

## Electronic Supplementary Information (EIS)

# Three Dimensional Palladium Nanoflowers with Enhanced Electrocatalytic Activity towards the Anodic Oxidation of Formic Acid

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### Preparation of Pd nanoflowers

Pd nanoflowers were synthesized as follows. Palladium chloride precursor ( $\text{PdCl}_2 \geq 99.5\%$ ) in the amount of 0.02 mmol was dissolved in two drops of HCl (36.5%), then added into a mixture of 40 mL benzyl alcohol ( $\geq 99\%$ ) and 3 mL oleic acid. The combination was then placed into a Teflon<sup>®</sup>-lined autoclave and conditioned at 140 °C for 6 hours, followed by separating and washing with ethanol, vacuum drying at 50 °C overnight. The yield of Pd-NF was *ca.* 90%. For comparison, Pd nanoparticles were prepared by the same procedures but without the addition of oleic acid.

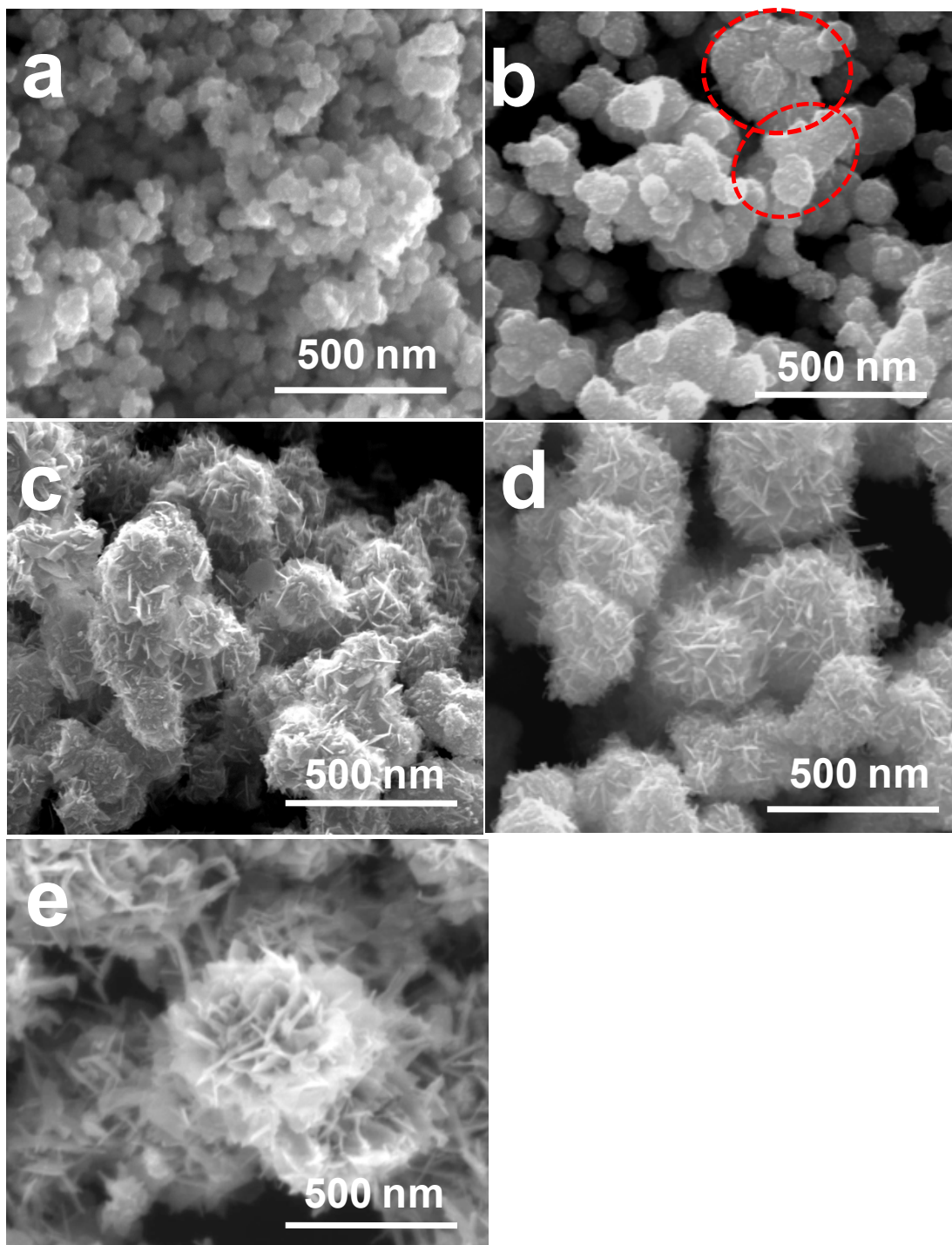
### **Catalysts characterization**

SEM images were recorded on a LEO 1530 VP field emission scanning electron microscope (Germany) operated at 5 kV and HRSEM image was recorded on Hitachi S-5500 (Tokyo, Japan) at 30 kV. High-resolution TEM images were recorded on a JEM-2100 transmission electron microscope (Tokyo, Japan) at 200 kV.

