

# Formic Acid Oxidation

- Recent trends in FAOR catalysts

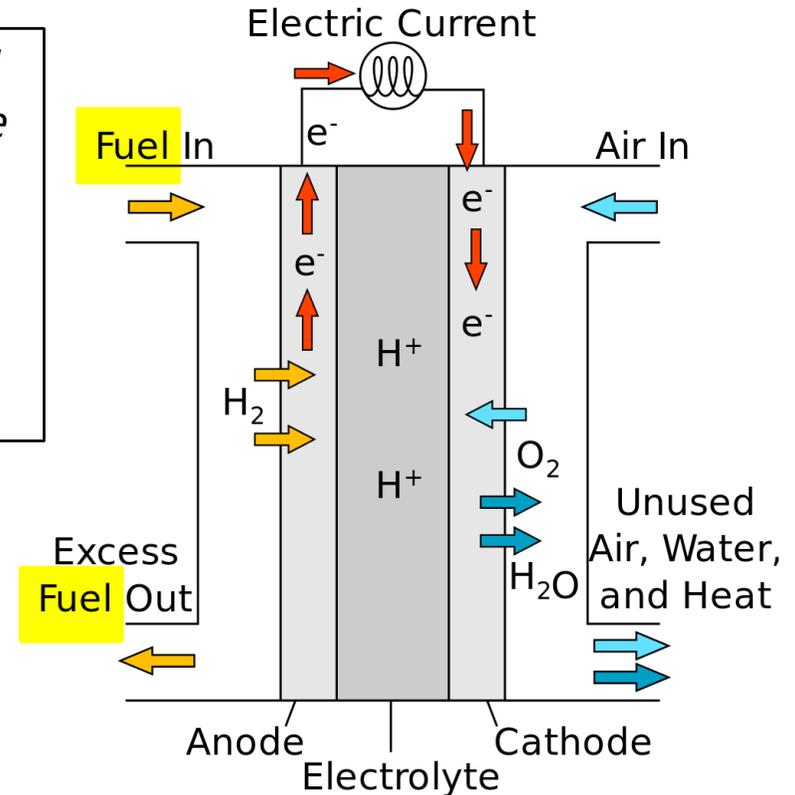
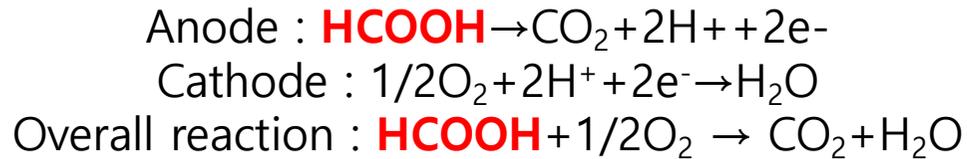
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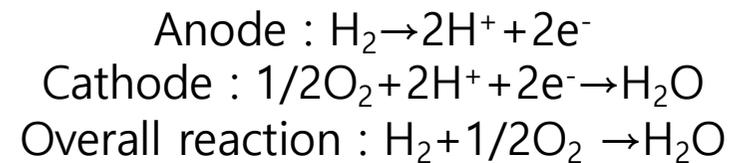
20158135 권용민

# Direct Formic Acid Fuel Cell (DFAFC)

*DFAFCs are a subcategory of PEMFC where the fuel (formic acid) is not reformed, but fed directly to the fuel cell.*



## Proton Exchange Membrane Fuel Cell (PEMFC)

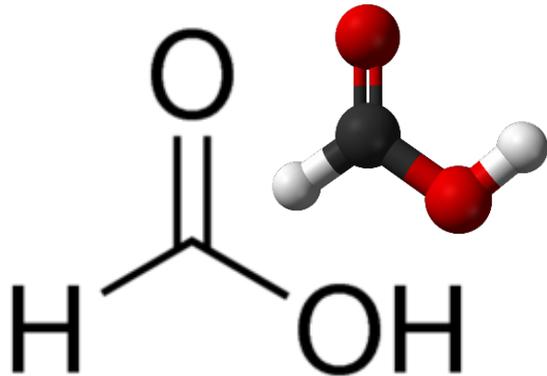


application : portable devices

# Why formic acid oxidation (FAOR)?

## Formic acid (HCOOH)

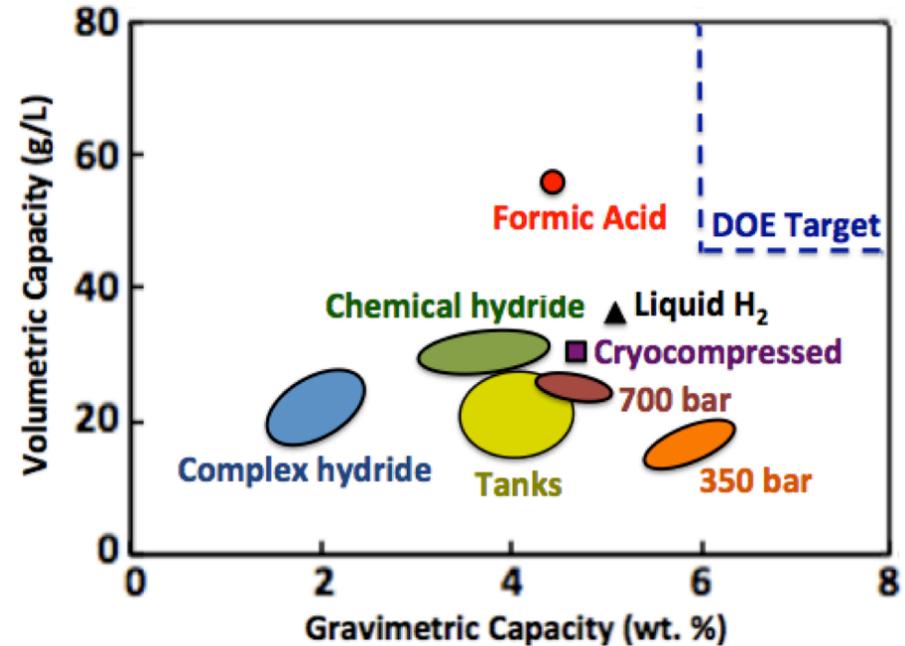
- Liquid state at ambient condition
- Non-toxic, non-corrosive, non-flammable
- high energy density



