

## Supporting Information

### Controlling Palladium Morphology in Electrodeposition from Nanoparticles to

### Dendrites via the use of Mixed Solvents

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ESI1: Assignment of the Raman spectra recorded in the three different MeCN-water solutions

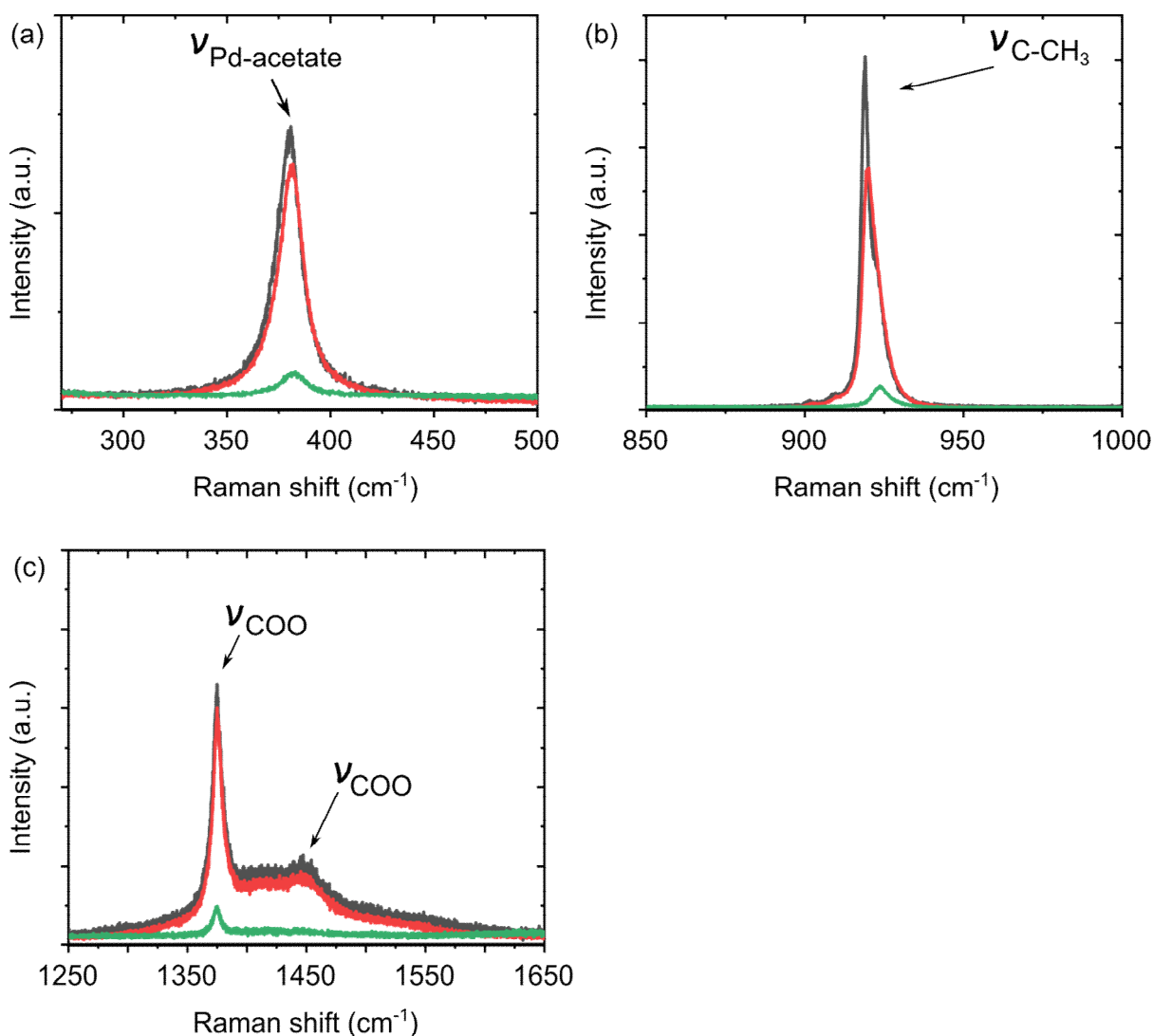
ESI2: Cyclic voltammetry of Pd-acetate in the three different MeCN-water solutions

