Supplementary Information

# Optimization Strategy for Fuel-Cell Catalysts Based on Electronic Effects

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Supplemental figures:

Figure S1. The cyclic voltammograms of the precursor solution of Pd (**A**), Cu (**B**), and Au (**C**) at different rotation rate. For co-deposition of Pd-Cu or Pd-Au, -0.4 V (vs. SCE) was used as the deposition potential so as to adjust the alloying degree based on the nominal ratio of precursors.
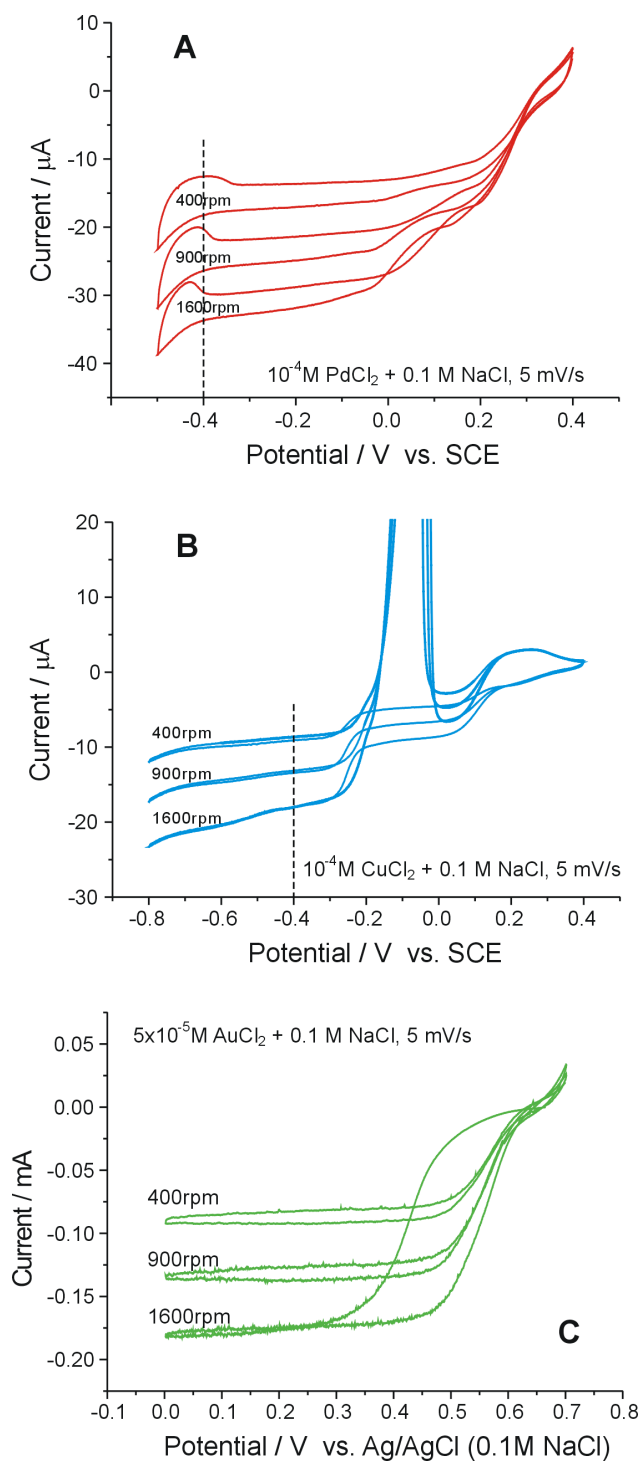
Figure S2. A representative result of grazing-incidence X-ray diffraction (GID) measurements for the Pd (alloy) electrode. The sensitive shift in the diffraction peaks reflects the strain in the Pd lattice and corresponds to an alloying degree very close to the nominal ratio of the precursors.
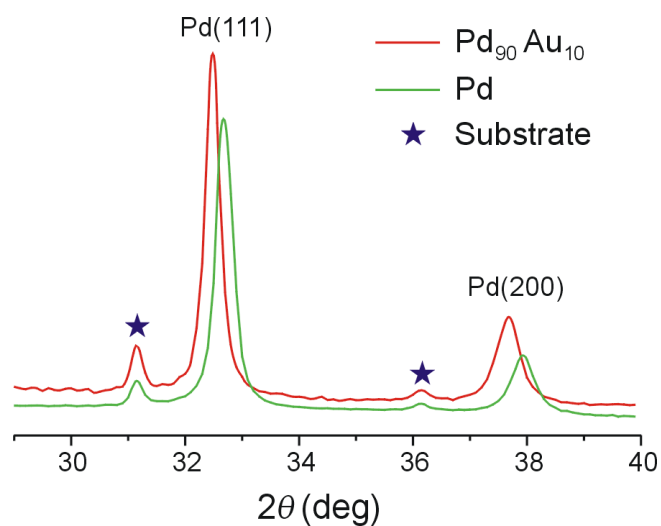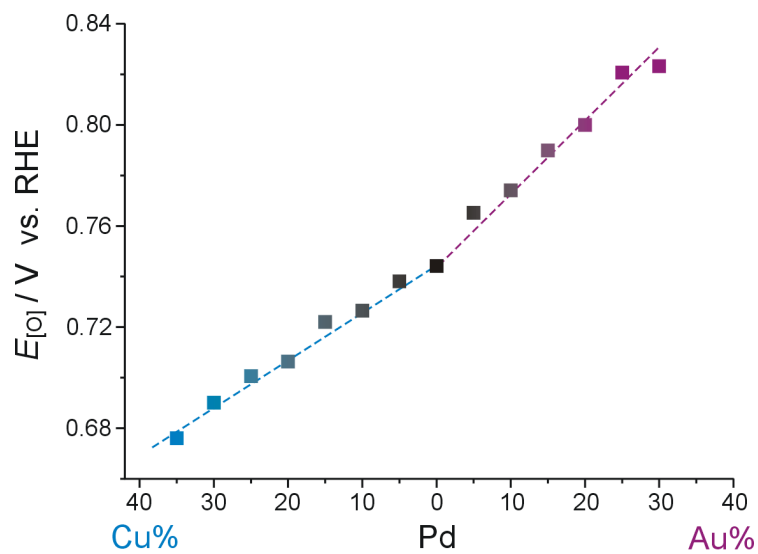

