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Supporting information

Improved Hydrogen Production from Formic Acid under Ambient Condition Using PdAu Catalyst on Graphene Nanosheets–Carbon Black Support

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Chemicals and materials

Formic acid (HCOOH, sinopharm Chemical Reagent Co., Ltd, ≥98%), sodium formate dehydrate ($HCOONa \cdot 2H_2O$, sinopharm Chemical Reagent Co., Ltd, ≥99.5%), carbon black (Vulcan XC-72, Cabot), palladium chloride ($PdCl_2$, Aladdin Reagent, Pd≥60%), sodium borohydride ($NaBH_4$, Aladdin Reagent, ≥98%), potassium gold chloride ($KAuCl_4 \cdot 2H_2O$, Aladdin Reagent, Au≥52%), sodium chloride (NaCl, Aladdin Reagent, ≥99%), sulfuric acid (H_2SO_4, Beijing Chemical Works, 98%), hydrochloric acid (HCl, Beijing Chemical Works, 36%~37%), potassium peroxodisulfate ($K_2S_2O_8$, Aldrich, ≥99%), phosphorus pentoxide (P_2O_5, Aldrich, ≥99.99%), potassium permanganate ($KMnO_4$, Sinopharm Chemical Reagent Co., Ltd, ≥99%), hydrogen peroxide (H_2O_2, Beijing Chemical Works, 30%), graphite powder (Alfa, 325 mesh) and nylon filter membranes (Aldrich, pore size 0.2 μm) were used as received. Ultrapure water with the specific resistance of 18.2 MΩ·cm was obtained by reversed osmosis followed by ion-exchange and filtration.

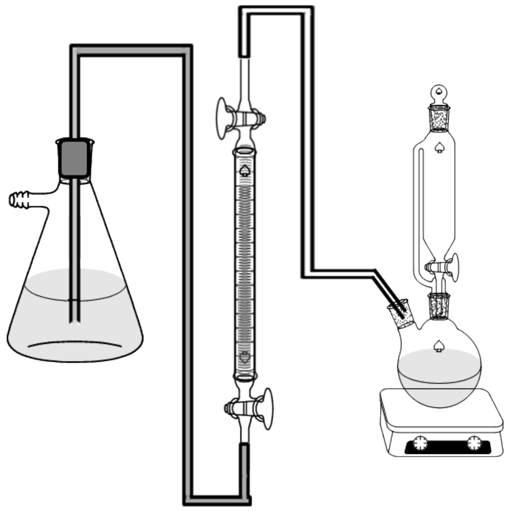

Figure S1. The illustration of apparatus for catalytic reaction.

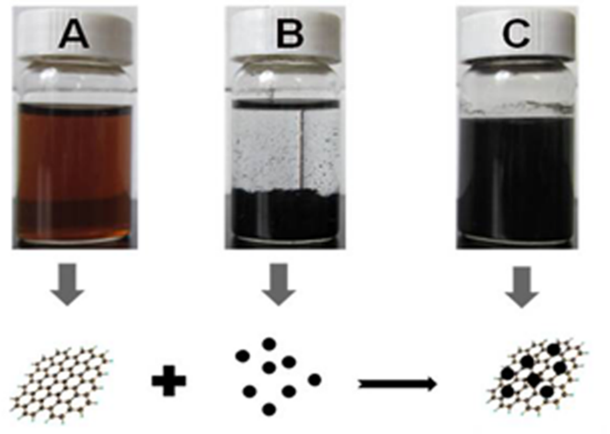

Figure S2. The pictures of different supports: A, GO; B, XC-72; C, GO-XC-72.

