

Supporting Information

Facile Synthesis and Electronic Structure Optimization of Sub-nanometer Palladium Clusters for Efficient Direct Synthesis of H₂O₂

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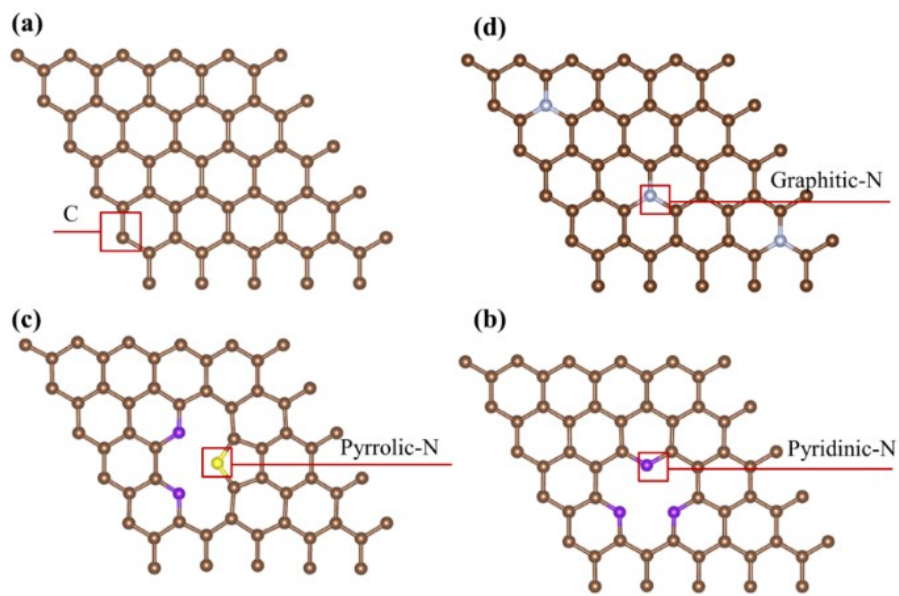


Figure S1. The models of (a) graphitic, (b) graphitic doped with Pyridinic-N, (c) graphitic doped with Pyrrolic-N and (d) graphitic doped with Graphitic-N.

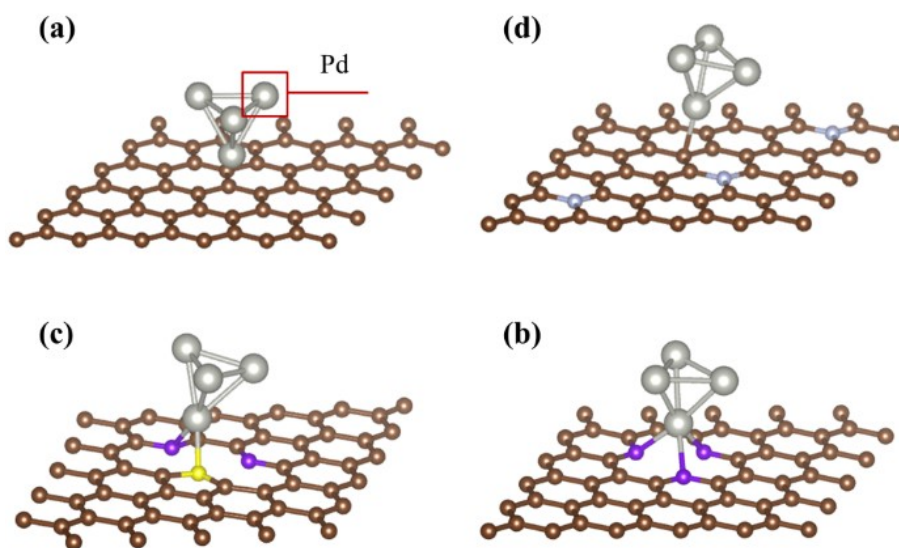


Figure S2. (a) The optimized models of Pd cluster adsorbed on (a) graphitic, (b) graphitic doped with Pyridinic-N, (c) graphitic doped with Pyrrolic-N and (d) graphitic doped with Graphitic-N.

