

Supporting Information

Effects of heat treatment atmosphere on the structure and activity of Pt₃Sn nanoparticle electrocatalysts: a characterisation case study

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Structural characterisation of the parent Pt₃Sn/C

The parent Pt₃Sn/C was characterised using TEM, XRD, XPS and XAFS, as described for the heat-treated samples in the main text. Its structure is largely similar to that of the Ar annealed sample. The TEM image (Figure S1, top) shows good dispersion of 2-3 nm diameter nanoparticles on the carbon support. The composition of nanoparticles was approximately identified using the lattice fringes observed in the HRTEM image (Figure S1, bottom left) by selected area Fourier-transformation (Figure S1, bottom right). The lattice fringes were indexed to the (111) and (200) facet of face centric cubic structure (fcc) of Pt or Pt₃Sn alloy. The fcc structure was also observed by the XRD patterns (Figure S2). The (220) peak of the parent Pt₃Sn/C was located between the standard references (JCPDS database), Pt and Pt₃Sn, suggesting Sn is incorporated into Pt structure, with the lattice parameter increasing from 3.930 Å (for the Pt/C, JM reference catalyst) to 3.975 Å. The extent of alloying from the lattice parameter is calculated to be ~49% using Vegard's law. The extent of alloying obtained by analysis of the Sn 3d XPS data (Figure S3) as the fraction of Sn present at Sn⁰ was 58 at% Sn. In contrast, the linear combination fitting of the Sn K edge XANES spectra (Figure S4) yielded a smaller amount of Sn⁰ or alloyed Sn, 15-25 at%. The mismatch between XPS and XANES aligns with the results presented in the main text for the heat treated samples. Finally, the EXAFS spectra of the parent Pt₃Sn/C on Pt L₃ and Sn K edges are shown in Figure S5, along with the corresponding first cell fits (Table S1). The fitting strategy is described in the main text. The extents of alloying from EXFAS fitting were estimated using the Pt-Pt bond length and $J_{\text{Pt-Sn}}$, and the results are listed in Table S2 along with the value measured by the other techniques described above. The extent of alloying of the parent Pt₃Sn/C, like that of the Ar sample, is between the air sample and the H₂ sample.

