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Supplementary Material

Highly Efficient Hierarchical Porous Carbon-Supported Pd-Based Catalysts for Additive-Free Dehydrogenation of Formic Acid

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Abstract: Formic acid (FA) is one of the most prospective hydrogen carriers for renewable energy transformation. In this context, the addition of extra-amine is always required for promoting the reactivity of FA, which is still a key challenge. Herein, we report a simple but effective strategy to synthesize Pd nanoparticles, supported on NH_2-functionalized, phosphorous-doped glucose-based porous carbon (NH_2-P-GC). The introduction of NH_2- groups on the support acts as an immobilized amine-additive for FA dehydrogenation, while phosphorus not only serves as an electronic promoter to keep Pd in the electronic deficient state for FA dehydrogenation, but also as an enlarger of the aperture size of the carbon. As a result, the Pd/NH_2-P-GC has exceptional catalytic activity, 100% H_2 selectivity, CO generation that is undetectable, and good reusability for hydrogen production from FA. In the additive-free dehydrogenation of aqueous FA solution, the initial turnover frequency (TOF) can reach 5126 h^{-1} at room temperature, which is substantially higher than the best heterogeneous catalyst so far recorded. Overall, the system's high activity, selectivity, stability, and simplicity in producing CO-free H_2/CO_2 gas from FA, without the need for any additive, makes it attractive for practical deployment.

Keywords: formic acid; dehydrogenation; amine functionalization; porous carbon; palladium nanoparticles

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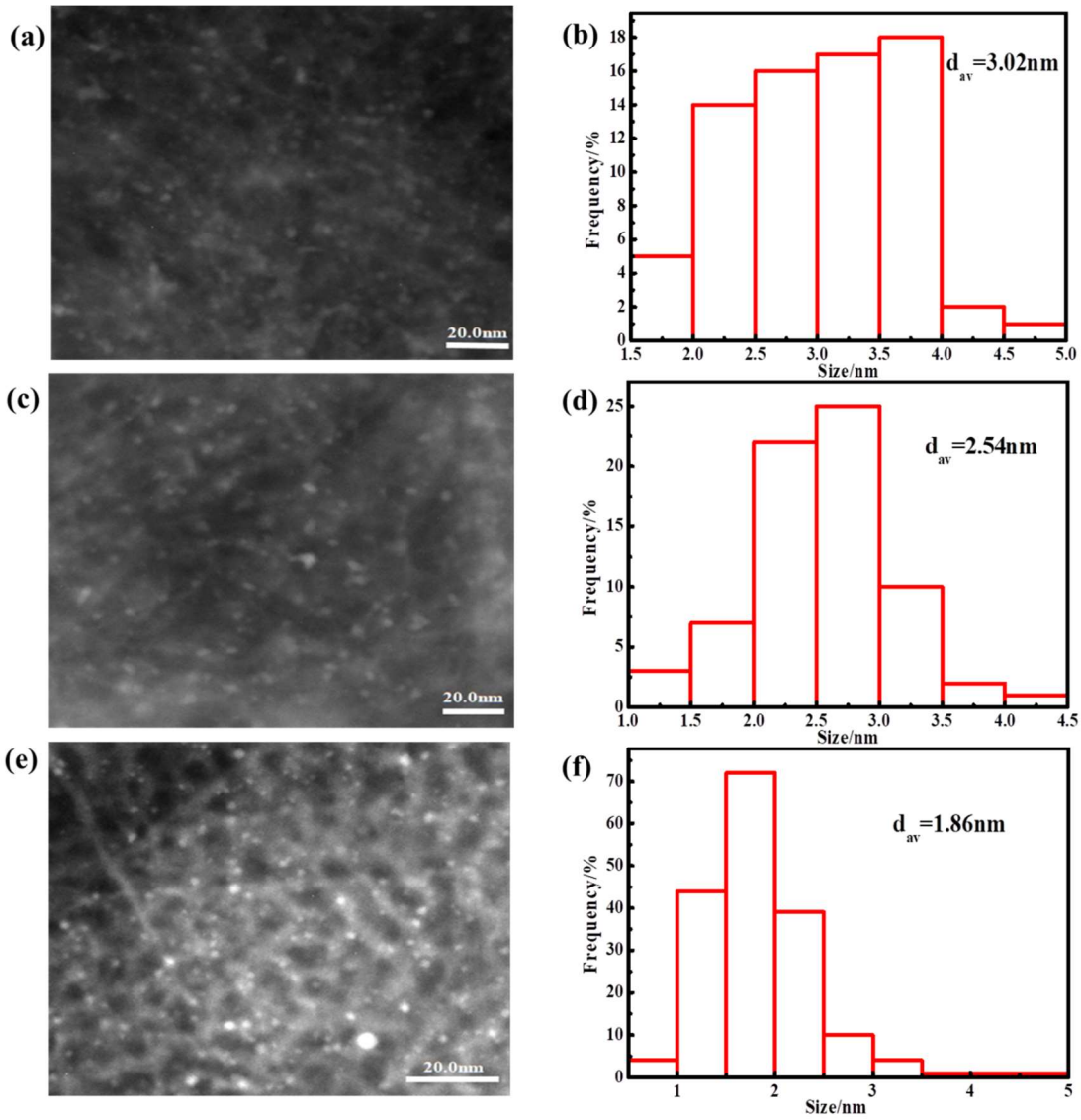

