

## **Supporting Information**

### **Structural Design and Facile Synthesis of a Highly Efficient Catalyst for Formic Acid Electrooxidation**

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## 1. Experimental section

### 1.1 Catalysts preparation

Pt decorated Pd/C (with different atomic ratio, Pd:Pt = 10:1, 15:1, 20:1 or 25:1) was prepared as follows. 6.8 ml 0.045 M PdCl<sub>2</sub> was added into 300 mL water. Then, 120 mg Vulcan XC-72R carbon was added into the above solution with stirring. Two hours later, 100 mL NaBH<sub>4</sub> solution (mole ratio, Pd<sup>2+</sup>: NaBH<sub>4</sub>=1:10) was slowly added into above suspension. The resulting suspension was further stirred and sonicated for 1 hour, respectively. Then, above suspension was transferred to ice-water bath with sonicating. In succession, a certain amount of 0.02 M H<sub>2</sub>PtCl<sub>6</sub> was added. After 1 hour sonicating, the mixture was filtered, washed and dried in vacuum oven at 60 °C for 12 hours.

For comparison, Pd/C, Pt/C, and PdPt alloy/C catalysts were prepared by the similar method. Typically, Pd/C was prepared as follows. 6.8 ml 0.045 M PdCl<sub>2</sub> was added into 300 mL water. Then, 120 mg Vulcan XC-72R carbon was added into the above solution with stirring. Two hours later, 100 mL NaBH<sub>4</sub> solution was slowly added into above suspension. In succession, the mixture was filtered, washed and dried in vacuum oven at 60 °C for 12 hours.

### 1.2 Physicochemical characterizations

The catalysts were characterized by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), X-ray diffraction (XRD), transmission electron microscopy (TEM), and CO-stripping measurements.

### 1.3 Electrochemical measurements

Electrochemical measurements were conducted with a CHI600 electrochemical analyzer and a conventional three-electrode electrochemical cell, in which a Pt plate and saturated calomel electrode (SCE, 0.242 V vs. normal hydrogen electrode) were used as the counter and reference electrodes, respectively. All potentials were quoted with respect to SCE. Each working electrode contained ca.  $28 \mu\text{g}/\text{cm}^2$  of Pd. In all electrochemical measurements, the current densities were normalized to the metal mass on the glassy carbon (GC) electrode (3 mm diameter). The working electrode was prepared according to the following procedure: 4 mg catalyst and 2 ml  $\text{H}_2\text{O}$  were mixed, and 5  $\mu\text{L}$  of the resulting slurry was spread on the surface of the glassy carbon (GC) electrode. After drying, 2  $\mu\text{L}$  of a Nafion (5 wt%) solution was spread on the surface of the catalyst electrode, and the working electrode was obtained.

Base cyclic voltammetry experiments were carried out in a 0.5 M  $\text{H}_2\text{SO}_4$  solution at a scan rate of 50 mV/s. To measure the amount of CO-like intermediates, base cyclic voltammetry experiments were performed on Pd/C and Pt decorated Pd/C electrodes, which had been pre-treated at a polarization potential of 0.15 V vs. SCE for 5 hours in  $\text{N}_2$ -saturated 0.5 M  $\text{H}_2\text{SO}_4$  and 8 M formic acid.

Cyclic voltammetry was performed in 0.5 M  $\text{H}_2\text{SO}_4$  and 0.5 M formic acid at a scan rate of 50 mV/s.

Chronoamperometry of Pt decorated Pd/C (atomic ratio, Pd:Pt = 20:1), commercial Pd/C and Pt/C on rotating electrode (1000 rpm) is tested in 0.5 M  $\text{H}_2\text{SO}_4$  and 0.5 M formic acid at a given potential of 0.1 V vs. SCE.

