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 acetylacetone $Pd(acac)_2$ (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 Ω/sq.

Table S1. Summary of electrocatalytic activity for Pd-derived thin film electrocatalysts.

Catalyst	η@10 mA cm^{-2} [mV] at η=0.35 V	Tafel slope [mV $decade^{-1}$]	Mass Activity [mA mg^{1-}]	ECSA [cm^2]	TOF (s^{-1}) at η=0.35 V
Pd_{40}	340	44	207	4.3	0.05
Pd_{60}	330	61	258	4.8	0.07
Pd_{90}	310	86	292	7.2	0.08
Pd_{120}	270	67	392	8	0.1
Pd_{180}	**240**	**40**	**560**	**20**	**0.2**

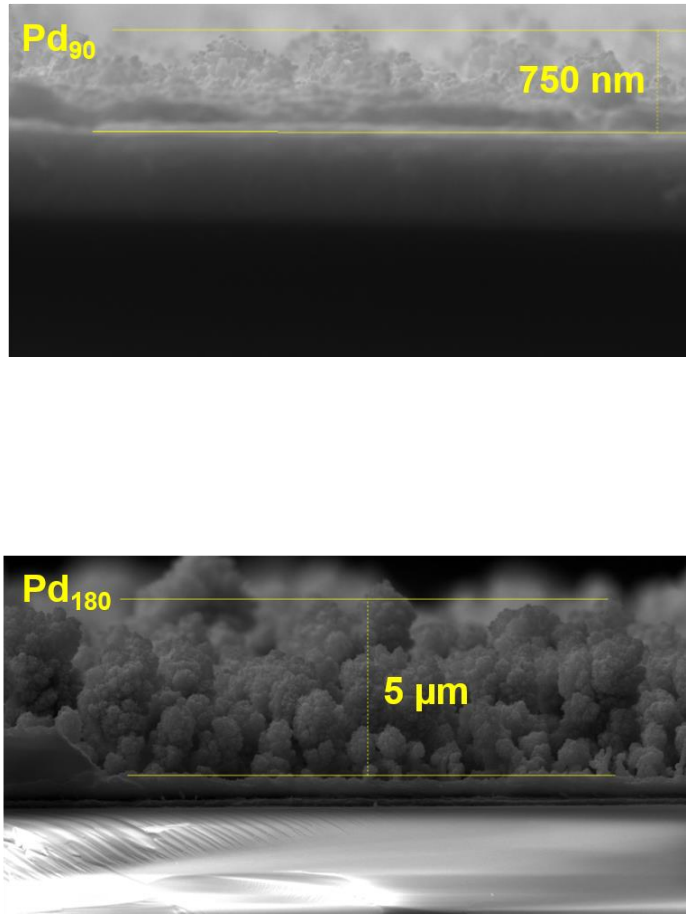

Figure S1. Cross-sectional scanning electron microscopy (SEM) images for Pd_{90} and Pd_{180} samples deposited on FTO via Aerosol-Assisted Chemical Vapor Deposition (AACVD) method.

