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Supplementary Information

Ultrafine PdAg nanoparticles immobilized on nitrogen-doped carbon/cerium oxide for superior dehydrogenation of formic acid

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1. Materials

Formic acid (HCOOH, Aladdin reagent Co., Ltd, >99%), silver nitrate ($AgNO_3$, Shanghai Makclin Biochemical Co., Ltd, 99.9%), potassium chloropalladite (K_2PdCl_4, Sigma-Aldrich Co. LLC, 99%), sodium borohydride ($NaBH_4$, Sinopharm Chemical Reagent Co., Ltd, >96%), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, Shanghai Makclin Biochemical Co., Ltd, ≥99.5%), 2-methylimidazole ($C_4H_6N_2$, Shanghai Makclin Biochemical Co., Ltd, ≥98%), N,N-Dimethylformamide (C_3H_7NO, Shanghai Makclin Biochemical Co., Ltd, ≥98.5%), nitric acid (HNO_3, Shanghai Makclin Biochemical Co., Ltd, 65%-68%), cerium nitrate hexahydrate ($CeN_3O_9 \cdot 6H_2O$, Shanghai Makclin Biochemical Co., Ltd, 99.95%), sodium carbonate (Na_2CO_3, Sinopharm Chemical Reagent Co., Ltd, >96%), sodium formate ($CHNaO_2$, Sinopharm Chemical Reagent Co., Ltd, 99.9%), vulcanxc-72 carbon (Cabot corporation, ≥97 %), multi-walled carbon nanotube (Shandong Dazhan nano materials Co., Ltd, 97%) 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.

2. Synthesis of zeolitic imidazolate framework (ZIF-8):

350 mg of $Zn(NO_3)_2 \cdot 6H_2O$ and 200 mg of 2-methylimidazole were placed in a 20 mL screw-top vial and dissolved in 15 mL of DMF. Three drops of HNO_3 were added to a

mixture with a Pasteur pipet, and complete dissolution was achieved by sonication. The vial was capped and placed in an oven at 120 °C for 24.

3. Synthesis of nitrogen-doped carbon:

The prepared ZIF-8 was transferred into a tube furnace and heat-treated at 900 °C for 2h with a heating rate of 5 ◦C/min in an argon flow to pyrolyze the organic species and zinc. The subsequent ultrasonication in deionized water, followed by washing with deionized water, , resulted in a nitrogen-doped carbon.

4. Catalytic measurement:

The PdAg/CeO_x-NPC pre-catalyst was placed in a two-necked round-bottomed flask (30 mL), which was placed in a water bath at a preset temperature (20-50 °C) under ambient atmosphere. A gas burette filled with water was connected to the reaction flask to measure the volume of released gas (lab temperature kept constant at 25 °C during measurements). When 2.5 mL of the mixed aqueous solution containing 3 mmol FA and 3 mmol SF was injected into the mixture, the volume of the released gas was monitored by recording the displacement of water in the gas burette

5. Durability testing of the catalysts:

For testing the durability of PdAg/CeO_x-NPC catalysts, 3 mmol FA was subsequently added into the reaction flask after the completion of the first-run decomposition of FA. Such test cycles of the catalyst for the decomposition of FA were carried out for 5 runs

at 30 °C by adding FA.

6. Calculation of turnover frequency (TOF)

The TOF reported here is an apparent TOF value based on the number of Pd and Ag atoms in catalyst, which is calculated from the equation as follow:

$$TOF = P_0V/(RTn_{PdAg}t)$$

Where P_0 is the atmospheric pressure (101325 Pa), V is the final generated volume of H_2/CO_2 gas, R is the universal gas constant (8.3145 m^3 Pa mol^{-1} K^{-1}), T is the room temperature (298 K), n_{PdAg} is the total mole number of Pd and Ag atoms in catalyst and *t* is the completion time of the reaction in hour.