Electrochemical CO stripping voltammograms were measured by the oxidation of pre-adsorbed CO ( $\text{CO}_{\text{ad}}$ ) in 0.5 M  $\text{H}_2\text{SO}_4$  at a scan rate of 50 mV/s. CO was introduced into 0.5 M  $\text{H}_2\text{SO}_4$  for 15 min to allow for complete adsorption of CO onto the catalyst. During this process, the working electrode was maintained at 0.15 V vs. SCE electrode. Excess CO in the electrolyte was then purged with high purity Ar for 15 min. The electrochemical surface area of the catalyst can be calculated with coulombic charges accumulated during CO adsorption and desorption after correcting for electric double-layer capacitance:

$$\text{ESA} = Q_{\text{co}} / (0.42 * m)^{[1,2]}$$

Where  $Q_{\text{co}}$  (mC) is the charge due to the CO adsorption/desorption in Figure S4, 0.42 mC  $\text{cm}^{-2}$  is the electrical charge associated with monolayer adsorption of CO on Pt or Pd, and  $m$  is the metal mass on the working electrode.

The above measurements were tested at room temperature. Before measurement, high purity Ar were purged for 10 min.

### **Acknowledgment**

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Table S1. Compositional, Structural, and Electrochemical Data for Pt/C, Pd/C, PdPt alloy/C (atomic ratio, Pd:Pt = 20:1), and Pt decorated Pd/C (atomic ratio, Pd:Pt = 20:1).

Catalysts	ICP-AES	Particle size/nm	ESA/m <sup>2</sup> g <sup>-1</sup>
Pt decorated Pd/C (Pd:Pt = 20:1)	19.8:1	5.1	49.05
PtPd alloy/C (Pd:Pt = 20:1)	19.9:1	5.0	49.29
Pd/C	/	5.1	48.75
Pt/C	/	5.1	25.48

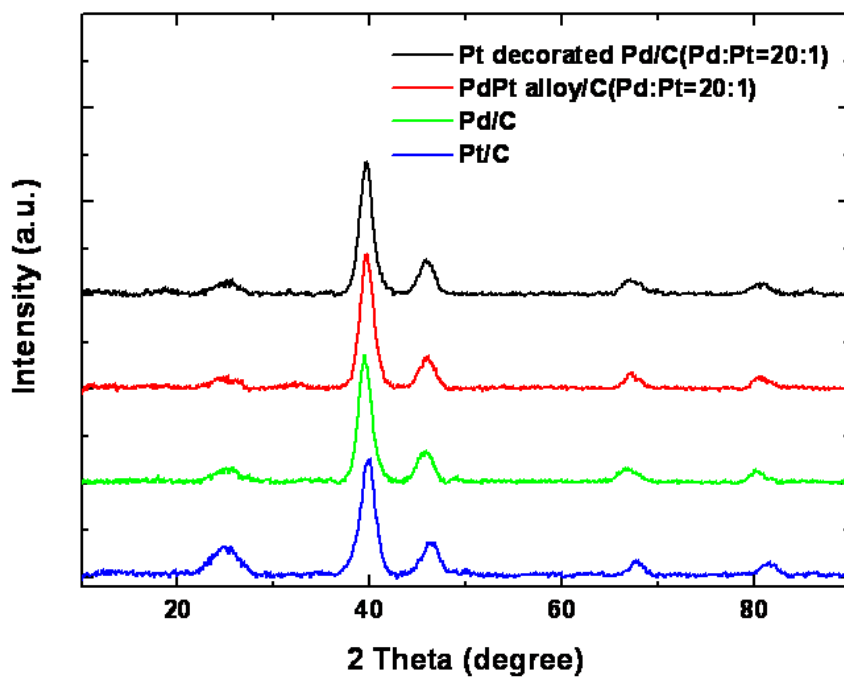


Fig. S1. XRD patterns of Pt/C, Pd/C, PdPt alloy/C (Pd:Pt = 20:1), and Pt decorated Pd/C (Pd:Pt = 20:1)