### **Electrochemical experiments**

The catalysts activities of electrooxidation of formic acid were evaluated at room temperature using an electrochemical workstation (CHI, Shanghai) with a three-electrode electrochemical cell. A saturated calomel electrode (SCE, 0.24 V vs. RHE) was used as the reference electrode and a Pt wire as the counter electrode. The working electrode was a glassy carbon disk electrode (0.19625 cm<sup>2</sup> electrode surface area). The working electrode was made as follows. The prepared Pd-NF or Pd-NP homogeneously mixed with conductive carbon black in a mass ratio of 1:4. The mixed catalyst then added into 0.25 wt.% Nafion/ethanol and ultrasonication for 20 minutes to obtain a 5 mg mL<sup>-1</sup> uniform suspension ink, as well as commercial BASF-20% Pd/C. After, 20  $\mu$ L ink was pipetted and spread on the polished glassy carbon electrode, finally, the metal loading on the working electrode was 0.1 mg for all the catalysts. The cyclic voltammetry (CV) data were measured in N<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M HCOOH electrolyte solution, with a scanning rate of 20 mV s<sup>-1</sup> at room temperature.

**Figure S1.**



**Figure S1.** SEM images of Pd products taken from different reaction time: 70min (a), 90min (b), 2 h (c), 3 h (d), and 6 h (e).

**Figure S2.**

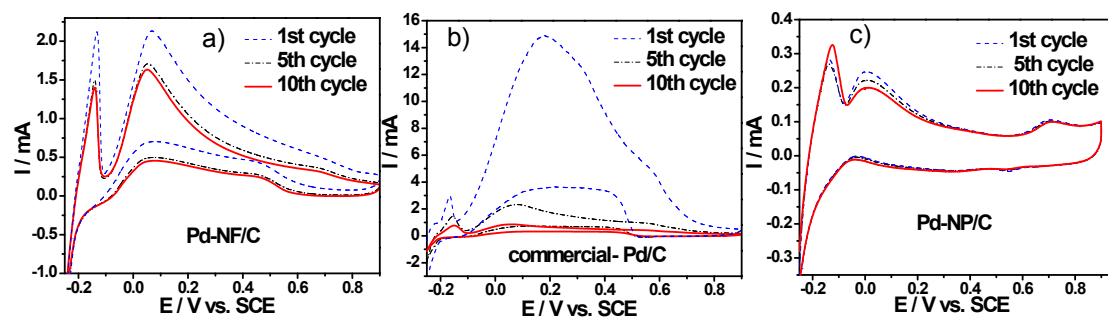


Figure S2. a), b) and c) are the cyclic voltammetry curves in different cycles for Pd-NF/C, commercial Pd/C and Pd-NP/C in  $\text{N}_2$ -saturated  $0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M HCOOH}$  solution with a scan rate of  $20 \text{ mV s}^{-1}$ . The loading of Pd on electrode is  $0.1 \text{ mg}$  for all catalysts.

**Figure S3.**

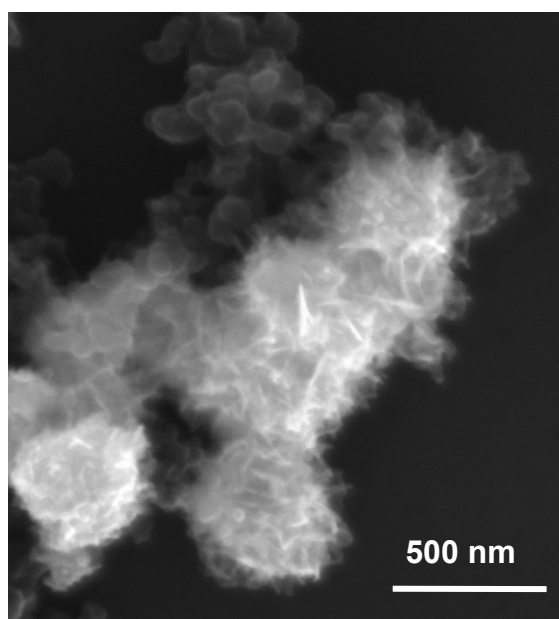


Figure S3. The morphology of the Pd-NFs/C after CVs of formic electro-oxidation.