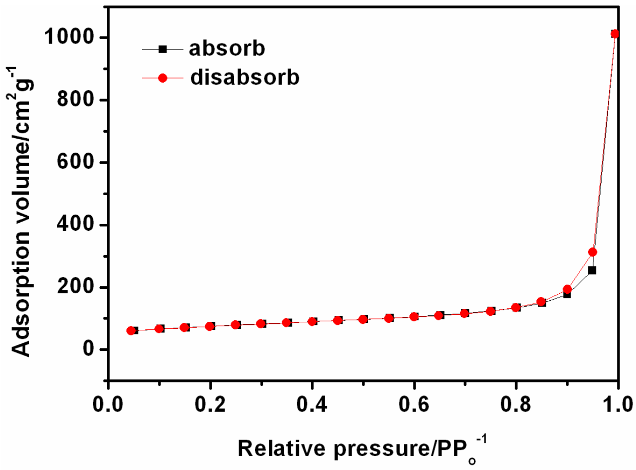

Figure S3. N_2 sorption isotherms of GO-CB.

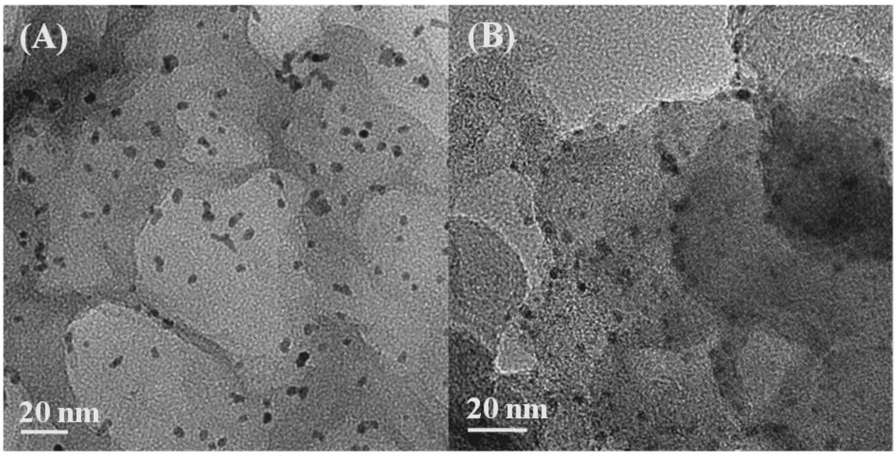

Figure S4. TEM images of (A) PdAu/GNs and (B) PdAu/CB.

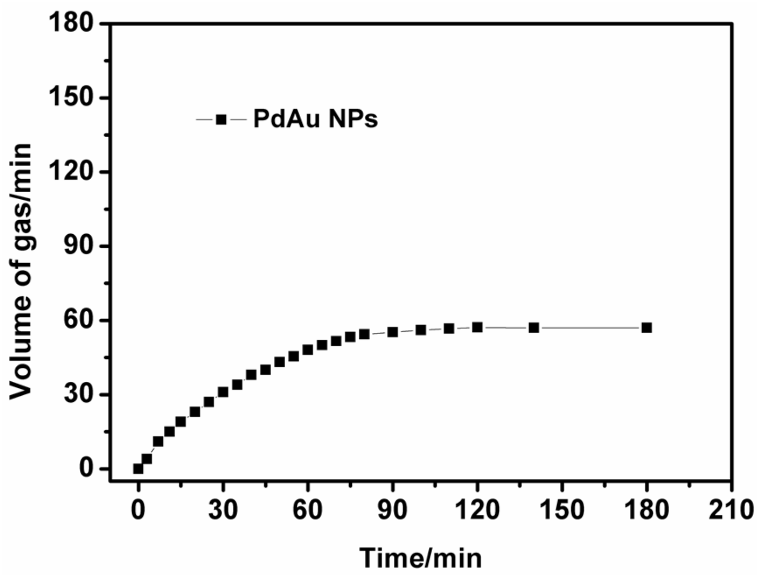

Figure S5. FA decomposition from 5 mL of solution containing 1 M FA and 1 M sodium formate using 10 mg (0.058 mmol) of PdAu NPs prepared without support.

Gas analysis of the generated gases was performed using a Techcomp GC 7900 gas chromatography Analyzer, wherein argon gas is chosen as carrying gas. Detailed gas analysis for CO was conducted by GC-TCD (GC column S/N: HO31b-04) using the corresponding calibration curves as shown in Figure S6A. And the calibration curves show excellent linearity with coefficients greater than 0.999.

