Supporting Information

Preserving the exposed facets of Pt₃Sn intermetallic nanocubes during order to disorder transition allows elucidation of effect of degree of alloy ordering on electrocatalysis

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Figure S1. (a) Shape distribution and (b) size distribution of synthesized Pt₃Sn calculated from around 300 particles shown in Figure 1a.



Figure S2. XRD pattern of synthesized Pt₃Sn cubes before loaded onto Vulcan carbon. The red labels indicate extra diffractions that is due to the L1₂ type ordering. The blue lines indicate the peak position and relative intensity from the reference. Thick layers of particles were drop casted onto XRD holder with fast drying to minimize self-assembly and the effect of preferred orientation, and the intensity ratios between the peaks to the (111) peak are very close to the bulk reference suggesting the synthesized nanocubes are close to fully ordered. The (110) peak was chosen for estimation of the degree of ordering throughout this study as it has the strongest intensity among the additional diffraction peaks.



Figure S3. Low magnification TEM images of (a) Acetic acid treated catalyst (c) 200°C treated catalyst and (e) 250 °C treated catalyst and corresponding size distribution of the edge length of Pt_3Sn cubes in (b), (d), (f), respectively showing that shape and size of the nanocubes are preserved. Scale bars = 50 nm.

Table S1. Calculation of the ordered domain size using the Scherrer equation and peak integration methods. A shape factor of 0.69 was applied for cubes to match the size measured from 300 cubes using TEM images in figure S1. The one-dimensional sizes of the ordered phase are: 9.3 nm; 8.0 nm and 5.2 nm for the acetic acid treated, thermal treated samples under 200°C and 250°C, respectively. In a 3-dimensional volume, the ratio for the three sample is 1: 0.63: 0.17, which is close to the ratio from peak integration: 0.95: 0.62: 0.29. The mismatch between 29.4% and 17% for the 250°C treated particles is understandable due to the assumption of same shape factor, however, the shape of the ordered domain may change during partial ordered-to-disordered transition.

| Post- synthesis treatment | 110 Peak position (degree) | FWHM (degree) | edge length from TEM* (nm) | ordered domain size τ* (nm) | % of original edge length | % of original volume | Integrated 110 peak area after normalized with {111} peak (a. u.) | % of size of initial ordered domain |
|---------------------------------|----------------------------------|------------------|--|--------------------------------------|------------------------------------|----------------------------|--|---|
| None | 31.66 | 0.67 | 9.3 ± 1.4 | 9.30 | 100.0 | 100.0 | 354.8 | 100.0 |
| Acetic acid | 31.66 | 0.67 | 8.9 ± 1.6 | 9.30 | 100.0 | 100.0 | 336.7 | 94.8 |
| 200 °C | 31.74 | 0.80 | 10.2 ± 1.5 | 7.97 | 85.7 | 62.9 | 218.6 | 61.6 |
| 250 °C | 31.79 | 1.25 | 9.3 ± 1.3 | 5.20 | 55.6 | 17.2 | 104.26 | 29.4 |

*The edge length from TEM measures the nanoparticle size, whereas the ordered domain size from XRD measures the crystallite size of the ordered domain. As expected, as the degree of ordering reduces the ordered domain size decreases while the edge length from TEM remains relatively constant.

Scherrer equation:

$$\tau = \frac{K\lambda}{\beta\cos\theta}$$

Where τ is the size of the ordered domain; *K* is the shape factor (here denoted as the shape of ordered domain); β is the line broadening at half the maximum intensity in radians, and θ is the Bragg angle.



Figure S4. (a) Potentiodynamic linear sweep voltammetry ORR plots for 60% ordered Pt_3Sn nanocubes in O_2 saturated 0.1 M HClO₄ at 25 °C with the working electrode rotating at 900, 1600, 2500 and 3600 rpm (b) Koutecký-Levich plots from data in (a) at different potentials ranging from kinetic control to mixed diffusion-kinetic control. The extrapolation of currents to infinite rotation speed (x = 0) represent the kinetic (diffusion free) currents.



Figure S5. k2 space for (a) Pt L3-edge (b) Sn K-edge.

| Sample | 95 % ordered | 60 % ordered | 30 % ordered | |
|----------------------|---------------|---------------|---------------|--|
| Pt-Pt CN | 5.77 ± 0.26 | 6.34 ± 0.19 | 6.29 ± 0.36 | |
| Pt-Pt NND (Å) | 2.793 ± 0.003 | 2.793 ± 0.002 | 2.791 ± 0.004 | |
| Pt-Pt σ ² | 0.005 ± 0.001 | 0.006 ± 0.001 | 0.006 ± 0.001 | |
| Pt-Sn CN | 2.33 ± 0.26 | 2.04 ± 0.15 | 1.87 ± 0.28 | |
| Pt-Sn NND (Â) | 2.814 ± 0.002 | 2.811 ± 0.002 | 2.817 ± 0.003 | |
| Pt-Sn σ ² | 0.008 ± 0.001 | 0.008 ± 0.001 | 0.008 ± 0.001 | |
| Sn-Pt CN | 10.88 ± 0.38 | 10.77 ± 0.46 | 9.29 ± 0.41 | |
| Sn-Pt NND (Å) | 2.814 ± 0.002 | 2.811 ± 0.002 | 2.817 ± 0.003 | |
| Sn-Pt σ ² | 0.008 ± 0.001 | 0.008 ± 0.001 | 0.008 ± 0.001 | |
| Sn-Sn CN | 5.38 ± 0.38 | 6.02 ± 0.51 | 3.58 ± 0.29 | |
| Sn-Sn NND (Å) | 4.015 ± 0.008 | 4.00 ± 0.01 | 4.02 ± 0.01 | |
| Sn-Sn σ ² | 0.007 ± 0.004 | 0.010 ± 0.004 | 0.006 ± 0.004 | |
| Sn-O CN | 1.92 ± 0.16 | 2.25 ± 0.19 | 3.38 ± 0.18 | |
| Sn-O NND (Â) | 2.044 ± 0.007 | 2.036 ± 0.007 | 2.040 ± 0.004 | |
| Sn-O σ ² | 0.006 ± 0.002 | 0.005 ± 0.003 | 0.005 ± 0.002 | |

Table S2. Summary of structural parameters obtained from EXAFS data.¹⁻³



Figure S6. XANES of (a) Pt L₃-edge and (b) Sn K-edge.