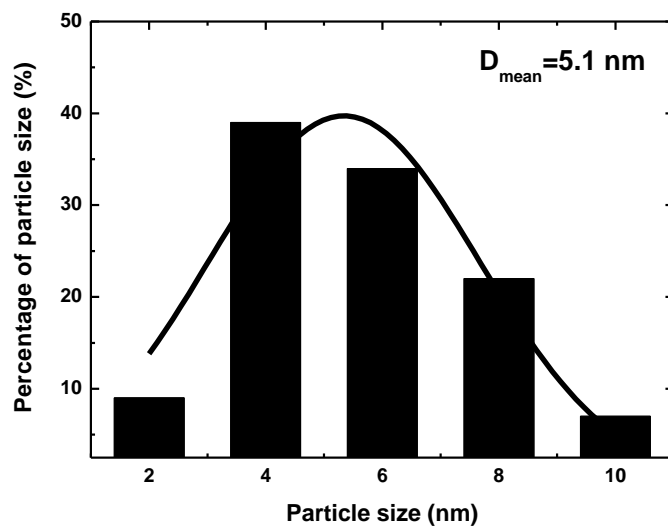
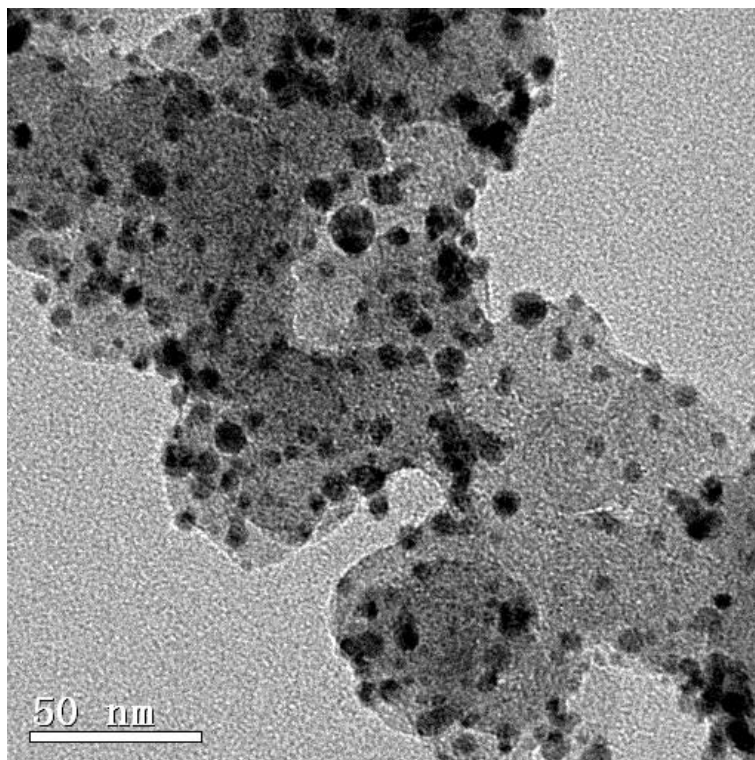


Fig. S2. Representative TEM image and corresponding size distribution histogram of Pd/C.

