Electronic Supplementary Information for

Strong Pyrrolic-N-Pd Interactions Boost the Electrocatalytic Hydrodechlorination Reaction on Palladium Nanoparticles

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This supplementary material is an 10-page document, which consists of 7 Figures and 1 Table.



Carbon; Nitrogen.

Figure S1. Schematical description of one graphene layer without N-doping (a), and with graphitic-N doping (b), pyridinic-N doping (c), and pyrrolic-N doping (d).

Calculation of the active Pd amount-normalized k_{obs} (k_{obs-N})

The electrochemically active surface area (ECSA, $m^2 g^{-1}$) is one useful index to describe the number of the active sites in N/G-Pd catalyst, and can be calculated from the PdO reduction peak in the corresponding cyclic voltammogram (CV) curve:

$$ECSA = \frac{Q}{4.05 \text{ Cm}^{-2} \times \text{m}_{Pd}}$$
(1)

Where m_{Pd} represents the Pd loading on the electrode for CV test; Q (C) is the total charge for reduction of PdO, and 4.05 C m⁻² is a conversion factor that exhibits the charge required to reduce a monolayer of PdO. With the equation (1) and the CV curves of the catalysts presented in **Figure S2**, we determined the ECSAs of N/G_{0.1}-430-Pd, N/G_{0.3}-430-Pd, N/G_{0.5}-430-Pd, N/G_{0.8}-430-Pd, N/G_{2.0}-430-Pd, N/G_{3.0}-430-Pd, N/G_{0.9}-430-Pd, N/G_{0.9}-430



Figure S2. Cyclic voltammograms (CVs) of N/G-Pd and C-Pd obtained in 0.1 M HClO₄ solution at a scanning rate of 50 mV s⁻¹: (a) N/G-900-Pd, C-Pd and N/G-430_{0.8}-Pd; (b) N/G-430_x-Pd, x denotes the mass ratio of the feeding melamine to GO.

With the ECSA value, the molar amount of the active sites in every gram of the catalysts (M, mol g⁻¹) can be estimated by

$$M = \frac{ECSA \times C_{Pd}}{N_A}$$
(2)

Where C_{pd} is the specific atomic concentration on Pd surface (1.27×10¹⁹ atoms m⁻²), and N_A refers to the Avogadro constant (6.02×10²³). After determining the value of M, the normalized k_{obs} (k_{obs-N}) for each electrode can be obtained by

$$k_{\rm obs-N} = \frac{k_{\rm obs}}{M \times m_{Pd}}$$
(3)

Where m_{Pd} is the Pd loading on the electrode for EHDC tests (g). k_{obs} refers to the apparent rate constant that is derived from the pseudo-first-order relationships between the -ln C/C_0 versus reaction time (Figure S3).





Figure S3. Pseudo-first-order representations of the EHDC reactions on C-Pd in N₂-saturated 50 mM Na₂SO₄ solution with 60 mg L⁻¹ 2,4-DCP under a cathode potential of -0.75, -0.80, -0.85 and -0.90 V: (a) C-Pd, (b) N/G_{0.8}-430-Pd, and (c) N/G-900-Pd; (d) Pseudo-first-order representations of the EHDC reaction on N/G_{0.1}-430-Pd, N/G_{0.3}-430-Pd, N/G_{0.5}-430-Pd, N/G_{0.8}-430-Pd, N/G_{2.0}-430-Pd and N/G_{3.0}-430-Pd under a cathode potential of -0.80 V.

Current efficiency determination

The current efficiency (CE%) of the EHDC reaction was calculated by:

$$CE\% = \frac{(n1Cp + n2 \times (Co - CP + Cp - CP)) \times F \times V}{Q} \times 100\%$$
(4)

where F is the Faraday constant, Q is the total consumed electric charge (C) that was directly read on electrochemical potentiostat. C_{P} , C_{o-CP} and C_{p-CP} refer to the concentrations (mM) of P, *o*-CP and *p*-CP. n₁ and n₂ are the electron numbers transferred in every molecular conversion of 2,4-DCP to P (n₁ = 4) and *o*-/*p*-CP (n₂ = 2), respectively, which are determined according to the conversion reactions:

$$2,4-DCP + 2H^{+} + 4e^{-} \rightarrow P + 2Cl^{-}$$
(5)

$$2,4-DCP + H^{+} + 2e^{-} \rightarrow CP + Cl^{-}$$
(6)



Figure S4. XPS survey spectra of N/G-900, N/G-900-Pd, N/G-430 and N/G-430-Pd.



Figure S5. Stability test for N/G-430-Pd. Operation conditions: cathode potential: -0.80 V; 60 mg L^{-1} of 2,4-DCP in one N₂-saturated 50 mM Na₂SO₄ solution.



Figure S6. High-resolution XPS N 1s spectra of all the N/G-430_x samples (x=0.1 - 3.0).



Carbon; Palladium; Oxygen; Nitrogen; Chlorine; Hydrogen.

Figure S7. The optimized configurations of the 2,4-DCP molecule adsorption on the catalyst (side view): (a) G-Pd, (b) graphitic-N/G-Pd, (c) pyridinic-N/G-Pd and (d) pyrrolic-N/G-Pd. The optimized configurations of the phenol molecule adsorption on the catalyst (side view): (a) G-Pd, (b) graphitic-N/G-Pd, (c) pyridinic-N/G-Pd, and (d) pyrrolic-N/G-Pd.



Figure S8. The optimized adsorption configurations for one HCl molecule on N/G-Pd (side view): (a) No N-doping, (b) graphitic-N doping, (c) pyridinic-N doping, and (d) pyrrolic-N doping.

Species	Adsorption energy / eV
C-Pd	-0.28
graphitic-N-Pd	-0.18
pyrrolic-N-Pd	-0.22
pyridinic-N-Pd	-0.23

 Table S1. The adsorption energy of HCl on the catalyst