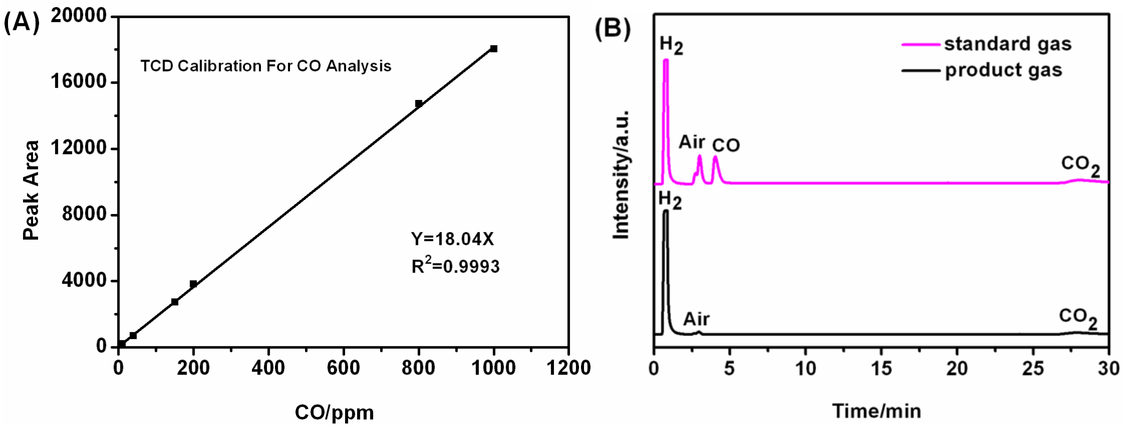

Figure S6. (A) A CO calibration curve for the GC-TCD for CO quantitative analysis. (B) Gas chromatograms of standard gas (0.2 mL, H_2:Air:CO:CO_2 = 1:1:1:1) and product gas (0.2 mL).

Mass analysis of the generated gases was performed using a ThermoStar^{TM} gas analysis system with GSD 320 mass spectrometer (Detection limit minimum: Faraday < 20 ppm, C-SEM < 1 ppm, 1-100 amu), wherein argon gas is chosen as cleaning gas. Before the reaction, the gas burette system was cleaned by argon until the mass spectral profile was obtained like Figure S7 (trace Ar). In this experiment, the gas burette system was modified by placement of trap (10 M NaOH solution) between the jacketed reactor and gas burette. The generated gas during the reaction was passed through the NaOH trap and the CO_2 was captured (The intensity of CO_2 in MS below E-11.). From Figure S7, 10 ppm CO in Ar can be found clearly at m = 28. However, no detectable CO peak can be found from the generated gas. Then the content of CO in generated gas below 10 ppm is concluded.

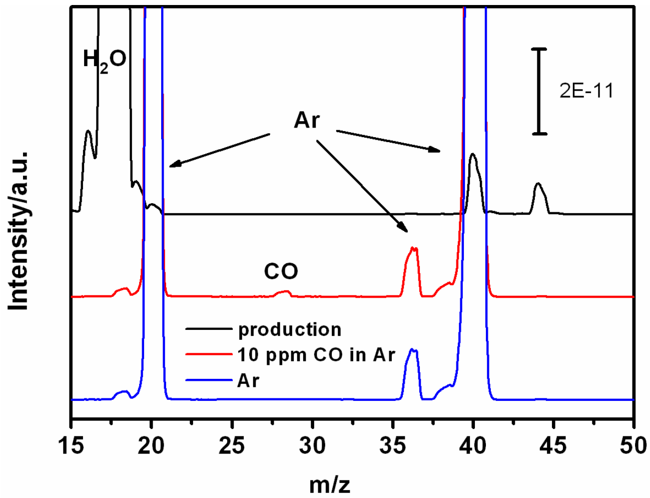

Figure S7. Mass spectral profiles of gases (C-SEM).