Figure S7. Table of fitting parameters and XPS of Pt^{Sn} , denoted as Pt in Sn environment, and Pt^{2+} (left column), Sn^{Pt} , denoted as Sn in Pt environment Sn^{2+} and Sn^{4+} (right column)⁴ on 95%, 60% and 30% ordered Pt_3Sn catalyst before and after activation by cyclic voltammetry.

| Table S3. Table of atomic | percentage of Pt and Sn in | different states extrapolate | d from XPS s | pectra in Fig | ure S11. |
|---------------------------|----------------------------|------------------------------|--------------|---------------|----------|
|---------------------------|----------------------------|------------------------------|--------------|---------------|----------|

| | 95% ord | ered | 60% ord | ered | 30% ordered | | |
|--------------------------------|------------------|-------|----------------|-----------|----------------|-----------|--|
| | as synthesized a | | as synthesized | activated | as synthesized | activated | |
| Sn ^{Pt} | 14.0% | 8.0% | 10.4% | 6.9% | 9.0% | 7.3% | |
| Sn ²⁺ | 2.6% | 2.7% | 9.8% | 0.0% | 10.7% | 0.0% | |
| Sn ⁴⁺ | 9.6% | 13.7% | 15.9% | 23.5% | 17.1% | 15.9% | |
| Pt ^{Sn} | 59.6% | 54.8% | 46.0% | 52.0% | 45.7% | 59.8% | |
| Pt ²⁺ | 14.0% | 20.5% | 17.8% | 17.7% | 17.4% | 17.1% | |
| Pt : Sn | 2.81 | 3.09 | 1.77 | 2.29 | 1.71 | 3.32 | |
| oxidized Sn : Sn ^{Pt} | 0.87 | 2.05 | 2.47 | 3.43 | 3.09 | 2.17 | |

The ratios are calculated via the formula below:

 $Pt: Sn = (Pt^{Sn}+Pt^{2+}) / (Sn^{Pt}+Sn^{2+}+Sn^{4+})$

Oxidized Sn: $Sn^{Pt} = (Sn^{2+}+Sn^{4+}) / Sn^{Pt}$



Figure S8. (a) Pt L₃-edge EXAFS (b) Sn K-edge EXAFS.



Figure S9. R_{mag} fits for (a) 95% ordered Pt (b) 60% ordered Pt (c) 30% ordered Pt (d) 95% ordered Sn (b) 60% ordered Sn (c) 30% ordered Sn.



Figure S10. R_{real} fits for (a) 95% ordered Pt (b) 60% ordered Pt (c) 30% ordered Pt (d) 95% ordered Sn (b) 60% ordered Sn (c) 30% ordered Sn.



Figure S11. K² space fits for (a) 95% ordered Pt (b) 60% ordered Pt (c) 30% ordered Pt (d) 95% ordered Sn (b) 60% ordered Sn (c) 30% ordered Sn.



Figure S12. CN of Sn-Pt, Pt-Pt, Sn-Sn, Pt-Sn and Sn-O calculated from EXAFS using a pair distribution function.



Figure S13. The ratio of ECSA_{Cu-upd} to its initial value after 1,000 and 10,000 cycles of ADT.



Figure S14: Low magnification TEM images of (a) acetic acid treated catalyst (c) 200°C treated catalyst and (e) 250 °C treated catalyst and corresponding size distribution of the edge length of Pt_3Sn cubes in (b), (d), (f), respectively after the 10,000 cycles of ADT showing that shape and size of the nanocubes are preserved. Scale bars = 50 nm

| | concentration | | /L) weight (ng) | | nmol | | atomic % | | |
|-------------|---------------|-----|-----------------|------|------|------|----------|----|-------|
| | Sn | Pt | Sn | Pt | Sn | Pt | Sn | Pt | Pt/Sn |
| 95% ordered | 44 | 157 | 220 | 785 | 1.85 | 4.02 | 32 | 68 | 2.17 |
| 60% ordered | 151 | 251 | 755 | 1255 | 6.36 | 6.43 | 50 | 50 | 1.01 |
| 30% ordered | 168 | 254 | 840 | 1270 | 7.08 | 6.51 | 52 | 48 | 0.92 |

Table S4. ICP-MS analysis of the electrolyte after 10,000 cycles of ADT showing that dissolution is significantly higherfor the less ordered nanocubes



Figure S15. Cyclic voltammograms of (a) 95% ordered (b) 60% ordered and (c) 30% ordered Pt₃Sn nanocubes, after 0, 1,000 and 10,000 cycles of ADT. The H_{upd} region in the box are shown in Figure 5a.



Figure S16. Schematic illustration of the steps for identical location HAADF-STEM imaging before and after ADT.



Figure S17. (a) (b) Fast Fourier transforms of Figure 5b and Figure 5d, respectively. The (110) diffraction spots pointed by the yellow arrows were used for inverse Fourier transforms shown in Figure 5c and Figure 5e. Scale bars = 5 nm⁻¹

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