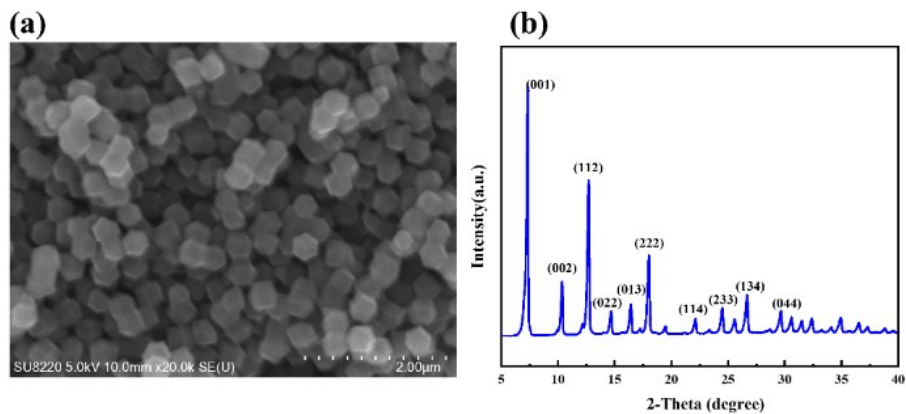


Figure S3. (a) SEM image of ZIF-8; (b)XRD spectra of ZIF-8

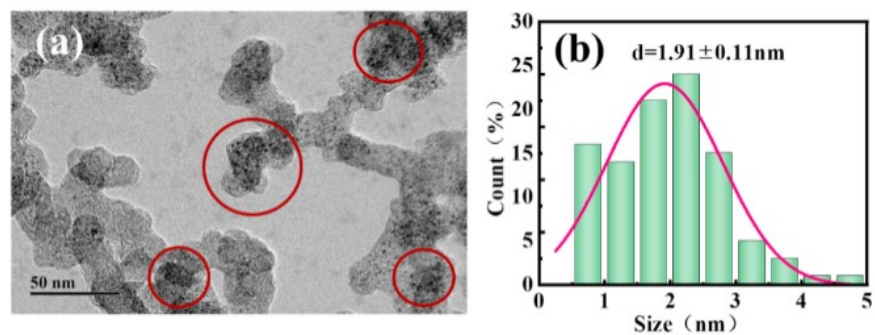


Figure S4. (a) TEM images of Pd/ XC-72. (b) Pd NPs size distribution of Pd/ XC-72.

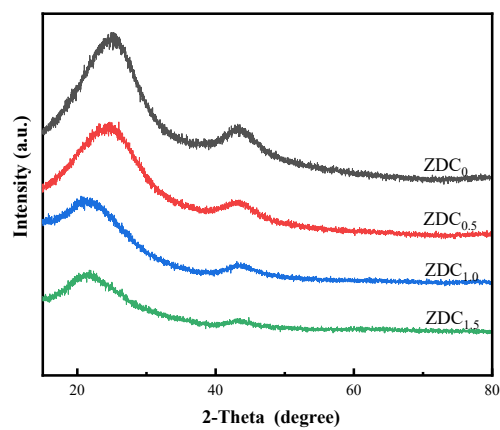


Figure S5. XRD spectra of ZDC_x.

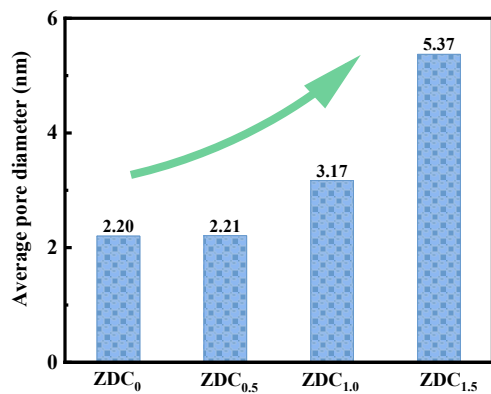


Figure S6. Average pore diameter of ZDC_X.

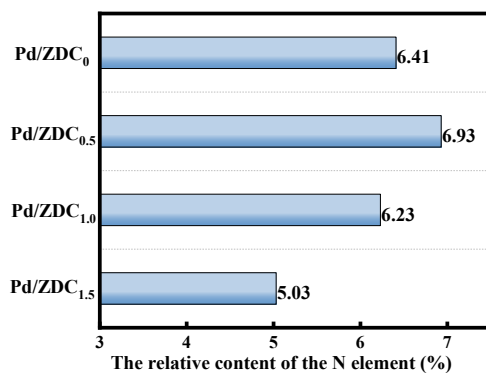


Figure S7. The relative content of the N element of ZDC₀, ZDC_{0.5}, ZDC_{1.0} and ZDC_{1.5}