Figure S3. A representative scanning-electron-microscopy (SEM) image of the surface of Pd (alloys) prepared by electrochemical deposition.
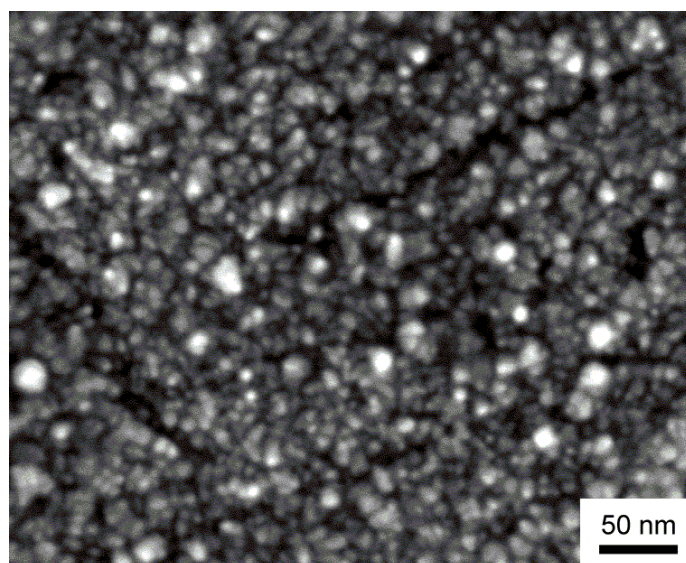
Figure S4. The cyclic voltammograms of Pd (alloys) recorded at a potential scan rate of 50 mV/s in 0.1 mol/L HClO$_4$.
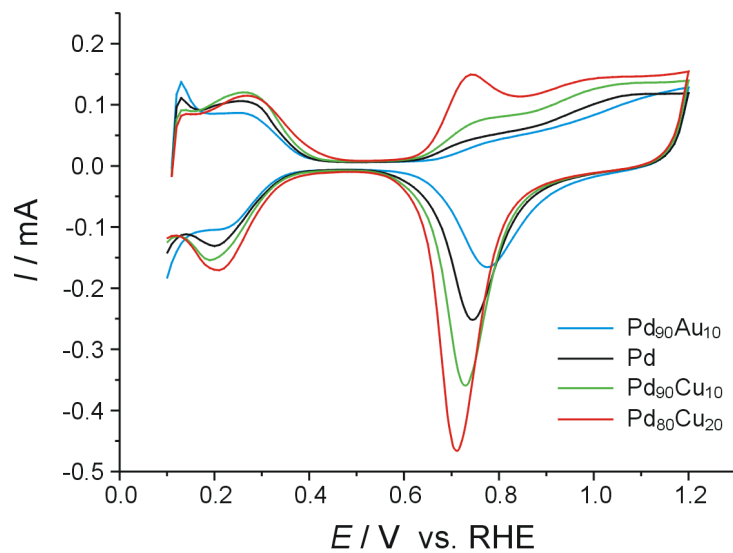
Figure S5. The dependence of the peak potential of surface-oxides stripping ($E_{[O]}$) on the alloying degrees of Pd-Cu and Pd-Au.

