**Supporting Information**

**for**

**An Enhanced Electrocatalytic Activity of Carbon-Supported Ordered Intermetallic Palladium-Lead (Pd$_3$Pb) Nanoparticles towards Electrooxidation of Formic Acid**

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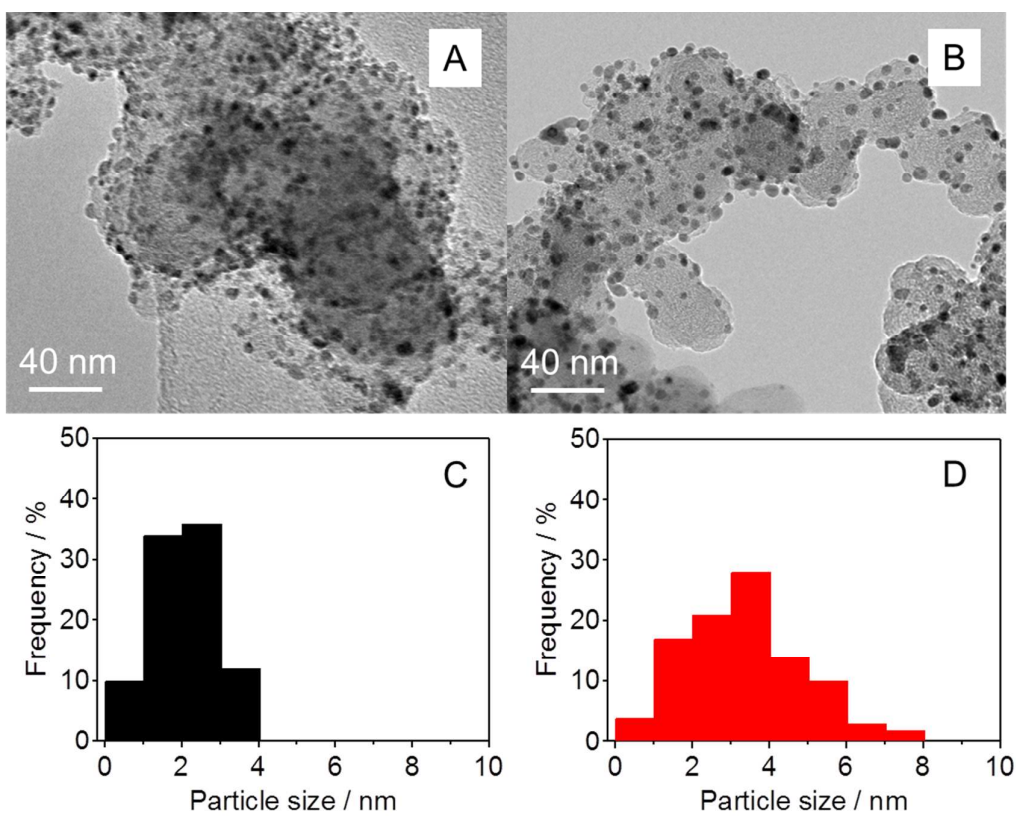
**Supporting Figures**

