

## Supplementary Information

# One-pot synthesis of single-crystalline PtPb nanodendrites with enhanced activity for electrooxidation of formic acid

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## Characterizations

### 1. Physical Characterizations

Automated Philips X'Pert Pro Super X-ray diffractometer was used to test the X-ray diffraction (XRD) measurements with Cu  $\alpha$  radiation operating at 40 kV  $\times$  40 mA. The  $2\theta$  degree varied from 20 to 90° at a scan rate of 20°·min<sup>-1</sup>. The morphology of PtPb SND was characterized by transmission electron microscopy (TEM, JEM-1400; TECNAI F30). The lattice constants were determined by Rietveld refinement using the X'pert High Score Plus software. The surface electronic structure of catalysts were characterization by X-ray photoelectron spectroscopy (XPS, PHI Quantum-2000). The atomic concentration and distribution were determined by energy-dispersive X-ray spectroscopy (EDS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES). The size distribution was computed by 200 particles.

### 2. Electrochemical Characterizations

The glassy carbon electrode (GC) was polished mechanically with sand paper (6#) and alumina powder with sizes of 5, 1, and 0.3  $\mu$ m respectively and then washed with Millipore water (18  $\Omega$ M·cm) in an ultrasonic bath. PtPb SND, Pd black and Pt/C-JM were ultrasonically dispersed in Millipore water (1 mg of catalyst/mL) to form the catalyst ink, which was dropped on the GC and left to dry. 5% Nafion was used to form a thin layer on the surface of catalysts. The electrochemical experiments were carried out in a three-electrode electrochemical cell connected to a PAR 263A potentiostat (EG&G) with a platinum foil counter electrode. All electrode potentials were quoted versus the saturated calomel electrode (SCE). The solution was deaerated by bubbling high-purity N<sub>2</sub> for 20 min before measurements, and this atmosphere was maintained by a flow of N<sub>2</sub> gas over it during the experiment. The working electrodes were cleaned by means of potential scans (200 mV s<sup>-1</sup>) in 0.1 M H<sub>2</sub>SO<sub>4</sub>, until a stable cyclic voltammogram (CV) was obtained. The activity of catalysts was tested in the electrolyte including 0.5 M HCOOH + 0.1 M H<sub>2</sub>SO<sub>4</sub> between -0.23 V and 0.25 V. All experiments were carried at room temperature (about 26 °C).

### 3. *In-situ* FTIR Characterizations

Electrochemical *in-situ* FTIR reflection spectroscopy measurements were conducted on a Nexus 870 spectrometer (Nicolet) equipped with a liquid nitrogen-cooled MCT-A detector. A CaF<sub>2</sub> disk was used as the IR window, and an IR cell with a thin layer configuration between the electrode and the IR window was approached by pushing the electrode against the window before FTIR measurement. *In-situ* FTIR spectras were collected using multi-stepped FTIR spectroscopy (MSFTIR) procedures. The resulting spectra were reported as the relative change in reflectivity and calculated as follows

$$\frac{\Delta R}{R} = \frac{R(E_S) - R(E_R)}{R(E_R)}$$

Where  $R(E_S)$  and  $R(E_R)$  are the single-beam spectra collected at sample potential  $E_S$  and reference potential  $E_R$ .

