

## Supporting Information

### Intermetallic Structures with Atomic Precision for Selective Hydrogenation of Nitroarenes

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### Experimental

#### Synthesis of Pt@mSiO<sub>2</sub> seeds

Pt@mSiO<sub>2</sub> was synthesized following previously reported literature with slight modifications.<sup>1</sup> In a 500 mL round bottom flask 8.4 g of tetradecyltrimethylammonium bromide (TTAB) was dissolved in 200 mL of deionized water. To this 103 mg of potassium tetrachloroplatinate (K<sub>2</sub>PtCl<sub>4</sub>) dissolved in 25 mL of deionized water was added to obtain a cloudy white solution, following which a septum was inserted on the flask. The cloudy solution was first homogeneously stirred at room temperature for 10 min and was then placed in a 50 °C oil bath under vigorous stirring for 15 minutes to obtain a clear solution. To this 284 mg NaBH<sub>4</sub> was dissolved in 15 mL cold water and then injected quickly into the clear Pt-TTAB solution. An additional needle was inserted into the septum to allow excess hydrogen generated in situ to vent. The needle was removed after 20 min, and the resultant mixture was stirred at 50 °C for 24 h. The brown Pt colloidal solution was centrifuged at 4 times at 4000 rpm (30 min each) to remove large Pt NPs. The supernatant solution of Pt NPs was then centrifuged at 14000 rpm for 15 min twice and concentrated into a final aqueous solution of 20 mL. The aqueous Pt NPs solution was then diluted to 150 mL, and 8 mL of a 0.05 M NaOH solution was added to obtain a pH of ~ 11. After stirring for 10 min, 3 mL 10% tetraethyl orthosilicate (TEOS) methanol solution was added dropwise to the above solution. The Pt@mSiO<sub>2</sub> NPs were obtained after stirring for 24 h at room temperature. The coated Pt@mSiO<sub>2</sub> NPs were then centrifuged and redispersed in 150 mL of methanol. Surfactant removal was carried out via refluxing the methanolic Pt@mSiO<sub>2</sub> NPs solution with an additional 15 mL of a concentrated HCl solution (36% assay) at 90 °C for 24 h. The refluxed solution was then centrifuged twice at 14000 rpm, and the collected Pt@mSiO<sub>2</sub> was washed thrice with methanol.

Table S1. ICP results of all PtM@mSiO<sub>2</sub> NPs (M=Sn, Zn, and Pb).

Entry	Pt (wt.%)	Secondary metal (wt.%)	Actual Pt/M in molar ratios
Pt@mSiO <sub>2</sub>	46.0	–	–
PtSn@mSiO <sub>2</sub>	27.5	16.3	1.02
Pt <sub>3</sub> Sn@mSiO <sub>2</sub>	57.8	10.6	3.3
PtZn@mSiO <sub>2</sub>	41.9	12.7	1.1
Pt <sub>3</sub> Zn@mSiO <sub>2</sub>	43.0	4.3	3.3
PtPb@mSiO <sub>2</sub>	36.0	34.7	1.1