Figure S1 TEM images of the commercially available (A) Pd NPs/CB (20 wt.%) and (B) as-prepared ordered intermetallic $Pd_3Pb$ NPs/CB. The size distribution of the (C) Pd NPs/CB and (D) $Pd_3Pb$ NPs/CB is shown in the histograms.
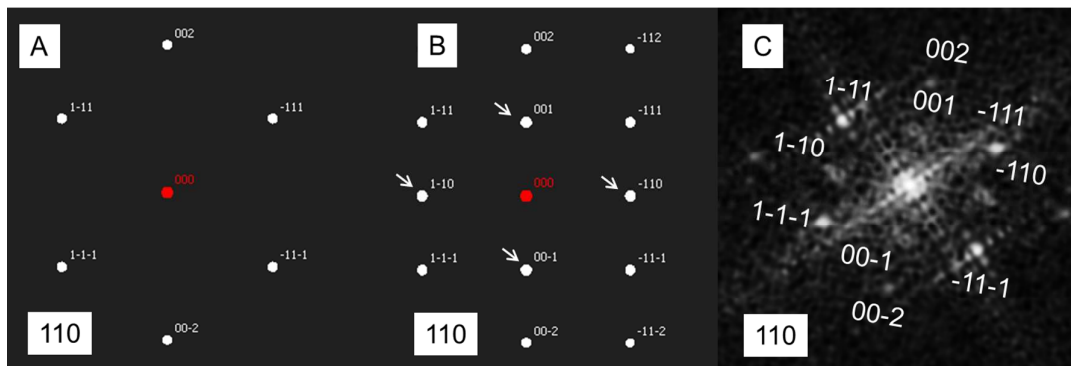
Figure S2. The simulated FFT profiles of (A) fcc (atomically disordered) and (B) $Cu_3Au$ (ordered intermetallic phase) type structures from 110 zone. (C) The FFT pattern obtained for ordered intermetallic $Pd_3Pb$ NP (see Figure 2B inset of the main text).
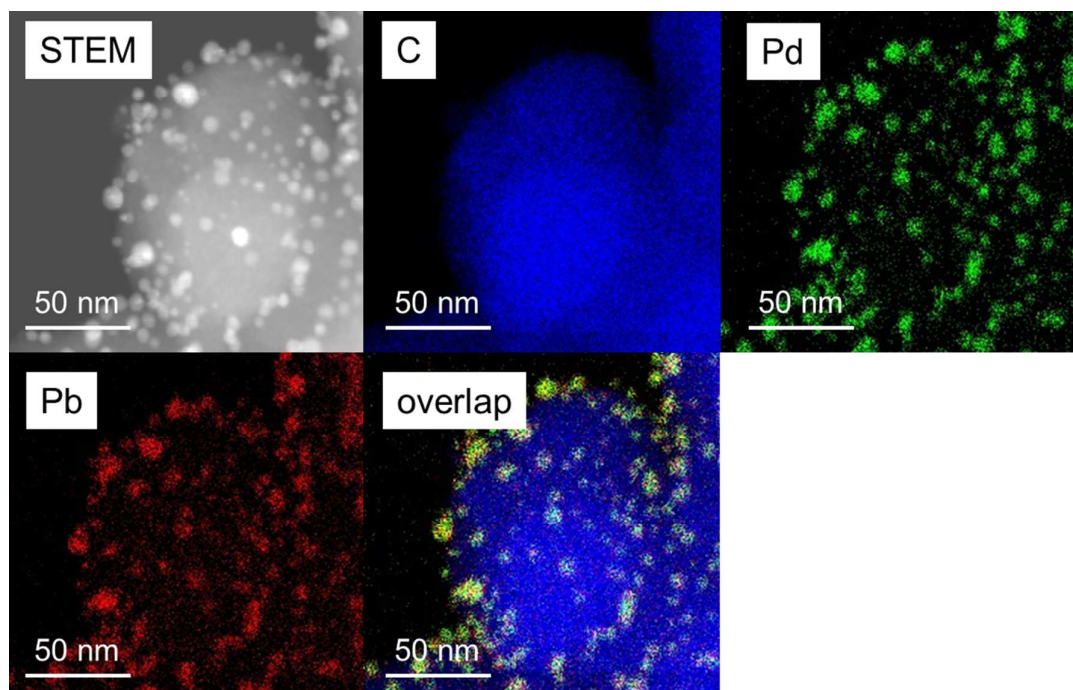
