Electronic Supplementary Information

Ultrafine Pd@PdPt nanowires with a single-atom alloy shell for efficient formate oxidation

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Density functional theory (DFT) calculations of Pd (111), PdPt\textsubscript{1} (111), Pt (111) and PdPt (111) surfaces were obtained by using Material studio 2019 through the local density approximation (LDA). An additional Coulomb potential ($U_{Pt} =$ 3.0 eV) and GGA+U functional was applied to states of 3d-orbit. Norm-conserving pseudopotentials were used altogether with a 400 eV of plane-wave energy cut off. The Brillouin zone was sampled with a $2 \times 2 \times 1$ Monkhorst-Pack grid. The force on each atom of the structure was fully optimized less than $10^{-4}$ eV/Å. A vacuum layer of 20 Å was incorporated into the slabs to avoid periodic interaction. The free energy ($G$) was computed using formula: $G = E + ZPE - T\Delta S$, where $E$ was the total energy, ZPE was the zero-point energy, the entropy ($\Delta S$) of each adsorbed state were carried out from DFT calculation, the thermodynamic corrections for gas molecules were obtained from standard tables.
Figures

**Fig. S1** (a) XRD pattern and (b) TEM image of the as-prepared Pd NWs.

**Fig. S2** (a) EDX spectra and (b) XRD pattern of Pd@PdPt NWs.

**Fig. S3** (a-c) Pt 4f and (d-g) Pd 3d XPS spectra of Pd@PdPt NWs (The black vertical dotted line indicates the standard binding energy).
Fig. S4 TEM images of (a) Pd@PdPt$_{0.011}$ NWs, (b) Pd@PdPt$_{0.018}$ NWs, (c) Pd@PdPt$_{0.024}$ NWs and (d) Pd@PdPt$_{0.029}$ NWs.

Fig. S5 CV curves of (a) Pd@PdPt$_{0.011}$ NWs, (b) Pd@PdPt$_{0.018}$ NWs, (c) Pd@PdPt$_{0.024}$ NWs and (d) Pd@PdPt$_{0.029}$ NWs in N$_2$-purged 1 M H$_2$SO$_4$/1 M H$_2$SO$_4$ + 0.5 M CH$_3$OH at 50 mV s$^{-1}$. 
**Fig. S6** The spacing between Pd atoms on Pd (111) and PdPt(111) surfaces.

**Fig. S7** Pt mass-normalized CV curves of Pd@PdPt_{0.024} NWs and Pt CC in N\textsubscript{2}-purged 1 M KOH + 0.5 M HCOOK at 50 mV s\textsuperscript{-1}.

**Fig. S8** Pd mass-normalized forward CV curves of Pd@PdPt\textsubscript{0.024} NWs and Pd CC in N\textsubscript{2}-purged 1 M KOH + 0.5 M HCOOK at 50 mV s\textsuperscript{-1}.

**Fig. S9** The atomic structures for (a) PdPt(111) surface and (b) Pt(111) surface.
**Fig. S10** Top and side views of the atomic structures for Pt (111) alloy surfaces with adsorbed CO*, H*, COOH*, OH*. C, grey; O, red; H, white; Pt, green.

**Fig. S11** Top and side views of the atomic structures for PdPt (111) alloy surfaces with adsorbed CO* and H*. C, gray; O, red; H, white; Pt, green; Pd, blue.
**Fig. S12** Chronoamperometric measurements of Pd@PdPt\textsubscript{0.024} NWs, Pd NWs and Pt CC in N\textsubscript{2}-purged 1 M KOH + 0.5 M HCOOK at 0.4 V.

**Fig. S13** (a) EDX spectrum (b)TEM image of Pd@PdPt\textsubscript{0.024} NWs after the stability test.