Figure S1. HRTEM image and histograms with Pd nanoparticle size distributions of Pd/P-GC (**a**,**b**); Pd/NH_2-GC (**c**,**d**) and Pd/NH_2-P-GC-Used (**e**,**f**).

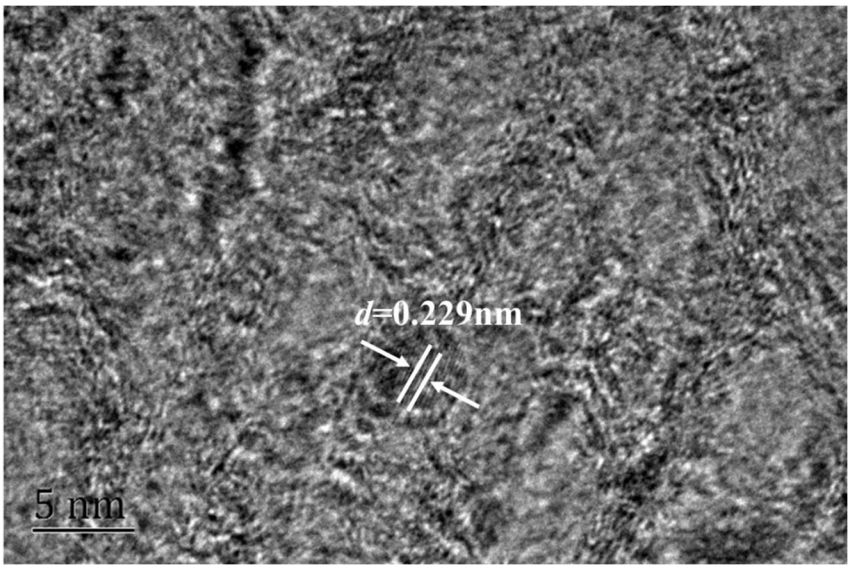

Figure S2. HRTEM image and corresponding FFT pattern of Pd/NH_2-P-GC.

