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In-situ regulation of formic acid oxidation via elastic strains

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ABSTRACT

The capability to actively control chemical reactions has enormous implications for energy generation and conversion. By integrating theory and experiments, we achieved an in-situ regulation of formic acid oxidation on a Pt (1 1 1) surface via externally applied strains. The first-principles theory predicted that compressive strains can lower the reaction overpotential to boost the formate pathway and alleviate CO poisoning on the Pt surface, while tensile strains should have the opposite effects. The experimental observations confirmed the theoretical predictions. Compressive elastic strains (approximately -0.4%) could create over 75 mV overpotential decrease, far beyond what was achieved in previous works. A mass activity (~700 mA/mg) of Pt was achieved in a broad potential range of 0.4–0.85 V (vs RHE) under compressive strains. There was no evident activity loss during the chronoamperometry test at 0.6 V. The first-principles theory, controlled synthesis and *in-situ* measurements were combined to achieve active control, which represents important progress in tuning the electrocatalytic activity of formic acid oxidation.

1. Introduction

Fuel cells can convert chemical energy into electricity using hydrogen gas or organic molecules as fuel sources. Formic acid, as a sustainable resource, can be produced as a side product in biomass transformation [1–5]. The electrochemical formic acid oxidation reaction (FAOR) has attracted recent interest thanks to the significant advantages that formic acid exhibits as a fuel in the fuel cell applications, including low operating temperatures, fast kinetics, and relatively low transport across the membrane [6–9]. Platinum (Pt) is one of the most studied catalysts in the FAOR because of its excellent and well documented electrocatalytic properties [2,10–13]. The FAOR reaction pathways on the Pt (1 1 1) surface have been established [13–19], including a direct pathway via COOH intermediates, formate medium and an indirect pathway retarded by CO poisoning.

Significant research efforts have been devoted to enhancing FAOR activity, with emphasis on the development of novel catalysts [20–25]. In this paper, we explore an alternative strategy in which elastic strains are applied to the Pt surface to optimize the catalytic activity. Elastic strains can be applied to metal catalysts either actively or passively. One of the most successful examples of passive straining includes core/shell nano-structures [22–27], and the effectiveness of the straining depends on the lattice misfits of the core/shell materials. However, materials with large lattice misfits are not necessarily good catalysts. Active straining, however, does not suffer from this limitation. One can apply strains - tension, compression, or even oscillations between them - directly to catalytically active materials via external loading as long as the materials can sustain the load, thereby allowing active control of surface strains. However, generating sufficient elastic strains on metal surfaces is highly challenging because metals tend to relax elastic strains through plastic deformations. Nonetheless, progress has been made in the active straining of metal catalysts. For example, elastic strains have been applied to metal films, including films composed of Au, Pt, Pd-derived metallic glasses, NiTi alloys, etc. to enhance their oxygen reduction reaction (ORR) activities [28–34]. We have recently developed an experimental approach to regulate the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) on metallic films [35–37]. To the best of our knowledge, there have been no studies to directly utilize elastic strain for tuning the FAOR. In this work, we extended the approach to the FAOR and an important motivation was to demonstrate that the well-known problem of CO poisoning on metal catalysts can be mitigated by elastic strains. Because CO poisoning is a common prob-

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lem in electrocatalysis, especially for CO_2 reduction reactions, our study will have a broad impact on electrocatalysis and could inspire future work in this emerging area of research.

2. Methodology

2.1. Computational methodology

The first principles calculations were performed based on density functional theory using the projector-augmented wave method as implemented in Vienna Ab-initio Simulation Package (VASP). The exchange and correlation functional was described by the Generalized Gradient Approximation (GGA) with the PBE parameterization. The energy cutoff of 500 eV for plane wave functions was used for structure optimization and self-consistent field calculations. A vacuum region of about 15 Å was used to eliminate interactions between the slabs. DFT-D3 functional was used to describe the dispersion correction [38], and the solvation effect due to water was described by an implicit solvation model [39]. More details are provided in the Supplementary material.

