Electronic Supplementary Information

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

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DFT calculation

Density functional theory (DFT) calculations of Pd (111), PdPt$_1$ (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 × 2 × 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 fomula: G = E + ZPE - TΔS, where E was the total energy, ZPE was the zero-point energy, the entropy (ΔS) of each adsorbed state were carried out from DFT calculation, the thermodynamic corrections for gas molecules were obtained from standard tables.

Figures
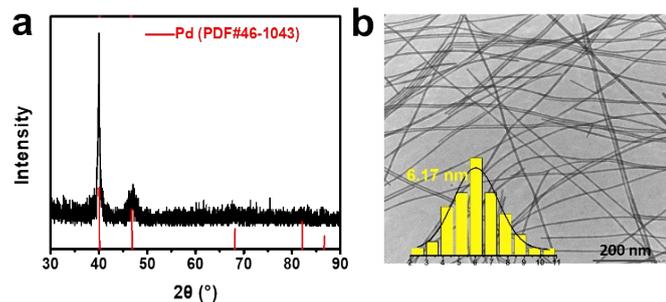
Fig. S1 (a) XRD pattern and (b) TEM image of the as-prepared Pd NWs.
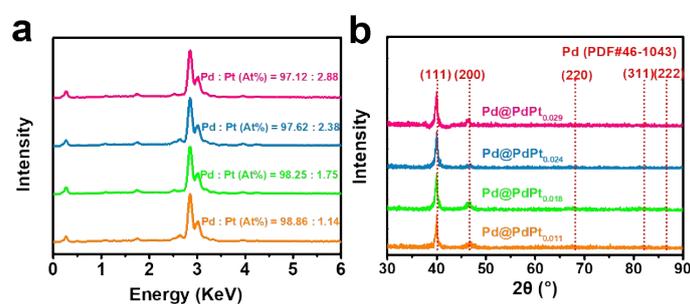
Fig. S2 (a) EDX spectra and (b) XRD pattern of Pd@PdPt NWs.
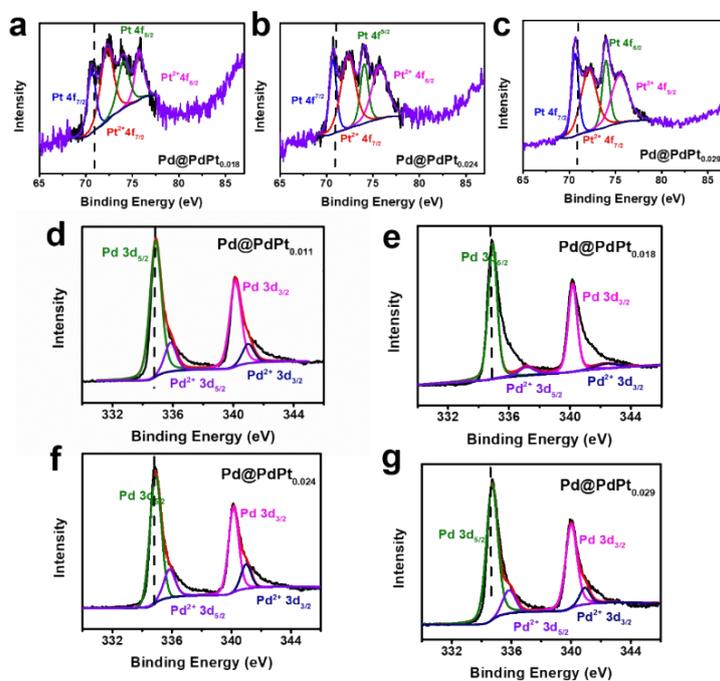
Fig. S3 (a-c) Pt 4f and (d-g) Pd 3d XPS spectra of Pd@PdPt NWs (The black vertical dotted line indicates the standard binding energy).
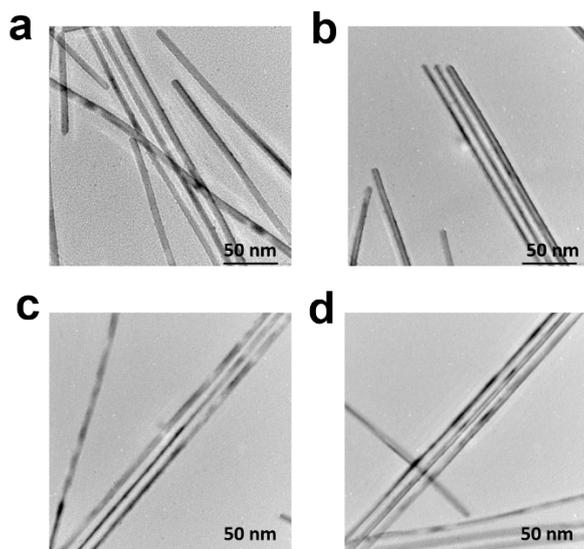
Fig. S4 TEM images of (a) Pd@PdPt$_{0.011}$ NWs, (b) Pd@PdPt$_{0.018}$ NWs, (c) Pd@PdPt$_{0.024}$ NWs and (d) Pd@PdPt$_{0.029}$ NWs.