Figure S3. Overview of HAADF-STEM image of Pd$_3$Pb NPs/CB and the corresponding mapping images.
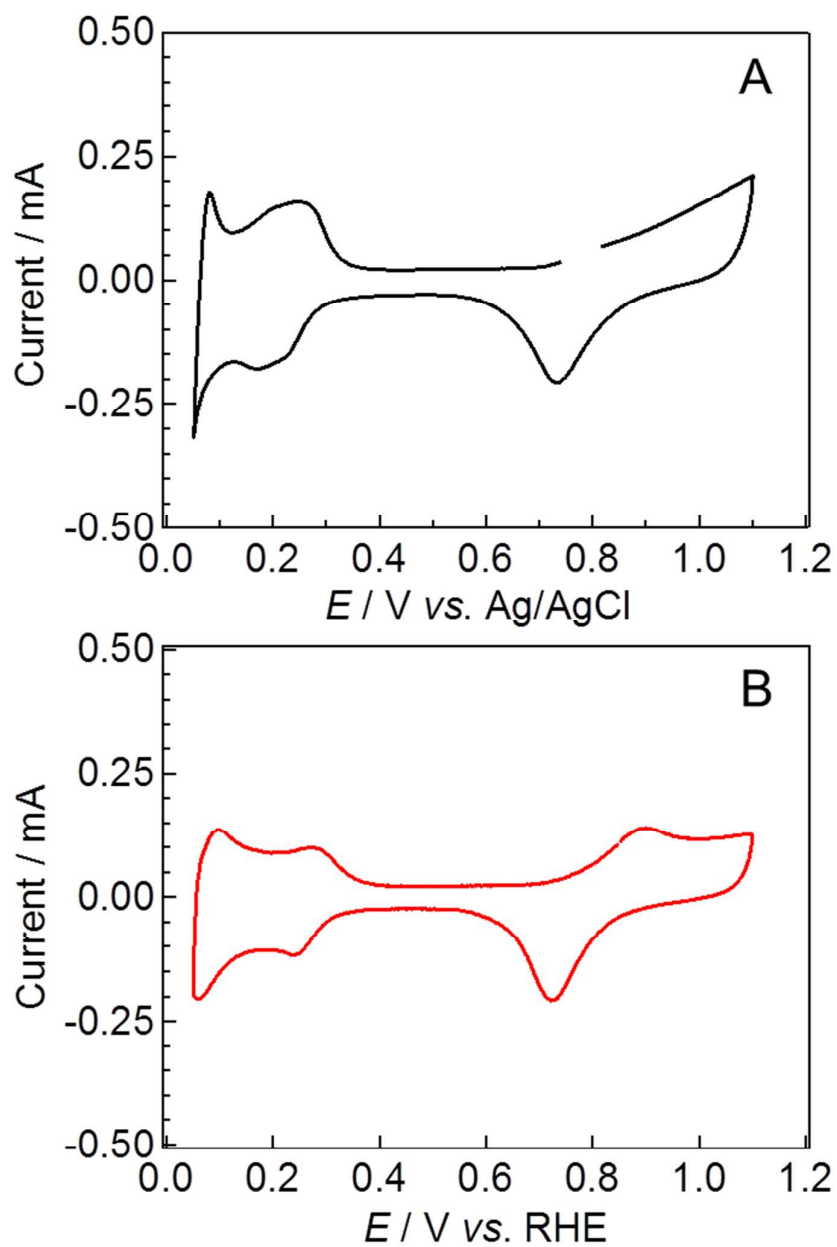
Figure S4. Cyclic voltammograms obtained for the commercially available (A) Pd NPs/CB and (B) Pd$_3$Pb NPs/CB after the 50 cycles' electrochemical treatment at a rate of 20 mVs$^{-1}$ between 0.05 and 1.1 V in a N$_2$-saturated 0.1 M HClO$_4$ aqueous solution.
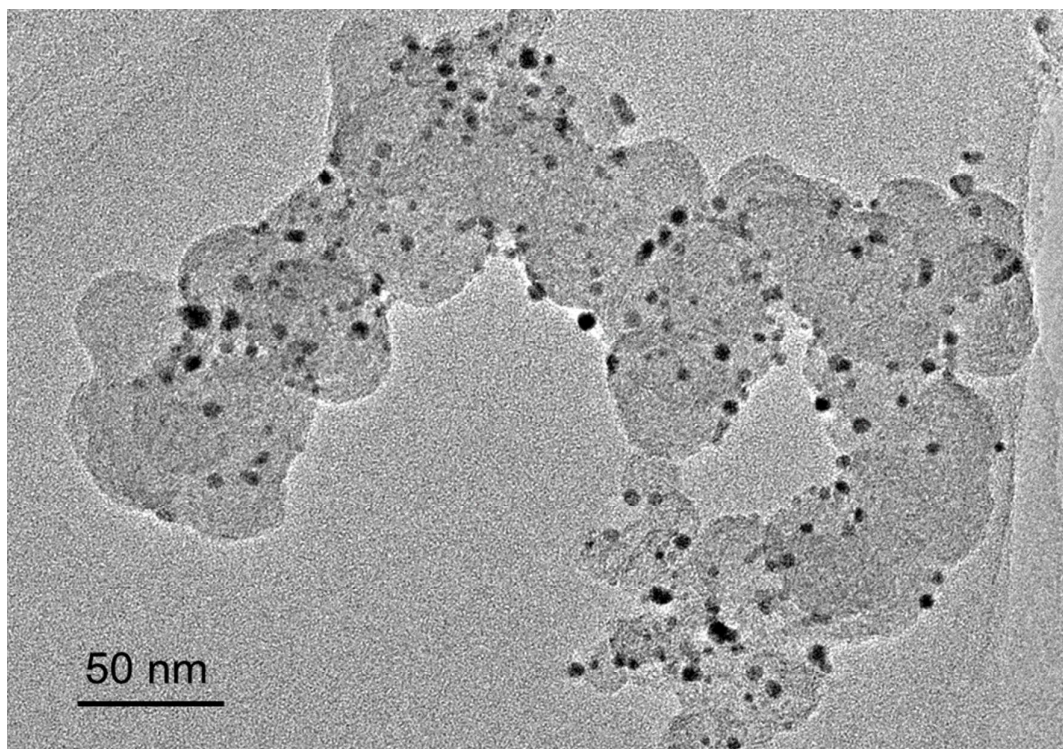
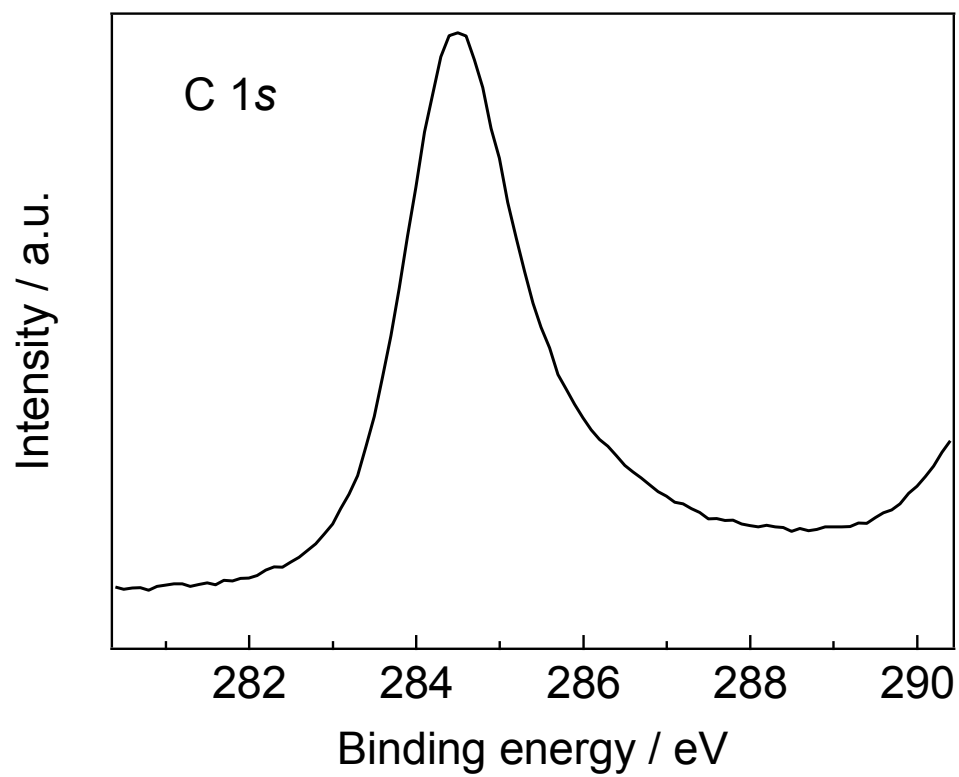Figure S5. TEM image of prepared Pd@Pd$_3$Pb NPs/CB.