-high H content



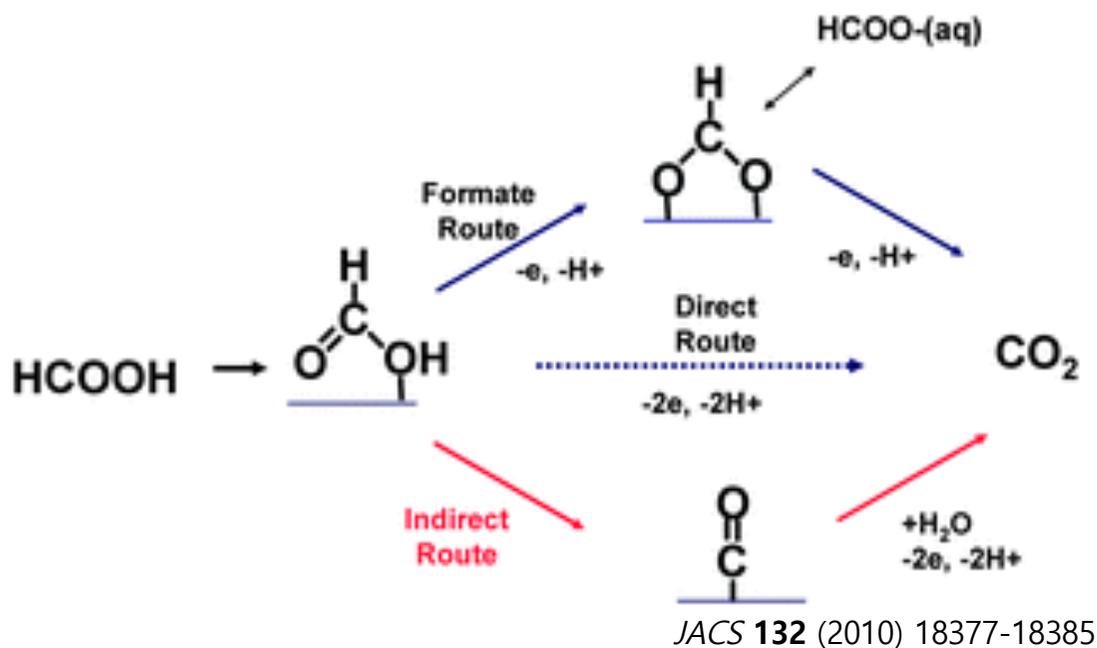
-easy storage



H<sub>2</sub>-PEMFC is limited by the high cost of miniaturized hydrogen containers, the potential dangers in the transport and use of hydrogen, and its low gas-phase energy density. For Direct Methanol Oxidation Fuel Cell (DMFC) liquid methanol has an impressive energy density (approximately 4900Wh L<sup>-1</sup>), but its electrocatalytic oxidation rate is very low relative to that of H<sub>2</sub>.

-*Journal of Power Series* **182** (2008) 124-132

# Mechanism ( $\text{HCOOH} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$ )



However, the detailed reaction intermediates and mechanisms are still elusive.

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## Theoretical Elucidation of the Competitive Electro-oxidation Mechanisms of Formic Acid on Pt(111)

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Received September 25, 2010; E-mail: timo.jacob@uni-ulm.de

**J | A | C | S**  
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Communication  
pubs.acs.org/JACS

Three proposed mechanisms exist for FAOR:

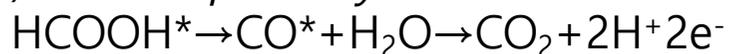
(i) *Direct pathway*



(ii) *Formate pathway*



(iii) *Indirect pathway*



(\*:adsorbed state)

## Importance of Acid–Base Equilibrium in Electrocatalytic Oxidation of Formic Acid on Platinum

Jiyong Joo,<sup>†,‡</sup> Taro Uchida,<sup>‡</sup> Angel Cuesta,<sup>§,⊥</sup> Marc T. M. Koper,<sup>‡,#</sup> and Masatoshi Osawa<sup>\*,‡</sup>

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<sup>⊥</sup>Leiden Institute of Chemistry, Leiden University, 2300 RA Leiden, The Netherlands

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*J. Phys. Chem. C* **2009**, *113*, 17502–17508

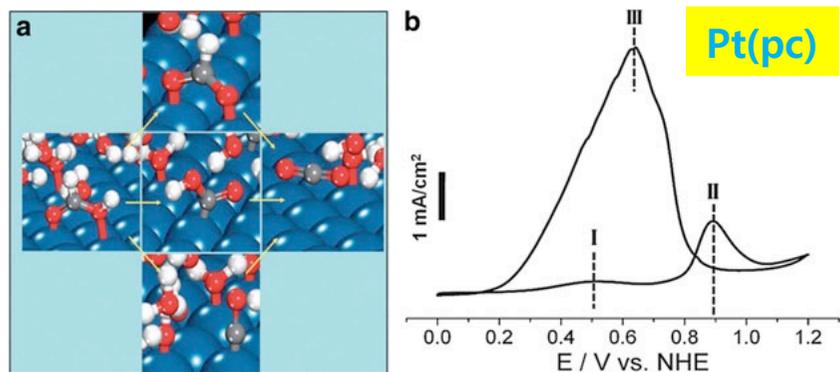
## Formic Acid Oxidation at Pt/H<sub>2</sub>O Interface from Periodic DFT Calculations Integrated with a Continuum Solvation Model

Hui-Fang Wang and Zhi-Pan Liu\*

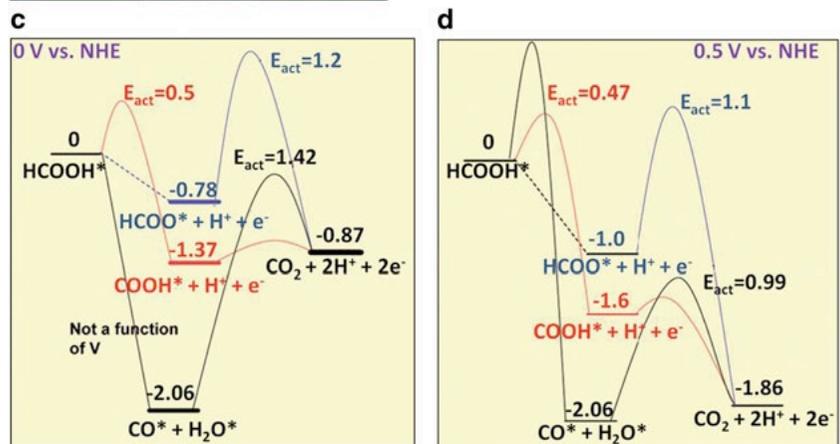
Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, MOE Key Laboratory for Computational Physical Sciences, Fudan University, Shanghai 200433, China

Received: June 26, 2009; Revised Manuscript Received: August 6, 2009

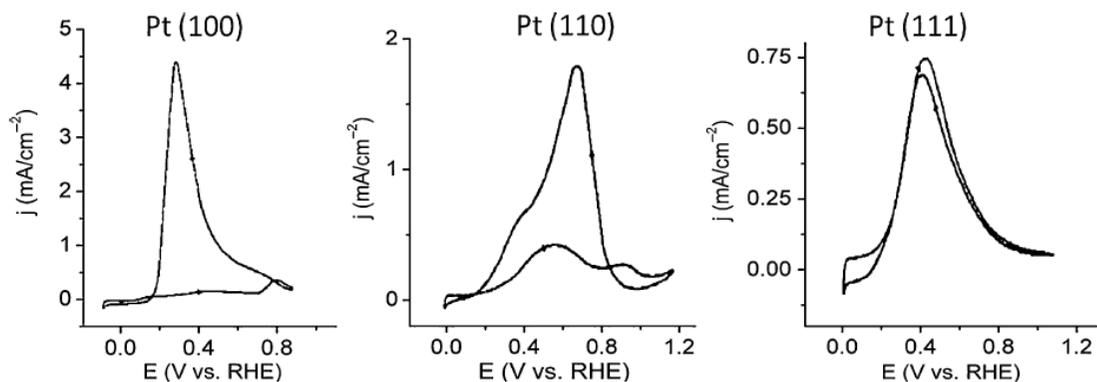
# Mechanism ( $\text{HCOOH} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$ )



**peak I** (~0.5V) : direct pathway, poisoning intermediates accumulated  
**peak II** (~0.9V) : reaction barrier of second step significantly reduced  
**peak III** (~0.6V) : removal of poisoning intermediate at high potential (oxidative stripping)