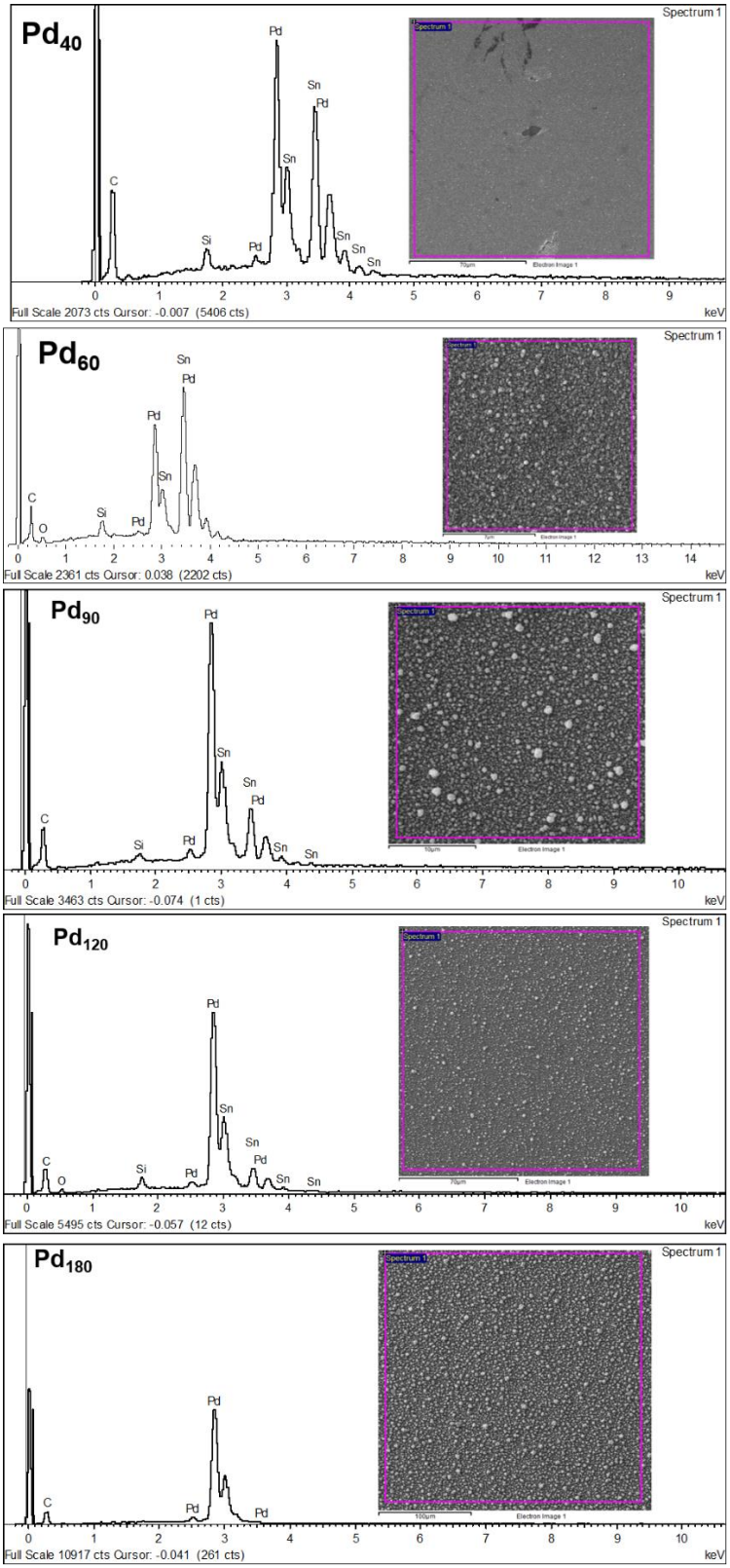

Figure S2: EDX spectra of Pd_{40} Pd_{60}, Pd_{90}, Pd_{120} and Pd_{180} films deposited on FTO substrate via Aerosol-Assisted Chemical Vapor Deposition (AACVD) method.