ESI3: High resolution ADF-STEM of a Pd NP on the (110) surface of the BDD TEM electrode

ESI4: Statistical analysis summary for Pd nanostructures obtained via electrodeposition

### ESI1: Assignment of the Raman spectra recorded in the three different MeCN-water solutions

Solution 1 is organic rich, 90% MeCN:10% water v/v ( $\chi_{\text{water}} = 0.243$ ). Solution 2 is equal by volume MeCN and water i.e. 50% MeCN:50% water v/v ( $\chi_{\text{water}} = 0.743$ ). Solution 3 is water rich, 90% MeCN:10% water v/v ( $\chi_{\text{water}} = 0.963$ ).<sup>1</sup>



**Figure S1:** Raman spectra of (a) Pd-acetate, and (b) C-CH<sub>3</sub> and (c) COO (in acetate) as function of water mole fraction  $\chi_{\text{water}}$ . Grey line represents  $\chi_{\text{MeCN}} = 0.757 + \chi_{\text{water}} = 0.243$  (90%:10% v/v), red line represents  $\chi_{\text{MeCN}} = 0.257 + \chi_{\text{water}} = 0.743$  (50%:50% v/v), and green line represents  $\chi_{\text{MeCN}} = 0.037 + \chi_{\text{water}} = 0.963$  (10%:90% v/v).

**Table S1:** Band assignment for Raman spectra of Figure 1 (main text).

Raman shift (cm <sup>-1</sup> )	Vibration	Comments
2253	C≡N stretching	Solution 1, Fig1a
2255	C≡N stretching	Solution 2, Fig1a
2260	C≡N stretching	Solution 3, Fig1a
2933	CH stretching	Solution 1, Fig1b
2936	CH stretching	Solution 2, Fig1b
2940	CH stretching	Solution 3, Fig1b
3200-3600	O-H stretch	Solution 3, Fig1b

Fig. 1 in the main text and Fig. S2 show the Raman spectral region of the CN bond. The component at higher wavenumbers (2260 cm<sup>-1</sup>) is associated with MeCN bound to water, i.e. bound MeCN, whilst that at 2250 cm<sup>-1</sup> is assigned to MeCN – MeCN interactions in bulk MeCN i.e. free MeCN.<sup>2</sup> By implementing the band-fitting procedures outlined by Shurvell et al,<sup>3</sup> it is possible to determine the fraction of free MeCN to total MeCN (free + water bound) for each different solution composition.

This method suggests that if  $C_{\text{total}}$  is the total concentration of one solvent (MeCN),  $C_{\text{free}}$  is the concentration of the free (unbound) MeCN and  $C_{\text{bound}}$  is the concentration of the MeCN-water associated solvent. We can then use the following equation to find  $C_{\text{Total}}$

$$C_{\text{Total}} = C_{\text{free}} + C_{\text{bound}} \quad (1)$$

For each species, the following relationship holds for the Raman spectra

$$I_i = J_i C_i \quad (2)$$

where  $I_i$  is the integrated band intensity,  $J_i$  is the molar scattering factor and  $C_i$  is the molar concentration of each species.