Figure S6. The formic-acid oxidation reaction (FAOR) over Pd. (**A**) *I-V* curves recorded using a rotating disk electrode at different rotation rates and a potential scan rate of 2 mV/s. Electrolyte: 0.1 mol/L $HClO_4$ solution containing 10^{-3} mol/L formic acid. (**B**) The Koutecký-Levich plot for the dependence of the diffusion-limiting current at 0.35 V (vs. RHE) on the rotation rate. A reaction electron number of ca. 2 can be calculated according to the slope of the regression line.
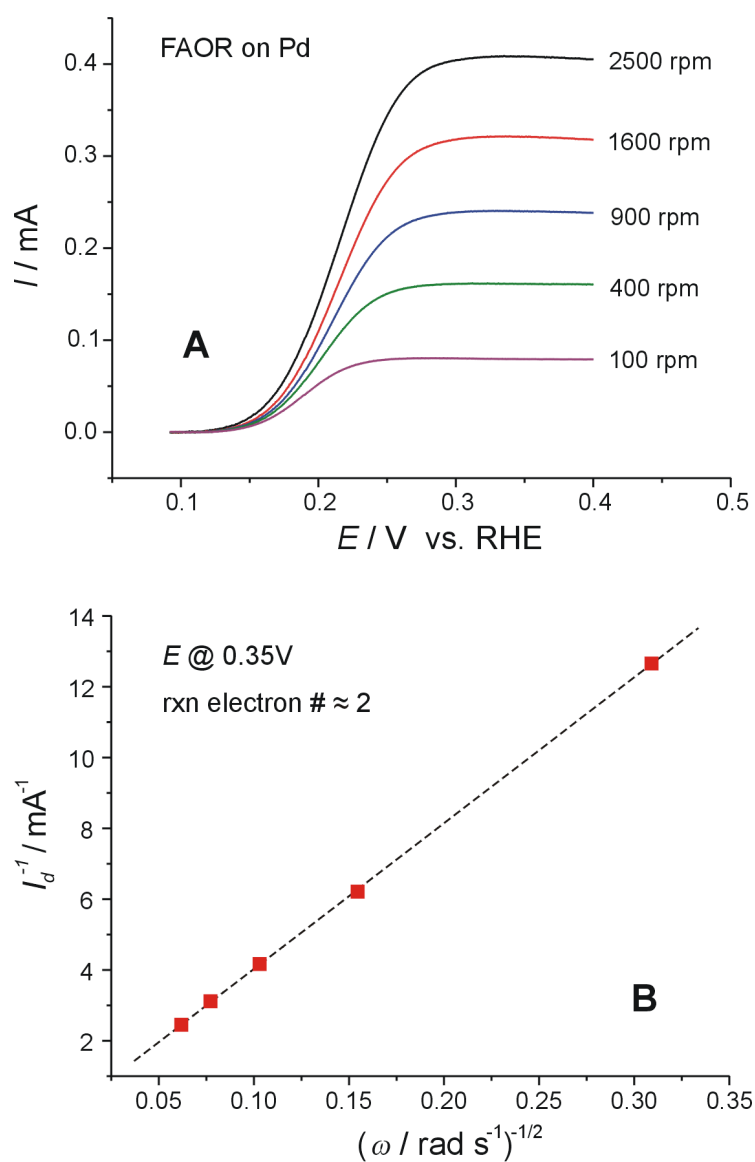
Figure S7. The energy diagram for possible dehydrogenation pathways of HCOOH on Pd(111). It can be seen that, although the *COOH intermediate is possible, the *OCHO* intermediate is favorable by 0.3 eV in energy. Furthermore, the *COOH intermediate is very easy to "slip" into the poisoning state (*CO). Considering Osawa et al. had also observed the *OCHO* intermediate on Pd in their ATR-FTIR[30], it is therefore reasonable to use the oxygen affinity as an adequate descriptor for the surface reactivity in this case.