

Supporting Information for:

Mechanistic studies into the selective production of 2,5-furandicarboxylic acid from 2,5-bis(hydroxymethyl)furan using Au-Pd bimetallic catalyst supported on nitrated carbon material

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1.1 Preparation of the AuPd/N-BN_xC nanocatalysts

By the Stober method, tetraethyl silicate (TEOS) was added to ethanol and NH₃OH to generate silica nanospheres of uniform size. The specific production method was as follows: 3.14 mL NH₃OH, 10 mL deionized water and 90 mL anhydrous ethanol were added to the flask, and 6 mL tetraethyl silicate was added drop by drop into the flask and stirred at 30 °C for 1.0 h. After the reaction, the silica nanoparticles were centrifuged and washed with ethanol three times. On account of a large number of hydroxyl groups on the surface of silica, the hydrophilicity was relatively strong, and the compatibility and dispersion of organic compounds were poor. Therefore, it must be modified organically. 3-Methylacroxypopyl trimethoxysilane (KH-570) was a typical silane coupling agent used for oxide surface modification. The modified silica surface of KH-570 contains vinyl, which greatly expands and improves the application performance of silica. Toluene was used as a solvent to prevent the KH-570 hydrolysate from polycondensation and reduce its coupling efficiency. The resulting SiO₂ nanospheres were added to 100 mL toluene and nitrogen was introduced. After 30 min, with the reflux device drop 6.0 mL KH-570, and heat the mixture under 90 °C for 24 h. After centrifugation, the solid was washed three times with toluene and then dried at 80 °C for 24 h. The resulting product was named v-SiO₂. After that, v-SiO₂ was further modified by precipitation polymerization. 0.2 g of v-SiO₂, 80 mg of AIBN and 60 mL acetonitrile was added into a single-neck flask, and 0.8 g polymeric monomer (Methylene-bis-acrylamide and Acrylamide) was added into nitrogen for 30 min after uniform ultrasonic dispersion. After sealing, it was reacted at 50 °C for 6.0 h in a water bath oscillator and then heated to 60 °C for 24 h. After the reaction, the sample should be centrifuged and washed with acetonitrile three times. The samples with different molar ratios of AM and MBA are recorded as SiO₂@N_xP, where the letter X represents the molar ratios of each element (x = 1, 2, 3, corresponding to AM: MBA = 1: 1, 2: 1, 3: 1, respectively).

Then SiO₂@N_xP was calcined in tubular furnace at 800 °C (heating rate 5 °C /min) for 2.0 h, and the product was named SiO₂@N_xC. To obtain a larger specific surface area, SiO₂@N_xC was treated with 40 wt% HF for 24 h to remove silica and obtain a hollow structure. The product was a porous bowl-shaped nitrogen-rich nitrated carbon material,

remember to BN_xC . It is also nitrified, and the sample is treated for 2.0 h with 30 wt% nitric acid in an oil bath equipped with a reflux device at 140 °C. And it was named $\text{N-BN}_x\text{C}$.

The bimetal was loaded onto the carrier by injection reduction method as follows: 1.0 wt% PVA aqueous solution was added into the mixed solution of PdCl_2 and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ to produce a stable AuPd nanoparticle solution. The molar ratio of Au to Pd was 1: 1 and metal load is 2.0 wt%, and the molar ratio of PVA: (Au + Pd) was 1.2: 1. The pH value was adjusted by adding HCl. Under the stirring condition of pH = 3, the freshly prepared sodium borohydride solution was dropped into it. The molar ratio of sodium borohydride to (Au + Pd) was 5: 1. Finally, the carrier was added, vigorously stirred at room temperature for 2.0 h, centrifuged, washed and dried by ethanol to obtain the final catalyst. The catalyst named $\text{Au}_1\text{Pd}_1/\text{N-BN}_x\text{C}$ was obtained.