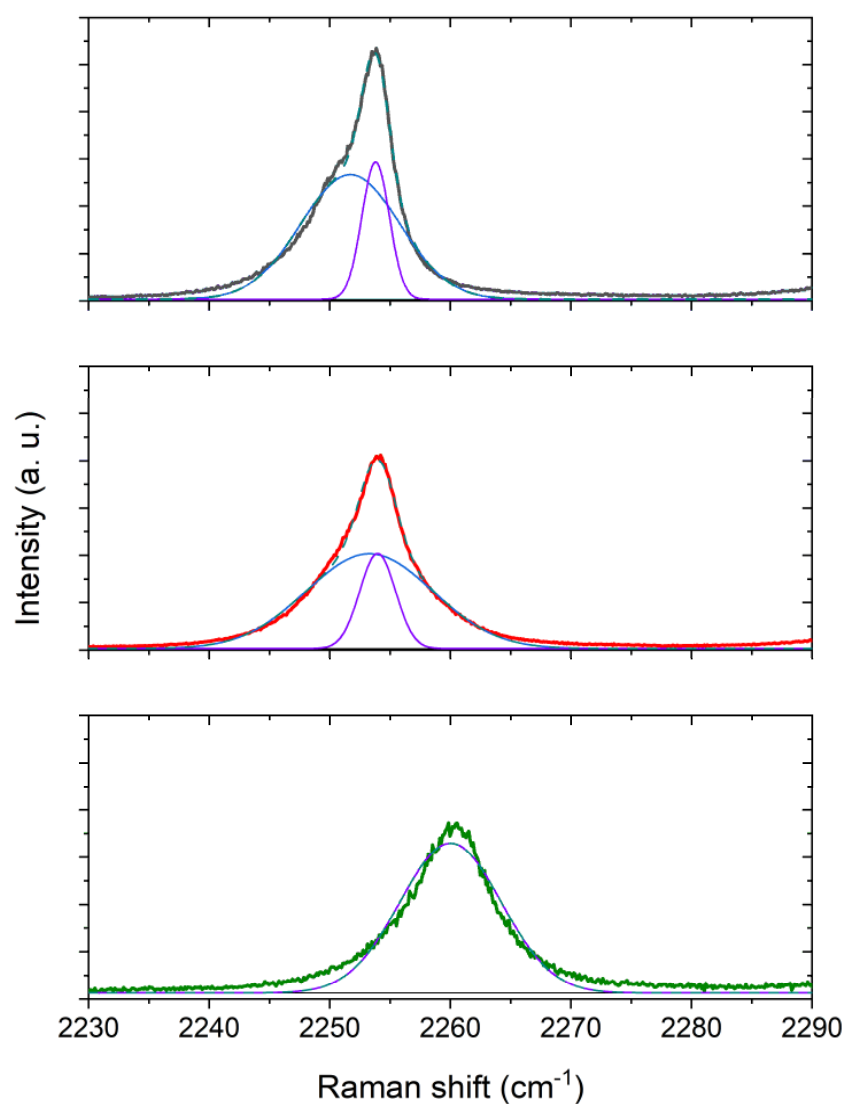
Combining both equations results in (3):

$$C_{\text{Total}} = \frac{I_{\text{free}}}{J_{\text{free}}} + \frac{I_{\text{bound}}}{J_{\text{bound}}} \quad (3)$$

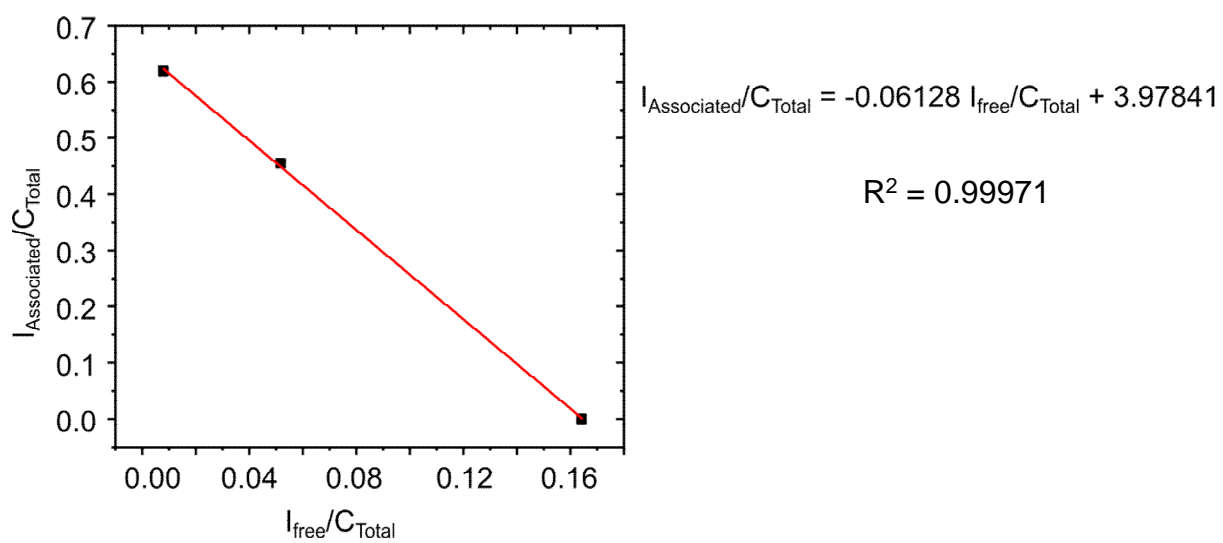
Equation 3 can be rearranged to (4)