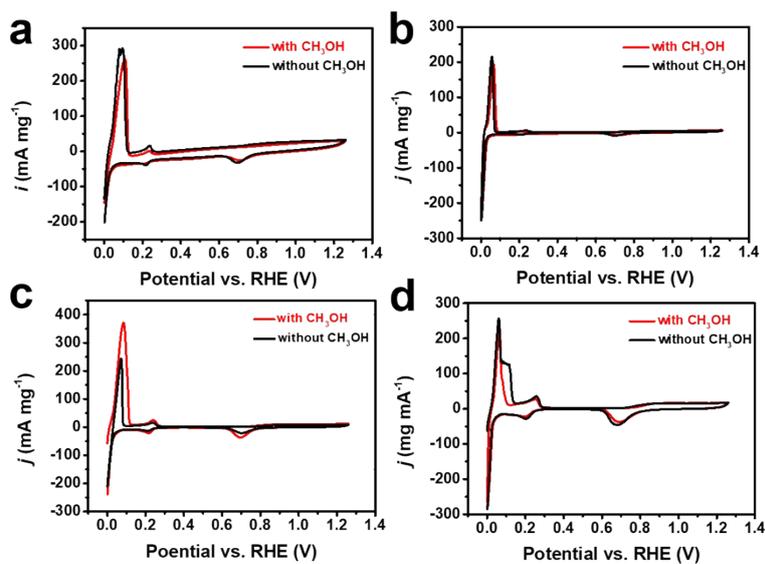
Fig. S5 CV curves of (a) Pd@PdPt$_{0.011}$ NWs, (b) Pd@PdPt$_{0.018}$ NWs, (c) Pd@PdPt$_{0.024}$ NWs and (d) Pd@PdPt$_{0.029}$ NWs in N$_2$-purged 1 M H$_2$SO$_4$/1 M H$_2$SO$_4$ + 0.5 M CH$_3$OH at 50 mV s^{-1}.
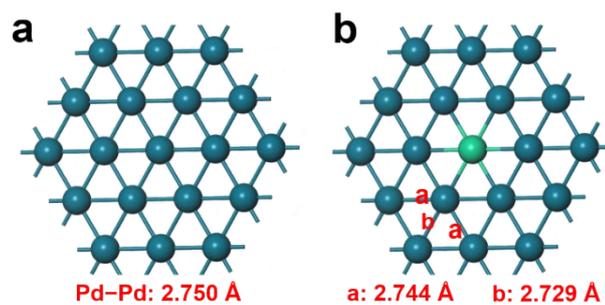
Fig. S6 The spacing between Pd atoms on Pd (111) and $PdPt_1$ (111) surfaces.
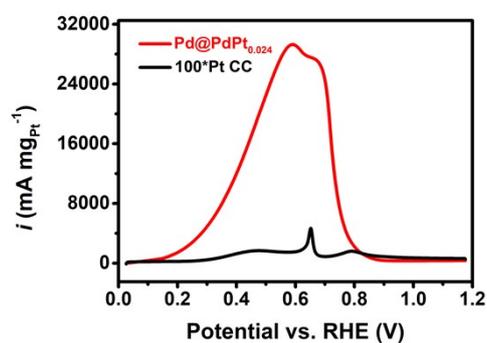
Fig. S7 Pt mass-normalized CV curves of $Pd@PdPt_{0.024}$ NWs and Pt CC in N_2-purged 1 M KOH + 0.5 M HCOOK at 50 mV s^{-1}.
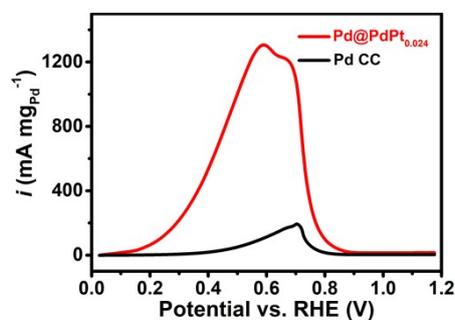
Fig. S8 Pd mass-normalized forward CV curves of $Pd@PdPt_{0.024}$ NWs and Pd CC in N_2-purged 1 M KOH + 0.5 M HCOOK at 50 mV s^{-1}.
