



# The ensemble effect of formic acid oxidation on platinum–gold electrode studied by first-principles calculations



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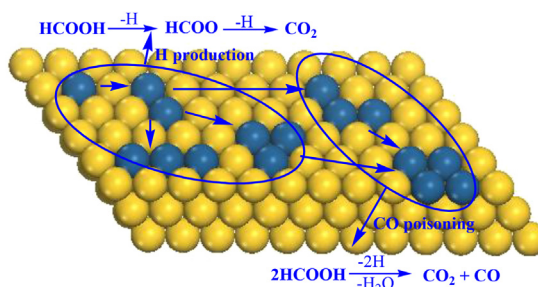
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## HIGHLIGHTS

- The mechanisms of HCOOH oxidation on a series of PtAu(111) surfaces are investigated.
- One Pt atom is required for the formate pathway.
- Three Pt atoms with a non-equilateral structure are needed for the dimer pathway.
- CO poisoning is induced by the non-equilateral Pt site upon PtAu(111).

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 25 August 2014

Received in revised form

18 November 2014

Accepted 17 December 2014

Available online 18 December 2014

### Keywords:

The ensemble effect

Formic acid oxidation

Platinum–gold bimetallic catalysts

Density functional theory

## ABSTRACT

The reaction mechanisms for HCOOH oxidation on a series of PtAu(111) alloy surfaces in the aqueous solution phase are investigated by density functional theory calculations. It is found that the dehydrogenation pathway of HCOOH oxidation occurs through the formation of formate with a barrier of 16.8 kcal mol<sup>-1</sup> and requires at least one Pt atom on the surface. In contrast, the CO formation pathway proceeds through the dimerization with a barrier of 5.6 kcal mol<sup>-1</sup>, for which at least three Pt atoms with a non-equilateral structure are required. The calculated average electrostatic potential, charge density difference, Bader charge and partial density of states all show obvious charge transfer from the alloy surface Pt atoms to HCOOH molecules, indicating that Pt sites are the reaction active center. Different ensemble of Pt sites on PtAu(111) surfaces can have significant impact on the catalysis performance for HCOOH oxidation. The non-equilateral Pt site upon PtAu(111) should be avoided to eliminate CO poisoning effect on Pt-based catalysts.

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## 1. Introduction

Direct formic acid fuel cells (DFAFCs), as power sources for portable electronic devices, have attracted great interest owing to

its diverse advantages, such as high energy density, non-toxic nature of formic acid, and fast oxidation kinetics [1–3]. However, the commercialization of DFAFCs is impeded by poor performance of catalysts for HCOOH electrooxidation [4]. Pt and Pt-group metals are known as the most promising electrocatalysts for HCOOH oxidation [5–10], and they have been extensively used as anode materials of DFAFCs. It is generally accepted that HCOOH could be oxidized to CO<sub>2</sub> on Pt electrodes via a dual-pathway mechanism consisting of direct and indirect pathways (Scheme 1) [11–14]. The

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direct pathway occurs via the dehydrogenation of HCOOH to form  $\text{CO}_2$  [15,16]. While the indirect pathway proceeds by the dehydration of HCOOH with formation of CO acting as the poisoning species, and then is oxidized to  $\text{CO}_2$  [17–19]. By using time-resolved surface-enhanced infrared absorption spectroscopy (SEIRAS), Osawa and co-workers [7,20] proposed the formate pathway of HCOOH oxidation, which operates through a HCOO intermediate resulted from the O–H bond scission of HCOOH. In order to rationalize the Pt catalysts poisoning effect, we have proposed a new dimer pathway for HCOOH oxidation [21], which involves the simultaneous formation of  $\text{CO}_2$  and CO via the HCOOH dimer in the elementary step.

Although Pt is the most extensively studied catalyst for HCOOH oxidation, the pure Pt catalysts are particularly vulnerable to CO-like species [22]. In order to avoid the “poisoning effect” on Pt, considerable efforts have been made to favor direct pathway by restricting large Pt surfaces through the introduction of another transition metal or noble metal, known as the third-body or the ensemble effect [23–26]. This approach not only reduces the consumption of Pt, but also enhances the activity of the catalysts for HCOOH electrooxidation. Among these Pt-based bimetallic catalysts, platinum–gold nanostructures have attracted special attention due to their good catalytic activity and stability [27–32]. In the last several years, various platinum–gold surfaces have been extensively investigated as the electrocatalyst for the HCOOH oxidation, such as Pt spontaneously deposited on Au(111) [33], Pt electrodeposited on Au [34], Pt-decorated Au nanoparticles [35–39] and platinum–gold alloy nanoparticles [27,40].