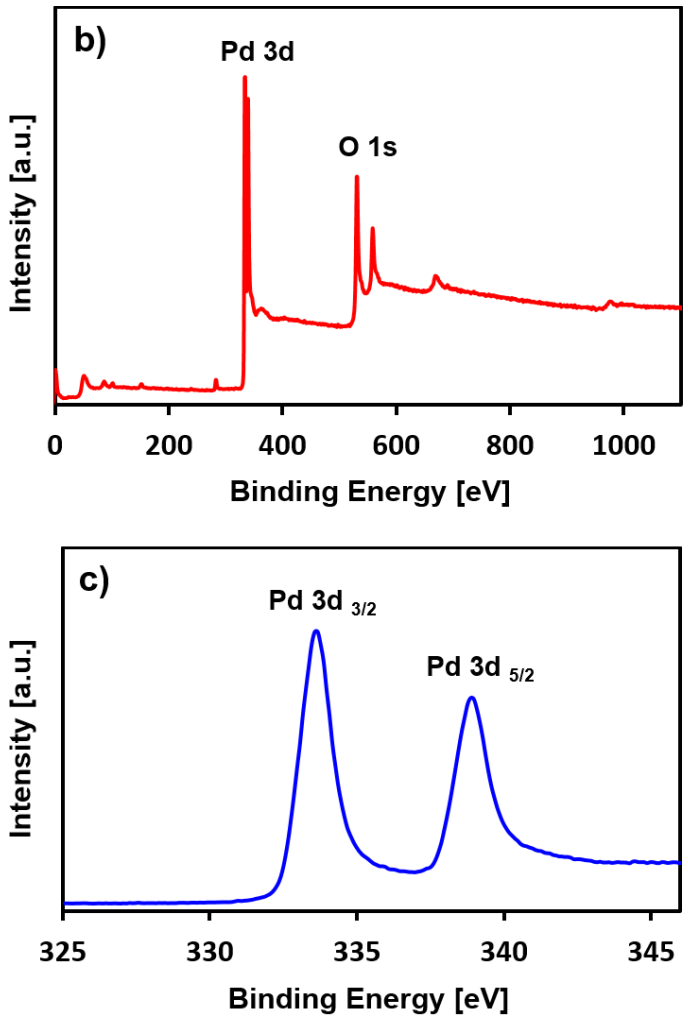

Figure S3. (**a**) XPS survey patterns of palladium film electrodes; (**b**) High resolution XPS study of Pd_{180} electrode showing binding energies for the Pd(0) state.

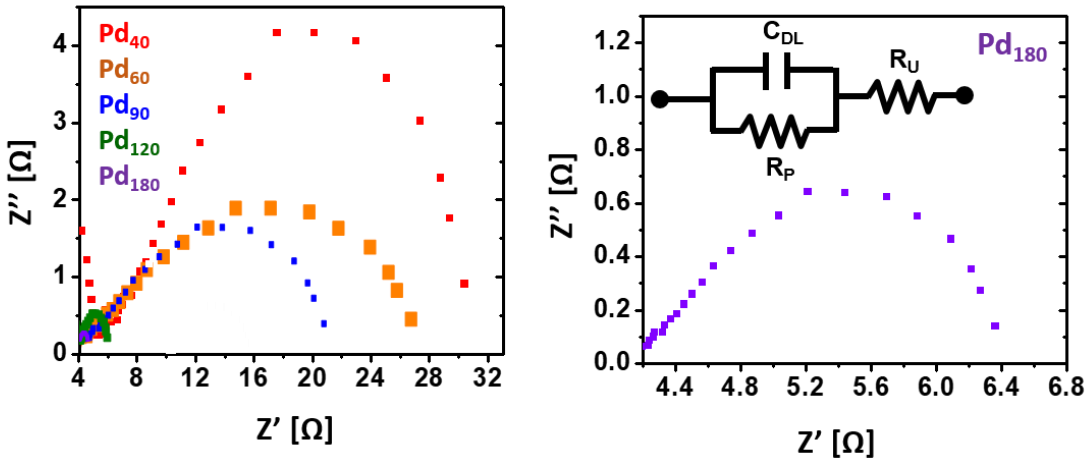

Figure S4. **(left)** Nyquist plot for Pd_{40}, Pd_{60}, Pd_{90}, Pd_{120}, and for Pd_{180} at an applied potential of 1.48 V vs. RHE in the frequency range of 0.1 Hz to 100 KHz. **(right)** Enlarged view of the Nyquist plot for Pd_{180}. For each EIS analysis, data was fitted employing Randles circuit with Nova software (inset figure). Charge transfer resistance for Pd_{40}≈ 15 Ω, Pd_{60}≈ 13 Ω, Pd_{90}≈ 11 Ω, Pd_{120}≈ 6 Ω, and Pd_{180}≈ 2.1 Ω is estimated by fitting a simplified Randles circuit.