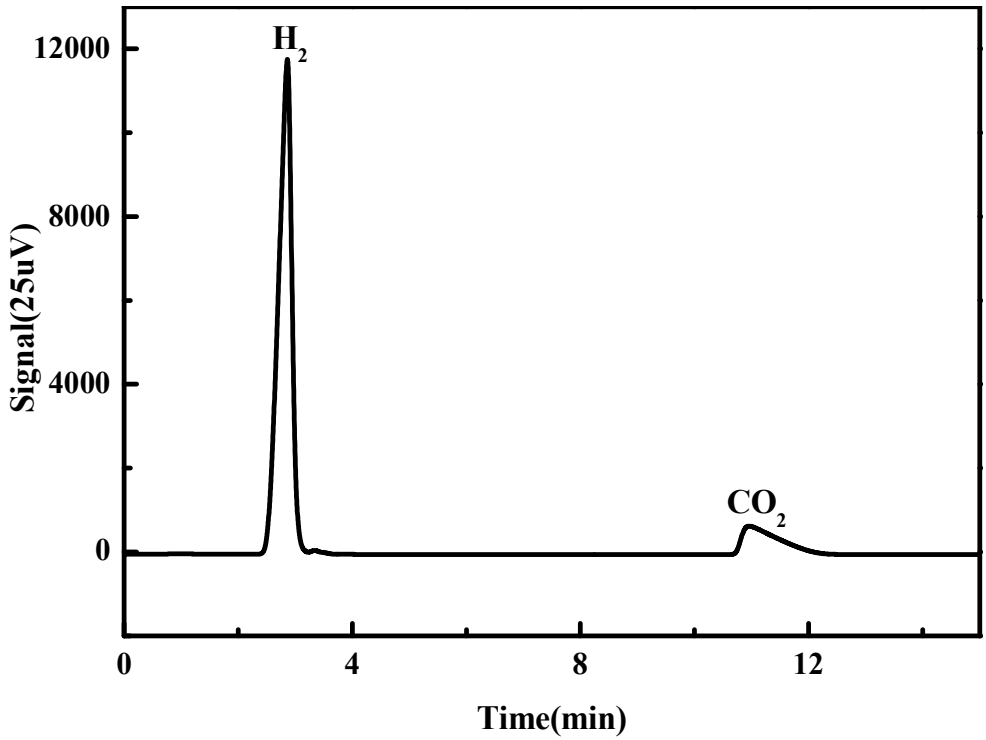

Figure S3. GC spectrum using TCD for the evolved gas from FA aqueous solution (1.0 M, 5.0 mL) over Pd/NH_2-P-GC hybrid at 298 K. (n_{metal}/n_{FA} = 0.0037).

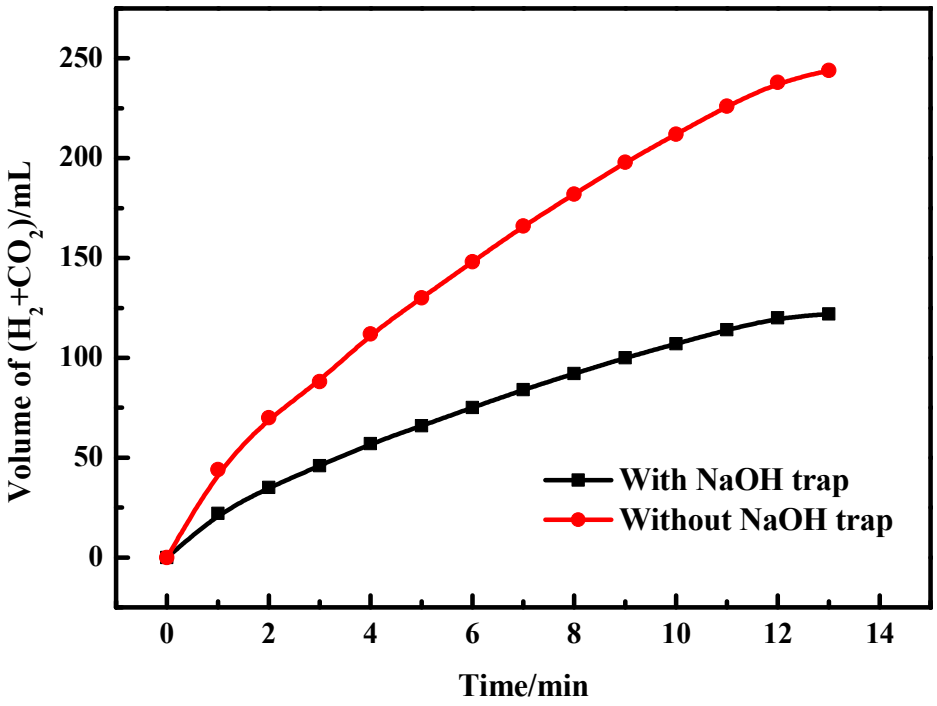

Figure S4. Volume of generated gas (H_2 + CO_2) versus time for the dehydrogenation of FA (1.0 M, 5.0 mL) without additive at 298 K over Pd/NH_2-P-GC with/without 10M NaOH trap. (n_{metal}/n_{FA} = 0.0037).