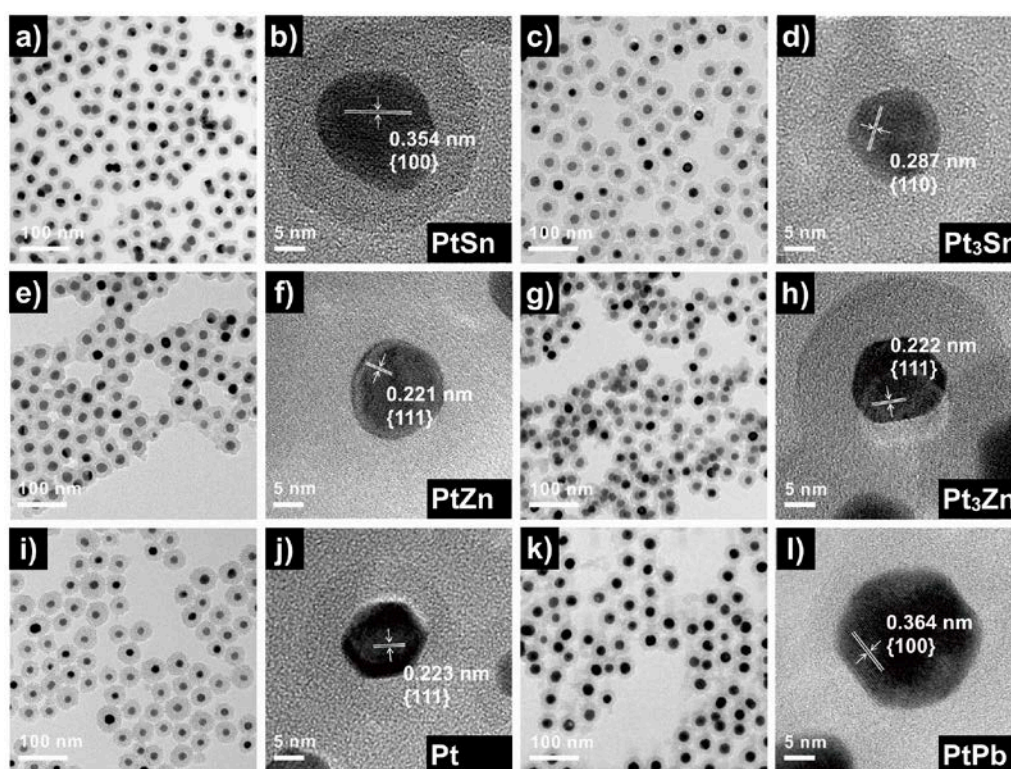


Figure S1. TEM images and HRTEM images of a), b) PtSn@mSiO<sub>2</sub>; c), d) Pt<sub>3</sub>Sn@mSiO<sub>2</sub>; e), f) PtZn@mSiO<sub>2</sub>; g), h) Pt<sub>3</sub>Zn@mSiO<sub>2</sub>; i), j) Pt@mSiO<sub>2</sub>; and k), l) PtPb@mSiO<sub>2</sub>

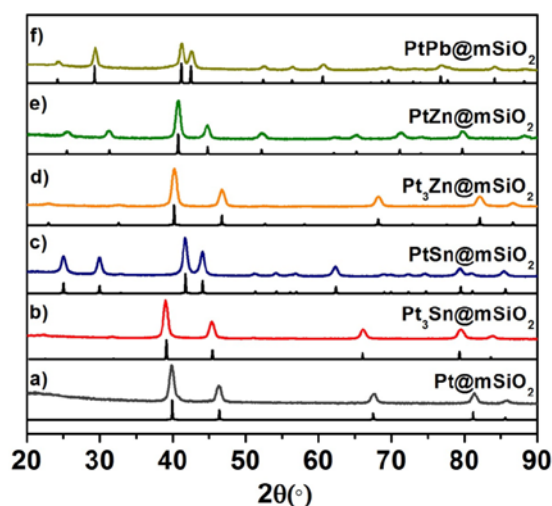


Figure S2. PXRD patterns of a) Pt@mSiO<sub>2</sub>; b) Pt<sub>3</sub>Sn@mSiO<sub>2</sub>; c) PtSn@mSiO<sub>2</sub>; d) Pt<sub>3</sub>Zn@mSiO<sub>2</sub>; e) PtZn@mSiO<sub>2</sub>; and f) PtPb@mSiO<sub>2</sub> with corresponding standard patterns (black vertical bars).

