Electronic Supplementary Information

Small amount of main group metal atoms matters: ultrathin Pdbased alloy nanowires enabling high activity and stability towards efficient oxygen reduction reaction and ethanol oxidation

Qiaoli Chen,*^{a+} Hui Jin, ^{a+} Tianchun Cheng, ^a Zhi Wang, ^a Yaoyao Ren,^a Jinshu Tian ^a and Yihan Zhu ^a

^a College of Chemical Engineering and State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology, Zhejiang University of Technology, Hangzhou 310014, Zhejiang, China.

[†] These authors contribute equally to this article.



Fig. S1 Diameter distributions of the PdBi naonwires (NWs).



Fig. S2 Fast Fourier transform (FFT) pattern of Fig.1d.



Fig. S3 The EDX spectra of (a) $Pd_{93}Bi_7 NWs$, (b) $Pd_{97}Bi_3 NWs$ and (c) $Pd_{99}Bi_1 NWs$.



Fig. S4 TEM image of (a) PdSn NWs and (b) PdPb NWs.



Fig. S5 (a) XPS full spectrum of $Pd_{89}Pb_{11}$ NWs, (b) Pd 3d spectrum, (c) Pb 4f spectrum.



Fig. S6 TEM images of PdBi NWs prepared at different conditions. (a) Without surfactant, (b) in presence of only ODA, (c) in presence of only DTAB, (d) in presence of ODA and CTAB, (e) in presence of ODA and CTAC, and (f) in presence of HDA and DTAB.



Fig. S7 TEM image of PdBi NWs synthesized under oxygen atmosphere.



Fig. S8 (a) CV curves of PdBi NWs/C recorded in Ar-saturated 0.1 M KOH solution at a scan rate of 50 mV s⁻¹. (b) ORR polarization curves recorded in O_2 -saturated 0.1 M KOH electrolyte at a rotation rate of 1600 rpm and a scan rate of 10 mV s⁻¹. (c) The half wave potential. (d) The comparisons in mass activity and specific activity at 0.90 V_{RHE}.



Fig. S9 (a) CV curves of PdPb NWs/C recorded in Ar-saturated 0.1 M KOH solution at a scan rate of 50 mV s⁻¹. (b) ORR polarization curves recorded in O_2 -saturated 0.1 M KOH electrolyte at a rotation rate of 1600 rpm and a scan rate of 10 mV s⁻¹. (c) The half wave potential. (d) The comparisons in mass activity and specific activity at 0.90 V_{RHE}.



Fig. S10 (a) CV curves of PdSn NWs/C recorded in Ar-saturated 0.1 M KOH solution at a scan rate of 50 mV s⁻¹. (b) ORR polarization curves recorded in O_2 -saturated 0.1 M KOH electrolyte at a rotation rate of 1600 rpm and a scan rate of 10 mV s⁻¹. (c) The half wave potential. (d) The comparisons in mass activity and specific activity at 0.90 V_{RHE}.



Fig. S11 ORR polarization curves of $Pd_{97}Bi_3$ NWs/C catalysts obtained at various rotation rates in O_2 -saturated 0.1 M KOH solutions at a scan rate of 10 mV s⁻¹. The inset shows corresponding Levich plots (n=4) at 0.4, 0.5, and 0.6 V_{RHE}.



Fig. S12 ORR polarization curves of $Pd_{89}Pb_{11}$ NWs/C catalysts obtained at various rotation rates in O_2 -saturated 0.1 M KOH solutions at a scan rate of 10 mV s⁻¹. The inset shows corresponding Levich plots (n=4) at 0.4, 0.5, and 0.6 V_{RHE}.



Fig. S13 EIS curves of $Pd_{97}Bi_3$ NWs/C, Pd NWs/C, and commercial Pt/C catalysts and commercial Pd/C catalysts.



Fig. S14 ORR polarization curves of (a) Pt/C, (b) Pd/C, (c) Pd NWs/C and (d) $Pd_{89}Pb_{11}$ NWs/C catalysts before and after 10,000 cycles.



Fig. S15 (a) CV curves of Pt/C, Pd/C, Pd NWs/C, $Pd_{97}Bi_3$ NWs/C and $Pd_{89}Pb_{11}$ NWs/C catalysts in Ar saturated 0.1 M KOH solution containing 0.3 M methanol at a scan rate of 50 mV s⁻¹. (b) ORR polarization curves in O₂-saturated 0.1 M KOH solution containing 0.3 M methanol.



Fig. S16 (a) CV curves in Ar-saturated 1 M KOH at a scan rate of 50 mV s⁻¹. (b) CV curves in Arsaturated 1 M KOH + 1 M ethanol at a scan rate of 50 mV s⁻¹. (c) Comparison of mass activity for various catalysts. (d) Current density-time curves of different catalysts in 1.0 M KOH + 1.0 M ethanol solution at 0.82 V.



Fig. S17 The crystal models for pure (a) Pd (111) (top view), and (b) main group metal (Bi, Pb or Sn)-doped Pd (111) (side view). The navy color represents Pd and the purple one for Bi, Pb or Sn.



Fig. S18 The PDOS of (a) PdBi slab, (b) PdPb slab and (c) PdSn alloy slab.