$$\frac{I_{\text{bound}}}{C_{\text{Total}}} = J_{\text{bound}} - \frac{J_{\text{bound}}I_{\text{free}}}{J_{\text{free}}C_{\text{Total}}} \quad (4)$$

A plot of  $I_{\text{bound}}/C_{\text{Total}}$  against  $I_{\text{Free}}/C_{\text{Total}}$  leads to a straight line with an intercept equal to  $J_{\text{bound}}$  and a slope equal to  $-J_{\text{bound}}/J_{\text{Free}}$ . The plot is shown in Fig. S3.



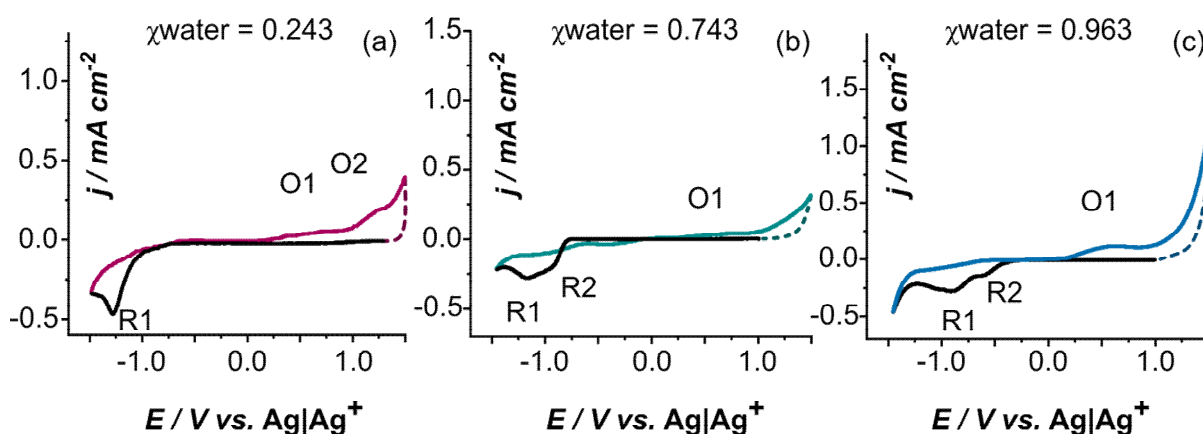
**Figure S2:** Band component fitting in the CN Raman spectral region. Grey line represents  $\chi_{\text{MeCN}} = 0.757 + \chi_{\text{water}} = 0.243$  (90%:10% v/v), red line represents  $\chi_{\text{MeCN}} = 0.257 + \chi_{\text{water}} = 0.743$  (50%:50% v/v), and green line represents  $\chi_{\text{MeCN}} = 0.037 + \chi_{\text{water}} = 0.963$  (10%:90% v/v).



**Figure S3:** Shurvell's plot corresponding to the integrated intensities of free and bound component of CN Raman stretching bands.

