Highly Active Pt$_3$Pb and Core–Shell Pt$_3$Pb–Pt Electrocatalysts for Formic Acid Oxidation

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Formic acid (FA), with high energy density (1740 Wh/kg, 2086 Wh/L) and easier storage and handling than H$_2$, is an attractive choice for chemical fuel in fuel cells, which could replace conventional batteries and at larger scale may possess higher efficiency than conventional combustion engines.1–5 However, due to the dominance of the indirect reaction pathway and strong poisoning effects,1,4,6 the development of direct formic acid fuel cells (DFAFCs) has been impeded by the low activity of existing electrocatalysts at desirable operating voltage (i.e., at low oxidation potential). Various efforts have been made to improve the electrocatalyst for FA oxidation, including the use of adatoms7–11 or making Pt-based alloys.12–28

Three possible reaction paths of FA oxidation have been proposed.6,29–32

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

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

(iii) $\text{HCOOH}^+ \rightarrow \text{CO}^+ + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2e^-$. 

Here, * represents an adsorbed state. Equation i is referred to as the direct pathway, where the removal of the first hydrogen atom from the C–H bond occurs to produce a hydroxy carbonyl, and then a second dehydrogenation step occurs at the O–H bond to produce CO$_2$. Equation ii is called the formate pathway, in which the dehydrogenation first occurs at the O–H bond to produce formate and then at the C–H bond to generate CO$_2$. Equation iii is known as the indirect pathway, in which CO$^+$ is produced by non-Faradaic dehydration of FA, then is further oxidized to CO$_2$. Both i and ii are accomplished by dehydrogenation (via different intermediates) to form CO$_2$ directly, so i and ii are sometimes referred to as a “direct pathway” jointly. Both experimental and computational results suggest that the dominance of the indirect reaction pathway, which generates the CO$^+$ poisoning intermediate, causes the problem of low activity at low oxidation potential. Pb has been identified as a promising adatom or alloying element to enhance FA activity at low oxidation potential. Pb

KEYWORDS: platinum · lead · electrocatalysis · formic acid oxidation · core–shell · nanostructure · nanocrystal

Formic acid is a promising chemical fuel for fuel cell applications. However, due to the dominance of the indirect reaction pathway and strong poisoning effects, the development of direct formic acid fuel cells has been impeded by the low activity of existing electrocatalysts at desirable operating voltage. We report the first synthesis of Pt$_3$Pb nanocrystals through solution phase synthesis and show they are highly efficient formic acid oxidation electrocatalysts. The activity can be further improved by manipulating the Pt$_3$Pb–Pt core–shell structure. Combined experimental and theoretical studies suggest that the high activity from Pt$_3$Pb and the Pt–Pb core–shell nanocrystals results from the elimination of CO poisoning and decreased barriers for the dehydrogenation steps. Therefore, the Pt$_3$Pb and Pt–Pb core–shell nanocrystals can improve the performance of direct formic acid fuel cells at desired operating voltage to enable their practical application.

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oxidation activity and CO-poisoning tolerance of electrocatalysts. Adding Pb into Pt electrocatalysts to enhance their activity has been demonstrated by both underpotential deposited Pb and PtPb alloys made by high-temperature annealing, as well as some Pt–Pb nanoparticles. Here, we report the first synthesis of Pt3Pb nanocrystals (NCs) and two types of core–shell structure based on such Pt3Pb NCs through solution phase synthesis and show they are highly efficient FA oxidation electrocatalysts, particularly at desirable low oxidation potential. By combining the design and functional testing of novel Pt3Pb, Pt3Pb–Pt core–shell NCs of varying shell thickness and morphology with density functional theory (DFT) calculations, we have identified that the origin of the activity enhancement is the elimination of CO poisoning and a lowered activation barrier for the desirable direct reaction pathway.

RESULTS AND DISCUSSION

To synthesize Pt3Pb NCs, Pt acetylacetonate [Pt(acac)2] and Pb acetylacetonate [Pb(acac)2] are dissolved in benzyl ether, oleic acid, oleylamine, and hexadecanethiol, and the reaction mixture is brought to 180 °C. The reducing agent, borane-triethylamine complex (BTEA), is injected into the reaction at 180 °C. After 30 min, Pt3Pb NCs of 3.7 nm diameter (σ < 5%) are purified and collected. Figure 1 shows the transmission electron microscope (TEM) images of the monodisperse Pt3Pb NCs with a size of 3.7 nm (σ < 5%). The interplanar distance measured from high resolution (HR) TEM is 2.34 Å (Figure S7), corresponding to the lattice spacing of the Pt3Pb {111} planes. The TEM-deduced lattice constant is 4.05 Å, which is consistent with the values calculated from X-ray diffraction (XRD) data (4.08 Å) and DFT calculation (4.13 Å). The stoichiometry of Pt:Pb = 3:1 is confirmed by both energy dispersive X-ray spectroscopy (EDX) (Pt79Pb21, σ < 5%) and inductively coupled plasma optical emission spectroscopy (ICP-OES) (Pt74Pb26, σ < 1%). Due to their extremely narrow size distribution, the Pt3Pb NCs readily form large-area superlattices (Figures S7–9). The combination of long-chain carboxylic acid, amine, and thiol as the capping agent (stabilizer) is essential to the synthesis of Pt3Pb NCs, although they can be substituted by similar ligands (Table S1). The synthesis in the absence of carboxylic acid and/or amine produces nanocrystals in a broad size distribution (Figures S3–5); in the absence of long-chain thiol, agglomerates are generated as the major product (Figure S6). The combination of hexadecylamine, adamantane-carboxylic acid, and hexadecanethiol produces nanorods in the PtPb phase, as reported by Yang et al.