## Structure sensitivity :

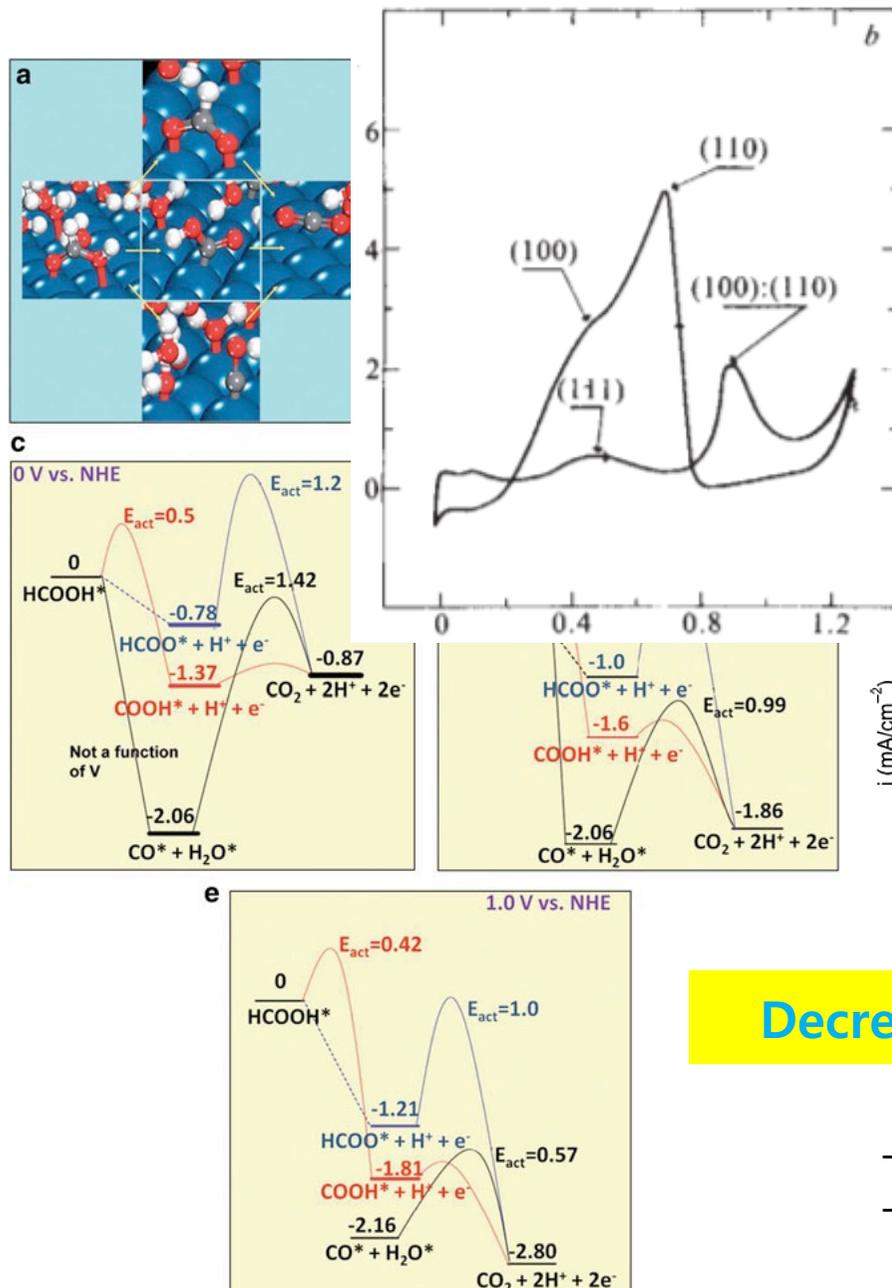


**Formic Acid Oxidation, Fig. 2** Electrooxidation of formic acid (0.26 M) on single crystal Pt electrodes with sweep rate: 50 mV/s (Reproduced by permission of Nature Publishing Group [6])

*Nature* **296** (1982) 137-138

- smallest poisoning effect on Pt(111)
- overall activity following trend of **Pt(100) > Pt(110) > Pt(111)**

# Mechanism ( $\text{HCOOH} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$ )

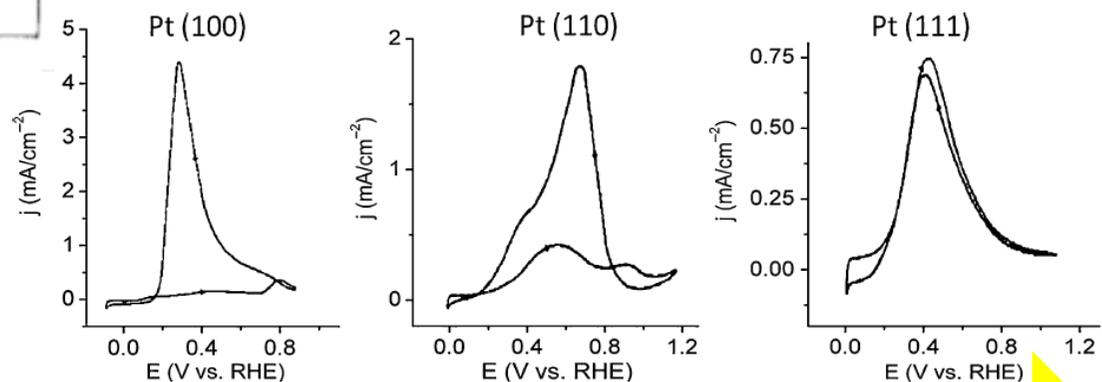


**Peak I** (~0.5V) : direct pathway, poisoning intermediates accumulated

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**Peak III** (~0.6V) : removal of poisoning intermediate at high potential (oxidative stripping)

**Structure sensitivity :**



**Decreasing poisoning effect & overall activity**

Nature 296 (1982) 157-160

- smallest poisoning effect on Pt(111)
- overall activity following trend of Pt(100) > Pt(110) > Pt(111)