## Supplementary Figures

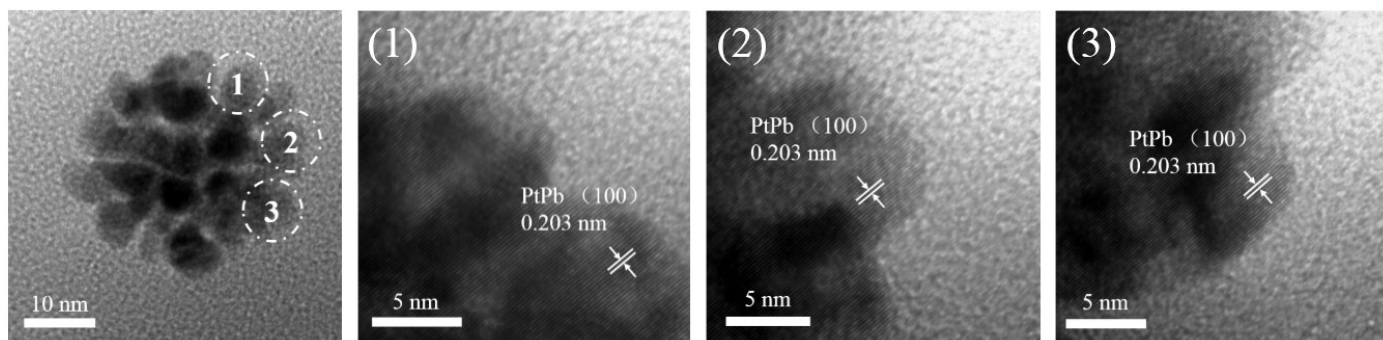


Fig. S1 TEM of a single PtPb SND and corresponding HRTEM images of three selected areas.

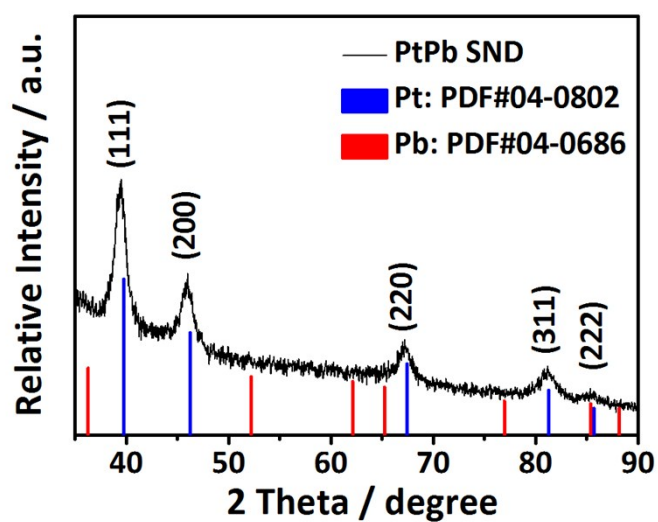


Fig. S2 XRD images of PtPb SND at a scan rate of  $20^{\circ}\cdot\text{min}^{-1}$ .

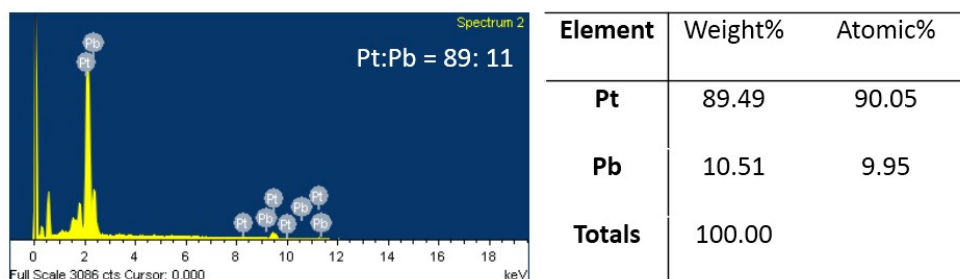


Fig. S3 EDS pattern and ICP-AED detection of PtPb SND.

To illustrate the change of electronic structure of PtPb SND, pure Pt nanoparticles were prepared by familiar method without the addition of Pb precursor. Corresponding XPS spectra of Pt 4f was displayed in Fig. S4(d).

