1) **Synthesis – TEM - XRD**

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.
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

3) Supplementary data for electrocatalysis
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 CO₂(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 Millipore water. Volume of catalysts solution cast on GC electrode: 15 µL (2mg/mL). The active area of the modified electrode was 0.032 cm². 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.