It has been found that the electrocatalytic activity of platinum–gold bimetallic catalysts depends strongly on the surface structure, the composition associated with the ensemble effect, and the variation of the density of active sites [35,36,41–44]. Although the ensemble effect plays dominant role in the catalysis of HCOOH oxidation on platinum–gold surfaces [28,45], as it increases the selectivity toward the HCOOH dehydrogenation, the underlying reaction mechanisms are still unclear and even controversial. Cuesta et al. [46] experimentally indicated that the dehydration pathway of HCOOH requires at least three contiguous Pt atoms and the dehydrogenation pathway requires at most two Pt atoms, while Park et al. [47] claimed that the dissociative adsorption of HCOOH to form CO requires at least two ensemble binding Pt sites and the direct oxidation of HCOOH does not require the presence of continuous neighboring Pt sites. In contrast, Kristian et al. [38]

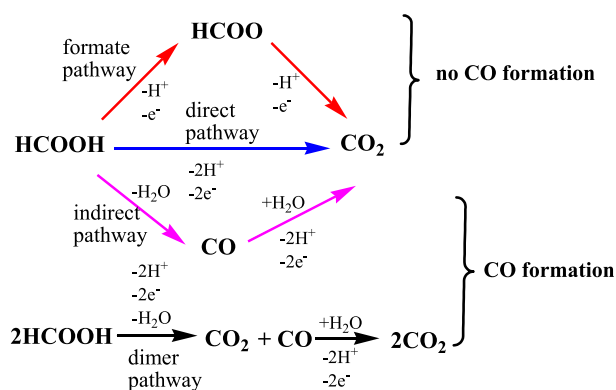
concluded that single isolated Pt atoms at lower Pt/Au ratio or 2–3 Pt atoms at higher Pt/Au ratio favor the dehydrogenation pathway due to the ensemble effect. Neurock et al. [48] theoretically predicted that the dehydrogenation pathway only requires a single Pt atom whereas the dehydration pathway needs a larger surface ensemble and stepped sites. The current theoretical calculations are consistent with experimental data for the dehydrogenation pathway. However, the experimental results for the dehydration pathway from different research groups do not agree with each other, not to mention the inconsistency between the theory and the experiment. It is therefore highly desirable to obtain a comprehensive understanding of the ensemble effect of HCOOH oxidation on PtAu surfaces.

The ensemble effect of HCOOH oxidation on platinum–gold surfaces remains unexplored theoretically at the molecular level, although several recent experimental and theoretical studies have addressed this issue [38,46–49]. In this work, in order to better understand the ensemble effect of HCOOH oxidation on platinum–gold surfaces we systematically studied the HCOOH oxidation on PtAu(111) surfaces with different platinum–gold structure and composition in an explicit water model. The theoretical results are expected to be helpful for the rational design of sustainable platinum–gold catalysts used in DFAFCs.

## 2. Models and computational details

Platinum–gold bimetallic catalysts have been obtained by the substitutional alloying of Pt into the Au layer [50–53]. To simulate different Pt active sites isolated by Au modifier, we replaced one, two, three, and four Au atoms on Au(111) with Pt atoms to form 1 Pt-doped, 2 Pt-doped, 3 Pt-equilaterally doped, 3 Pt-linearly doped, 3 Pt-non-equilaterally doped, and 4 Pt-doped Au(111) surfaces, respectively. Although there are actually three Pt atoms in the supercell for 1 Pt-doped Au(111) surface, this structure assures that each Pt active site is isolated by Au modifier and the density of Pt active sites is of highest. So-structured platinum–gold surfaces were used for the present calculations. Our calculations were performed by using a periodic three-layer slab with a  $p(3 \times 3)$  unit cell, where the atoms in the top layer were allowed to be fully relaxed, whereas those in the two bottom layers were fixed at their bulk-truncated structures. The vacuum region between slabs is 10 Å, which is sufficiently large to ensure that the interactions between repeated slabs in a direct normal to the surface are negligible. The aqueous solution phase was modeled using 20 explicit water molecules chosen to fill up the vacuum region. The height of the background region was chosen so as to match the density of water near a metal surface of  $0.86 \text{ g cm}^{-3}$  at 0 K [46,54–58]. Initially the water molecules were oriented in the vacuum region with a hexagonal bilayer and subsequently optimized. In view of the fact that a HCOOH molecule matches two water molecules in size and structure, when a formic acid molecule is incorporated into the surface, two water molecules in the water solution phase are removed.

The calculations were based on the plane-wave pseudopotential density functional theory (DFT) periodic slab approach [59,60] by using the generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [61,62], as implemented in the Cambridge sequential total energy package (CASTEP) code [63]. The GGA–PBE functional has been widely used to study the small molecules oxidation on noble metal surfaces and the obtained results are often reliable [64–66]. It is found that our calculated lattice constant is 4.19 Å for the bulk Au, which is in close agreement with the experimental value of 4.07 Å (error of 2.9%) [67]. Integrations in reciprocal space used a  $2 \times 2 \times 1$  Monkhorst–Pack  $k$ -point grid during configurations optimization



**Scheme 1.** Mechanistic scheme for HCOOH electrochemical oxidation along the formate pathway (red line), direct pathway (blue line), indirect pathway (purple line), and the dimer pathway (black line) proposed by our study. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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