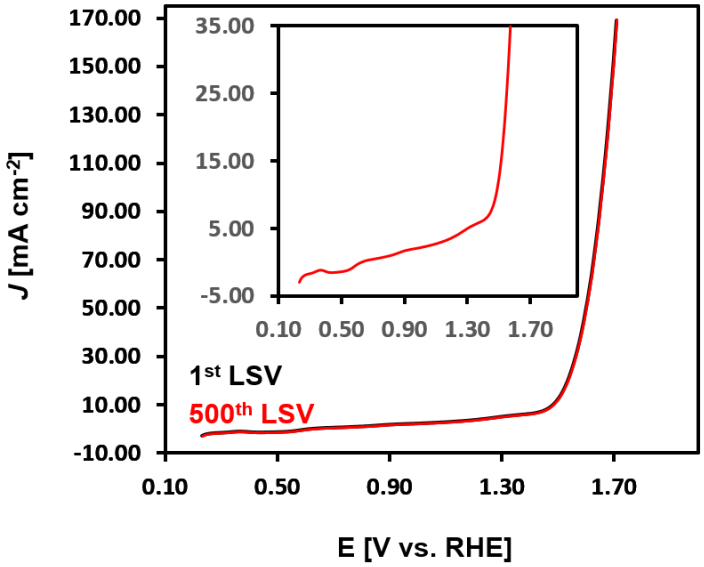

Figure S5. Forward potential sweeps during 1st (black line) and 500th (Red line) LSV run for Pd_{180} electrocatalytic material in 0.1 M KOH electrolyte solution at the scan rate of 10 mV s^{-1}. (Inset shows enlarged view of the LSV in 0.1 M KOH electrolyte solution)

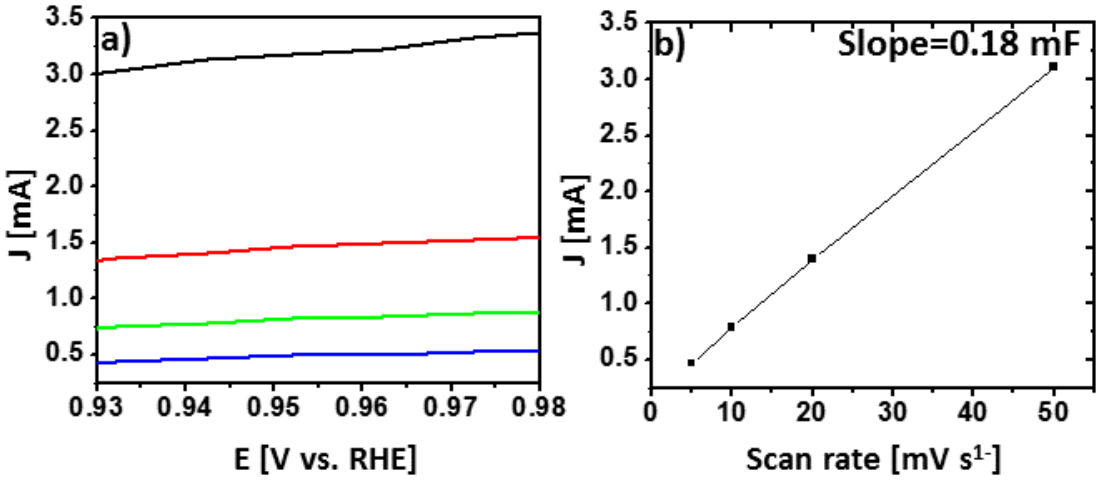

Figure S6. Double layer capacitance measurements for evaluating the electrochemically active surface area for Pd_{40} type electrocatalytic system in 0.1 M KOH electrolyte solution. **(a)** cyclic voltammogram for Pd_{40} measured at varying scan rate such as (blue) 5 mV s^{1-} (green) 10 mV s^{1-} (red) 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 cm^2.

