Supporting Information

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CHEMICALS AND REAGENTS:

All the chemicals and reagents were of analytical grade, obtained from Aldrich and were used as received without any purification step otherwise noted. Palladium acetylacetonate Pd(acac)$_2$ (99.9%) was obtained from Sigma Aldrich, Toluene (99.99%) from Sigma Aldrich, KOH (99.99%) from Sigma Aldrich. FTO coated glass substrates are obtained from Dyesol with a resistance value of approximately 15 $\Omega$/sq.
Table S1. Summary of electrocatalytic activity for Pd-derived thin film electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>η@10 mA cm(^2) [mV] at η=0.35 V</th>
<th>Tafel slope [mV decade(^{-1})]</th>
<th>Mass Activity [mA mg(^{-1})]</th>
<th>ECSA [cm(^2)]</th>
<th>TOF (s(^{-1})) at η=0.35 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(_{40})</td>
<td>340</td>
<td>44</td>
<td>207</td>
<td>4.3</td>
<td>0.05</td>
</tr>
<tr>
<td>Pd(_{60})</td>
<td>330</td>
<td>61</td>
<td>258</td>
<td>4.8</td>
<td>0.07</td>
</tr>
<tr>
<td>Pd(_{90})</td>
<td>310</td>
<td>86</td>
<td>292</td>
<td>7.2</td>
<td>0.08</td>
</tr>
<tr>
<td>Pd(_{120})</td>
<td>270</td>
<td>67</td>
<td>392</td>
<td>8</td>
<td>0.1</td>
</tr>
<tr>
<td>Pd(_{180})</td>
<td>240</td>
<td>40</td>
<td>560</td>
<td>20</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Figure S1. Cross-sectional scanning electron microscopy (SEM) images for Pd$_{90}$ and Pd$_{180}$ samples deposited on FTO via Aerosol-Assisted Chemical Vapor Deposition (AACVD) method.
Figure S2: EDX spectra of Pd$_{40}$, Pd$_{60}$, Pd$_{120}$, and Pd$_{180}$ films deposited on FTO substrate via Aerosol-Assisted Chemical Vapor Deposition (AACVD) method.
**Figure S3.** (a) XPS survey patterns of palladium film electrodes; (b) High resolution XPS study of Pd$_{180}$ electrode showing binding energies for the Pd(0) state.
Figure S4. (left) Nyquist plot for Pd40, Pd60, Pd90, Pd120, and for Pd180 at an applied potential of 1.48 V vs. RHE in the frequency range of 0.1 Hz to 100 KHz. (right) Enlarged view of the Nyquist plot for Pd180. For each EIS analysis, data was fitted employing Randles circuit with Nova software (inset figure). Charge transfer resistance for Pd40≈ 15 Ω, Pd60≈ 13 Ω, Pd90≈ 11 Ω, Pd120≈ 6 Ω, and Pd180≈ 2.1 Ω is estimated by fitting a simplified Randles circuit.

Figure S5. Forward potential sweeps during 1st (black line) and 500th (Red line) LSV run for Pd180 electrocatalytic material in 0.1 M KOH electrolyte solution at the scan rate of 10 mV s⁻¹. (Inset shows enlarged view of the LSV in 0.1 M KOH electrolyte solution)
Figure S6. Double layer capacitance measurements for evaluating the electrochemically active surface area for Pd₁₀ type electrocatalytic system in 0.1 M KOH electrolyte solution. (a) cyclic voltammogram for Pd₁₀ measured at varying scan rate such as (blue) 5 mV s⁻¹ (green) 10 mV s⁻¹ (red) 20 mV s⁻¹ (black) 50 mV s⁻¹ in the non-faradaic region, where all the current is supposed to be due to capacitive charging (b) charging current at the fixed potential of 0.955 V vs. RHE is plotted as a function of scan rate while slope giving the value of $C_{dl}$. Electrochemically active surface area is found to be 4.3 cm².

Figure S7. Double layer capacitance measurements for evaluating electrochemically active surface area for Pd₁₀ type electrocatalytic system in 0.1 M KOH electrolyte solution. (a) cyclic voltammogram for Pd₁₀ measured at varying scan rate such as (blue) 5 mV s⁻¹ (green) 10 mV s⁻¹ (red) 20 mV s⁻¹ (black) 50 mV s⁻¹ in the non-faradaic region, where all the current is supposed to be due to capacitive charging (b) charging current at the fixed potential of 0.955 V vs. RHE is plotted as a function of scan rate while slope giving the value of $C_{dl}$. Electrochemically active surface area is found to be 4.8 cm².
Figure S8. Double layer capacitance measurements for evaluating electrochemically active surface area for Pd$_{90}$ type electrocatalytic system in 0.1 M KOH electrolyte solution. (a) cyclic voltammogram for Pd$_{90}$ measured at varying scan rate such as (blue) 5 mV s$^{-1}$ (green) 10 mV s$^{-1}$ (red) 20 mV s$^{-1}$ (black) 50 mV s$^{-1}$ in the non-faradaic region, where all the current is supposed to be due to capacitive charging. (b) charging current at the fixed potential of 0.955 V vs. RHE is plotted as a function of scan rate while slope giving the value of $C_{dl}$. Electrochemically active surface area is found to be 7.2 cm$^2$.

Figure S9. Double layer capacitance measurements for evaluating electrochemically active surface area for Pd$_{120}$ type electrocatalytic system in 0.1 M KOH electrolyte solution. (a) cyclic voltammogram for Pd$_{120}$ measured at varying scan rate such as (blue) 5 mV s$^{-1}$ (green) 10 mV s$^{-1}$ (red) 20 mV s$^{-1}$ (black) 50 mV s$^{-1}$ in the non-faradaic region, where all the current is supposed to be due to capacitive charging. (b) charging current at the fixed potential of 0.955 V vs. RHE is plotted as a function of scan rate while slope giving the value of $C_{dl}$. Electrochemically active surface area is found to be 8 cm$^2$. 
Figure S10. Double layer capacitance measurements for evaluating electrochemically active surface area for Pd$_{180}$ type electrocatalytic system in 0.1 M KOH electrolyte solution. (a) cyclic voltammogram for Pd$_{180}$ measured at varying scan rate such as (blue) 5 mV s$^{-1}$ (green) 10 mV s$^{-1}$ (red) 20 mV s$^{-1}$ (black) 50 mV s$^{-1}$ in the non-faradaic region, where all the current is supposed to be due to capacitive charging (b) charging current at the fixed potential of 0.955 V vs. RHE is plotted as a function of scan rate while slope giving the value of $C_{dl}$. Electrochemically active surface area is found to be 20 cm$^2$.

Figure S11. Scanning electron microscopy (SEM) images for palladium film electrode after repetitive LSVs and CCE tests.