# Limitations in FAOR : Poisoning



## CARBON MONOXIDE (CO) POISONING



**CAN'T BE  
SEEN**



**CAN'T BE  
SMELLED**



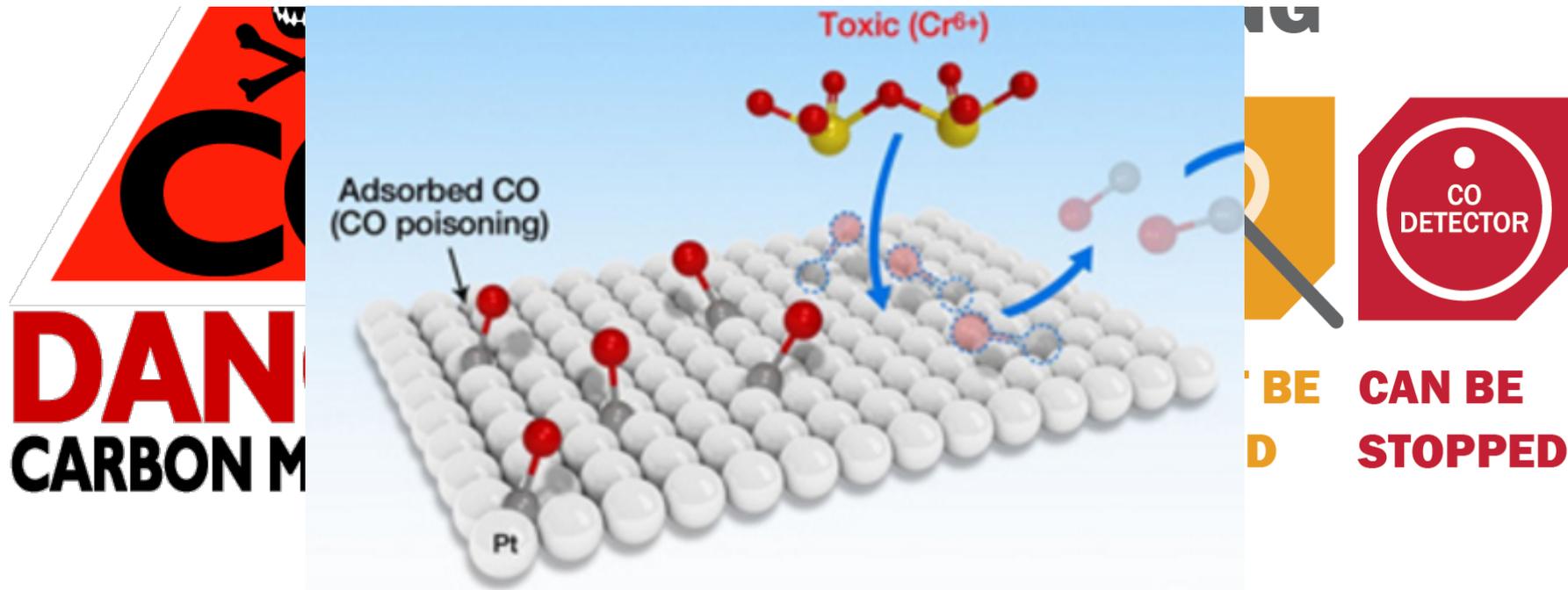
**CAN'T BE  
HEARD**



**CAN BE  
STOPPED**

# Limitations in FAOR : Poisoning

- Poisoning problems with CO intermediate, existing Pt-based electrocatalysts can accomplish FA oxidation at extremely positive potentials (without technological interest).
- The development of direct formic acid fuel cells (DFAFCs) has been impeded by the low activity of existing electrocatalysts at desirable oxidation voltage (at low oxidation potential).



**poisoning & activity should be considered simultaneously**

Ideal catalyst : working at low potentials, together with an ability to prevent the formation of CO and resist the poisoning

# Solution : introducing foreign metals

*J. Electroanal. Chem.*, 65 (1975) 587–601  
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*J. Electroanal. Chem.*, 150 (1983) 79–88  
 Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

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## ELECTROCATALYSIS BY FOREIGN METAL MONOLAYERS: OXIDATION OF FORMIC ACID ON PLATINUM\*

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(Received 21st July 1975)

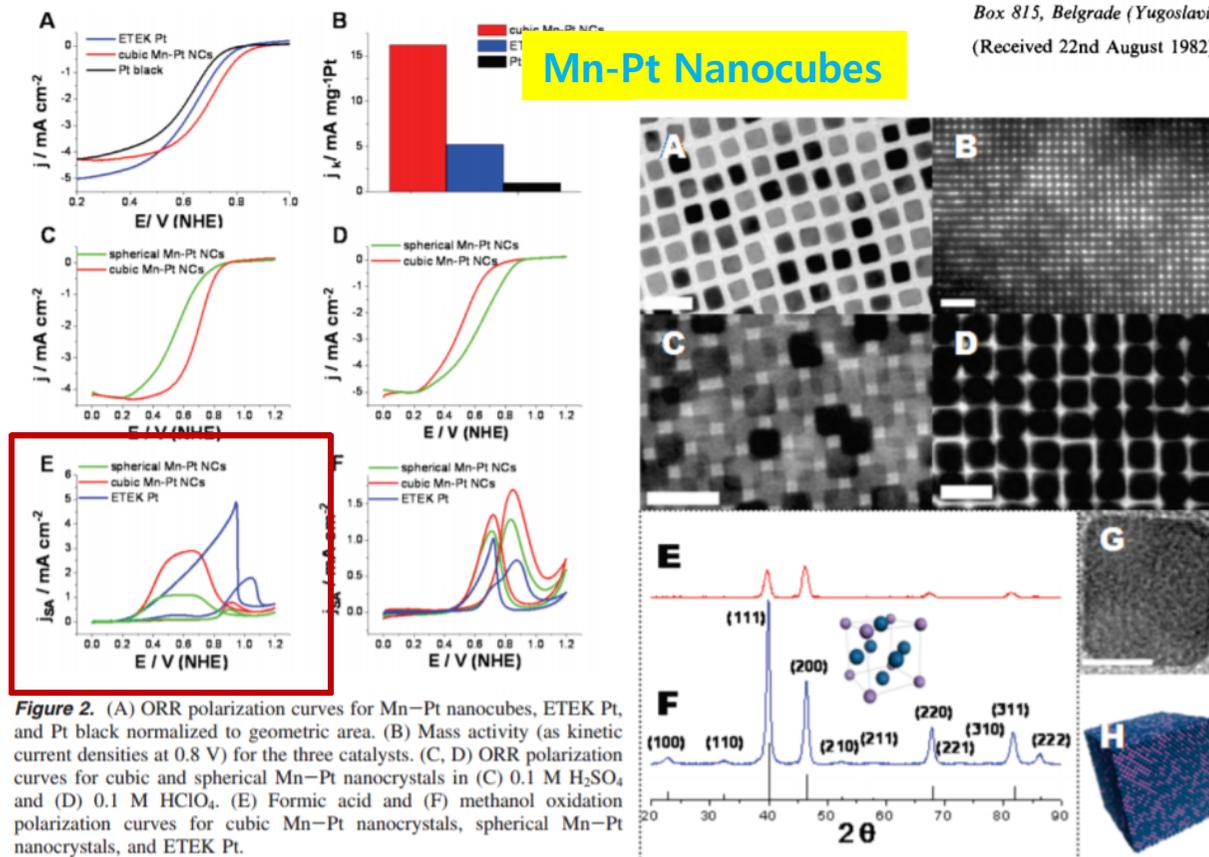
## STRUCTURAL EFFECTS IN ELECTROCATALYSIS

### OXIDATION OF FORMIC ACID AND OXYGEN REDUCTION ON SINGLE-CRYSTAL ELECTRODES AND THE EFFECTS OF FOREIGN METAL ADATOMS

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(Received 22nd August 1982)



- Modifying Pt-Pt distance by lattice contraction while maintaining the favorable Pt electronic properties

- However, still peak current achieved at high oxidation potential with low activity and selectivity.

# Solution : introducing foreign metals

## Highly Active Pt<sub>3</sub>Pb and Core–Shell Pt<sub>3</sub>Pb–Pt Electrocatalysts for Formic Acid Oxidation

Yijin Kang,<sup>†</sup> Liang Qi,<sup>‡</sup> Meng Li,<sup>§</sup> Rosa E. Diaz,<sup>⊥</sup> Dong Su,<sup>⊥</sup> Radoslav R. Adzic,<sup>§</sup> Eric Stach,<sup>⊥</sup> Ju Li,<sup>‡</sup> and Christopher B. Murray<sup>†,‡,\*</sup>

<sup>†</sup>Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States, <sup>‡</sup>Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States, <sup>§</sup>Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973, United States, and <sup>⊥</sup>Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, United States

ARTICLE

- Pt<sub>3</sub>Pb NCs, Pt<sub>3</sub>Pb@Pt NCs prepared via solution phase synthesis

### Ordered intermetallic compounds

- Modulating Pt-Pt distances are expected to mitigate CO poisoning, by reducing bridge sites and eliminating 3-fold hollow adsorption sites.