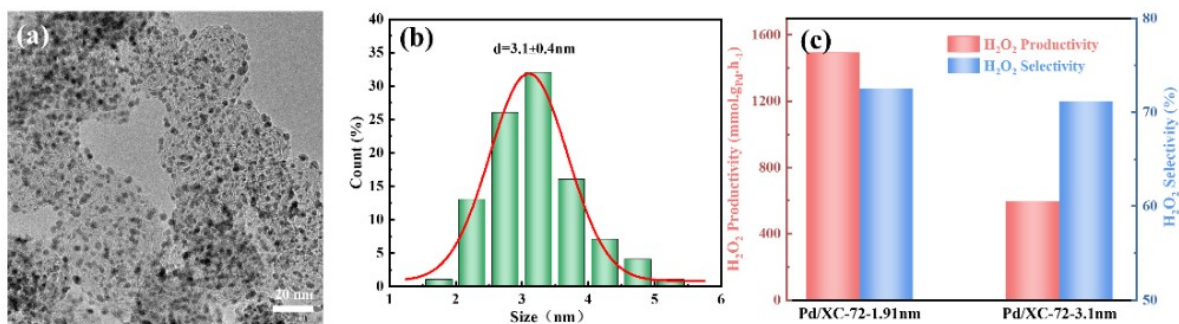


Figure S8. (a) TEM image of Pd/XC-72-3.1nm, (b) Pd NPs size distribution of Pd/XC-72, (c) evaluation results of catalytic performance of Pd/XC-72-1.91nm and Pd/XC-72-3.1 nm.

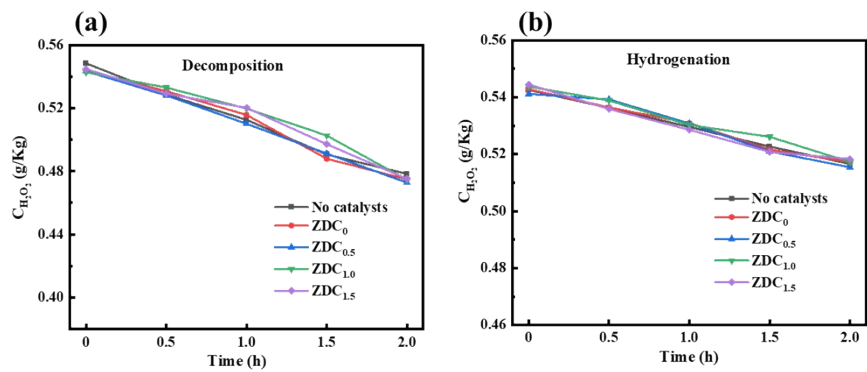


Figure S9. (a) H_2O_2 decomposition and (b) hydrogenation test for ZDC_X carriers.

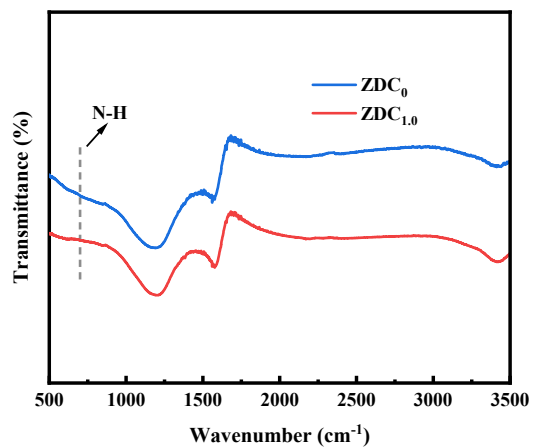


Figure S10. FTIR spectra of ZDC_0 and $ZDC_{1.0}$.