2.2. Electrochemical measurements

The chemicals, Pt thin film synthesis, catalyst characterization are described in the Supplementary material. Electrochemical studies of the FAOR were carried out using a three electrode system, whereas the Metro (Multi Autolab 204) electrochemistry workstation and Instron machine. The initial clyclic voltammetry (CV) scans were collected from 0 to 1.15 V under the Argon (Ar, ultra-high purity of 99.999%) saturated 0.1 M $HClO_4$ using the scan rate of 50 mV s^{-1}. CVs of the FAOR were obtained in an Ar-saturated 0.1 M $HClO_4$ + 0.1 M HCOOH electrolyte with the same scan rate. Chronoamperometry tests were performed at 0.6 V_{RHE}. The CVs collected without FA (Fig. S1), with FA at 0% and −0.4% strain (Fig. S2) were shown in the Supplementary material. All the experiments were repeated five times to confirm reproducibility. More details are depicted in the Supplementary material.

3. Results and discussion

Previous works indicated that formate (HCOO) adsorbate in the bidentate configuration with two oxygen atoms bounded to Pt surface is one of the key intermediates involved in the FAOR [10,13,40–43]. In addition, FAOR can also take place via an indirect pathway through CO formation and subsequent oxidation of CO to CO_2. Hence, we focus on the two key pathways as shown in Fig. 1a. We first determine the free energy diagrams for the two pathways, as shown in Fig. 1b. Note that the free energies of the reactant HCOOH (G_{HCOOH}) and the product CO_2 (G_{CO2}) are known quantities, independent of the surface [44,45]. In the free energy diagram, we set G_{HCOOH} = 0. The free energies of the intermediate CO (G_{CO}) in the indirect oxidation and HCOO (G_{HCOO}) in the formate pathway were computed from first-principles. For the indirect oxidation, the adsorption of CO on Pt (1 1 1) is highly stable with a free energy gain of −1.1144 eV. As a result, the oxidation of CO* to form CO_2 is endothermic with a free energy increase of 0.8634 eV. The CO poisoning on the Pt surface was attributed to the strongly adsorbed CO along with the high energy cost for its oxidation. As for the formate pathway, the formation of *HCOO is endothermic with ΔG of 0.2803 eV, which is the overpotential determining step for FAOR.