-immunity to CO poisoning, enhanced current density for FAOR, shift in the onset of oxidation potential

(J.Am.Chem.Soc. 2004, 126, 4043-4049)

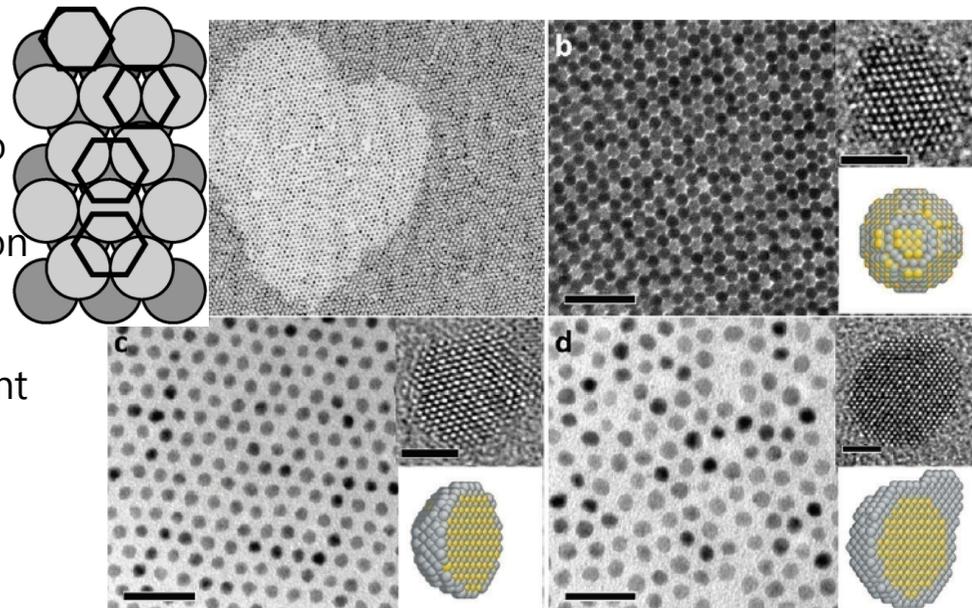


Figure 1. TEM images and (insets) HRTEM images of (a, b) Pt<sub>3</sub>Pb NCs, (c) Pt<sub>3</sub>Pb–Pt (type A) NCs, and (d) Pt<sub>3</sub>Pb–Pt (type B) NCs. Scale bars: (a) 100 nm, (b, c, d) 20 nm, (insets) 2 nm.

# Solution : introducing foreign metals

Increased activity (0.1M sulfuric acid + 0.5M FA)

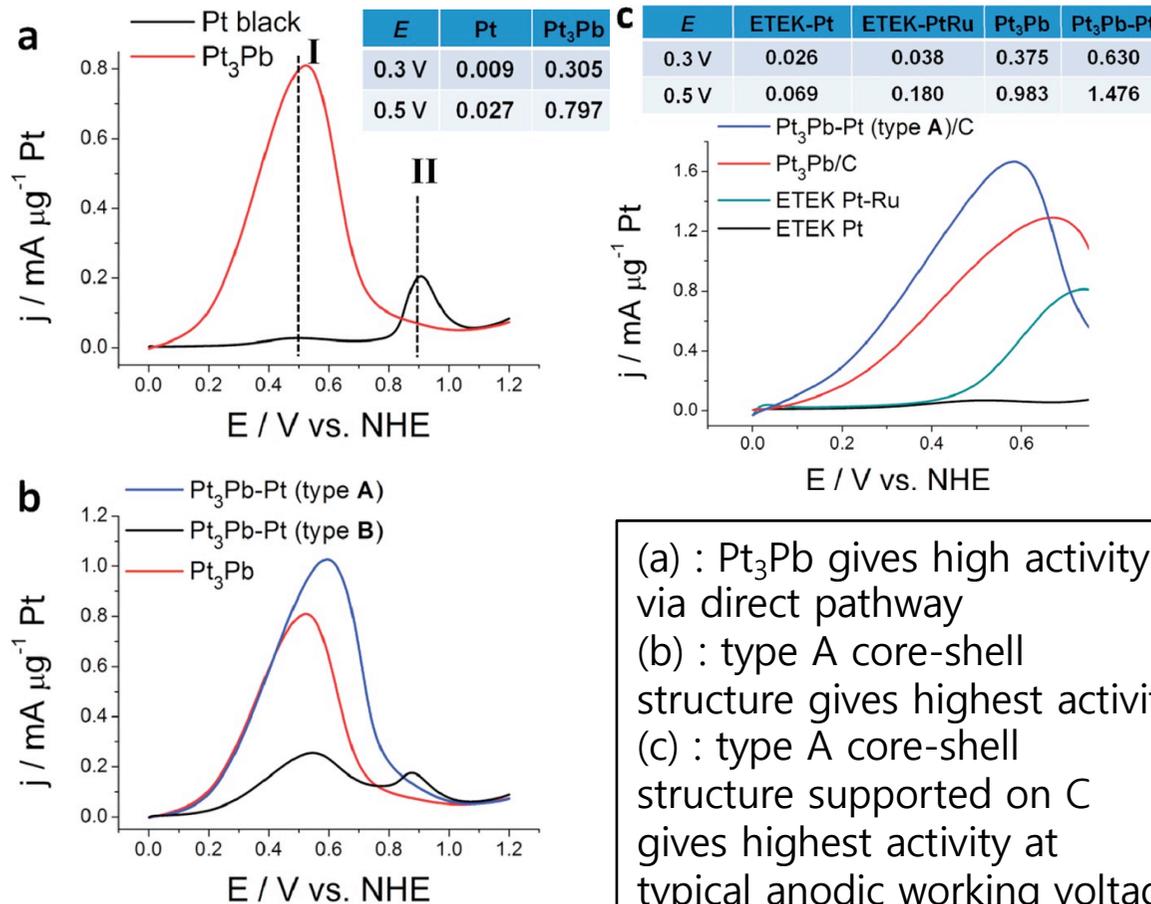


Figure 5. Polarization curves of (a) formic acid oxidation on Pt black and Pt<sub>3</sub>Pb, (b) formic acid oxidation on Pt–Pb nanostructures, and (c) maximum activities of formic acid oxidation on carbon-supported catalysts. Tables in a and c present the activities ( $\text{mA } \mu\text{g}^{-1} \text{Pt}$ ) of electrocatalysts at 0.3 and 0.5 V.

Reduced poisoning

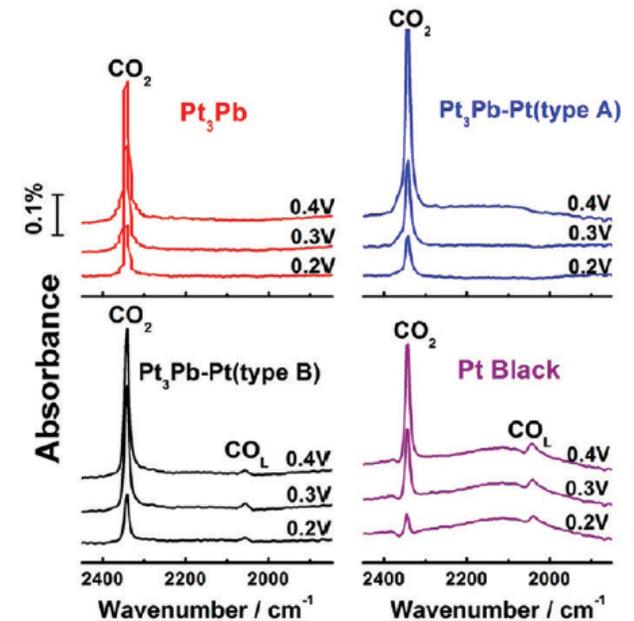


Figure 6. *In situ* IRRAS spectra for formic acid oxidation on Pt–Pb nanostructures and Pt black.