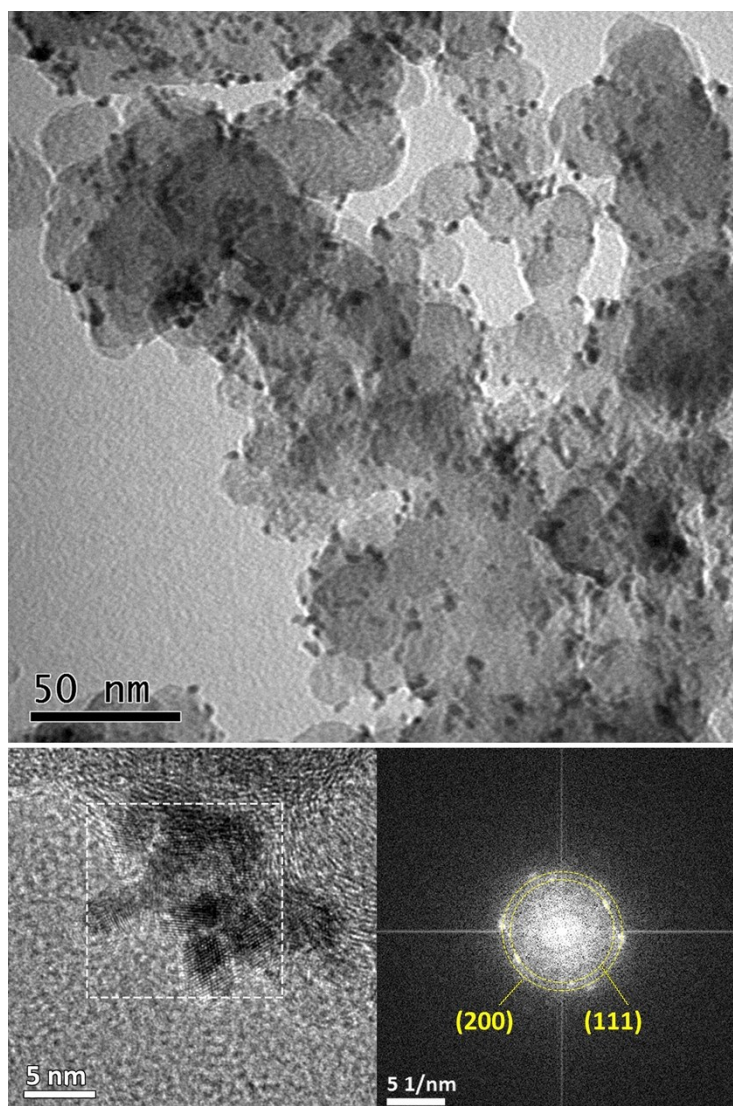


Figure S1. (top) TEM and (bottom left) HRTEM images of the parent PtSn nanoparticles; the FFT pattern on the bottom right is derived from the selected area (dashed white box) of the image.

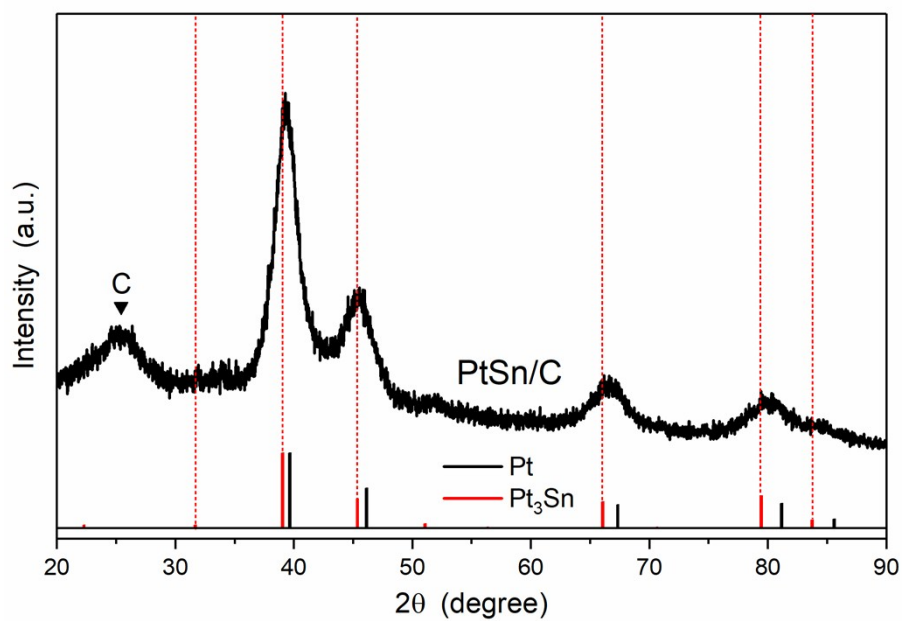


Figure S2. XRD pattern of the parent PtSn/C.

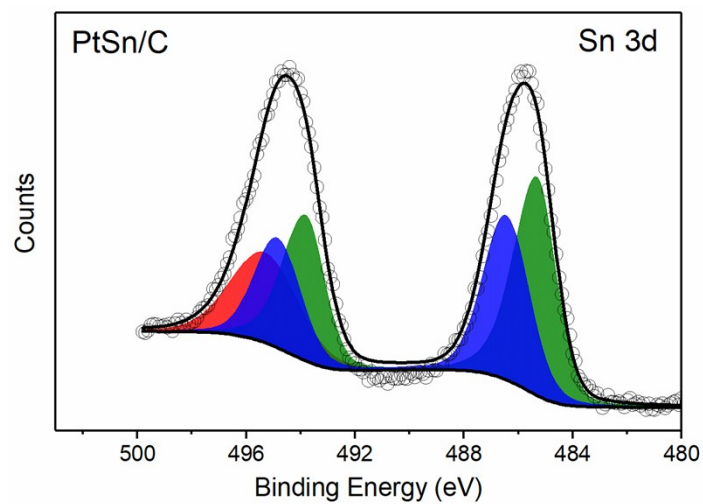


Figure S3. Sn 3d XPS spectrum of the parent PtSn/C and fitting. Peak deconvolution shown corresponding to Sn⁰ (green), Sn^{IV} (blue), and metallic Sn 3d_{3/2} (red).