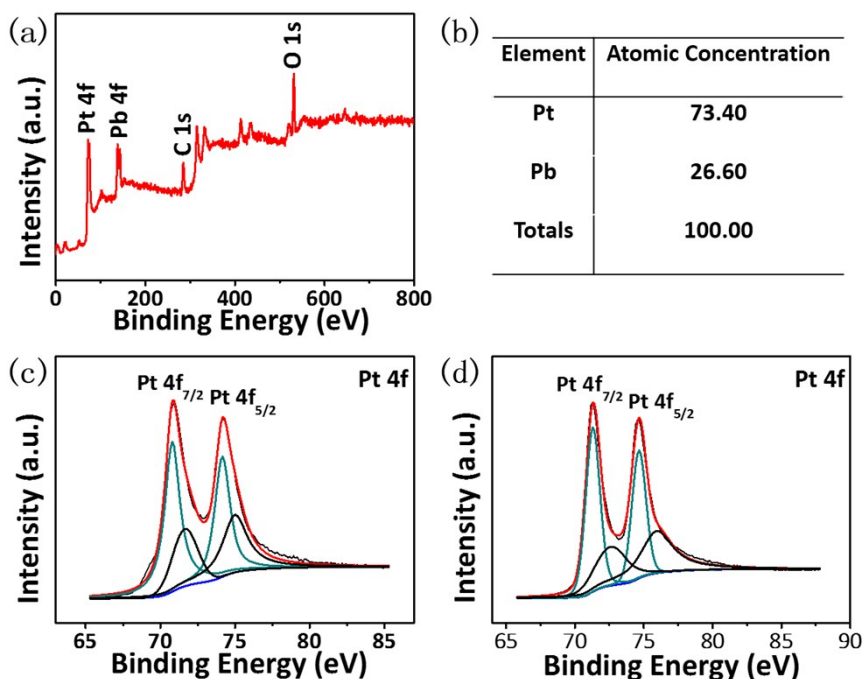


Fig. S4 (a) Wide survey XPS spectrum with (b) corresponding atomic concentration and core-level XPS patterns for Pt 4f of (c) PtPb SND and (d) Pt nanoparticles. In (c) and (d), the red line and blue line correspond to the fitting curve and background. The green line and black line correspond to the pure Pt phase and Pt-O phase.

Table S1 Binding energy of Pt 4f in PtPb SND and Pt nanoparticles

Sample	Phase	Binding Energy	
		4f 7/2	4f 5/2
PtPb SND	Pt	70.8	74.1
	Pt-O	71.7	75.0
Pt nanoparticles	Pt	71.3	74.6
	Pt-O	72.7	76.0

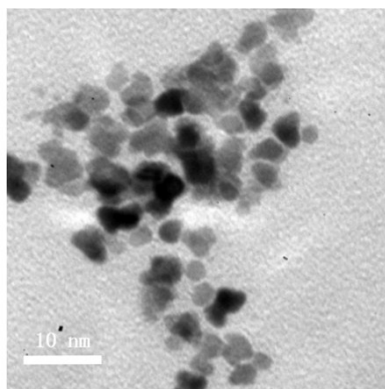


Fig. S5 The TEM image of Pt nanocrystals. The synthesis condition is same as that of PtPb SND except for the absence of precursor of  $\text{Pb}(\text{NO}_3)_2$ .

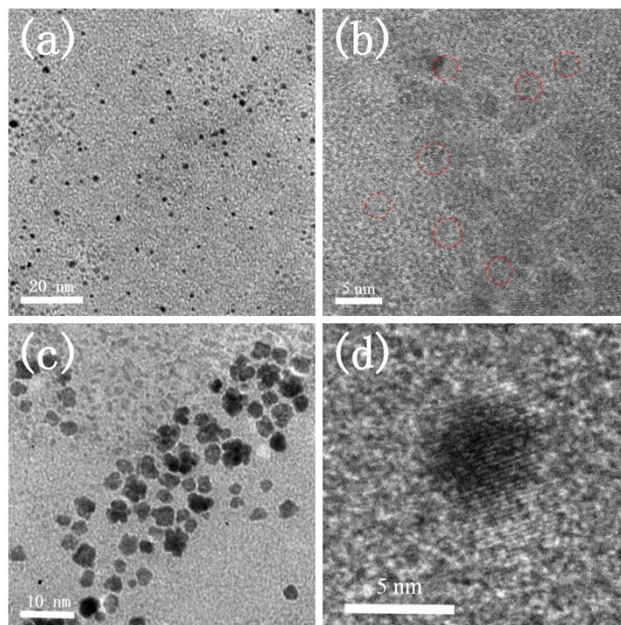


Fig. S6 TEM images of PtPb SND obtained using the standard procedure at different reaction time of (a and b) 10 min and (c and d) 20 min.

