

Figure S1. (a) HAADF image of Pd/C and relevant EDS elemental (Pd and C) mappings (b and c).

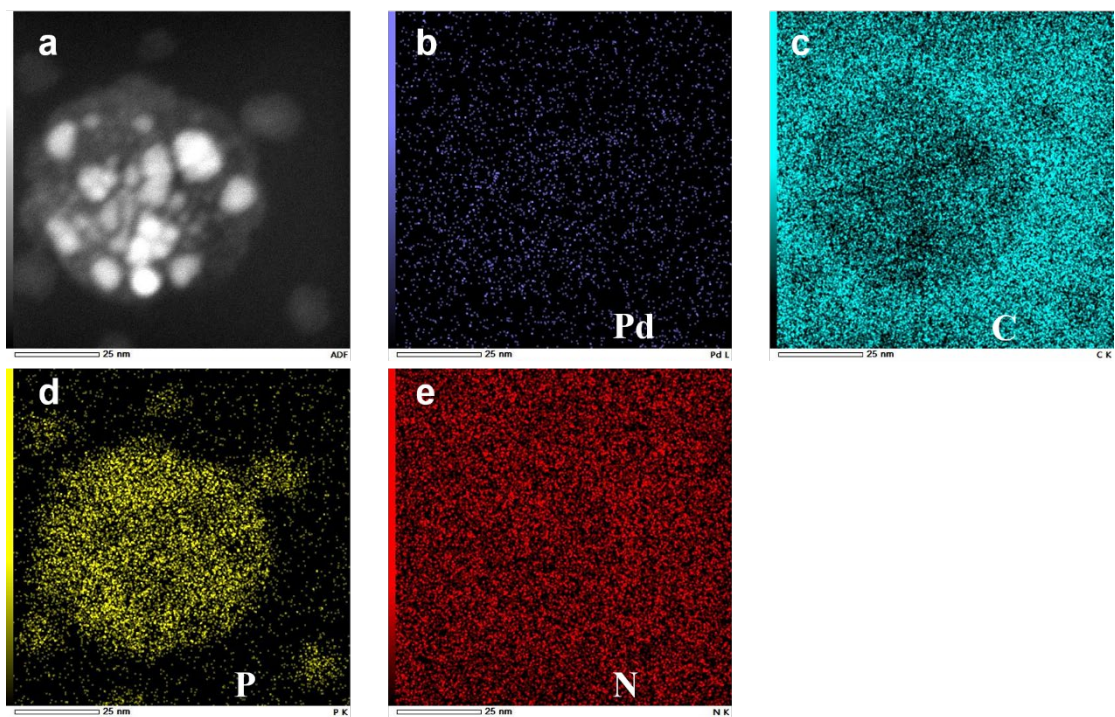


Figure S2. (a) HAADF image of Pd₃P_{0.95}/NC and relevant EDS elemental (Pd, C, P and N) mappings (b, c, d and e).

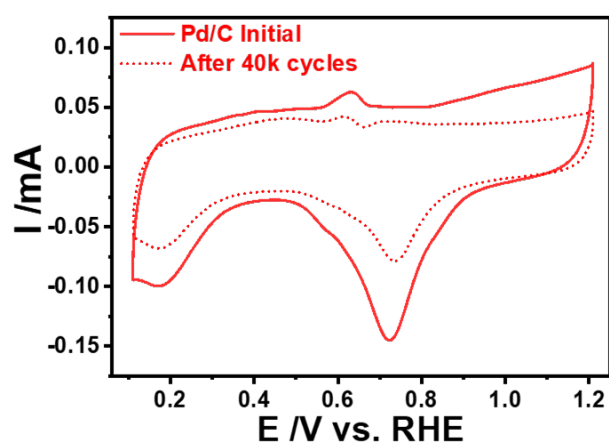


Figure S3. CV curves of Pd/C before and after ADT.