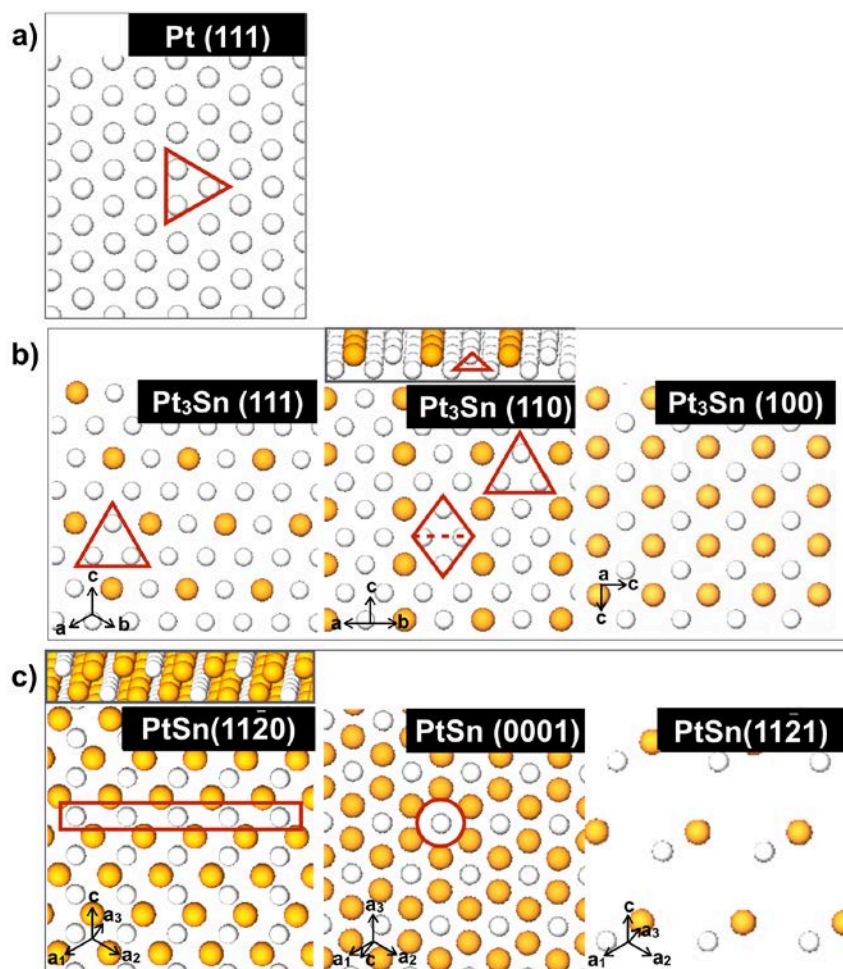


Figure S3. Surface structures of ideal a) Pt (111), b) Pt<sub>3</sub>Sn (111), (110) and (100), and c) PtSn (1120), (0001), and (1121). Pt (white circles) and Sn atoms (yellow circles) are shown, along with Pt threefold sites (red triangles in b), fourfold sites (red rhombus in b), bridge sites (red rectangle in c), and single Pt (circle in c).

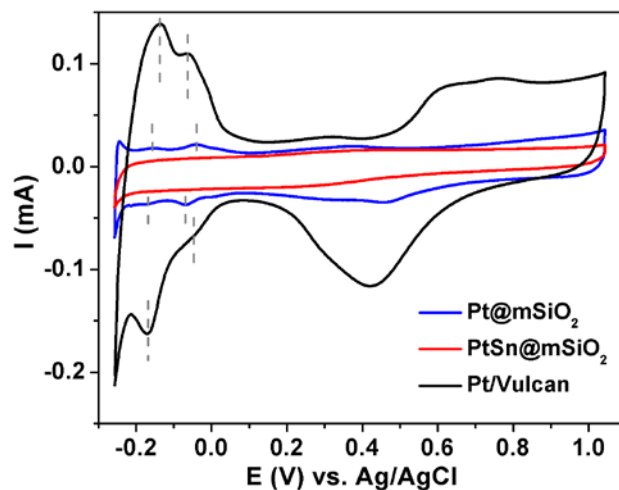
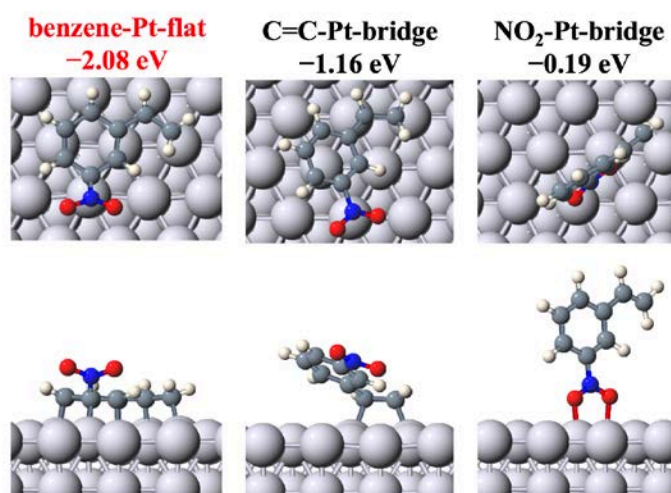