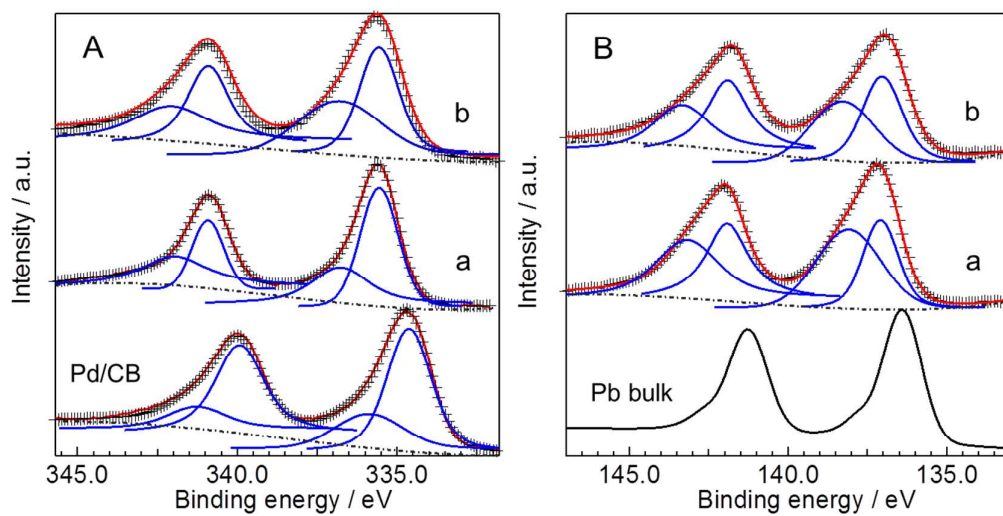Figure S6. XPS profile in the C 1*s* region.