in-situ infrared reflection absorption spectra (IRRAS)  
 2343 $\text{cm}^{-1}$  : asymmetric stretch vibration of  $\text{CO}_2$   
 2030 $\text{cm}^{-1}$  : linear bound CO

# Solution : introducing foreign metals

## DFT calculation

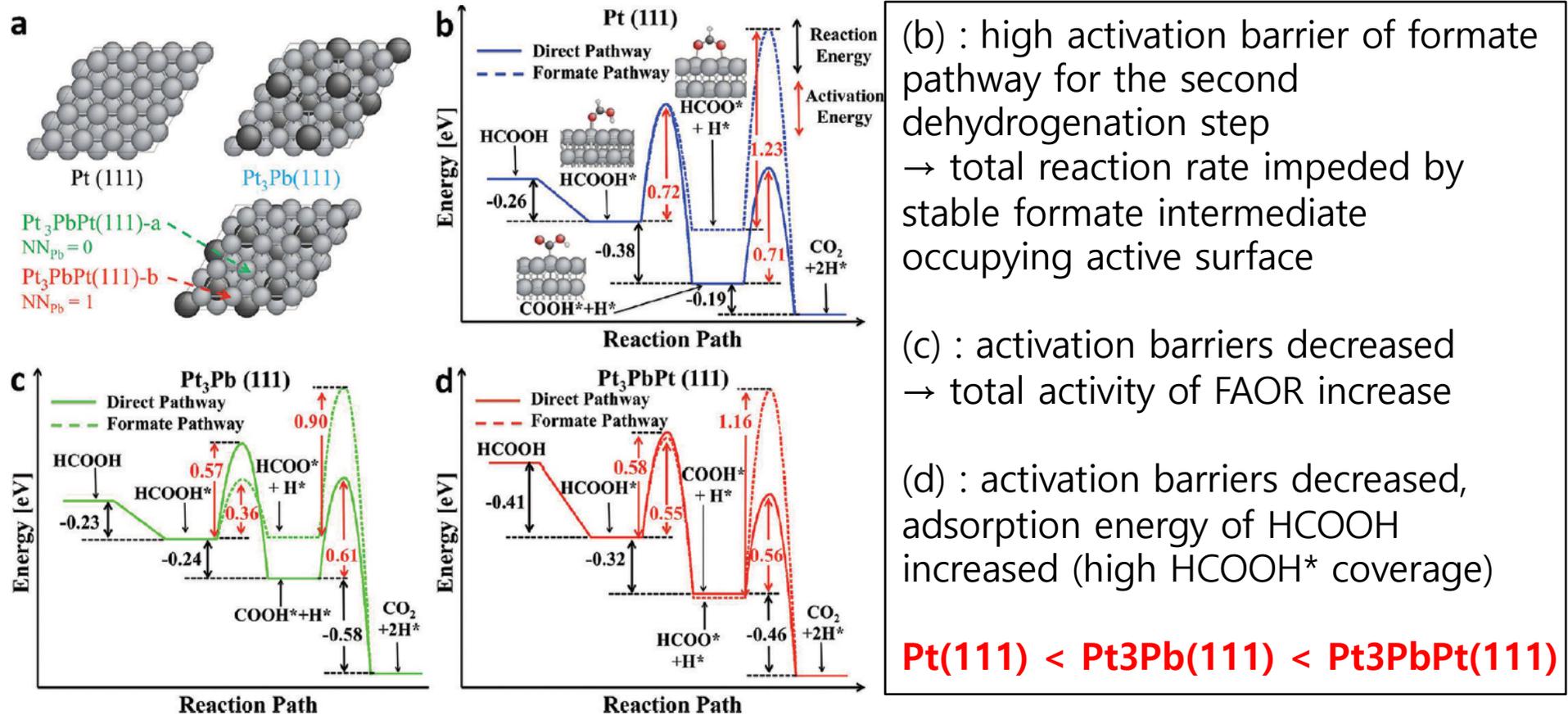


Figure 7. (a) Surface models of Pt(111), Pt<sub>3</sub>Pb(111), and Pt<sub>3</sub>Pb–Pt(111) atoms. Gray (black) stands for Pt (Pb) atoms. (b, c, d) Reaction pathways of HCOOH → CO<sub>2</sub> + 2H\* with reaction/activation energies of elementary steps on different model surfaces. Here the final product H\* is located at the most stable adsorption site on the corresponding surface; thus three surfaces have different total reaction energies because of different H adsorption strengths.

# Solution : introducing foreign metals

## A Facile Synthesis of MPd (M = Co, Cu) Nanoparticles and Their Catalysis for Formic Acid Oxidation

Vismadeb Mazumder,<sup>†</sup> Miaofang Chi,<sup>‡</sup> Max N. Mankin,<sup>†</sup> Yi Liu,<sup>†</sup> Önder Metin,<sup>§</sup> Daohua Sun,<sup>||</sup> Karren L. More,<sup>‡</sup> and Shouheng Sun<sup>\*,†</sup>

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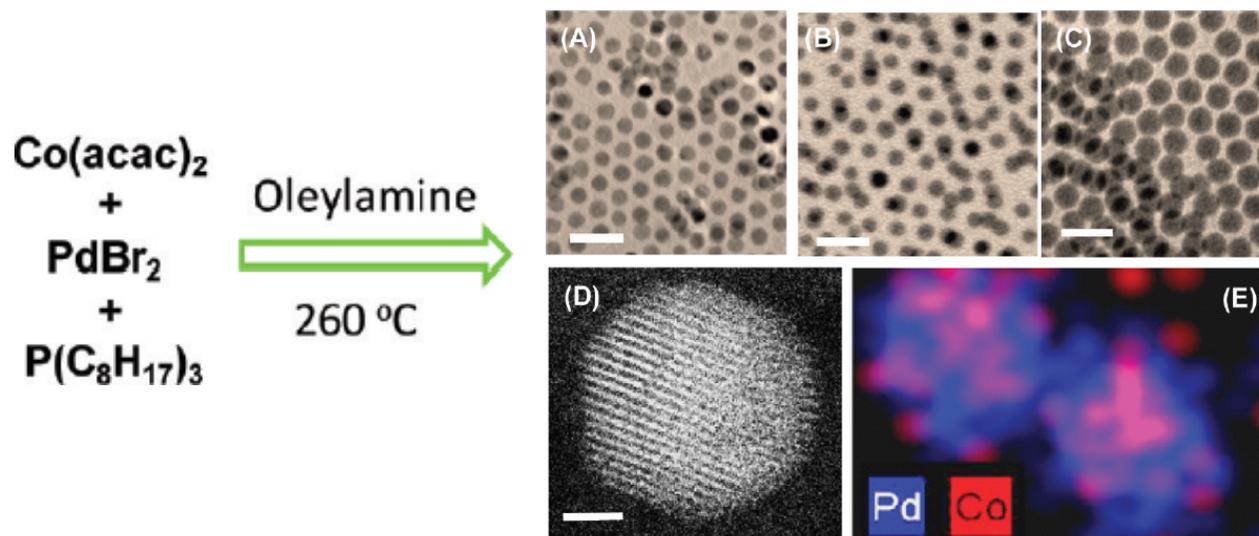


Figure 1. TEM images of (A) 8 nm, (B) 5 nm, and (C) 12 nm  $\text{Co}_{60}\text{Pd}_{40}$  NPs (scale bar = 25 nm). (D) A high-angle annular dark-field (HAADF) STEM image of a 8 nm  $\text{Co}_{60}\text{Pd}_{40}$  NP (scale bar = 2 nm). (E) EDS elemental maps for Co (red) and Pd (blue) within two individual 8 nm  $\text{Co}_{60}\text{Pd}_{40}$  NPs indicating the distribution of the two elements within each NP.