Figure S4. CV spectra of  $\text{H}^+$  electro-reduction for intermetallic  $\text{PtSn@mSiO}_2$ ,  $\text{Pt@mSiO}_2$  and commercial  $\text{Pt/Vulcan}$ .  $\text{H}_2$  Electro-reaction of evolution ( $2\text{H}^+ \rightleftharpoons \text{H}_2$ ) occurs at -0.2-0.1 V region (vs.  $\text{Ag/AgCl}$ ) for both forward and backward scans, and the subsequent  $\text{H}_2$  desorption and adsorption due to this electro-reaction occurs at  $\sim 0$  V. In -0.2  $\sim$  0.1 V, commercial  $\text{Pt/Vulcan}$  and  $\text{Pt@mSiO}_2$  are both active for the  $\text{H}^+$  electro-reduction reaction.  $\text{Pt@mSiO}_2$  has weaker peak intensity and some voltage shift compared to commercial  $\text{Pt/Vulcan}$ , likely due to the large sizes of  $\text{Pt@mSiO}_2$  (14 nm) presenting low surface area-to-volume ratio and less undercoordinated Pt at corner, edge and kink sites. Specifically,  $\text{Pt@mSiO}_2$  sample has two tails ( $\sim 0$  V) in forward and backward scans, corresponding the  $\text{H}_2$  adsorption and desorption. Intermetallic  $\text{PtSn@mSiO}_2$  shows only one tail as the backward scan corresponding the desorption of  $\text{H}_2$  from the electro-reaction, but the absence of adsorption tail indicates a negligible  $\text{H}_2$  adsorption on  $\text{PtSn}$  surfaces in the liquid phase at room temperature.

### 3-nitrostyrene on Pt(111)



### 3-nitrostyrene on PtSn(11 $\bar{2}$ 0)

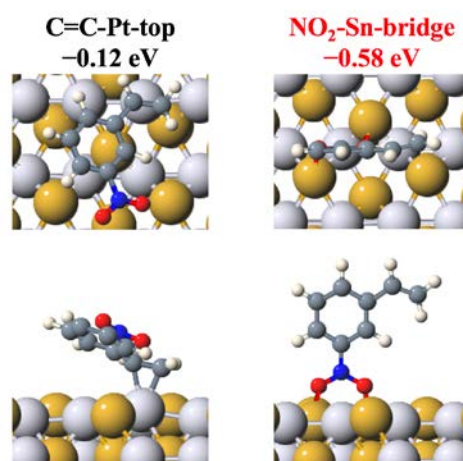


Figure S5. DFT results of 3-nitrostyrene adsorption on Pt(111) and PtSn(11 $\bar{2}$ 0) in different configurations. Pt (Sn) in surfaces are given by light grey (brown) spheres; C, N, O and H atoms in 3-nitrostyrene are shown by small grey, blue, red and white spheres. Top (bottom) panel is the top (side) view.