## ESI2: Cyclic voltammetry of Pd-acetate

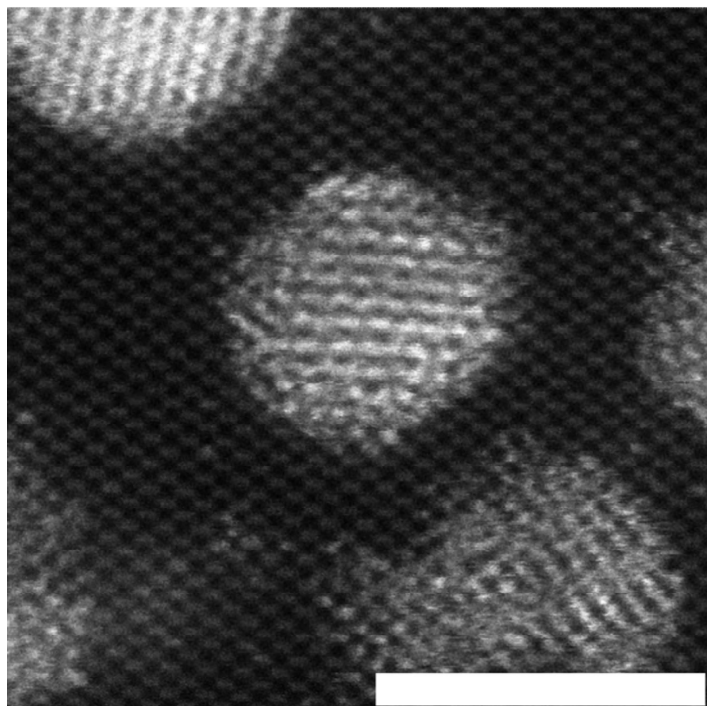
Figure S4 shows the first cycle of CVs recorded for Pd-acetate in various water containing MeCN solutions, for  $\chi_{\text{water}}$  (a) 0.243, (b) 0.743, and (c) 0.963, at a scan rate of  $0.1 \text{ V s}^{-1}$  cycled from +1.0 V to -1.5 V and back to +1.5 V. In the negative direction scan, at  $\chi_{\text{water}} = 0.243$ , one reduction peak (R1) is observed, while increasing  $\chi_{\text{water}}$  leads to the emergence of a new reduction peak (R2) and a shift of R1 to more positive potentials. Electrodeposition was achieved by applying a defined overpotential,  $\eta$ , according to  $\eta = E_{\text{dep}} - E_{\text{ocp}}$ , where  $E_{\text{dep}}$  is the applied potential and  $E_{\text{ocp}}$  is the open circuit potential.  $E_{\text{ocp}}$  was treated as an estimate of the formal equilibrium potential, by recording OCP under conditions where a substantial amount of Pd had been electrodeposited on the electrode surface ( $E_{\text{dep}} = -1.3 \text{ V}$  for 20 mins). Solution 1,  $\eta = -1.50 \text{ V} - (-0.50 \text{ V}) = -1.00 \text{ V}$ , solution 2,  $\eta = -1.45 \text{ V} - (-0.45 \text{ V}) = -1.00 \text{ V}$ , and solution 3,  $\eta = -1.25 \text{ V} - (-0.25 \text{ V}) = -1.00 \text{ V}$ .



**Figure S4:** First cycle CVs for studying the electrochemical behaviour of Pd-acetate at  $v = 0.1 \text{ V/s}$  (a) 90% MeCN:10% water v/v ( $\chi_{\text{water}} = 0.243$ ), (b) 50% MeCN:50% water v/v ( $\chi_{\text{water}} = 0.743$ ), (c) 10% MeCN:90% water v/v ( $\chi_{\text{water}} = 0.963$ ).