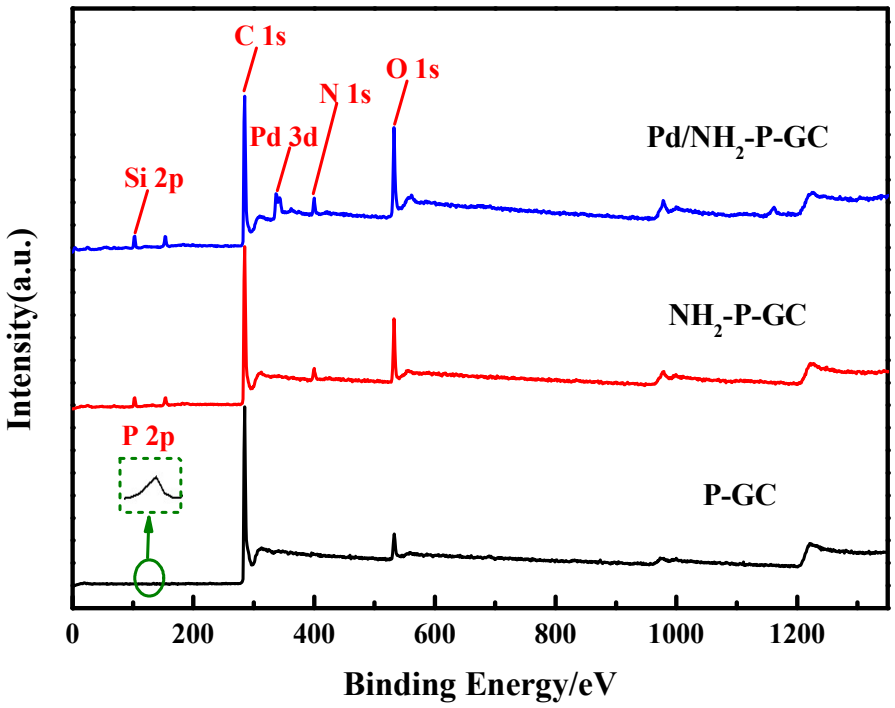

Figure S5. XPS survey spectra of Pd/NH_2-P-GC, NH_2-P-GC and P-GC.

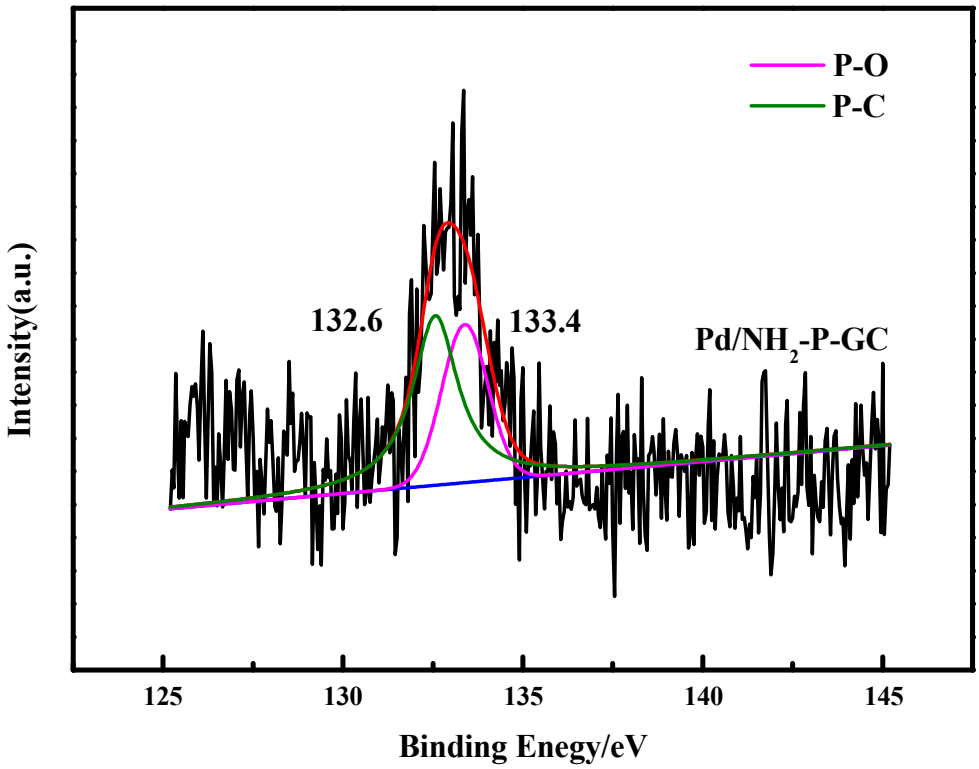

Figure S6. High-resolution XPS spectra of P 2p in Pd/NH_2-P-GC.