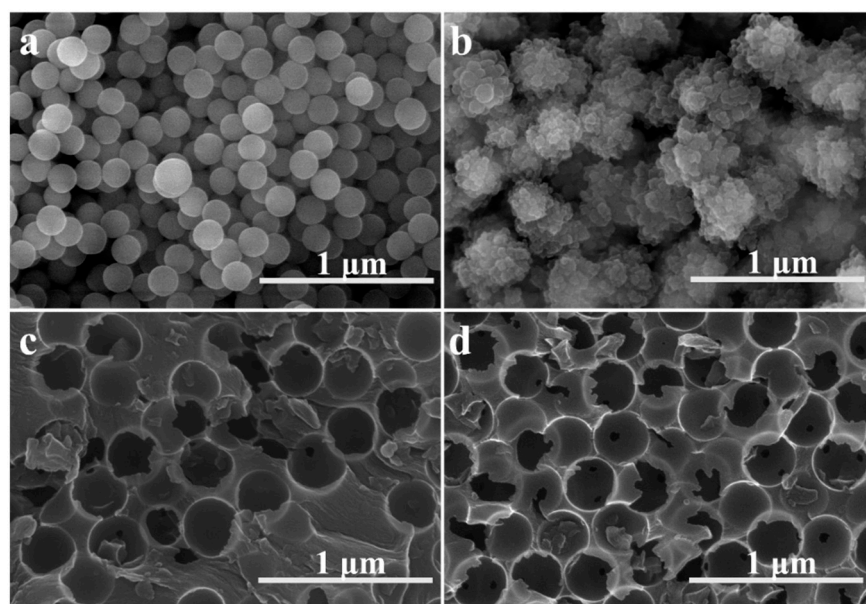


Figure S1. SEM images of SiO_2 (a), $\text{SiO}_2@\text{N}_x\text{P}$ (b), BN_xC (c), and $\text{N-BN}_x\text{C}$ (d).

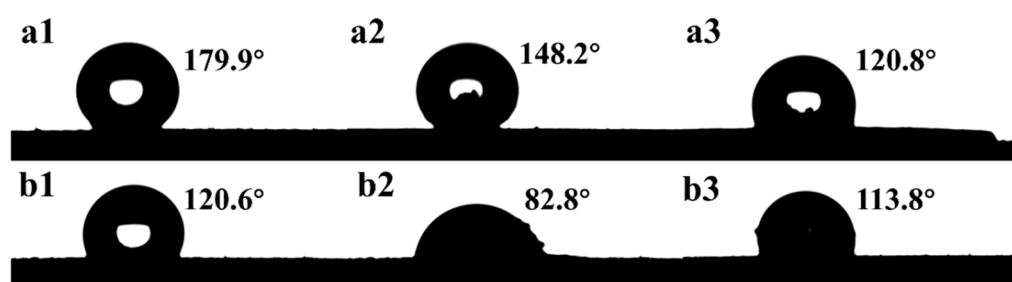


Figure S2. Contact angle data of BN_xC (a1-a3) and $\text{N-BN}_x\text{C}$ (b1-b3) ($x = 1, 2, 3$, corresponding to MBA:AM = 1:1, 1:2, 1:3, respectively).

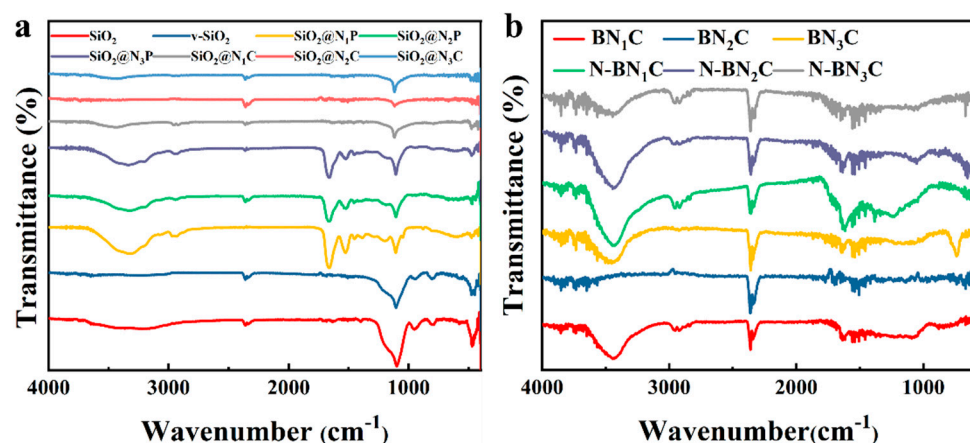


Figure S3. FTIR spectra of SiO₂, v-SiO₂, SiO₂@N_xP, SiO₂@N_xC (a), BN_xC and N-BN_xC (b) ($x = 1, 2, 3$, corresponding to MBA: AM = 1: 1, 1: 2, 1: 3).