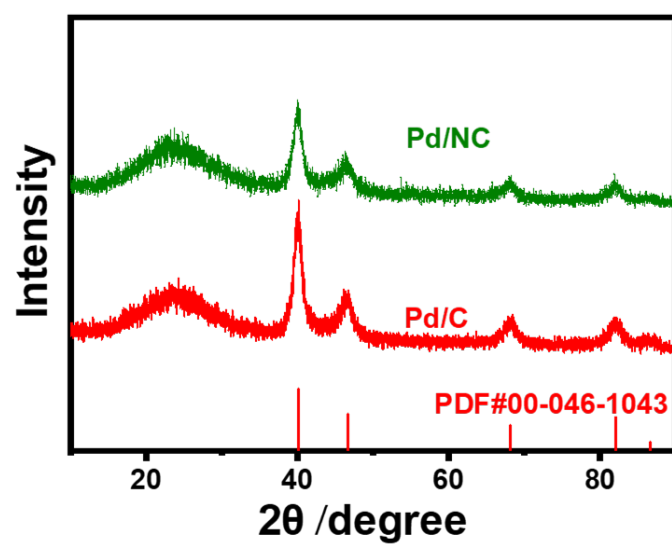


Figure S4. XRD spectra of Pd/NC and Pd/C.

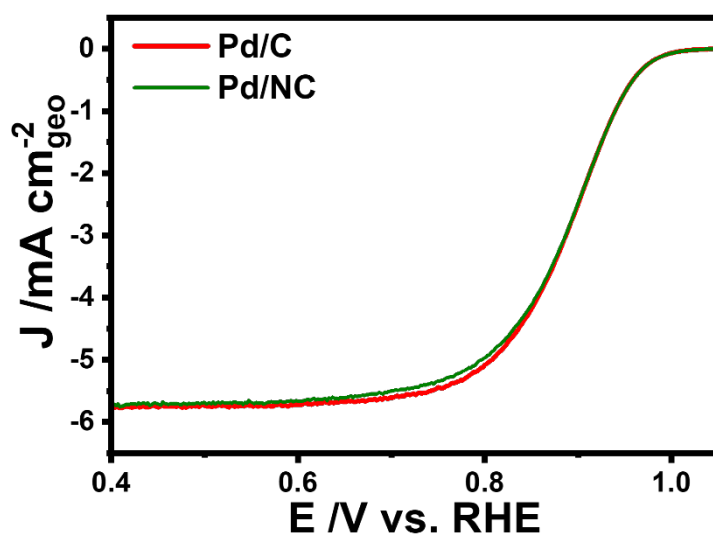


Figure S5. ORR polarization curves of Pd/NC and Pd/C.

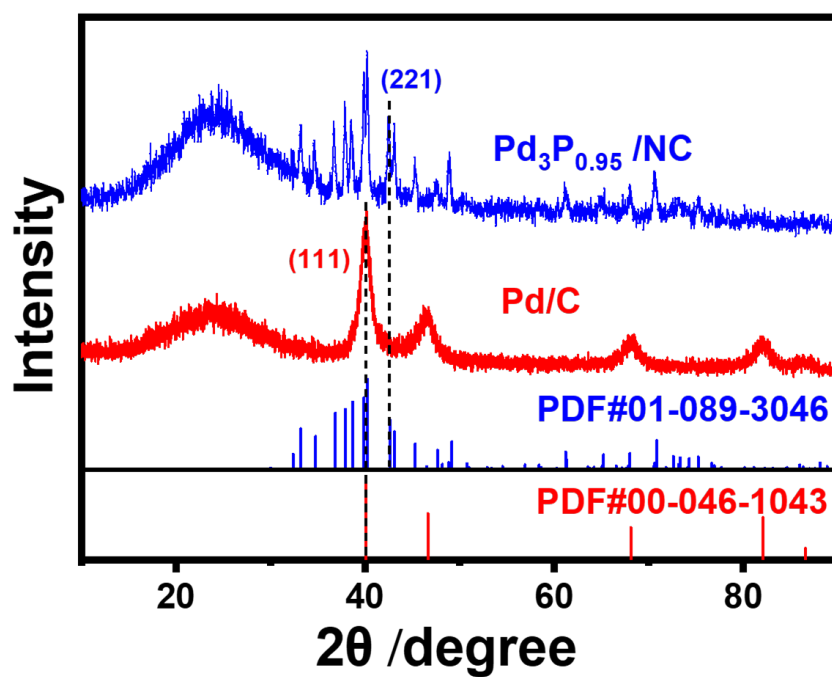


Figure S6. XRD spectra of catalysts and the marking of diffraction peaks corresponding to specific crystal faces displayed by TEM.

We used software to calculate the reduction charge of surface $\text{Pd}(\text{OH})_2$. Using CHI760E software, select the last circle of the CV curve, select **Peak Definition** function, select **Gaussian** peak shape and determine. Select the **Manual Results** function, from the base of the peak to make the tangent line (**Figure S7**), can directly read the corresponding charge quantity value.