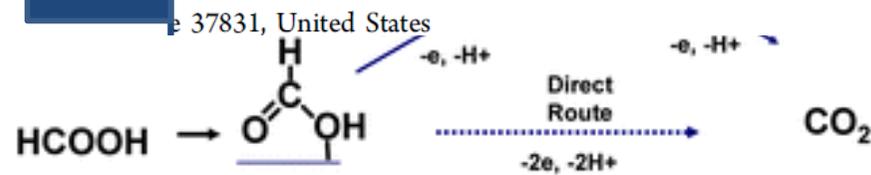
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- more active than the commonly used Pt catalysts
- direct 2e oxidation leads to less CO poisoning/deactivation than Pt catalysts

Pd



- enhances the reaction rate of limiting step (HCOOH adsorption/dissociation on the Pd surface)
- oxophilic property or transition metals in the alloy structure facilitates 2e oxidation of HCOOH.

M

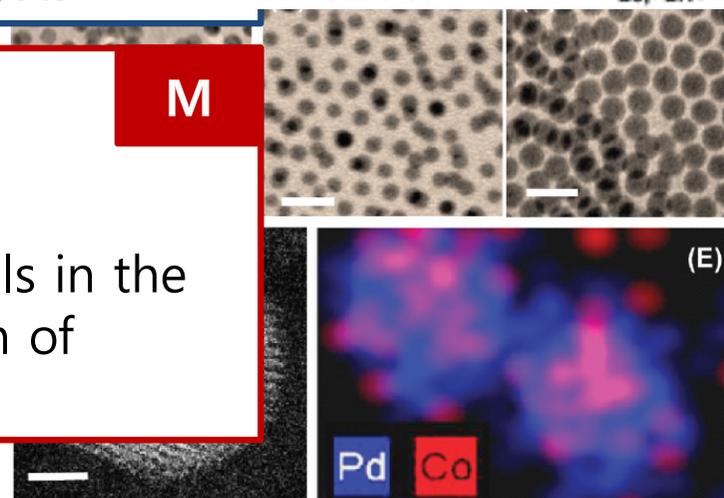


Figure 1. TEM images of (A) 8 nm, (B) 5 nm, and (C) 12 nm Co<sub>60</sub>Pd<sub>40</sub> NPs (scale bar = 25 nm). (D) A high-angle annular dark-field (HAADF) STEM image of a 8 nm Co<sub>60</sub>Pd<sub>40</sub> NP (scale bar = 2 nm). (E) EDS elemental maps for Co (red) and Pd (blue) within two individual 8 nm Co<sub>60</sub>Pd<sub>40</sub> NPs indicating the distribution of the two elements within each NP.

# Solution : introducing foreign metals

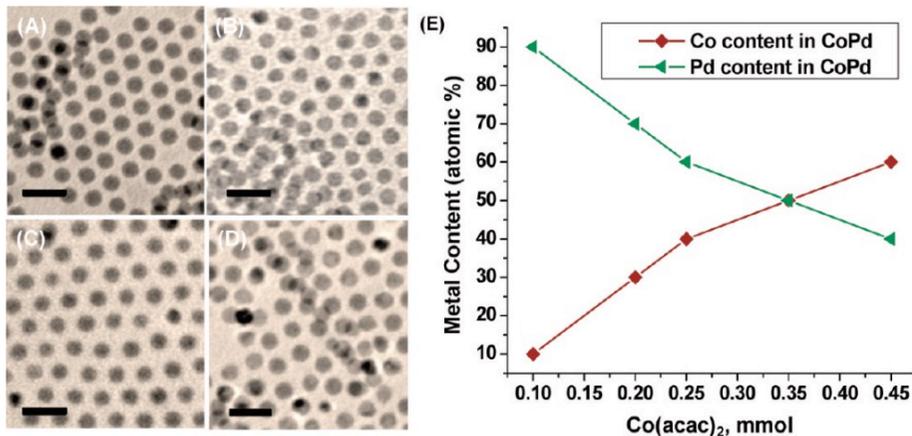


Figure 3. TEM images of the 8 nm CoPd NPs of different compositions synthesized via incrementing the Co precursor concentrations under otherwise identical synthesis conditions: (A)  $\text{Co}_{10}\text{Pd}_{90}$ , (B)  $\text{Co}_{30}\text{Pd}_{70}$ , (C)  $\text{Co}_{40}\text{Pd}_{60}$  and (D)  $\text{Co}_{50}\text{Pd}_{50}$  NPs (scale bar = 25 nm). (E) Relationship between the amount of Co precursor and the Co and Pd contents within the NPs at constant  $\text{PdBr}_2$  of 0.30 mmol.