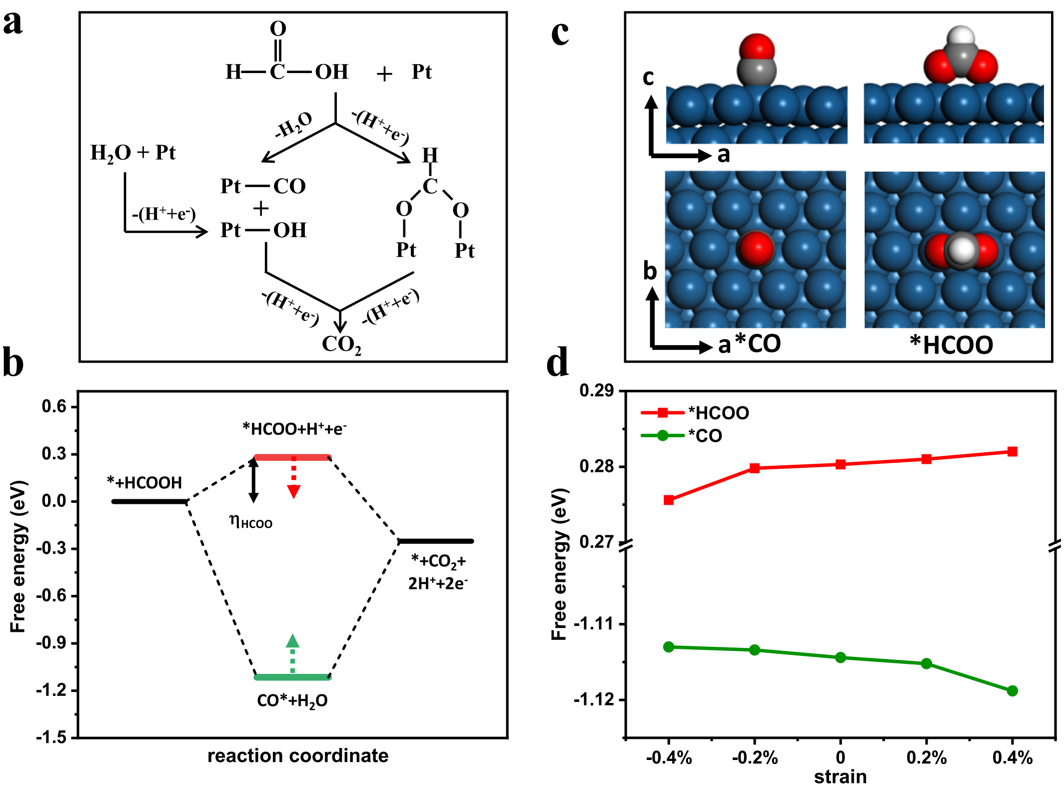

Fig. 1. (a) Reaction pathways for the oxidation of formic acid on Pt (1 1 1) surface. (b) Free energy diagram for the reaction pathways shown in (a). The free energies of the reactant (HCOOH), intermediates (HCOO and CO) and product (CO_2) are represented by horizontal bars. The dashed horizontal bar indicates the mid-point free energy of the reactant and the product. (c) Computational models displaying the adsorption of the reaction intermediates (HCOO and CO) on the Pt (1 1 1) surface in the side (upper) and top (bottom) view. (d) Change in the free energy of *HCOO and *CO on Pt (1 1 1) surface as a function of the applied strain. Positive and negative strains correspond to uniaxial tension and compression, respectively.

Fig. 1d shows the changes of G_{HCOO} and G_{CO} as functions of the uniaxial strain along the b axis (Fig. 1c) on the Pt (1 1 1) surface. G_{HCOO} increased and G_{CO} decreased monotonically as functions of the strain. In particular, the compression lowered G_{HCOO}, while the tension increases it. On the contrary, the compression increases G_{CO} while the tension lowered it. Therefore, the compressive strains are expected to boost the formate pathway of FAOR by lowering G_{HCOO} and the overpotential η_{HCOO}. Furthermore, compression can also alleviate CO poisoning by increasing G_{CO}, reducing the CO binding on the surface. In other words, the compressive strains were predicted to enhance the oxidation of formic acid: the larger the strain, the greater the enhancement. The tensile strains were predicted to have the opposite effects on the FAOR.

To probe the influence of the elastic strains on the FAOR experimentally, we first fabricated 20 nm Pt thin films by DC-magnetron sputtering, which allowed for controllable synthesis, similar to our previous work [34]. The strain was applied *in-situ* during the FAOR and evaluated using a three-electrode facility with Ar-saturation in acidic media (0.1 M $HClO_4$ + 0.1 M HCOOH). The experimental setup was similar to our previous studies [35,37]. After assembling of the electrocatalytic work station and strain-controlled working electrode system, the electrochemical test was firstly passed through 100 CV scans using a sweep rate of 50 mV s^{-1} to achieve a stable state on the surface of the Pt electrode. The 20 nm Pt films on the polymethyl methacrylate (PMMA) substrates were then sustained to the strain cycle as depicted in Fig. 2a. During the strain tuning of the electrocatalysis process, the electrode was held at the specified strains while multiple CV scans (0%, ±0.2% and ±0.4%) were performed. The peaks in the region of 0.10–0.28 V were related to hydrogen adsorption and desorption on the Pt. The oxidation/reduction peaks of the Pt thin films appeared at approximately 0.7 V/0.60 V. When a strain was applied, the oxidization/reduction peaks shifted to approximately 0.83 V/0.59 V. This Pt oxidation potential shift was due to the strain, which significantly enhanced of the catalytic dehydrogenation reactions rather than the dehydration of formic acid [14]. When the strain was applied *in-situ* (*e.g.*, at −0.4% nominal strain), it could create over ~75 mV overpotential decrease. Fig. 2b displays the shift of the CVs versus each tensile strain values of 0%, 0.2% and 0.4%. Fig. 2b shows a systematic shift of the CV curve as a function of strain, whereas the applied tensile strain moves CVs to the right (lower current and higher overpotential), thus decreasing catalytic oxidation activity. Due to the relaxation effect of PMMA substrate, the unloading went to 0% has minor difference as the loading section. As shown in Fig. 2c, compressive strains yielded the opposite trend, that is, they caused the CV curves to shift upward with much higher current density, increasing the activity. The significant activity enhancement could be attributed to the strain effect weakening the CO accumulation on the Pt surface during the FAOR and simultaneously enhancing the electrochemical activity [1,10,39].

Fig. 2d depicts the voltage change induced by the strain and confirms the following important traits, (1) The voltage change was approximately linearly with the elastic strain for Pt films in the strain range from 0 to 0.4%. The magnitude of the slope was ~185 mV per 1% strain, which is far beyond what was achieved in previous work; (2) The compressive strain increased the FAOR activity. The −0.4% strain led to a decrease in the overpotential with 75.6 mV. This matched with the theoretical predictions, as depicted in the Fig. 1. (3) The experimental data clearly demonstrated the strain effect in the FAOR, which can offer useful guidance for the regulation of other electrocatalytic systems. After the electrocatalytic FAOR proceeded for 2000 s at strains of 0.4% and −0.4%, nearly no change was occurred (Fig. S3), suggesting the highelectrocatalytic stability.