Figure S7. XPS profiles in the (A) Pd $3d$ and (B) Pb $4f$ regions for (a) as-prepared Pd$_3$Pb NPs/CB and (b) after Ar$^+$ etching for 1 s.

Table S1. Summarized XPS analysis

| Entry | Position ($Pd^0$) / eV | Position ($Pb^0$) / eV | Atomic ratio of Pd and Pb / Pd : Pb |
|---|---|---|---|
| Pd NPs/CB | 334.63 | – | – |
| Pb bulk | – | 136.4 | – |
| As-prepared Pd$_3$Pb NPs/CB | 335.12 | 137.05 | 60.5 : 39.5 |
| Pre-treated Pd$_3$Pb NPs/CB [a] | 335.41 | 137.04 | 15.0 : 85.0 |
| After Ar$^+$-etching Pd$_3$Pb NPs/CB [b] | 335.47 | 136.98 | 20.1 : 79.9 |

a) The potential was scanned at 100 mV s$^{-1}$ 50 times between 0.05 and 1.1 V vs. RHE in 0.1 M HClO$_4$.

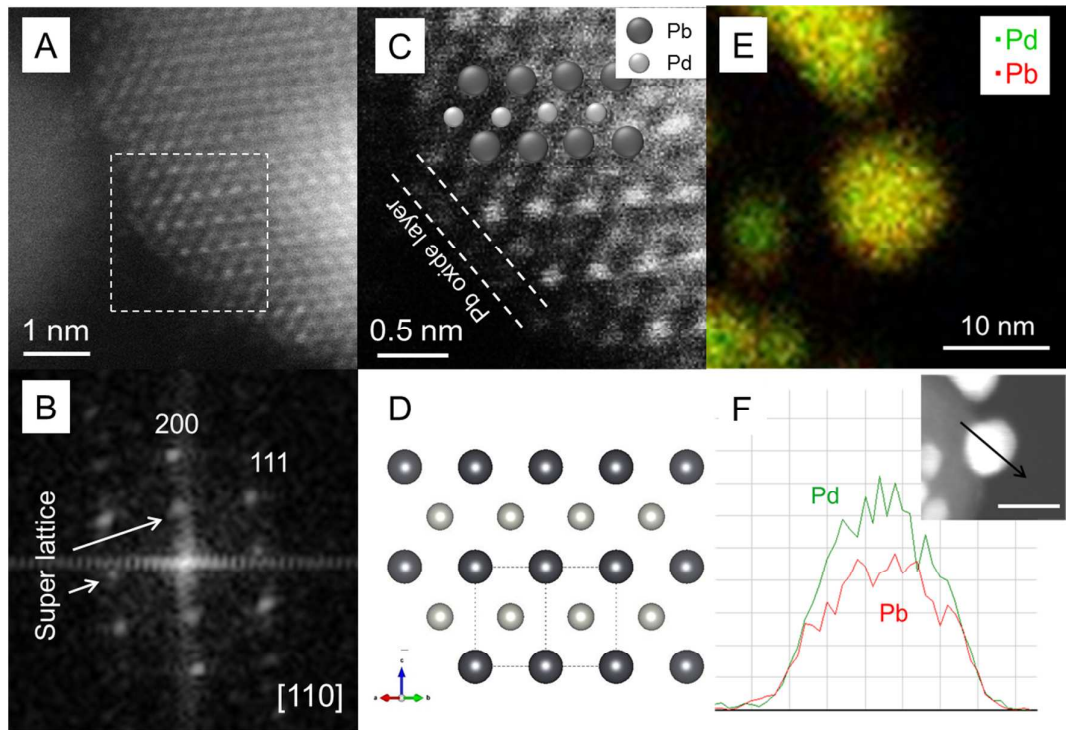b) Ar$^+$-etching was performed at 0.5 Pa and 30 W for 10 s.

Figure S8 (A) Atomic resolution HAADF-STEM image of the as-prepared $Pd_3Pb$ NP.

(B) FFT pattern and (C) image expansion corresponding to the area outlined by the

dot square in the image of (A). (D) Crystal structure of ordered intermetallic $Pd_3Pb$

at [110] zone. (E) STEM-EDS mapping profile image and (F) line profile. Scale bars

are 10 nm.