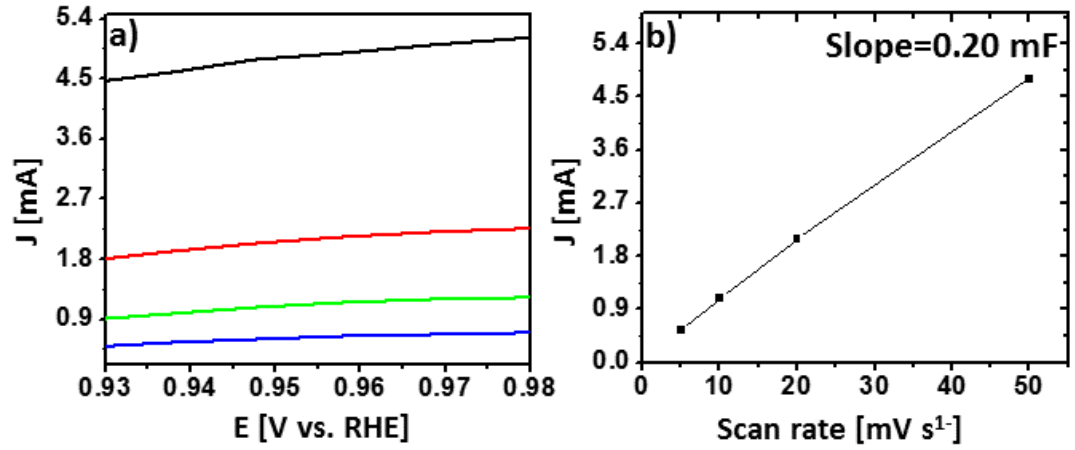

Figure S7. Double layer capacitance measurements for evaluating electrochemically active surface area for Pd_{60} type electrocatalytic system in 0.1 M KOH electrolyte solution. **(a)** cyclic voltammogram for Pd_{60} measured at varying scan rate such as (blue) 5 mV s^{1-} (green) 10 mV s^{1-} (red) 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 cm^2.

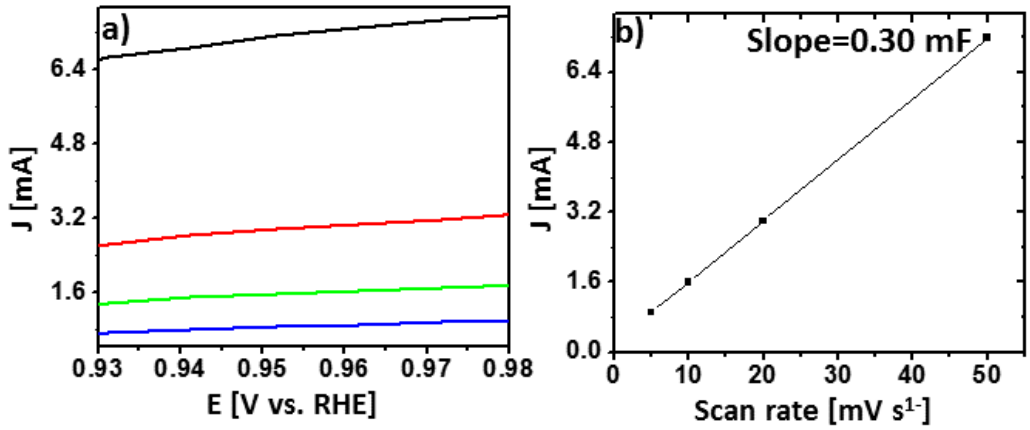

Figure S8. Double layer capacitance measurements for evaluating electrochemically active surface area for Pd_{90} type electrocatalytic system in 0.1 M KOH electrolyte solution. **(a)** cyclic voltammogram for Pd_{90} measured at varying scan rate such as (blue) 5 mV s^{1-} (green) 10 mV s^{1-} (red) 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.