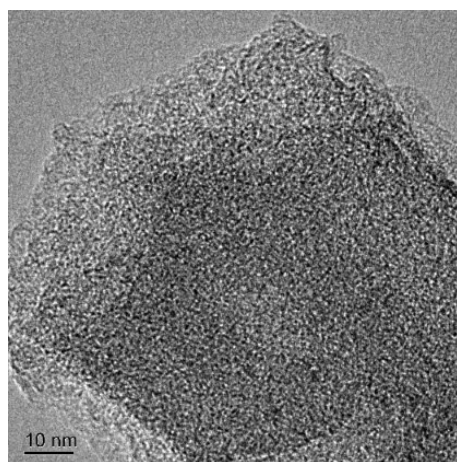


Figure S11. TEM of $Pd/ZDC_{1.0}$ catalyst after four cyclic experiments

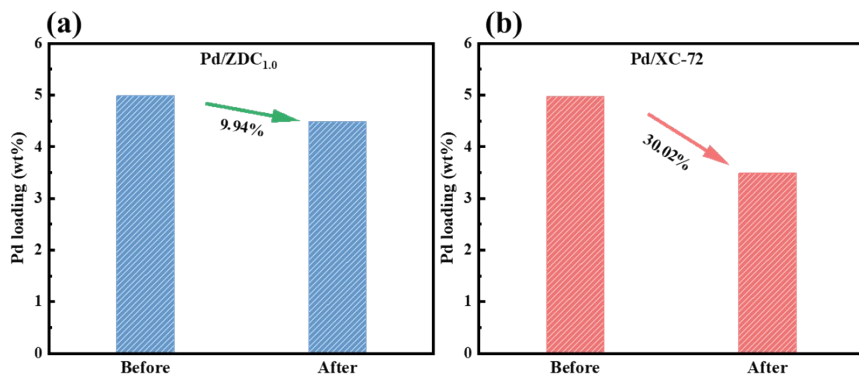


Figure S12. The Pd leaching rate of catalysts after cycling experiments, (a) Pd/ZDC_{1.0}, (b) Pd/XC-72.

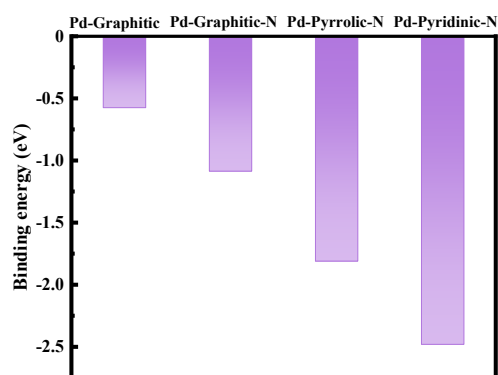


Figure S13. Binding energy of Pd cluster adsorbed on pristine graphitic and graphitic doped with graphitic-N, pyrrolic-N and pyridinic-N.

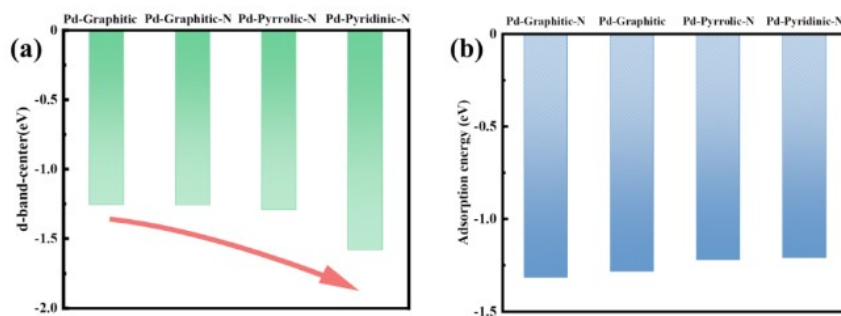


Figure S14. (a) The d-band-center of Pd cluster adsorbed on graphitic and graphitic doped with graphitic-N, pyrrolic-N and pyridinic-N. (b) Adsorption energy of O₂ on Pd-Graphitic, Pd-Graphitic-N, Pd-pyrrolic-N and Pd-pyridinic-N

Table S1 The Pd loading of catalysts measured by ICP-AES

catalysts	theoretical Pd loading (wt%)	actual Pd loading (wt%)	residual Zn (wt%)
Pd/ZDC ₀	5.0	4.865	N/A
Pd/ZDC _{0.5}	5.0	4.902	N/A
Pd/ZDC _{1.0}	5.0	4.934	N/A
Pd/ZDC _{1.5}	5.0	4.896	N/A
Pd/XC-72	5.0	4.878	/

Δ: N/A indicates that no corresponding element has been detected.

Table S2. Structural parameters of ZDC_x.

catalyst	S _{BET} (m ² /g)	V _{mic} (cm ³ /g)	V _{mes} (cm ³ /g)
Pd/ZDC ₀	1230.51	0.44	0.24
Pd/ZDC _{0.5}	1845.97	0.61	0.41
Pd/ZDC _{1.0}	2964.64	0.75	1.60
Pd/ZDC _{1.5}	3088.89	0.82	3.32