FTIR analysis of SiO₂, v-SiO₂, SiO₂@N_xP, SiO₂@N_xC, BN_xC, and N-BN_xC was carried out. The results were shown in Figure S2. It can be seen that the sample absorption peak is consistent with the standard spectrum of SiO₂. The strong and wide absorption peak at 1100 cm⁻¹ was Si-O-Si antisymmetric stretching vibration, and the peaks at 799 cm⁻¹ and 470 cm⁻¹ were Si-O bond symmetric stretching vibration and bending vibration. The wide peak at 3447 cm⁻¹ was the structural H₂O-OH antisymmetric stretching vibration, the peak at 1654 cm⁻¹ was the H-O-H bending vibration peak of water, and the peak at 958 cm⁻¹ was the absorption peak of Si-OH bending vibration. And it could be found that the peak at 958 cm⁻¹ disappears, after calcination, indicating that Si-OH was completely coagulated into the Si-O-Si bond. Moreover, the Si-O-Si bond completely disappeared after the removal of silica, and the benzene ring skeleton vibration peak appeared at 1654 cm⁻¹, C-C bond and C-H bond absorption peak at 1024 cm⁻¹ and 2918 cm⁻¹, respectively. A characteristic absorption peak of -NH₂ appeared at 3449 cm⁻¹.

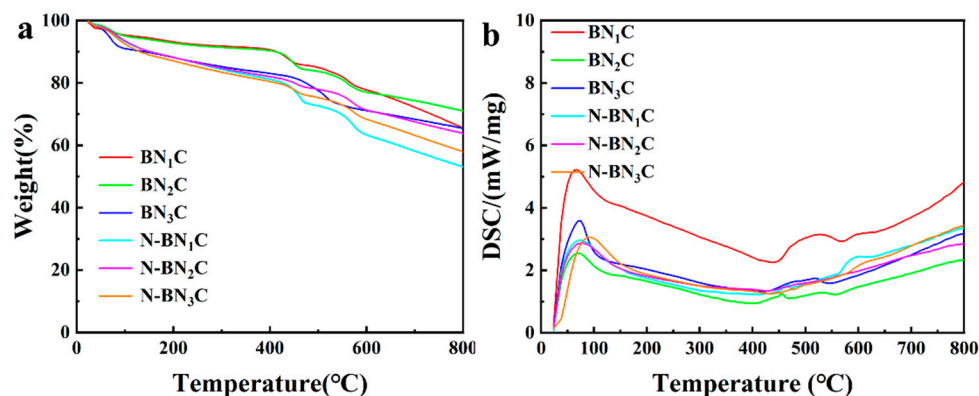


Figure S4. TG(a) and DSC(b) curves of BN_xC and N-BN_xC (x=1,2,3, respectively).

The thermal stability of BN_xC and N-BN_xC was tested by the TG-DSC method, as shown in Figure. S3. BN_xC had a small mass loss at high temperatures, of which BN₂C was the most stable. After nitrification, the mass loss was more, but it was also very stable, and N-BN₂C in N-BN_xC had the best thermal stability. A peak was found in the DSC curve at around 500 °C, which corresponds to a violent exothermic process in the sample near this temperature. It had to do with graphite or graphene.

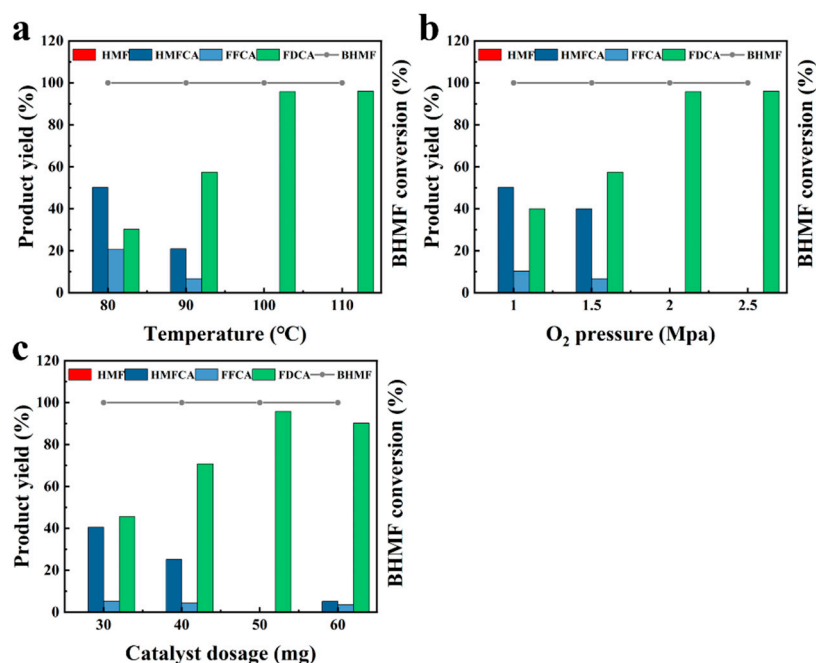


Figure S5. The effects of reaction temperature (a), oxygen pressure (b) and catalyst dosage (c) were investigated with Au₁Pd₁/N-BN₂C as catalyst.

