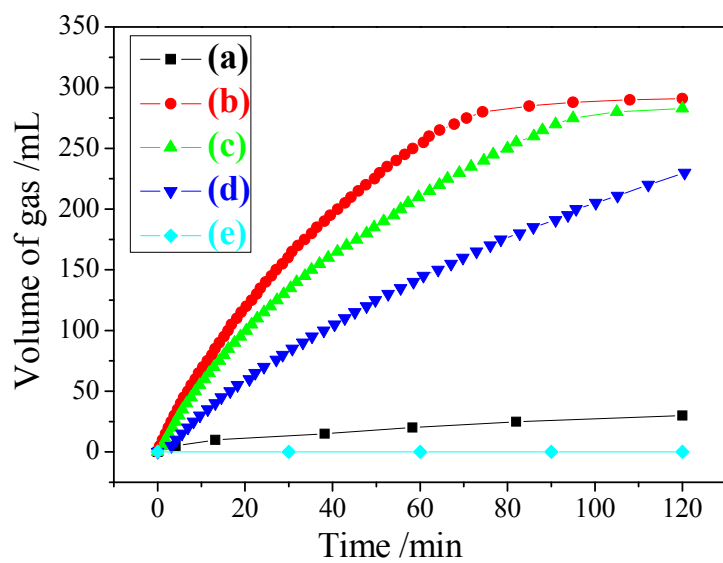


Figure S8. Gas generation by decomposition of FA/SF(1 M/0.33 M, 5 ml) with different ratios of Ag/Pd supported on rGO vs time (a) Pd/rGO, (b) Ag_{0.1}Pd_{0.9}/rGO, (c) Ag_{0.2}Pd_{0.8}/rGO, (d) Ag_{0.5}Pd_{0.5}/rGO, (e) Ag/rGO ($n_{AgPd}/n_{FA} = 0.02$) at 298 K under ambient atmosphere.

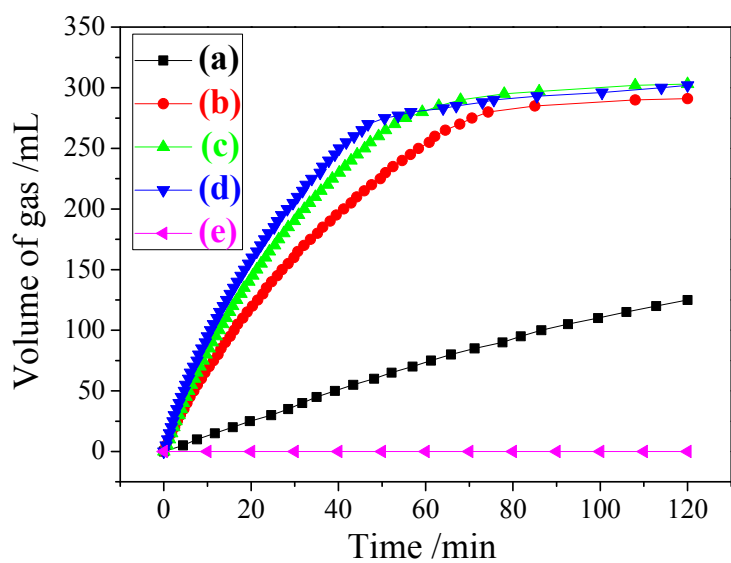


Figure S9. Gas generation by decomposition of FA/SF with different FA molar percents ($n_{FA} = 5$ mmol) (a) 100%, (b) 75%, (c) 60%, (d) 50%, (e) 0% catalyzed by Ag_{0.1}Pd_{0.9}/rGO ($n_{AgPd}/n_{FA} = 0.02$) at 298 K under ambient atmosphere.

Table S1. The initial TOF values calculated during the first 20 min of the reactions in the decomposition of FA catalyzed by various heterogeneous catalysts.

Catalyst	FA (mmol)	Additive (mmol)	Tem. (K)	n_{catalyst} (mmol)	TOF _{initial} (mol H ₂ · mol catalyst ⁻¹ · h ⁻¹) ^a	Ref.
AgPd/rGO	5.0	HCOONa (3.35)	298	0.100	105.2	This work
Pd- poly(allyl-amine)	15.2	None	295	0.040	46.1	38
Ag@Pd	10.0	None	293	0.200	15.5	6
CoAuPd/C	5.0	None	298	0.100	36.9	8

Calculation methods:

$$x_a = \frac{P_{\text{atm}} V_{H_2} / RT}{n_{(FA+SF)}} \quad (1)$$

Where x_a is conversion, P_{atm} is the atmospheric pressure, V_{H_2} is the generated volume of H₂ gas within 20 min, R is the universal gas constant, T is the room temperature (298 K), $n_{(FA+SF)}$ is the total molar number of reactants of FA and SF.

$$\text{TOF} = \frac{P_{\text{atm}} V_{H_2} / RT}{n_{\text{AgPd}} t} \quad (2)$$

Where V_{H_2} is the generated volume of H₂ gas within 20 min, n_{AgPd} is the molar number of AgPd catalyst, t is the reaction time (20 min) in hour.

$$R_m = \frac{n_{(FA+SF)}}{n_{FA}} \quad (3)$$

Where the R_m is the theoretical molar ratio of H₂ to CO₂ based on equations (1) and (2), n_{FA} is the molar number of FA.

References

- S1 W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* 1958, **80**, 1339.
S2 N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva, A. D. Gorchinskiy, *Chem. Mater.* 1999, **11**, 771.