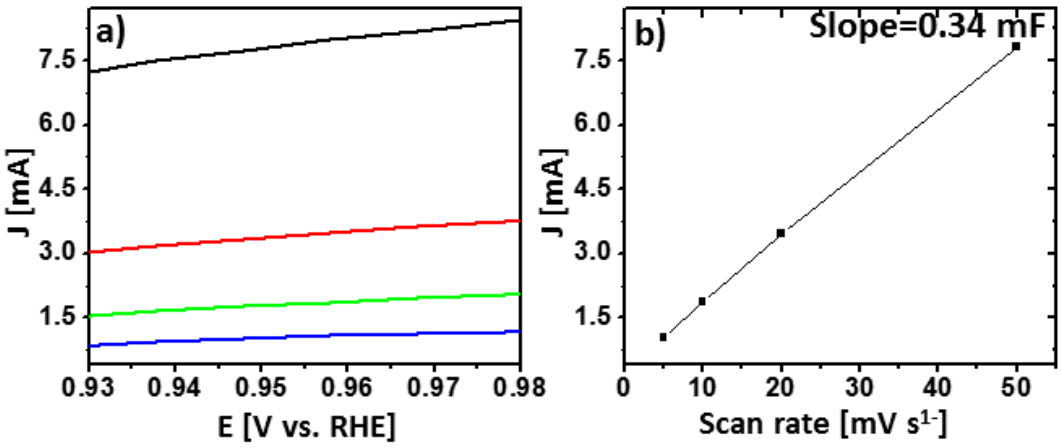

Figure S9. Double layer capacitance measurements for evaluating electrochemically active surface area for Pd_{120} type electrocatalytic system in 0.1 M KOH electrolyte solution. **(a)** cyclic voltammogram for Pd_{120} measured at varying scan rate such as (blue) 5 mV s^{1-} (green) 10 mV s^{1-} (red) 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.

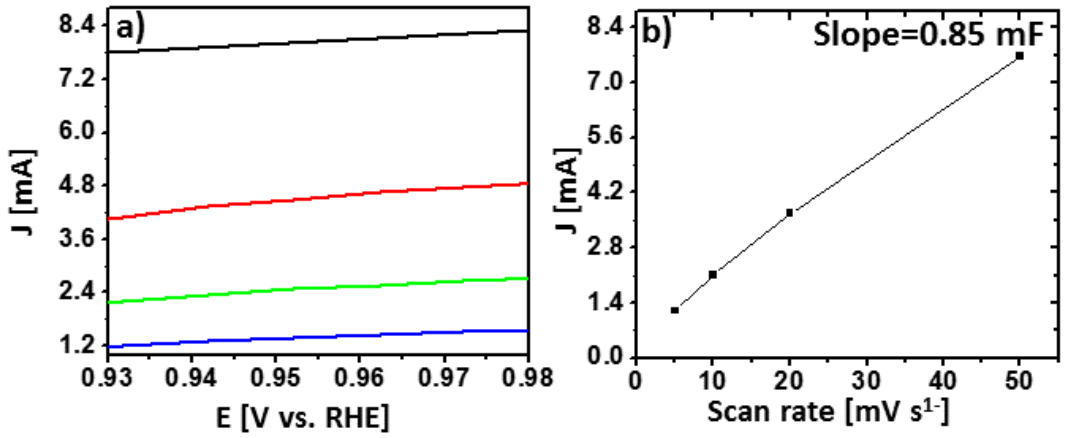

Figure S10. Double layer capacitance measurements for evaluating electrochemically active surface area for Pd_{180} type electrocatalytic system in 0.1 M KOH electrolyte solution. **(a)** cyclic voltammogram for Pd_{180} measured at varying scan rate such as (blue) 5 mV s^{1-} (green) 10 mV s^{1-} (red) 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.

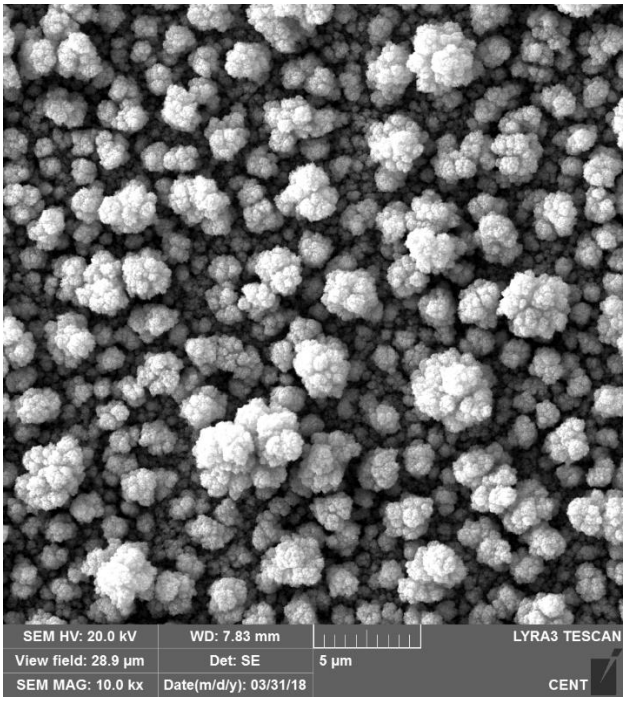

Figure S11. Scanning electron microscopy (SEM) images for palladium film electrode after repetitive LSVs and CCE tests.