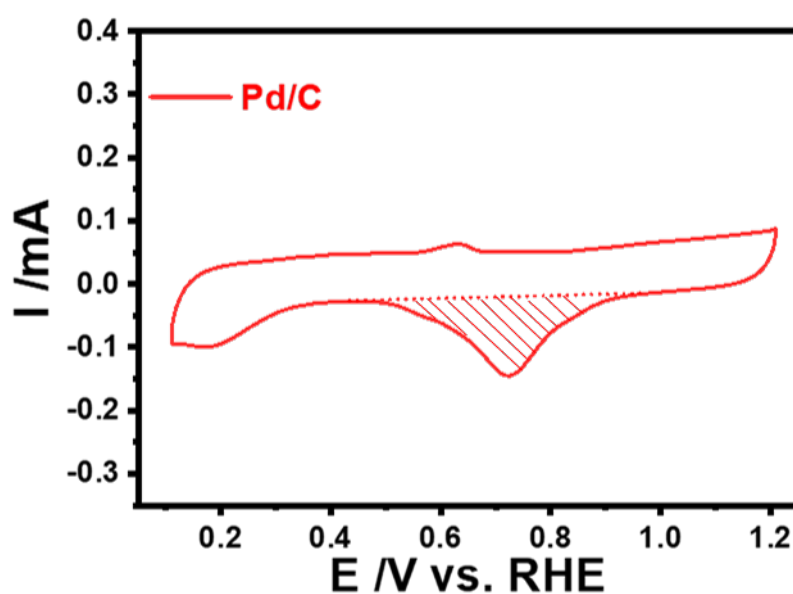


Figure S7. Schematic diagram of the reduction peak position of $\text{Pd}(\text{OH})_2$.

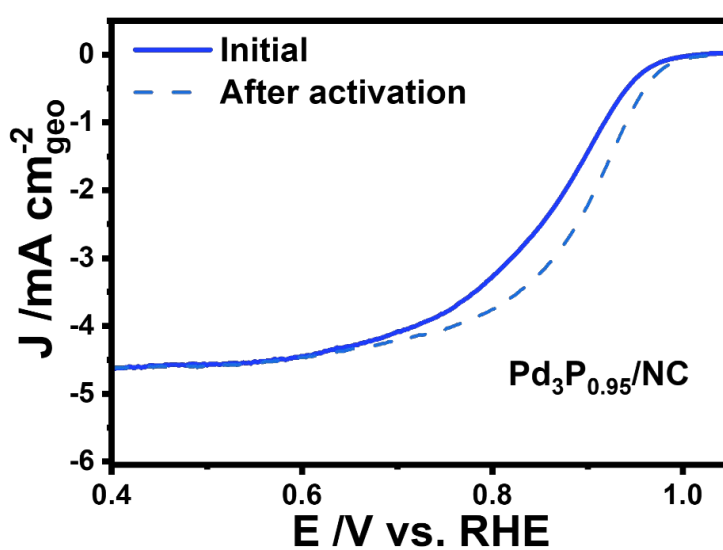


Figure S8. ORR polarization curves of $\text{Pd}_3\text{P}_{0.95}/\text{NC}$ before and after activation.

Table S1. XPS peak position of Pd 3d_{5/2} for these two catalysts Pd/C and Pd₃P_{0.95}/NC.

Sample	Pd ⁰ 3d _{5/2} Position	Pd ⁰ 3d _{3/2} Position	Pd ²⁺ 3d _{5/2} Position	Pd ²⁺ 3d _{3/2} Position
Pd/C	335.67eV	341.05 eV	337.04 eV	342.20 eV
Pd ₃ P _{0.95} /NC	335.82eV	340.90 eV	338.12 eV	343.35 eV

Table S2. ICP-OES results of the prepared samples.

Sample	Pd (wt%)	P (wt%)
Pd/C	15.1455	-
Pd ₃ P _{0.95} /NC	15.5143	9.4953

Table S3. ESA, SA, and MA of catalysts before and after ADT.

Sample	Electrochemical specific area (m ² g ⁻¹)	Initial- SA, @0.90V (mA cm ⁻²)	Initial- MA, @0.90V (mA μgPd ⁻¹)	10k-MA, @0.90V (mA μgPd ⁻¹)	40k-MA, @0.90V (mA μgPd ⁻¹)
Pd/C	18.12	1.171	0.212	0.180	0.131
Pd ₃ P _{0.95} /NC	18.00	0.998	0.175	0.210	0.186