Supporting information

Dimethylformamide-mediated synthesis of water-soluble platinum nanodendrites for ethanol oxidation electrocatalysis

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1) <u>Synthesis – TEM - XRD</u>

Taking into account the protocol described in the main body of the manuscript, nanodendrites with an 'average' degree of **porosity** were obtained using a precursor concentration of 15 mM. 'Less-porous' (or 'more compact') dendrites were obtained by using 3 mM Pt(acac)₂. On the contrary, 'more porous' dendrites were prepared when using 30 mM precursor. Typically 1 hour was sufficient in all cases to obtain nanodendrites. The application of prolonged reaction time, even up to 24 h (after the 1h aging) did not affect the final dendrite size.

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Fig. S1 TEM images for samples Pt1-PEI (images a & a'), Pt2-PEI (b & b'), Pt3-PEI (c & c')



Fig. S2 Early stages of dendrite formation (aliquot taken after the first 20 min of reflux for sample Pt2-PEI)



Fig. S3 XRD measurement for sample Pt1-PEI



Fig. S4 XRD measurement for sample Pt2-PEI

2) Advanced electron microscopy techniques - Additional data for Pt dendrites

Video showing the 3D reconstruction of the nanodendrites of sample 'Pt1-PEI', obtained by 3D-Tomography (see Experimental section). The 3D reconstruction is presented as a rendering in which intensity differences actually represent the projected thickness along a certain direction. In addition, the middle part of the movie shows slices through the 3D reconstruction (see attached file).





Fig. S5 HAADF-STEM images for sample Pt1-PEI



Fig. S6 HAADF-STEM image for sample Pt2-PEI



Fig. S7 HAADF-STEM image for sample Pt3-PEI



Fig. S8 'Unsupported' Pt nanodendrites (single powder sample, no use of electrode)



Fig. S9 Pt nanodendrites assembled on GC electrode



Fig. S10 (a) Cyclic voltammograms measured at GC-Pt3-PEI electrodes in 0.5 M NaOH and 0.5 M CH₃CHO (black curve with an oxidation peak at 0.125V) or 0.5 M NaOH and 0.5M CH₃COONa (red curve with no oxidation peak). Scan rate was 50 mV/s. (b) Cyclic voltammograms measured at GC-Pt3-PEI electrode in deaerated aqueous solution of 0.5M NaOH and purged $CO_2(g)$ for increasing purging time. Scan rate: 50 mV/s.



Fig. S11 Consecutive cyclic voltammograms recorded at GC-Pt2-PEI electrode in 1M ethanol and 1M NaOH for a potential window of -0.7V to 0.5V (a,b,c) and narrow potential window of -0.7V to 0V (orange dashed curves in (c)). Scan rate was 50 mV/s.



Fig. S12 Cyclic voltammograms recorded at GC-Pt2-PEI electrode in 0.1 M HClO₄. Scan rate was 100 mV/s.



Fig. S13. Test of Pt3-PEI reusability: A maximum of 900 cyclic voltammograms recorded at the same GC-Pt3-PEI modified electrode in three freshly prepared and deaerated alkaline solutions of 1M ethanol and 1M NaOH. Prior to immersion into the new solution, the GC-Pt3-PEI modified electrode was washed persistently with Mil lipore water. Volume of catalysts solution cast on GC electrode: $15 \ \mu L \ (2mg/mL)$. The active area of the modified electrode was $0.032 \ cm^2$. Scan rate was 50 mV/s.



Fig. S14 TEM images of Pt3-PEI nanodendrites after 300 cyclic voltammograms recorded in 1M ethanol and 1M NaOH aqueous solution. The scale bar is 20 nm at both images.