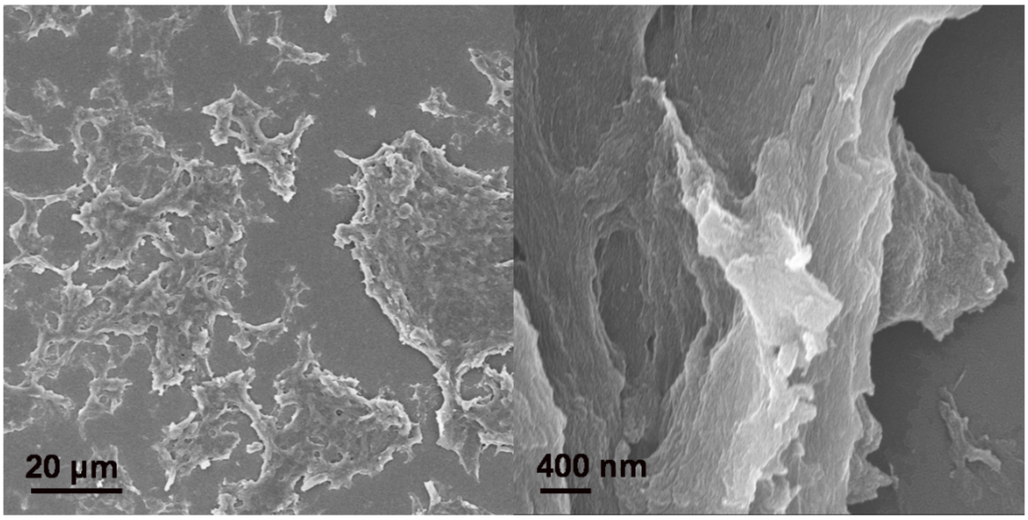

Figure S8. SEM images of PdAu/GNs after the reaction.

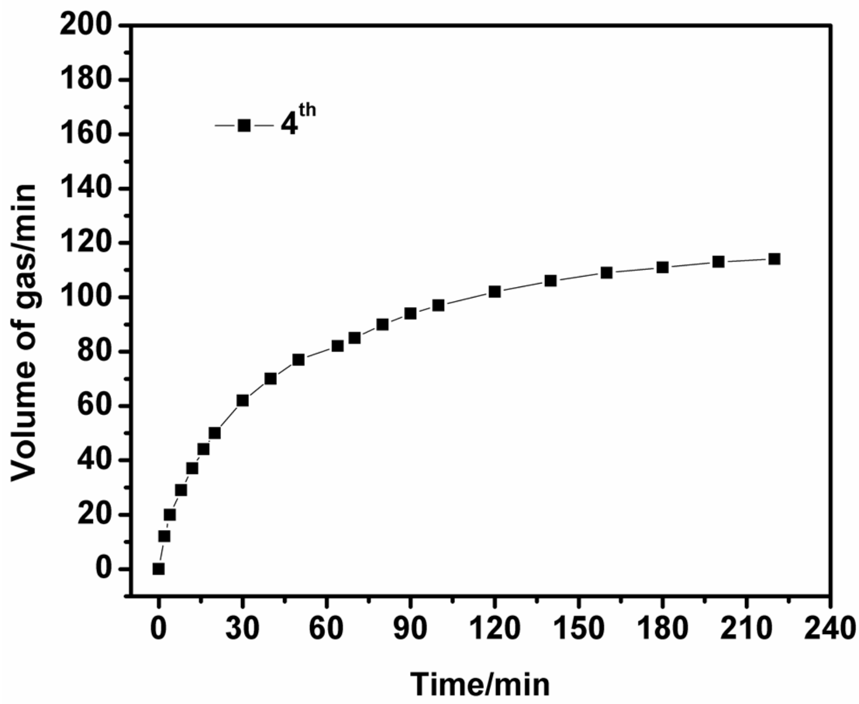

Figure S9. The 4th cycle testing of formic acid decomposition on PdAu/GNs-CB.