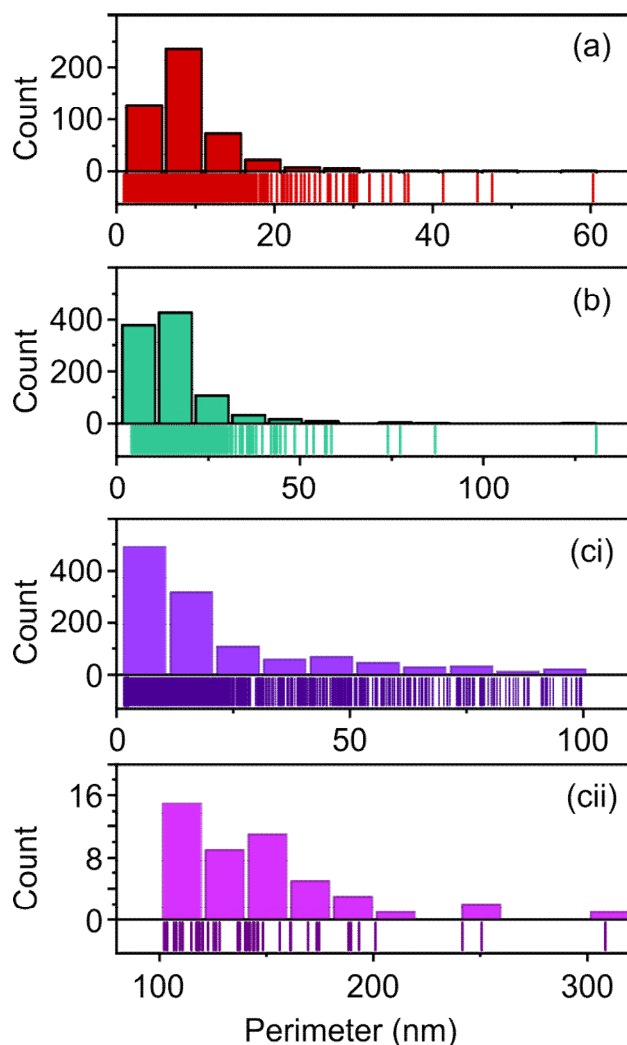
**ESI3: High resolution ADF-STEM of a Pd NP on the (110) surface of the BDD TEM electrode**

At an electrodeposition potential of  $\eta = -1$  V for  $t_{\text{dep}} = 50$  s in the MeCN rich solution there is evidence of Pd NP epitaxial growth, Fig. S5. Assuming a parallel orientation, the theoretical lattice parameter for Pd is 3.8907 Å whilst that for diamond is 3.567 Å, resulting in a lattice mismatch of  $(3.8907-3.567)/3.8907=8.3\%$ .



**Figure S5:** ADF-STEM of Pd NPs electrodeposited from  $1 \times 10^{-3}$  M Pd-acetate in (a) 90% MeCN:10% water v/v ( $\chi_{\text{water}} = 0.243$ ) at an electrodeposition potential of  $\eta = -1$  V for  $t_{\text{dep}} = 50$  s. Scale bar = 3 nm.

## ESI4: Statistical analysis summary for Pd nanostructures obtained via electrodeposition



**Figure S6:** Histogram summary analysis of the perimeter of Pd nanostructures electrodeposited using the following solutions; (a = solution 1) 90% MeCN:10% water v/v ( $\chi_{water} = 0.243$ ), (b = solution 2) 50% MeCN:50% water v/v ( $\chi_{water} = 0.743$ ), and (c = solution 3) 10% MeCN:90% water v/v ( $\chi_{water} = 0.963$ ). Perimeter values are extracted from the ADF-STEM images presented in Figures 2 and 5. Note: solution 3 led to two statistical distributions, (ci) represents the perimeter distribution for the NPs and nanostructures, and (cii) represents the perimeter distribution of the agglomerated nanostructures (nano-fractal like).

### References:

1. D. D. Kragten, R. A. van Santen, M. K. Crawford, W. D. Provine and J. J. Lerou, *Inorganic Chemistry*, 1999, **38**, 331-339.
2. J. R. Reimers and L. E. Hall, *Journal of the American Chemical Society*, 1999, **121**, 3730-3744.
3. J. M. Alía and H. G. M. Edwards, *Vibrational Spectroscopy*, 2004, **34**, 225-230.