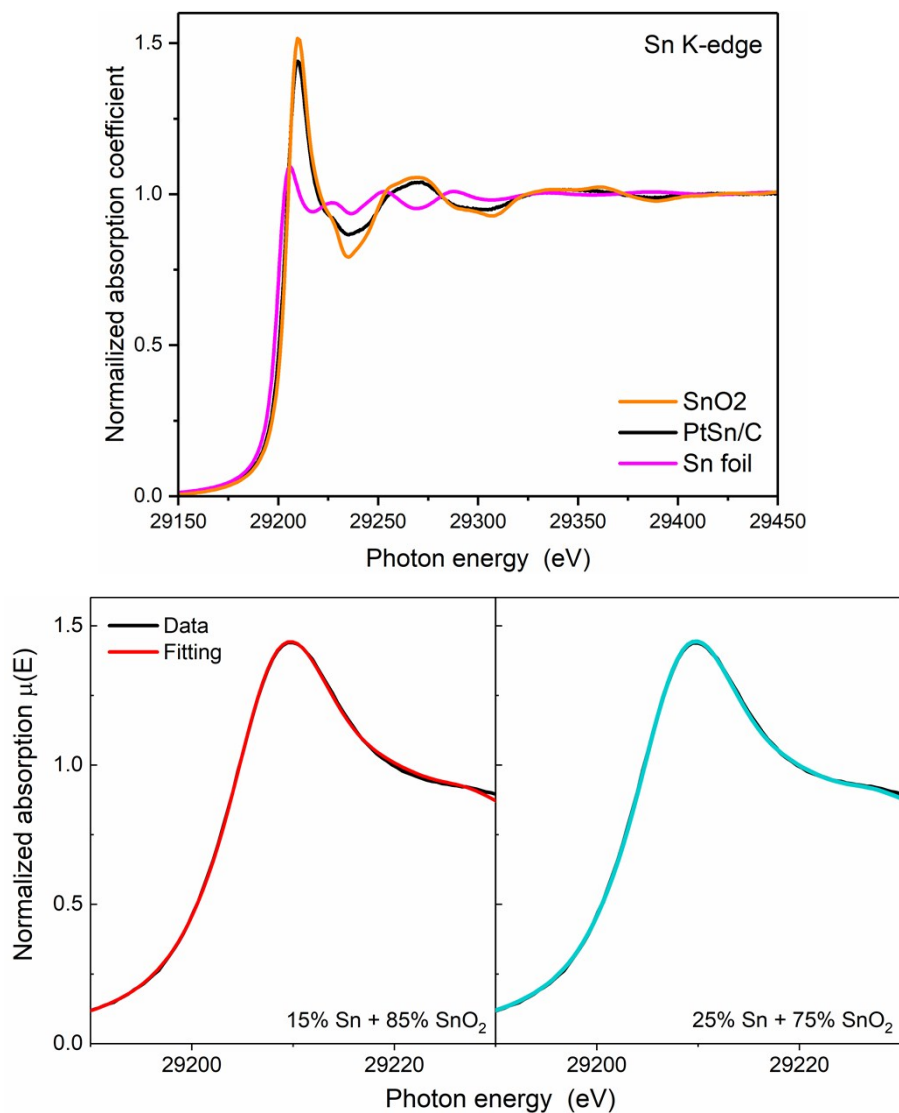


Figure S4. (top) XANES spectra of the parent PtSn/C along with the SnO₂ reference and Sn foil spectra, (bottom) linear combination fitting of the whiteline region. SnO₂ and Sn foil (red line) or the Sn K-edge spectra of the H₂ treated sample collected under H₂ (cyan line) are used as references for the fittings. The goodness of the fit (R-factor) for the fits are 0.02% (red) and 0.004% (cyan).