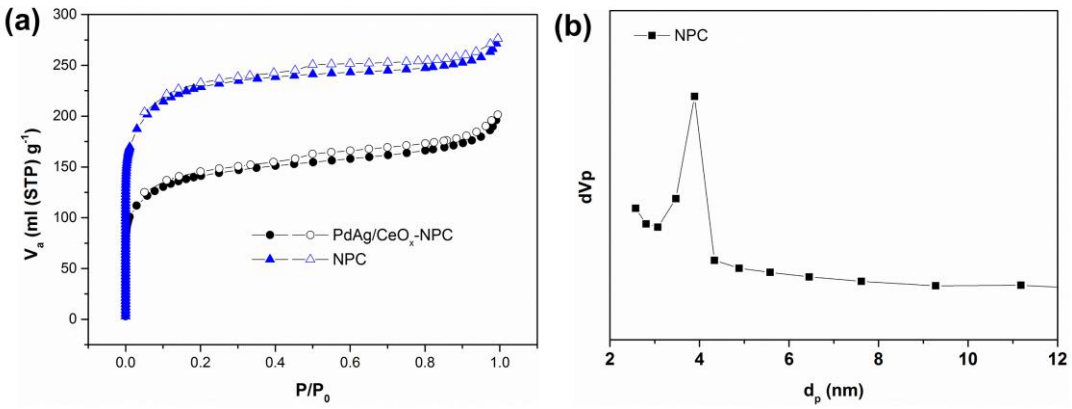

Figure S1 (a) N_2 sorption isotherms and (b) the corresponding pore size distributions of PdAg/CeO_x-NPC and NPC/MXene.

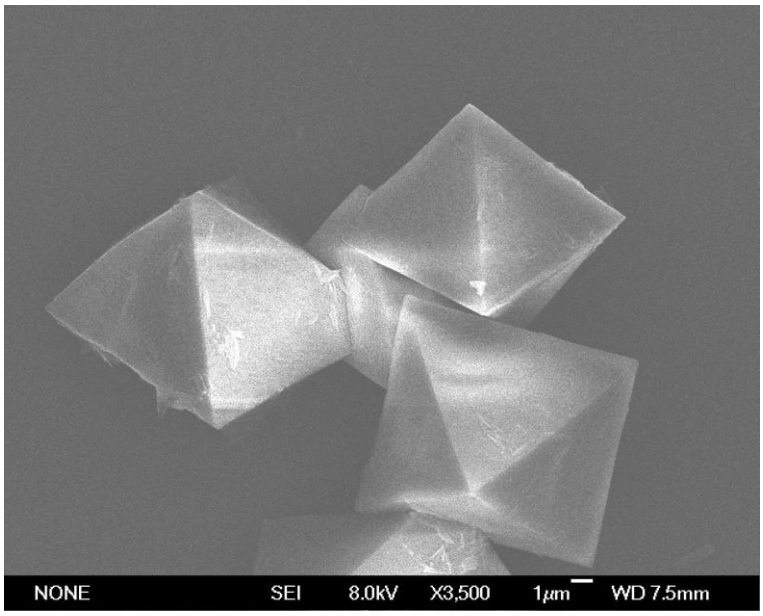

Figure S2 SEM image of pristine ZIF-8.

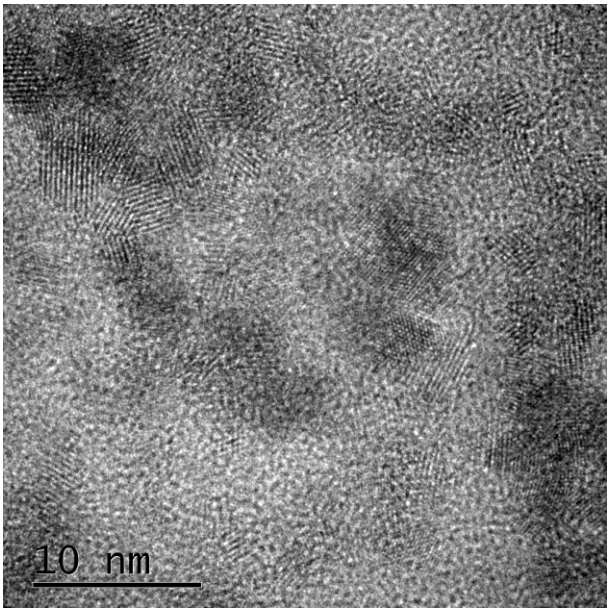

Figure S3 TEM image of PdAg/CeO_x-NPC.