Figure S9 (A) Atomic resolution HAADF-STEM image of the electrochemically 50 cycles-treated $Pd_3Pb$ NP. (B) FFT pattern and (C) image expansion corresponding to the area outlined by the dot square in the image of (A). (D) Crystal structure of ordered intermetallic $Pd_3Pb$ at [121] zone. (E) STEM-EDS mapping profile image and (F) line profile. Scale bars are 10 nm.
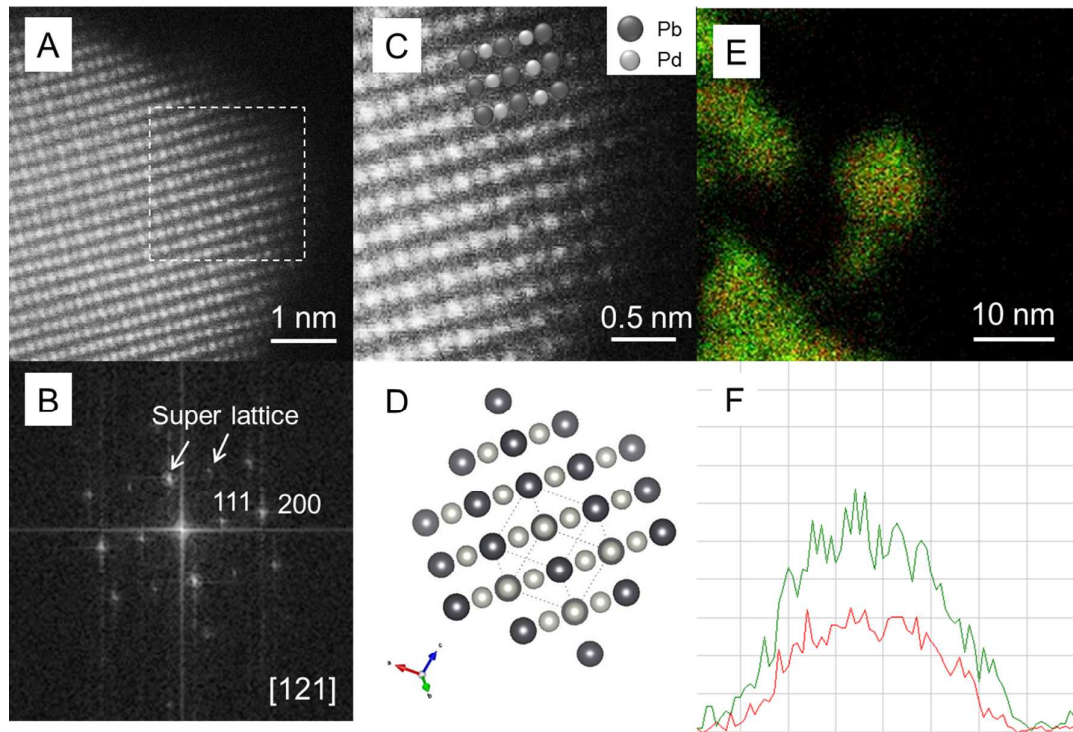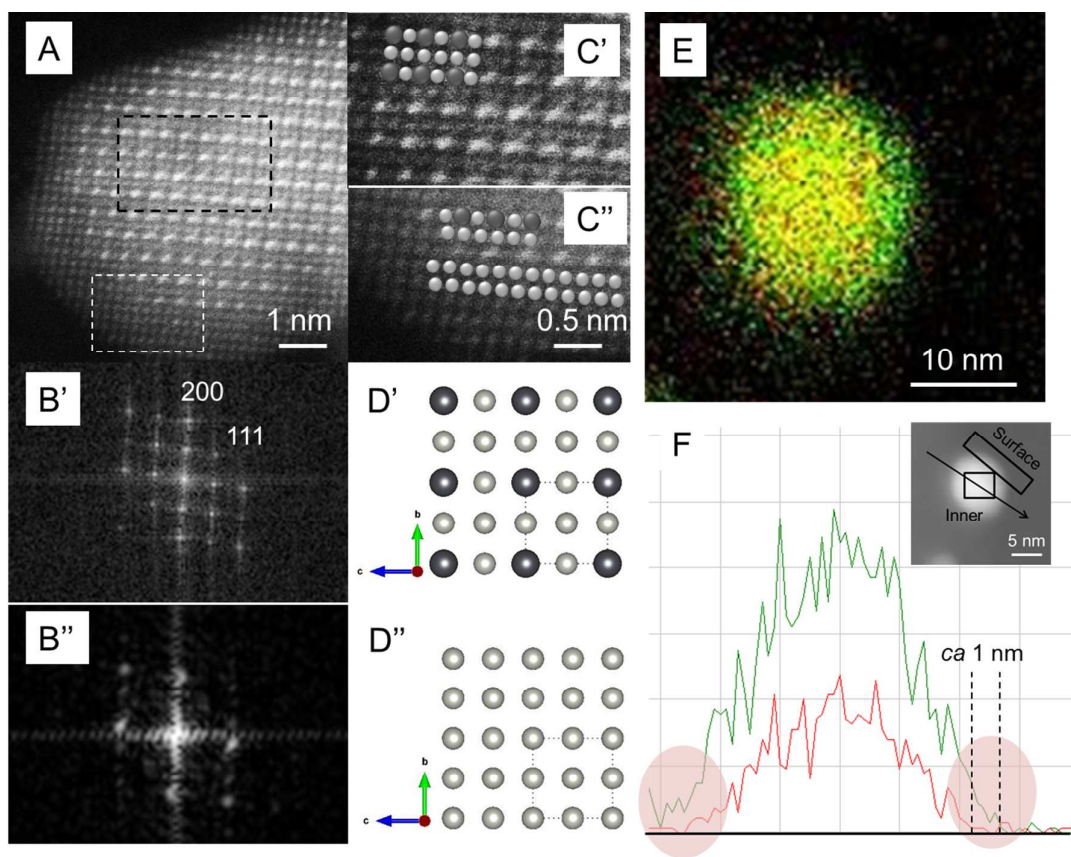
Figure S10 (A) Atomic resolution HAADF-STEM image the electrochemically 100 cycles-treated $Pd_3Pb$ NP. (B) FFT pattern and (C) image expansion corresponding to the area outlined by the dot square in the image of (A). (D) Crystal structure of ordered intermetallic $Pd_3Pb$ at [100] zone. (E) STEM-EDS mapping profile image and (F) line profile. The ' and '' in B, C and D indicate the inner and suface region, respectively.
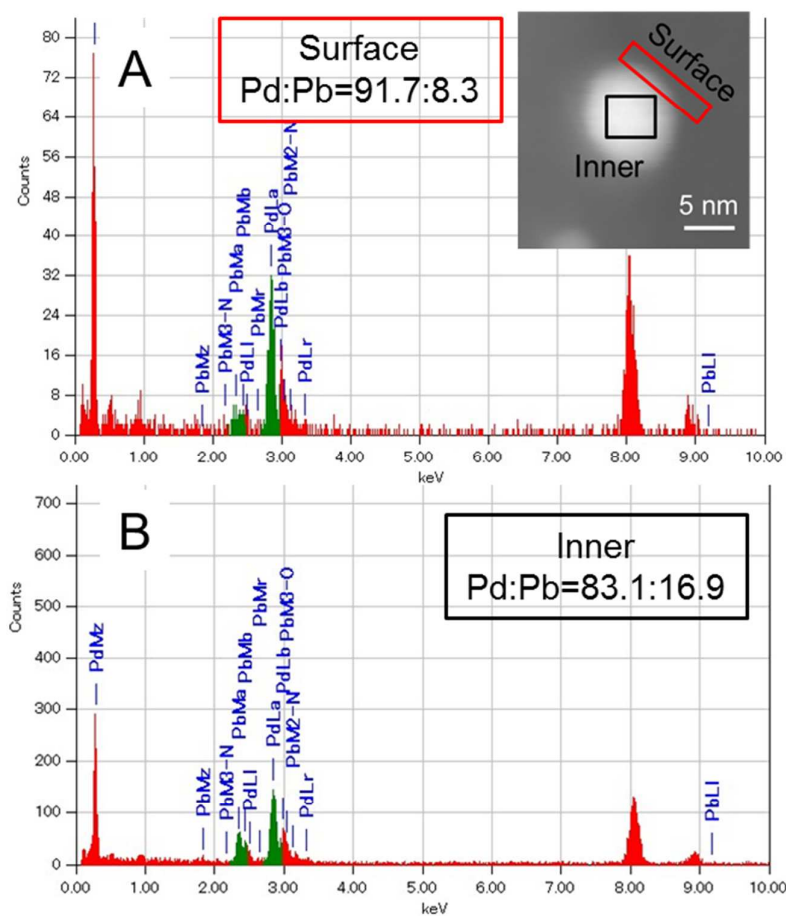
Figure S11. EDS profiles in the (A) surface and (B) inner regions of electrochemically treated ordered intermetallic Pd$_3$Pb NPs/CB. Inset : STEM image of the Pd$_3$Pb NPs.
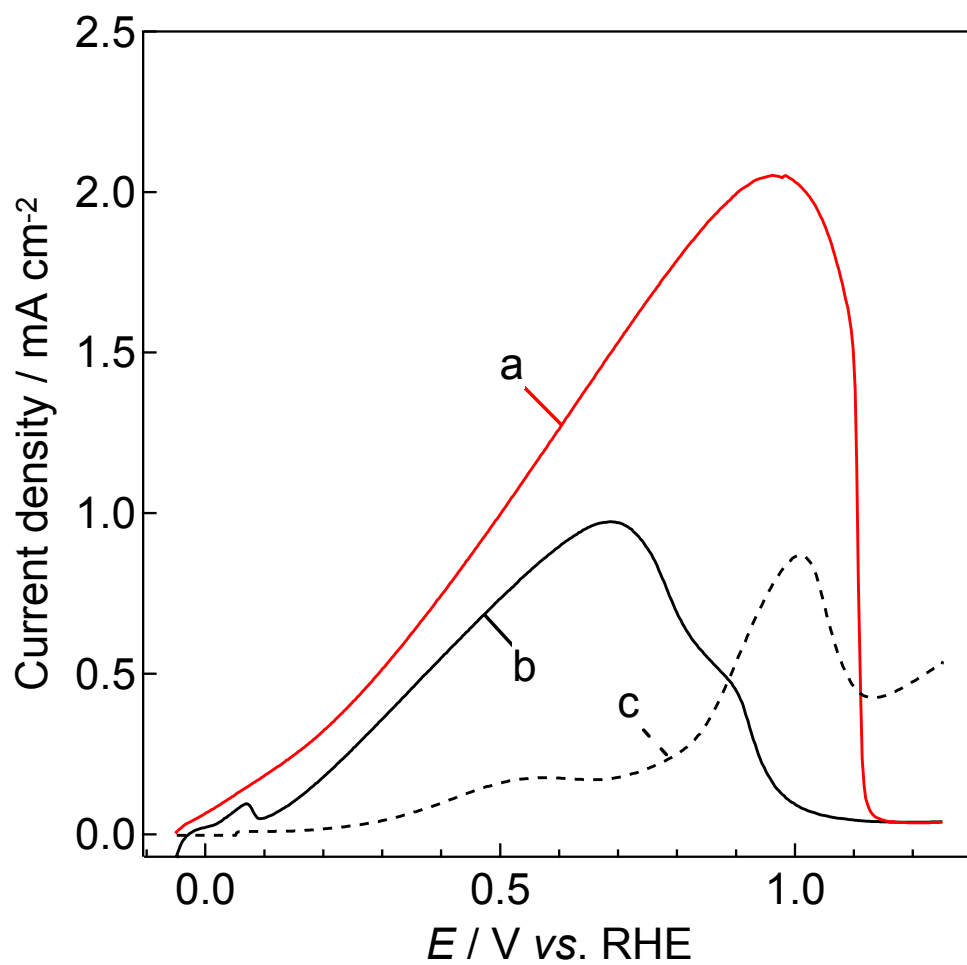
Figure S12 Anodic sweep voltammograms for FA oxidation over (a) electrochemically treated Pd$_3$Pb NPs/CB , (b) Pd NPs/CB and (c) Pt NPs/CB at 20 mV s$^{-1}$ in 0.1 M HClO$_4$ + 0.5 M FA.
