Electronic Supplementary Information for

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

Peng Wang\textsuperscript{a,b}, Xuelin Shi\textsuperscript{b}, Chunhong Fu\textsuperscript{b}, Xiangjun Li\textsuperscript{b}, Junxi Li\textsuperscript{b}, Xiaoshu Lv\textsuperscript{b}, Yinghao Chu\textsuperscript{a,*}, Fan Dong\textsuperscript{b}, Guangming Jiang\textsuperscript{b,*}

\textsuperscript{a} College of Architecture and Environment, Sichuan University. Chengdu, 610065, China

\textsuperscript{b} Engineering Research Center for Waste Oil Recovery Technology and Equipment, Ministry of Education, Chongqing Technology and Business University, Chongqing 400067, China

*Corresponding author. Tel.: +86-23-62768316; Fax: +86-23-62768317.

E-mail address: jiangguangming@zju.edu.cn (G.M. Jiang)

chuyinghao@scu.edu.cn (Y. H. Chu)

This supplementary material is an 10-page document, which consists of 7 Figures and 1 Table.
**Figure S1.** Schematic 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, m² 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:

$$ECSA = \frac{Q}{4.05 \, \text{C m}^{-2} \times m_{\text{Pd}}}$$  \hspace{1cm} (1)

Where $m_{\text{Pd}}$ represents the Pd loading on the electrode for CV test; Q (C) is the total charge for reduction of PdO, and 4.05 C m² 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/G₀.₁-430-Pd, N/G₀.₃-430-Pd, N/G₀.₅-430-Pd, N/G₀.₈-430-Pd, N/G₂.₀-430-Pd, N/G₃₀-430-Pd, N/G-900-Pd and C-Pd catalyst to be 16.67, 17.09, 16.85, 14.80, 21.66, 21.61, 19.06 and 24.08 m² g⁻¹.

**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-430₀.₈-Pd; (b) N/G-430ₓ-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

\[ M = \frac{\text{ECSA} \times C_{\text{Pd}}}{N_A} \]  

(2)

Where \( C_{\text{Pd}} \) is the specific atomic concentration on Pd surface (\(1.27 \times 10^{19}\) atoms m\(^{-2}\)), and \( N_A \) refers to the Avogadro constant (\(6.02 \times 10^{23}\)). After determining the value of M, the normalized \( k_{\text{obs}} \) (\( k_{\text{obs-N}} \)) for each electrode can be obtained by

\[ k_{\text{obs-N}} = \frac{k_{\text{obs}}}{M \times m_{\text{Pd}}} \]  

(3)

Where \( m_{\text{Pd}} \) is the Pd loading on the electrode for EHDC tests (g). \( k_{\text{obs}} \) 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 N$_2$-saturated 50 mM Na$_2$SO$_4$ 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:

\[
CE\% = \left(\frac{n_1 C_p + n_2 \times (C_o - CP + C_p - CP)) \times F \times V}{Q}\right) \times 100\%
\]

where \(F\) is the Faraday constant, \(Q\) is the total consumed electric charge (C) that was directly read on electrochemical potentiostat. \(C_p\), \(C_{oCP}\) and \(C_{pCP}\) refer to the concentrations (mM) of \(P\), \(o\)-CP and \(p\)-CP. \(n_1\) and \(n_2\) are the electron numbers transferred in every molecular conversion of 2,4-DCP to \(P\) \((n_1 = 4)\) and \(o-/p\)-CP \((n_2 = 2)\), respectively, which are determined according to the conversion reactions:

\[
2,4\text{-DCP} + 2H^+ + 4e^- \rightarrow P + 2Cl^-
\]

\[
2,4\text{-DCP} + H^+ + 2e^- \rightarrow CP + Cl^-
\]
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 N$_2$-saturated 50 mM Na$_2$SO$_4$ solution.
Figure S6. High-resolution XPS N 1s spectra of all the N/G-430$_x$ samples ($x=0.1$ - $3.0$).
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.
**Table S1.** The adsorption energy of HCl on the catalyst

<table>
<thead>
<tr>
<th>Species</th>
<th>Adsorption energy / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Pd</td>
<td>-0.28</td>
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<tr>
<td>graphitic-N-Pd</td>
<td>-0.18</td>
</tr>
<tr>
<td>pyrrolic-N-Pd</td>
<td>-0.22</td>
</tr>
<tr>
<td>pyridinic-N-Pd</td>
<td>-0.23</td>
</tr>
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