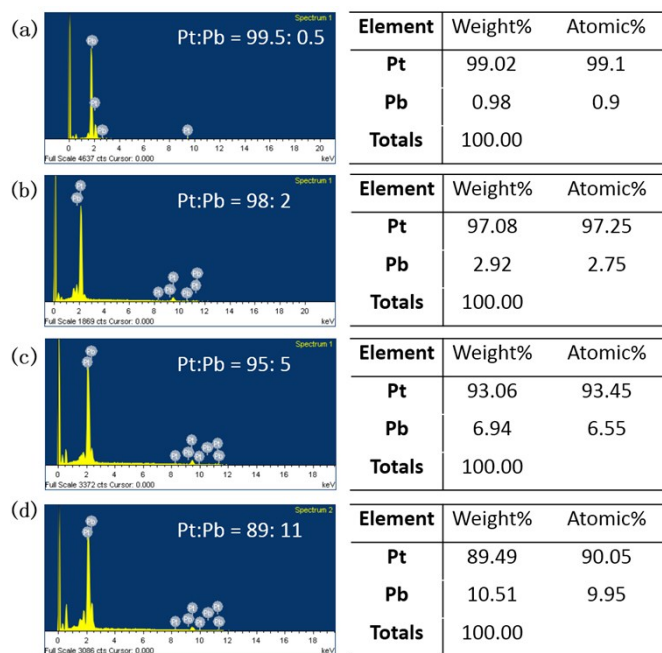


Fig. S7 EDS and ICP-AES detections at the reaction time of (a) 30min, (b) 40min, (c) 120min and (d) 180 min.

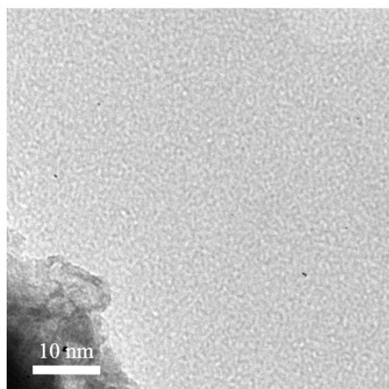


Fig. S8 The TEM image of reaction liquid. The synthesis condition is same as that of PtPb SND except for the absence of precursor of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ . The black part is the edge of Cu foil.

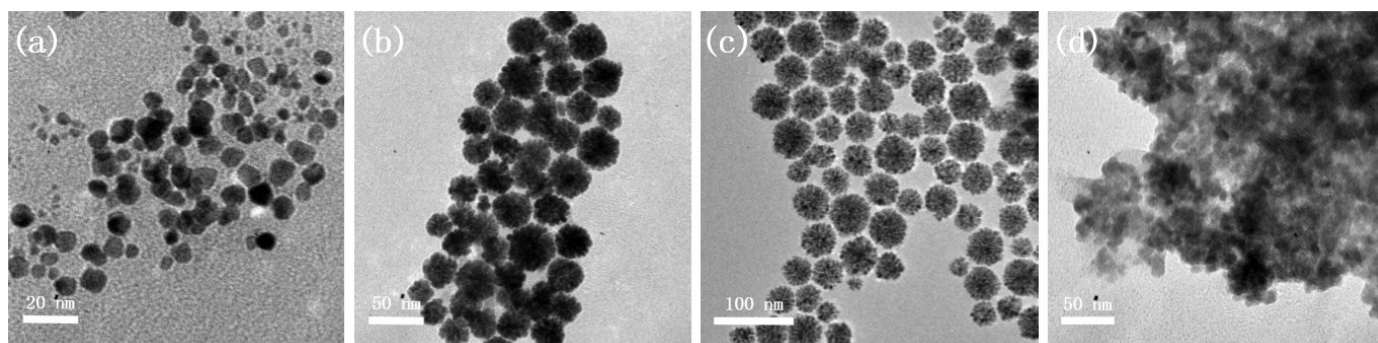


Fig. S9 TEM images of PtPb nanocrystals synthesized by (a) KF, (b) KCl, (c) KBr and (d) KI.