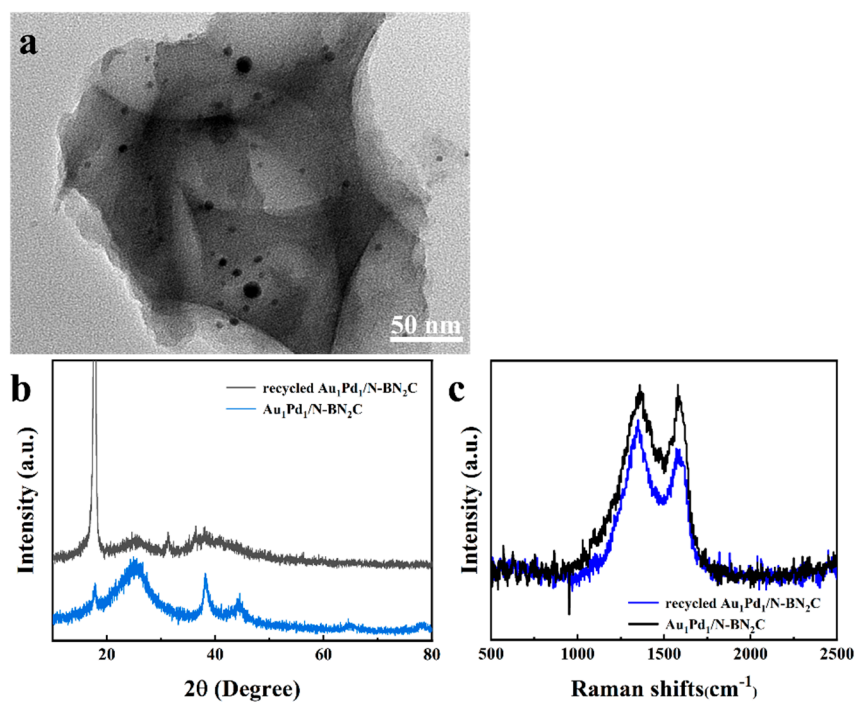


Figure S6. TEM images of recycled Au₁Pd₁/N-BN₂C (a), XRD (b) and Raman (c) spectra of Au₁Pd₁/N-BN₂C and recycled Au₁Pd₁/N-BN₂C.

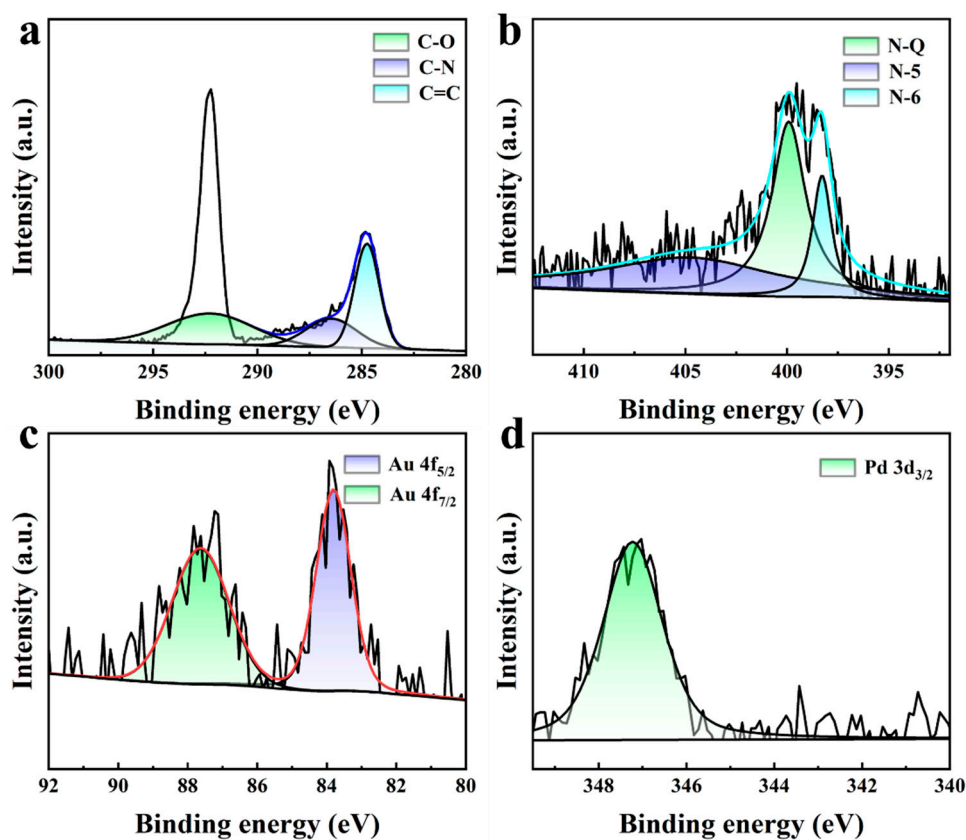


Figure S7. C 1s (a), N 1s (b), Au 4f (c) and Pd 3d (d) XPS spectra of recycled Au₁Pd₁/N-BN₂C.