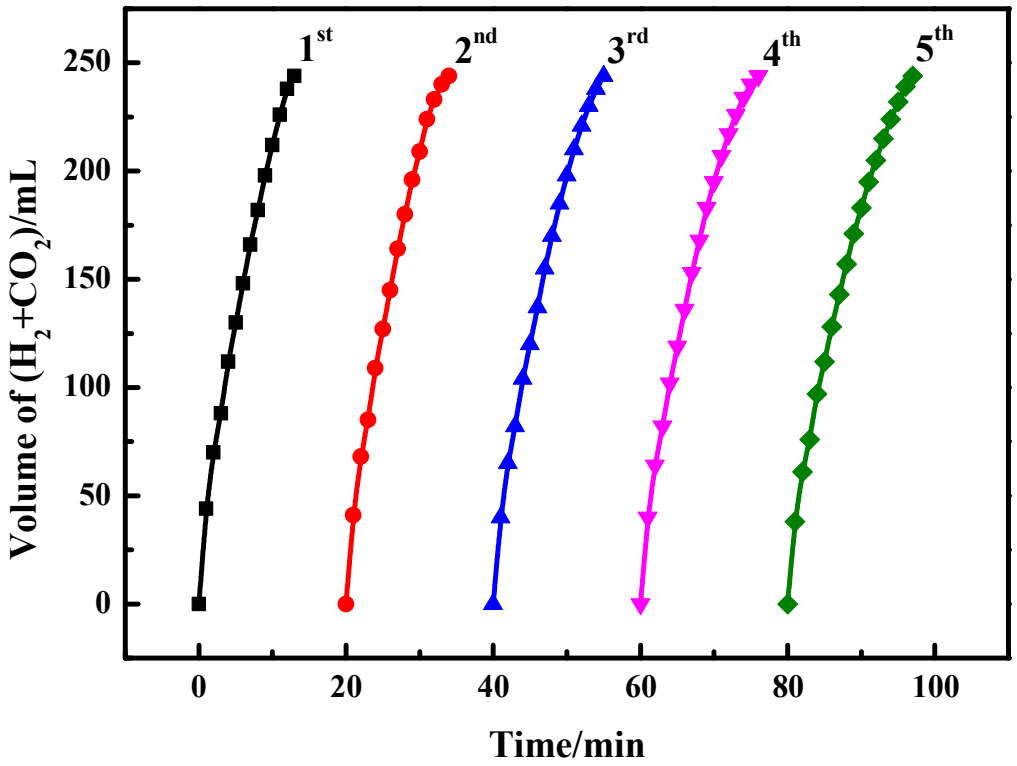

Figure S7. Recyclability of Pd/NH_2-P-GC for FA dehydrogenation.

Table S1. ICP-OES (Pd) and XPS analyses (P, N, C, and Si) for Pd/NH_2-P-GC before/after dehydrogenation reaction.

Conditions	Pd (wt%)	P (at%)	N (at%)	C (at%)	Si (at%)
Fresh prepared	2.10	0.53	5.97	75.98	6.05
After reusability test	2.12	0.45	3.89	78.98	5.12

Table S2. Initial TOF values for the decomposition of FA without additive over various heterogeneous catalysts.

Catalyst	Additive (mmol)	Tem. (K)	$TOF_{initial}$ (mol H_2 mol catalyst$^{-1}h^{-1}$)	Ea (kJ mol^{-1})	Ref.
$Ni_{0.4}Pd_{0.6}/NH_2$-N-rGO	None	298	954.3	-	1
AuPd-MnOx/ZIF-8-rGO	None	298	660.7	-	2
CoAuPd/C	None	298	80.0	-	3
$Ni_{0.4}Au_{0.15}Pd_{0.45}$/C	None	298	12.4	-	4
Au@Pd/N-mrGO	None	298	109.3	-	5
CoAuPd/DNA-rGO	None	298	104.4	-	6
PdAu-MnOx/N-SiO_2	None	298	785	26.2	7
$Pd_{60}Au_{40}$/ZrSBA-15-AP	None	298	1185	42.5	8
CrAuPd/N-SiO_2	None	298	730	49.8	9
Pd/IMIP-1	None	298	356	46.5	10
Pd/mpg-C_3N_4	None	298	144	29.1	11
AgPd	None	298	150	22.0	12
PdAg-MnO_x/N-SiO_2	None	298	482	72.4	13
Ag@Pd/C	None	298	96	-	14
$Au_{0.5}Pd_{0.5}/NH_2$-N-rGO	None	298	4446	-	15
$Pd_{60}Au_{40}$/HPC-NH_2	None	298	3763	64.8	16
Ag_1Pd_4/UiO-66	None	298	107	29.66	17
Pd/$CN_{0.25}$	None	298	752	48.8	18
Pd/NMC-400	None	298	913	36.9	19
Pd/NHPC-NH_2	None	298	1265	46.3	20
AP-SiO_2@PDA-NGO@Pd	None	298	1588	51.5	21
IrPdAu/NH_2-SBA-15	None	298	4737	30.14	22
Pd/NH_2-P-GC	None	298	5126	22.44	**This work**

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