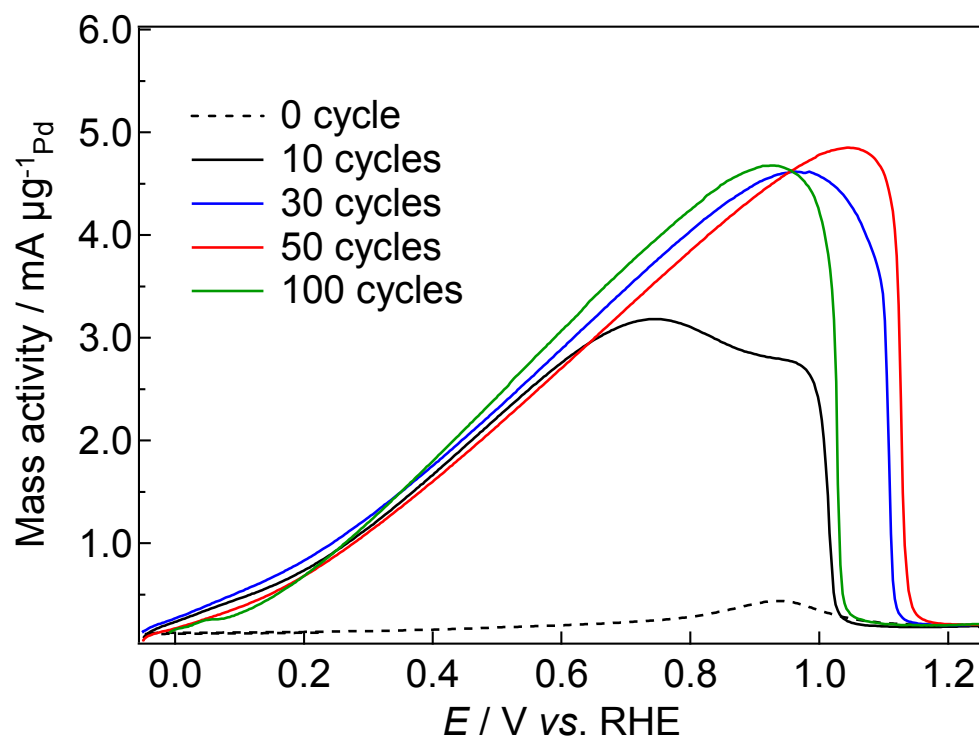
Figure S13 Electrochemical oxidation of FA over ordered intermetallic Pd$_3$Pb NPs/CB at 20 mV s-1 in 0.1 M HClO$_4$ + 0.5 M FA, depending on the number of potential scan in the electrochemical treatment each cycle.
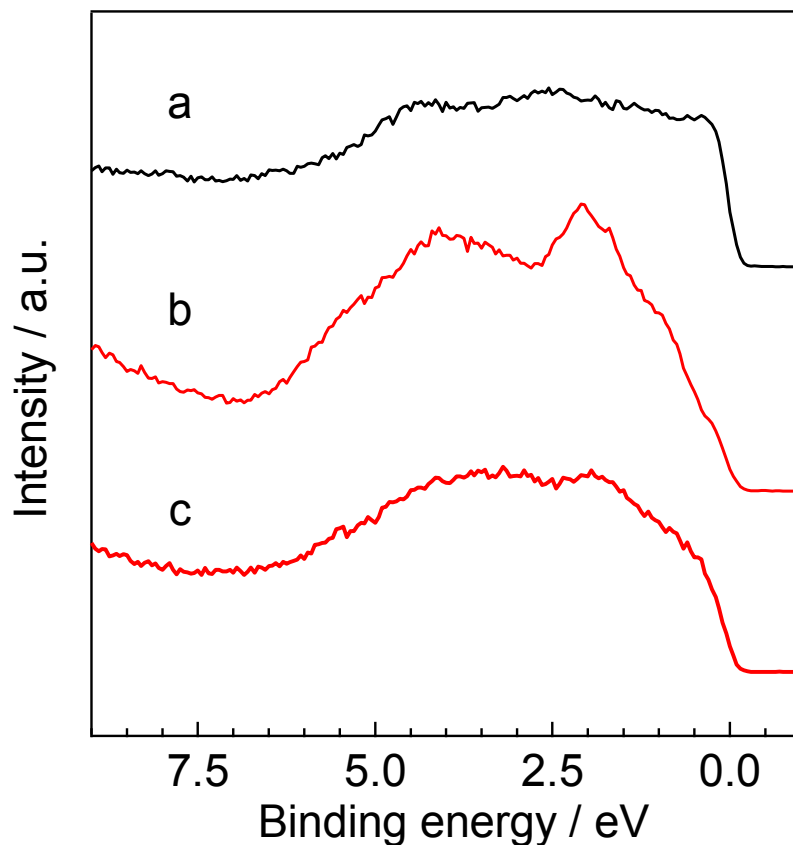
Figure S14 HAXPES profiles in the valence band region for (a) commercially available Pd NPs/CB, (b) as-prepared ordered intermetallic $Pd_3Pb$ NPs/CB and (c) electrochemically treated ordered intermetallic $Pd_3Pb$ NPs/CB.

$$d - band\ center$$
$$= \int_{-6\ eV}^{0\ eV} (Binding\ Energy(E) \times Intensity(E))\ dE \bigg/ \int_{-6\ eV}^{0\ eV\ (Ef)} Intensity(E)\ dE$$