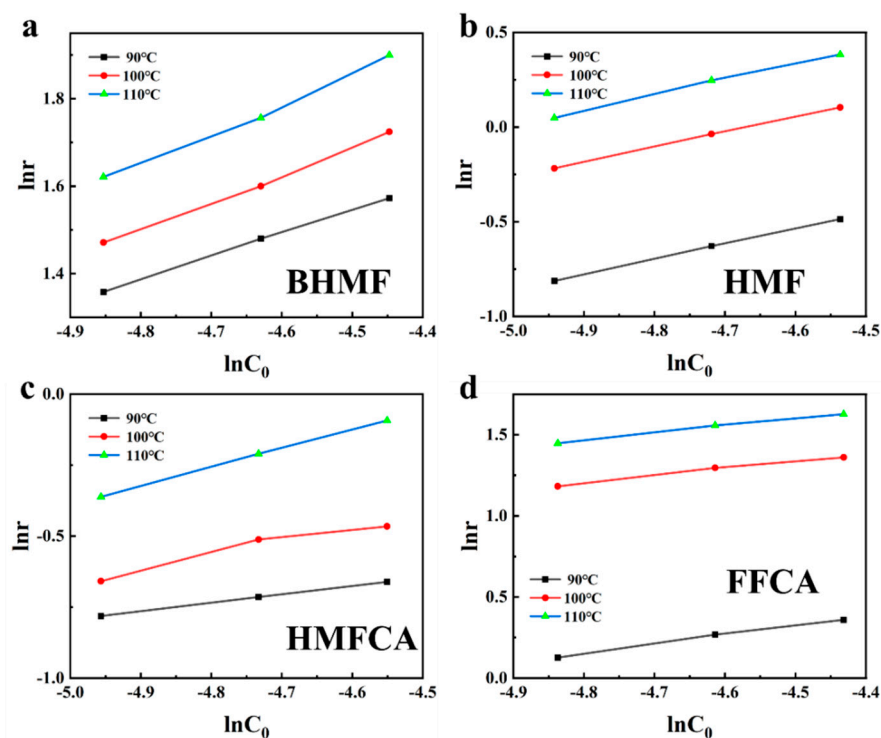


Figure S8. $\ln r$ versus the initial concentration of BHMf (a) HMF (b), HMfCA (c) and FFCA (d) ($\ln C_0$).

Table S1. Kinetic parameters of BHMf conversion in water (k_1).

Temperature/ $^{\circ}\text{C}$	Temperature/K	K_1 (h^{-1})	$T^{-1}/(10^{-3} \cdot \text{K}^{-1})$	$\ln(k_1)$
90	363.15	25.47	2.75	3.24
100	373.15	44.62	2.68	3.80
110	383.15	69.46	2.61	4.24

Table S2. Kinetic parameters of HMF conversion in water (k_1).

Temperature/ $^{\circ}\text{C}$	Temperature/K	K_1 (h^{-1})	$T^{-1}/(10^{-3} \cdot \text{K}^{-1})$	$\ln(k_1)$
90	363.15	18.51	2.75	2.92
100	373.15	27.85	2.68	3.33
110	383.15	36.32	2.61	3.59

Table S3. Kinetic parameters of HMfCA conversion in water (k_1).

Temperature/ $^{\circ}\text{C}$	Temperature/K	K_1 (h^{-1})	$T^{-1}/(10^{-3} \cdot \text{K}^{-1})$	$\ln(k_1)$
90	363.15	1.99	2.75	0.69
100	373.15	5.71	2.68	1.74
110	383.15	18.62	2.61	2.92

Table S4. Kinetic parameters of FFCA conversion in water (k_1).

Temperature/°C	Temperature/K	K_1 (h ⁻¹)	$T^{-1}/(10^{-3} \cdot K^{-1})$	$\ln(k_1)$
90	363.15	23.92	2.75	3.17
100	373.15	40.98	2.68	3.71
110	383.15	63.24	2.61	4.15