- Peak appears at lower potentials for high Co content

- Higher peak current than the elemental Pd NPs

→ More rapid  $\text{HCOOH}$  adsorption and activation

-stronger current with higher Co content

- positive shift of reduction peak

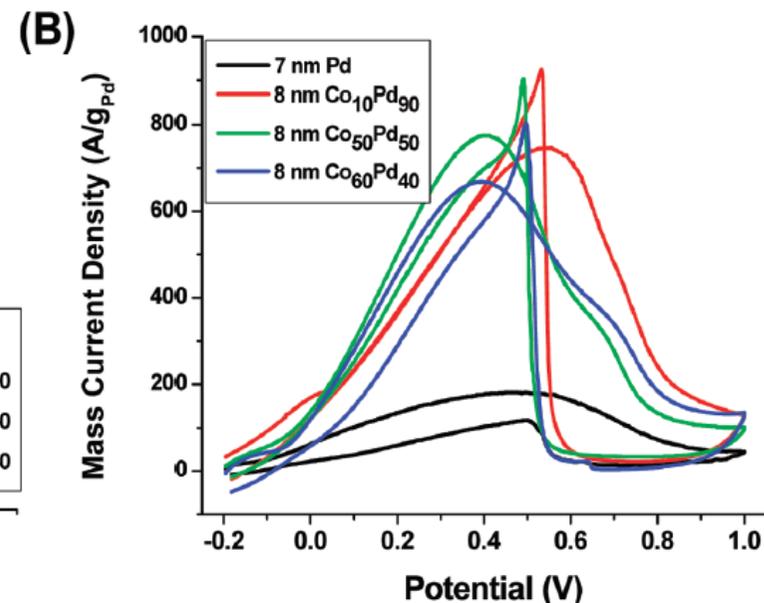
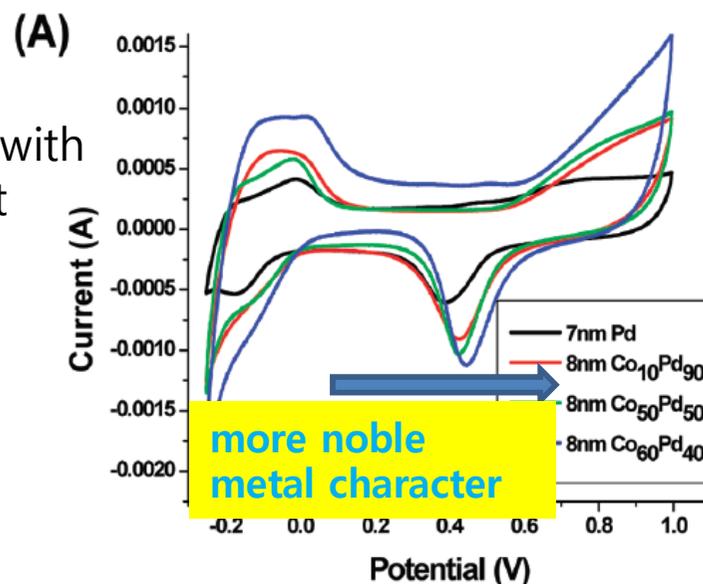
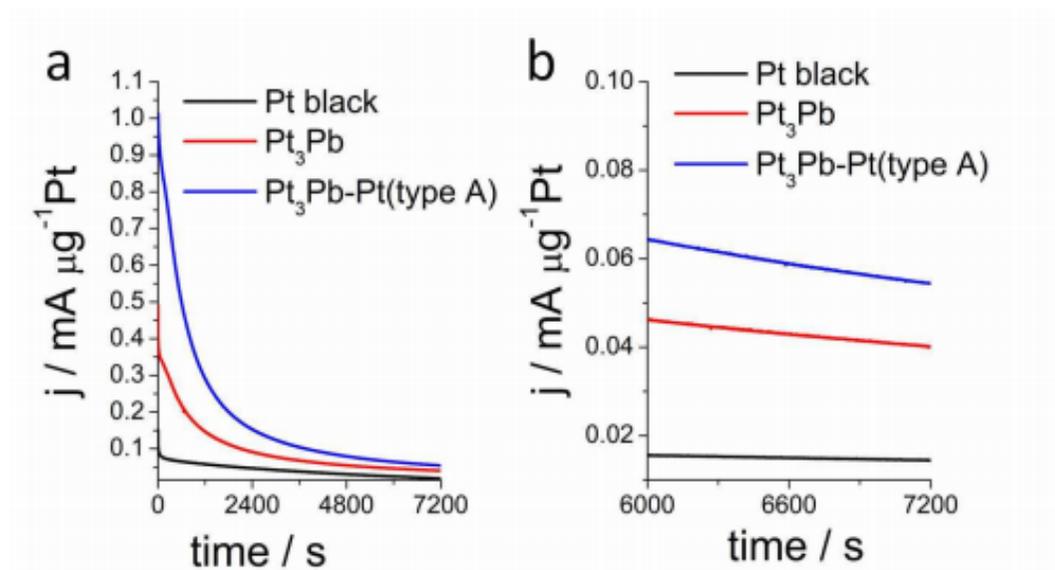


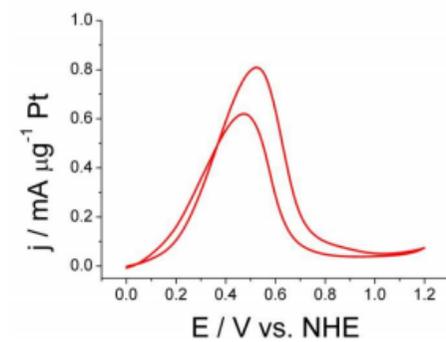
Figure 4. (A) Cyclic voltammograms of the 7 nm Pd NPs and the 8 nm CoPd NPs with three different compositions at 25 °C in  $\text{N}_2$  saturated 0.1 M  $\text{HClO}_4$  (scan rate: 50 mV/s). (B) NP mass current densities vs applied potential in 0.1 M  $\text{HClO}_4$  and 2 M  $\text{HCOOH}$  at 25 °C (scan rate: 50 mV/s).

# Conclusion

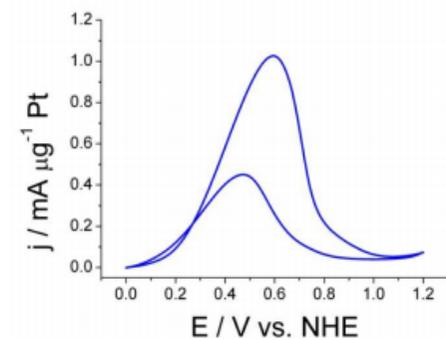
- Various catalysts have been developed with no poisoning and high activity surpassing Pt black
- Materials with very similar chemical compositions can be manipulated by control of nanoscale structures to obtain high catalytic activities
- Low-cost catalyst with non noble metal



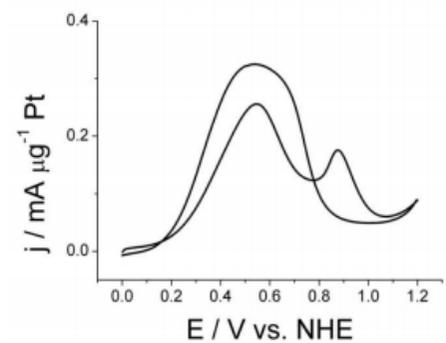
**Figure S16.** Chronoamperometric curves (at 0.4V) of formic acid oxidation on Pt<sub>3</sub>Pb, Pt<sub>3</sub>Pb-Pt(type A), and Pt black.

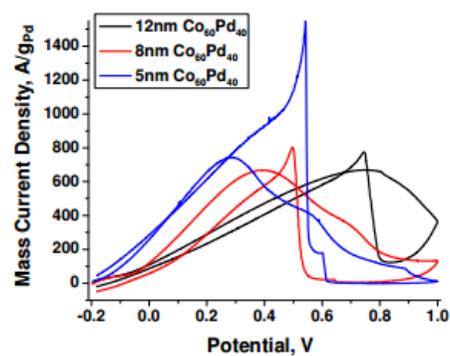


**Figure S17.** Polarization curve of formic acid oxidation on Pt<sub>3</sub>Pb.

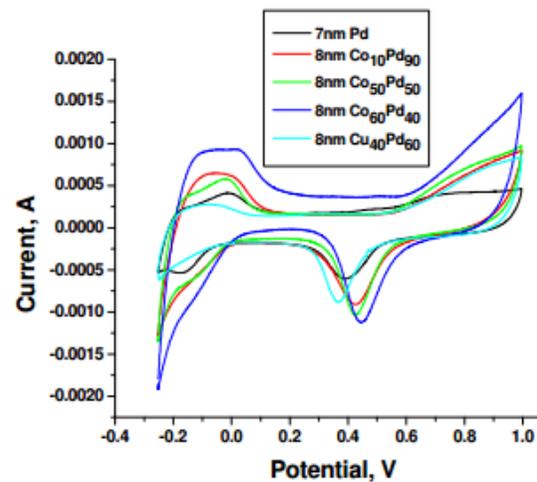


**Figure S18.** Polarization curve of formic acid oxidation on Pt<sub>3</sub>Pb-Pt(type A).





Name of Catalyst	Peak Current (at 300mV)	Peak Potential
5nm Pd	440 A/g	411 mV
5nm Co <sub>60</sub> Pd <sub>40</sub>	737 A/g	293 mV
8nm Co <sub>60</sub> Pd <sub>40</sub>	686 A/g	396 mV
12nm Co <sub>60</sub> Pd <sub>40</sub>	384 A/g	739 mV



**Figure S6.** CV's of 8 nm Cu<sub>40</sub>Pd<sub>60</sub> NPs, 7 nm Pd NPs and 8 nm CoPd NPs with three different

**Figure S5.** Size dependent catalysis observed for 5 nm, 8 nm and 12 nm Co<sub>60</sub>Pd<sub>40</sub> NPs.

compositions obtained at 25 °C (scan rate: 50 mV/s).