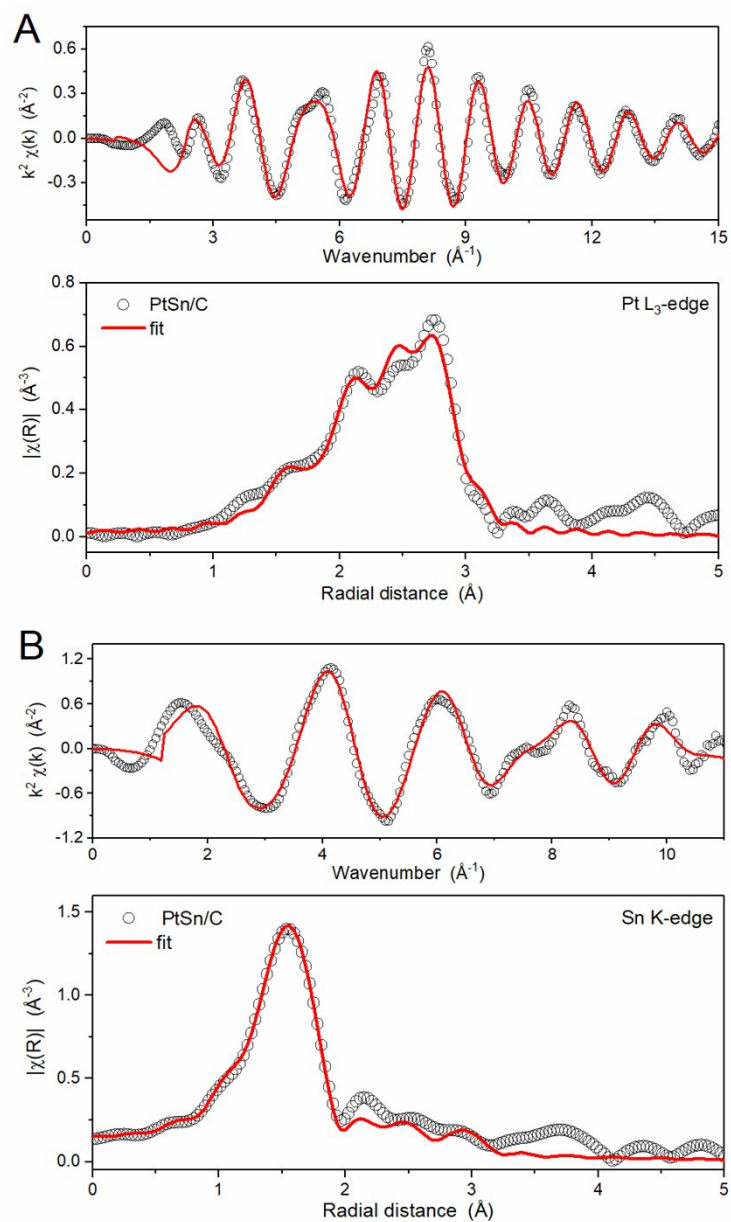


Figure S5. k²-weighted EXAFS spectra and their Fourier transforms (not phase-corrected) of the parent PtSn/C at (A) Pt L₃-edge and (B) Sn K-edge. The data points and the fittings are plotted as empty dots and red lines, respectively.

Table S1. EXAFS data fitting results of as-prepared samples

Samples	Shell	N	R(Å)	$\sigma^2 \times 10^2$ (Å)	$J_{\text{Pt-Sn}}$ (%)	R-factor (%)
PtSn/C	Pt-O	0.3(1)	1.97(2)	0.2(4)	24	1.54
	Pt-Pt	7.9(6)	2.760(7)	0.92(8)		
	Pt-Sn	0.7(4)	2.82(2)	0.9(4)		
	Sn-O	4.1(4)	2.06(1)	0.4(2)		
	Sn-Pt	3(1)	2.82(2)	0.9(4)		

N, the coordination number for the absorber-backscatterer pair; R, the average absorber-backscatterer distance; σ^2 , the mean square relative displacement.

Table S2 Extent of alloying calculated using the various structural characterisation methods.

Characterisation method	$J_{\text{Pt-Sn}}$ from EXAFS	XPS	XANES*	XRD	EXAFS
Pt₃Sn/C	24%	58%	15-25%	49%	20%

*using the Sn foil (lower end of range) or Pt₃Sn data (upper end of range) as one of reference spectra