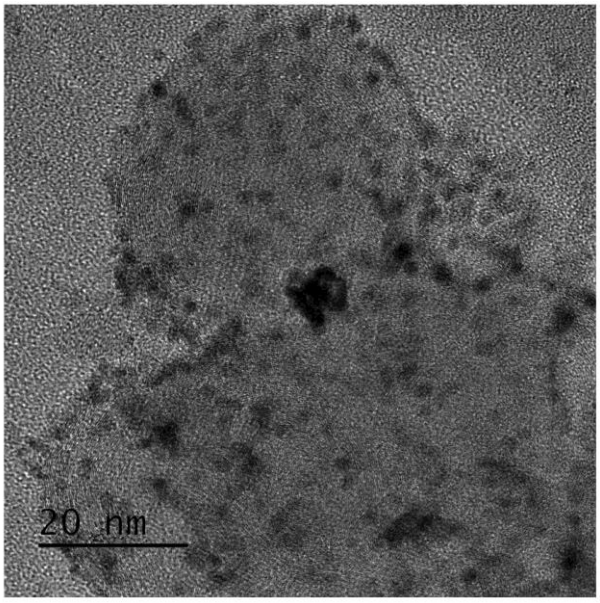

Figure S4 TEM image of PdAg/CeO_x-XC 72R.

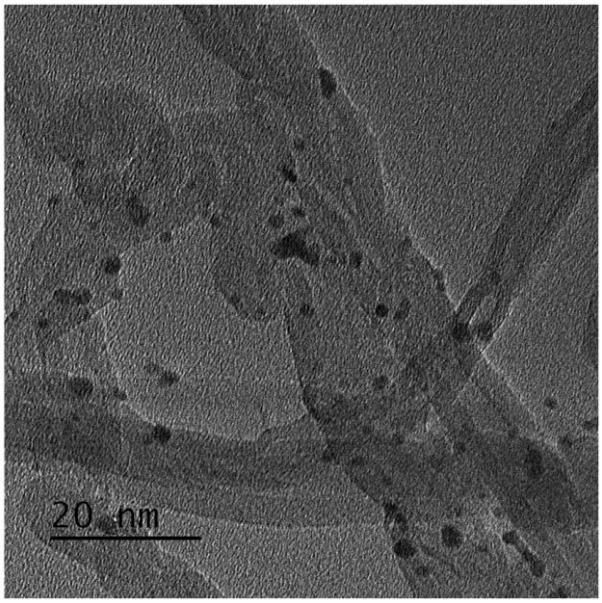

Figure S5 TEM image of PdAg/CeO_x-MNCTs.

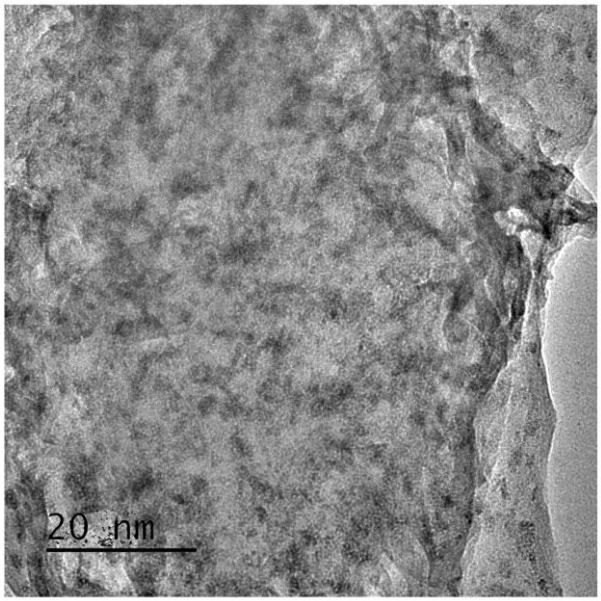

Figure S6 TEM image of PdAg/CeO_x-rGO.