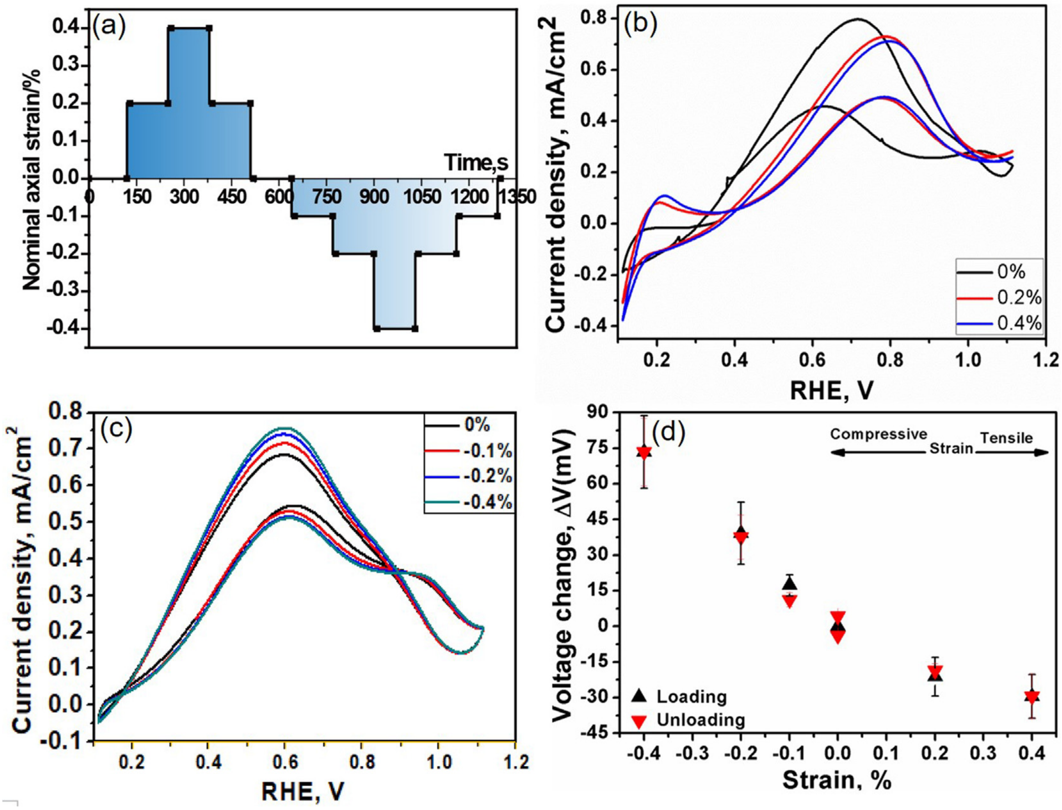

Fig. 2. (a) Schematic illustration of the loading history on Pt films deposited on PMMA substrate, showing progressively increasing tensile and compressive strains. (b) Representative view of CVs obtained at tensile strains of 0%, 0.2% and 0.4%. (c) Representative CVs obtained at compressive strains of 0%, −0.1%, −0.2% and −0.4%. (d) Voltage change versus strain calculated in the current density range of 0.55 to 0.65 mA/cm^2. Note the systematic shift of oxidation and reduction peaks in CV curves with strain.