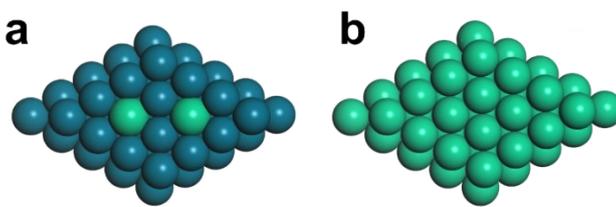
Fig. S9 The atomic structures for (a) PdPt(111) surface and (b) Pt(111) surface.
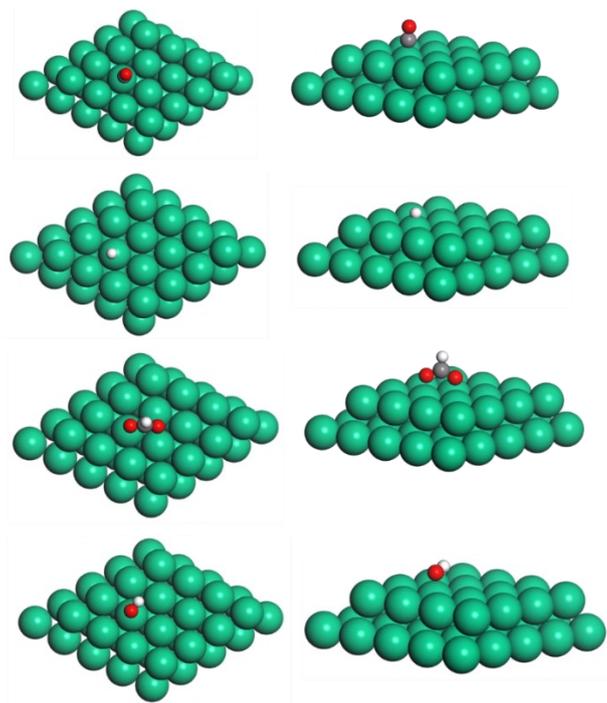
Fig. S10 Top and side views of the atomic structures for Pt (111) alloy surfaces with adsorbed CO*, H*, COOH*, OH*. C, grey; O, red; H, white; Pt, green.
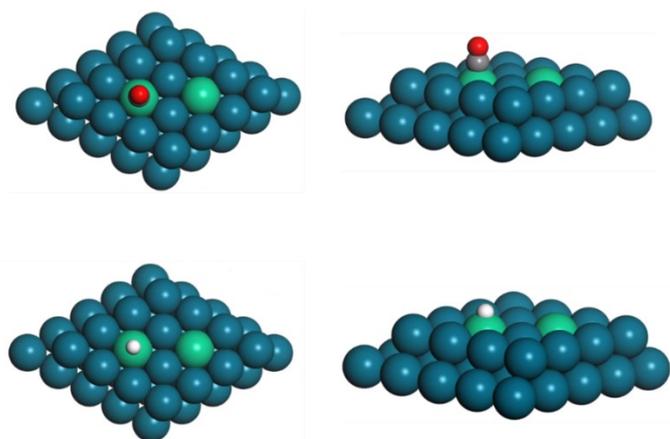
Fig. S11 Top and side views of the atomic structures for PdPt (111) alloy surfaces with adsorbed CO* and H*. C, gray; O, red; H, white; Pt, green; Pd, blue.
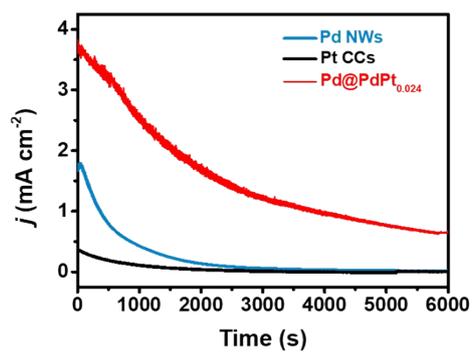
Fig. S12 Chronoamperometric measurements of Pd@PdPt$_{0.024}$ NWs, Pd NWs and Pt CC in N$_2$-purged 1 M KOH + 0.5 M HCOOK at 0.4 V.
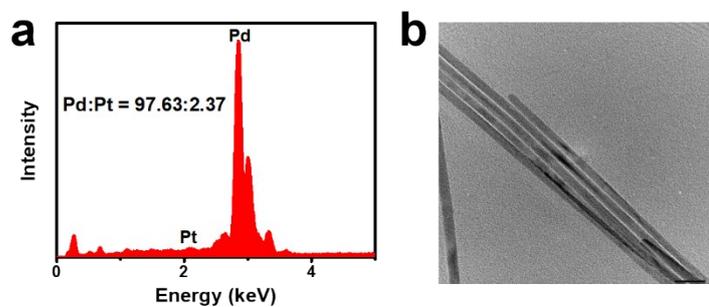
Fig. S13 (a) EDX spectrum (b)TEM image of Pd@PdPt$_{0.024}$ NWs after the stability test.