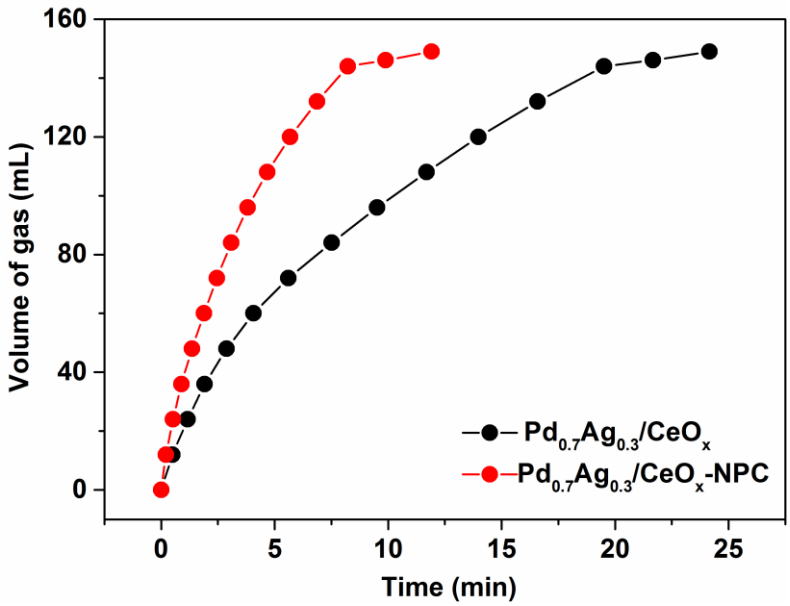

Figure S7 Gas generation from FA decomposition versus time over $Pd_{0.7}Ag_{0.3}/CeO_x$-NPC and $Pd_{0.7}Ag_{0.3}/CeO_x$. The molar ratio of catalyst/FA = 0.0083.

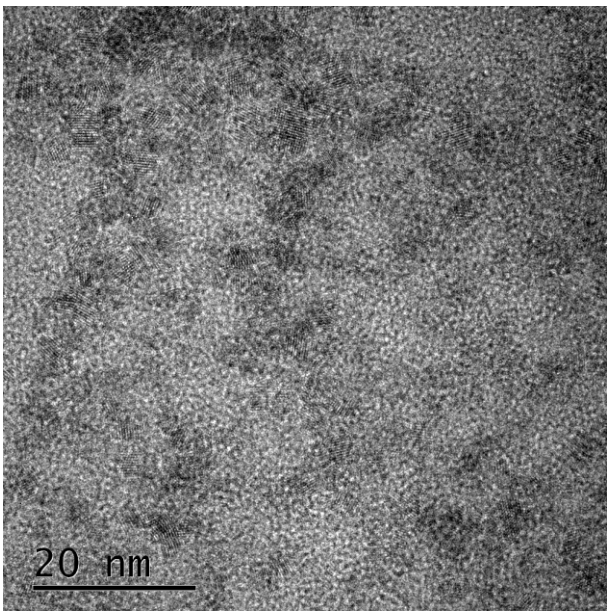

Figure S8 TEM image of the PdAg/CeO_x-NPC after the fifth cycle at 303 K.

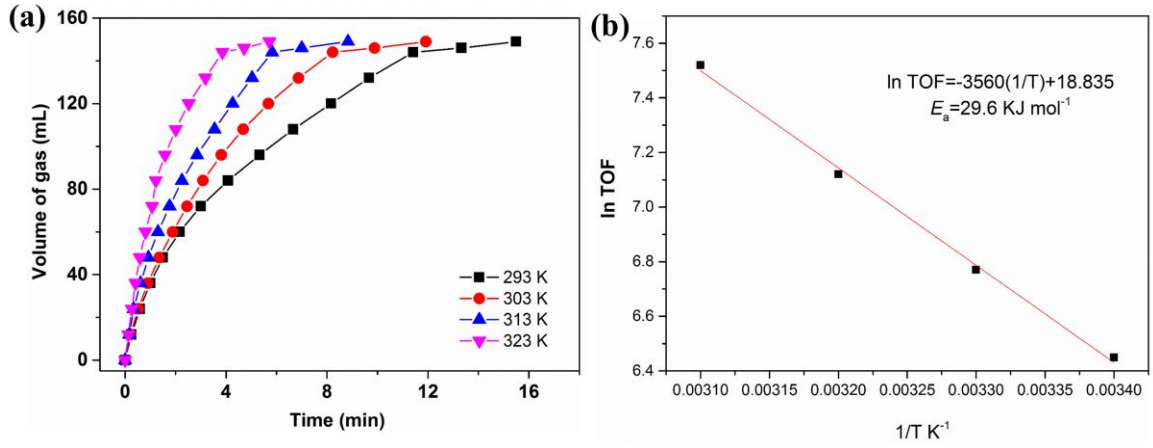

Figure S9 Gas generation from FA decomposition versus time over $Pd_{0.7}Ag_{0.3}/CeO_x$-NPC at different reaction temperatures (a); arrhenius plot (ln(TOF) vs. 1/T (b). The molar ratio of catalyst/FA = 0.0083.

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