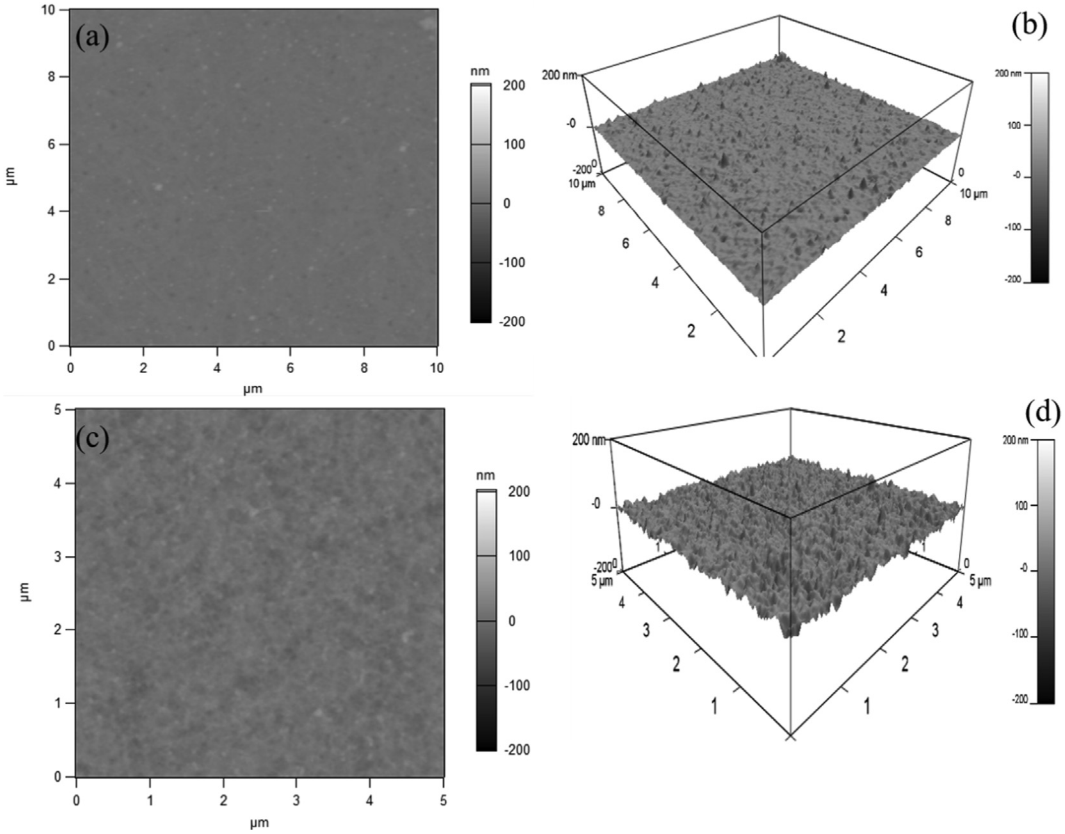

Fig. 3. Atomic force microscopy (AFM) images of the fresh (a and b) and spent (c and d) Pt thin films.

To ascertain the stability during the strain tuning of the FAOR, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were performed on the as-synthesized and spent Pt thin films after the FAOR. As shown in Fig. S4a, the XRD pattern mainly present the peaks of the PMMA substrate and Pt film exhibited (111), (200) and weak (220) planes. XRD patterns of the Pt films before and after the experiments showed nearly the same crystal phase, with no other measurable phases, confirming the high stability during the strain tests. XPS survey (Fig. S4b) of the spent metal Pt thin films showed the existence of Pt, C and O and there is no Cl to be formed, indicating that electrolyte only adsorbed on the surface. The Pt and C spectra are shown in Fig. 3c and d, confirming that Pt^0 was present on the surface of the spent Pt films [35].

Scanning electron microscopy (SEM, Fig. S5) images of the as-prepared and spent Pt films after the FAOR indicated that the Pt films did not exhibit any mechanical damage such as cracking or delamination. Based on the AFM analysis (Fig. 3) of the Pt films after electrochemical FAOR tests, the films still exhibited a low roughness values (Ra = 2.9 nm) that wree close to the fresh one, suggesting that the geometric current density was the proper way to measure the electrocatalytic FAOR performance. To examine the surface homogeneity, surface mapping (Fig. S6) was measured using a SuperView optical surface profiler to measure the feature heights from <1.5 nm up to 10,000 μm. The Pt thin films exhibited homogeneous surfaces before and after the FAOR. All these data confirmed the high stability of the Pt films during the strain tuning of the FAOR.

4. Conclusions

In conclusion, through the combination of first-principle modeling and in-situ experiments, we demonstrated that externally applied elastic strains can strongly regulate the FAOR activities of Pt thin films in a predictable way. The first-principles theory predicted that the uniaxial compressive strains could lower the overpotential for the FAOR, boost the formate pathway of FAOR, reduce the CO binding on the surface, and alleviate the CO poisoning on the Pt (111) surface. The uniaxial tensile strains were predicted to have the opposite effects. The experiments confirmed the theoretical predictions and revealed that the compressive elastic strains promote the FAOR. The integration of experimental and computational study offers new insights into the *in-situ* tuning of electrocatalytic reactions.

CRediT author statement

Gang Lu: Theory calculation, writing. **Kai Yan:** Idea, experimental work, writing, submission.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2020.07.004.

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