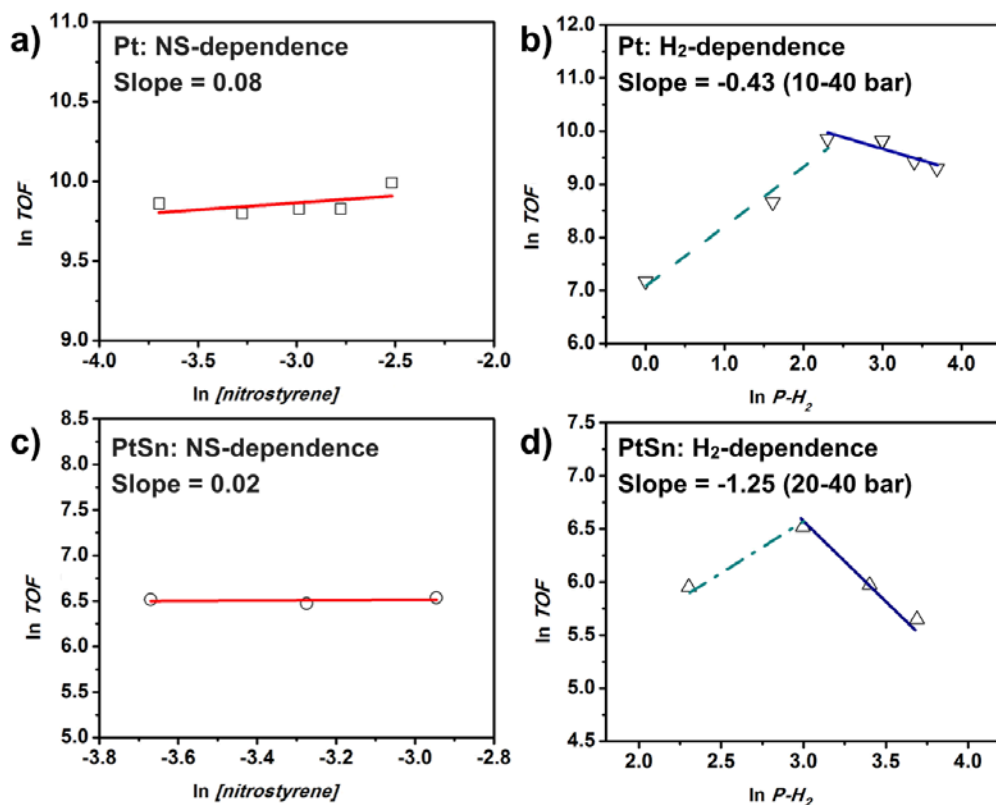


Figure S6. For Pt@mSiO<sub>2</sub>: the dependence of reaction rate on a) 3-nitrostyrene (NS) concentration, and b) H<sub>2</sub> pressure. The slope is a) is 0.08, indicating a near zero reaction order, and the slope in b) is -0.43. For PtSn@mSiO<sub>2</sub>: c) the dependence of reaction rate on 3-nitrostyrene concentration, and d) H<sub>2</sub> pressure. The slope in c) is 0.02, indicating a near zero order reaction, and the slope in d) is -1.25, showing a near negative first reaction order to H<sub>2</sub>. For Pt, nitrostyrene substrate varies from 50, 75, 100, 125, and 150 mg; H<sub>2</sub> pressure ranges from 10, 20, 30 and 40 bars. For PtSn, nitrostyrene substrate varies from 50, 75, and 100 mg; H<sub>2</sub> pressure ranges from 20, 30, and 40. All other reaction conditions were controlled as the same: 2 mL toluene as a solvent, 20 mg xylene as internal standard and 80 °C. The reaction rate was calculated at the initial reaction time.

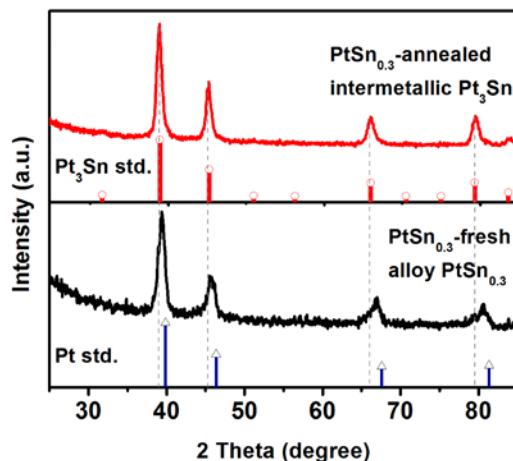


Figure S7. PXRD patterns of alloyed  $\text{PtSn}_{0.3}@\text{mSiO}_2$  alloy (black curve, directly after synthesis), and intermetallic  $\text{Pt}_3\text{Sn}@\text{mSiO}_2$  (red curve, after annealing). The diffraction peaks of alloy  $\text{PtSn}_{0.3}$  slightly shift to lower angle due to lattice expansion by addition of Sn. The intermetallic  $\text{Pt}_3\text{Sn}$  agrees well with the  $\text{Pt}_3\text{Sn}$  standard. Intermetallic phase shifts more to the lower angles in contrast to the alloy phase.