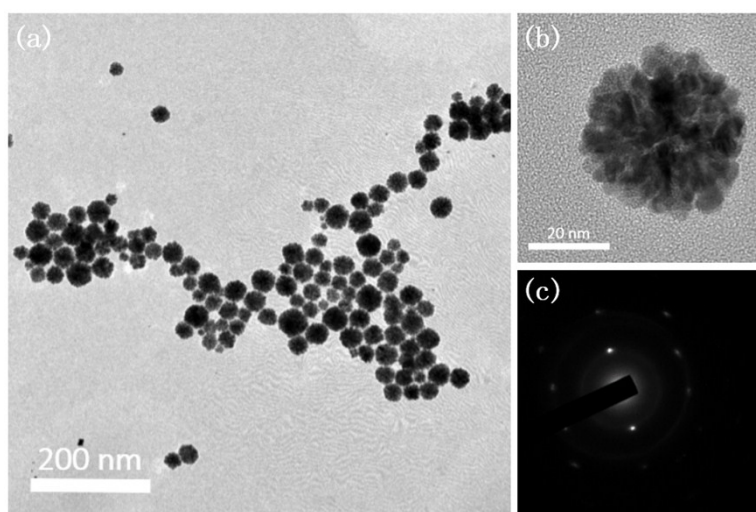


Fig. S10 (a) The TEM image of PtPb SND after durability test, (b) the HRTEM image of a single nanocrystal and (c) the corresponding SAED pattern.

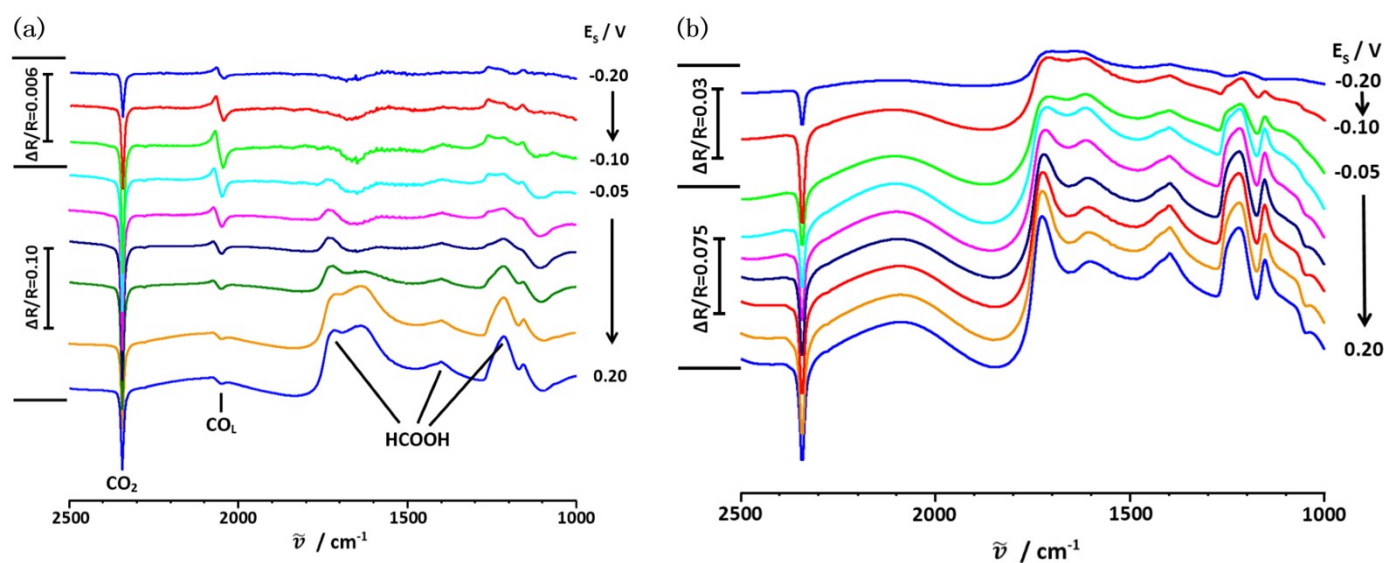


Fig. S11 *In-situ* FTIR spectra of HCOOH oxidation on (a) Pt/C-JM and (b) Pd black at different potentials.  $E_s$  was varied from -0.20 to 0.20 V,  $E_R = -0.25$  V vs. SCE.