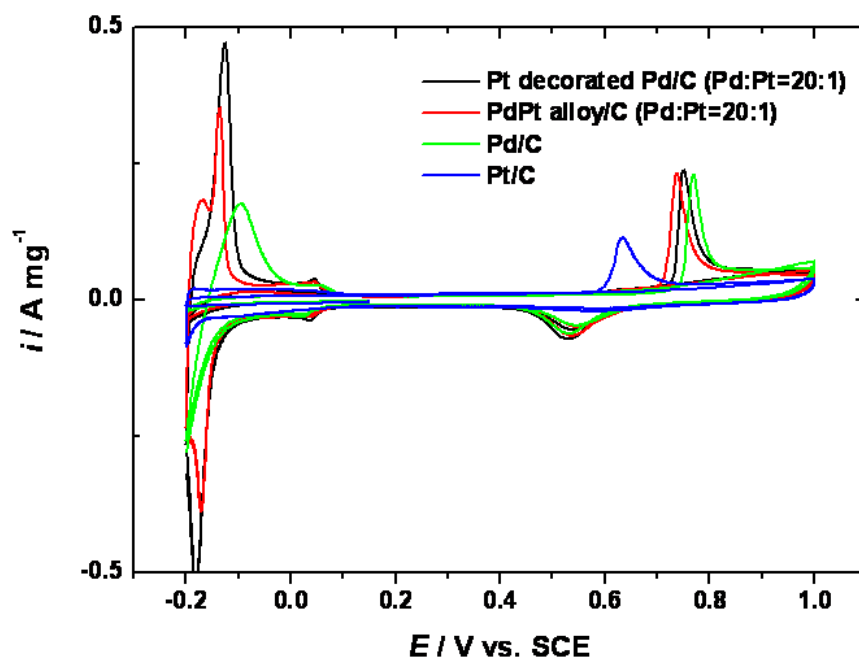


Fig. S3. CO-stripping measurements of Pt/C, Pd/C, PdPt alloy/C (Pd:Pt = 20:1), and Pt decorated Pd/C (Pd:Pt = 20:1)



Table S2. Electrochemical data from CO-stripping measurements for Pt/C, Pd/C, PdPt alloy/C (Pd:Pt = 20:1), and Pt decorated Pd/C (Pd:Pt = 20:1)

Catalysts	Onset potential (V vs. SCE)	Peak potential (V vs. SCE)
Pt decorated Pd/C (Pd:Pt = 20:1)	0.724	0.751
PdPt alloy/C (Pd:Pt=20:1)	0.700	0.737
Pd/C	0.738	0.769
Pt/C	0.577	0.631

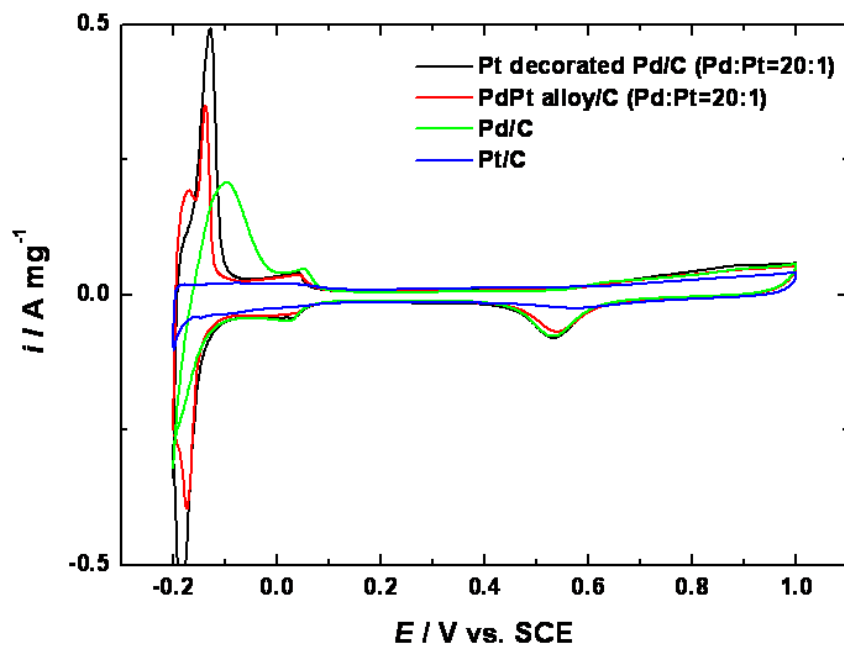


Fig. S4. Cyclic voltammograms in  $\text{N}_2$ -saturated 0.5 M  $\text{H}_2\text{SO}_4$  on Pt/C, Pd/C, PdPt alloy/C and Pt decorated Pd/C. Scan rate:  $50 \text{ mV s}^{-1}$  (room temperature).

## References

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- (2) Vidakovic, T.; Christov, M.; Sundmacher, K. *Electrochim. Acta* 2007, 52, 5606.