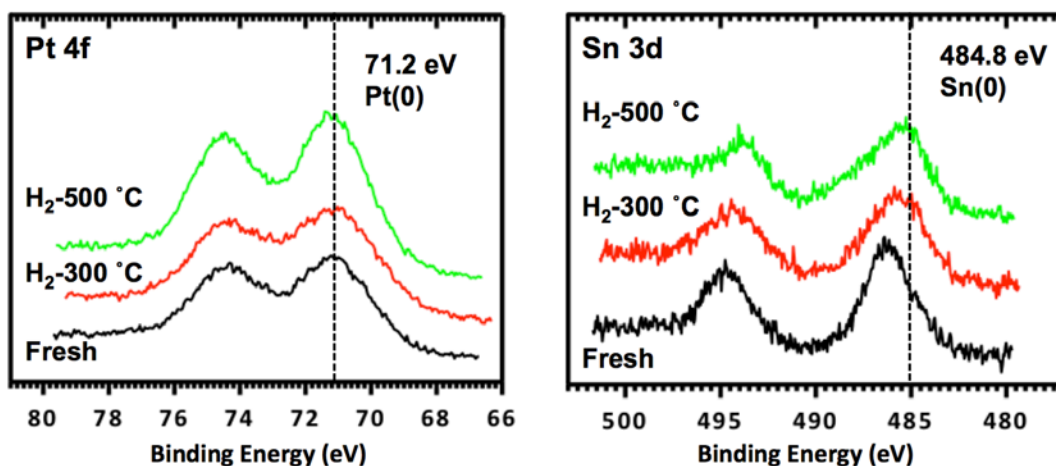
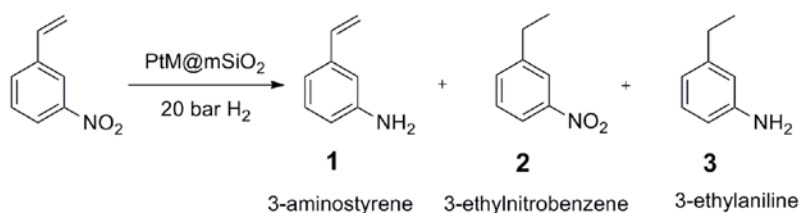


Figure S8. AP-XPS spectra of  $\text{PtSn}_{0.3}@\text{mSiO}_2$  during *in situ* reductions. Pt stays as a metallic state in both fresh and reduced samples. The fresh sample has  $\text{SnO}_x$  peaks and transitions to metallic state after high-temperature reduction. The  $\text{SnO}_x$  on the fresh sample can be formed during the sample handling. However, they may readily exist during the TEG reduction. Atomic Pt/Sn ratios of fresh, reduced in  $300^\circ\text{C}$ , and reduced in  $500^\circ\text{C}$  are respectively 1.33, 1.90 and 2.28.

Table S2. Catalytic results of fresh and annealed PtSn<sub>0.3</sub>@mSiO<sub>2</sub> for 3-nitrostyrene hydrogenation.



Entry	Catalyst	Time (h)	Conversion (%)	Selectivity		
				<b>1</b>	<b>2</b>	<b>3</b>
1	Fresh PtSn <sub>0.3</sub> @mSiO <sub>2</sub>	1	3.2	>99	—	—
		9	63.3	>99	—	—
2	Annealed Pt <sub>3</sub> Sn@mSiO <sub>2</sub>	0.5	>99	—	—	>99
		1	>99	—	—	>99

a. Reaction condition: 1 mg catalyst, 50 mg 3-nitrostyrene, 20 mg xylene as internal standard, 2 mL toluene as solvent, 80 °C, and 20 bar H<sub>2</sub>.

#### Reference

- 1 S. H. Joo, J. Y. Park, C. K. Tsung, Y. Yamada, P. Yang and G. A. Somorjai, *Nat. Mater.*, 2009, **8**, 126.