As it has been demonstrated that catalytic reactions could be sensitive to the morphology of the catalyst, to better study the catalytic properties of Pt3Pb, we prepare two more Pt–Pb core–shell nanostructures as control systems for comparison. We use the as-synthesized Pt3Pb as seeds upon which to grow a second Pt layer. High-temperature growth facilitates the Pt precursor decomposition, inducing growth on any possible seed sites, usually forming islands as well as layers, while at lower temperature slower growth allows Pt to grow uniformly onto Pt3Pb seeds at a low yield, forming an epitaxial layer. Figure 1c and d present the TEM images of these as-synthesized Pt3Pb–Pt NCs. The size of Pt3Pb–Pt NCs (here, we name them as “Pt3Pb–Pt(type A)”) by slow growth is 4.0 nm (σ = 6%), slightly larger than the original Pt3Pb NCs, while the size of Pt3Pb–Pt NCs (here, we name them as “Pt3Pb–Pt(type B)”) by rapid growth is 4.9 nm (σ > 10%) at broadened size distribution. Many Pt3Pb–Pt(type B) NCs adopt an elongated morphology rather
than a uniform spherical morphology, indicating an island structure (Figures 2, S14). The monodisperse Pt3Pb–Pt(type A) NCs form a large-area superlattice as readily as the original Pt3Pb NCs (Figures S11, S12). Due to their broad size and shape distribution, Pt3Pb–Pt(type B) NCs form only small-area superlattices (Figure S13). The composition of Pt3Pb = 83:17 (σ < 5%) for Pt3Pb–Pt(type A) and Pt3Pb = 92:8 (σ < 5%) for Pt3Pb–Pt(type B) is determined by both EDX and ICP-OES. The Pt/Pb ratio of a Pt3Pb NC covered with a monolayer of Pt is calculated to be 82:18 (at a size of 4.0 nm), which is in good agreement with the Pt3Pb–Pt(type A) composition. Figure 3 presents the EDX line scans of three types of Pt–Pb NCs. A Pt-rich shell for Pt3Pb–Pt(type B) can be clearly seen as shown in the shadowed regions of Figure 3c. The difference between Pt3Pb and Pt3Pb–Pt(type A) is not apparent, because it is difficult for the equipped EDX detector to resolve the Pt shell as thin as a monolayer. As shown in Figure 4, the XRD pattern of Pt3Pb–Pt(type A) is similar to Pt3Pb with an fcc structure. Compared to Pt3Pb and Pt3Pb–Pt(type A), the XRD pattern of Pt3Pb–Pt(type B) is shifted to a greater 2-theta angle (i.e., smaller lattice constant), indicating a Pt-rich composition. Noting that the alloy phase could transform into an intermetallic phase upon annealing, we employ this phenomenon to investigate the composition and structure of these Pt–Pb NCs. After annealing at 600 °C for 30 min, the NC structures could be converted from the A1 phase to the ordered L12 phase (AuCu3 structure), and phase segregation is observed (Figure 4). The major peaks of Pt3Pb NCs fit the Pt3Pb intermetallic phase. The trace impurity peaks are ascribed to the slight excess of Pt in the NCs. Pt3Pb–Pt(type A) NCs show an increased amount of Pt, and the Pt3Pb–Pt(type B) NCs exhibit even stronger signals for the pure Pt phase. These XRD data, with EDX and ICP-OES data and TEM images, support the claimed Pt–Pb structures and proposed mechanism of the Pt layer growth.

Figure 5a shows the electrochemical performance of Pt3Pb NCs (treated by UV/ozone), compared to that of pure Pt (Pt black, Aldrich). As described earlier, FA oxidation on electrocatalysts follows both direct (including the formate pathway) and indirect pathways, corresponding to peak I and peak II in Figure 5a, respectively. The indirect pathway dominates the reactions on Pt catalysts, making the Pt unsuitable for DFAFC. However, on Pt3Pb the direct pathway is more favorable, with little reaction occurring via the indirect pathway. At 0.3 V (typical anodic working voltage in DFAFC), the FA oxidation activity on Pt3Pb is 33 times greater than that on Pt. Figure 5b presents a comparison of activities for the different Pt–Pb nanostructures. The Pt3Pb–Pt(type A) NCs show the highest activity toward FA oxidation. The activity on Pt3Pb–Pt(type B) NCs is much lower than that on the other two Pt–Pb nanostructures, while a peak at higher potential is observed, indicating FA oxidation on Pt3Pb–Pt(type B) NCs does occur via the indirect pathway. It is worth noting that the Pt–Pb electrocatalysts demonstrated in Figure 5a and b are dense films (Figure S10) rather than supported catalysts. In a commercial fuel cell catalyst, ETEK Pt, Pt is supported on high surface area carbon (Vulcan-72R), which enables much higher catalyst utilization of ETEK Pt. To make the Pt–Pb electrocatalysts comparable to the commercial electrocatalysts, we load Pt–Pb NCs onto Vulcan-72R (Figure S15). The resulting
Pt$_3$Pb/C and Pt$_3$Pb-Pt(type A)/C catalysts exhibit high activities, which are about 15 and 25 times (at 0.3 V) higher respectively than the corresponding activity of the commercial Pt/C catalyst (Figure 5c). Figure 6 shows in situ infrared reflection absorption spectra (IRRAS) of FA oxidation on different catalysts. The positive-going band at 2343 cm$^{-1}$ is attributed to the asymmetric stretch vibration of CO$_2$, the product of FA oxidation. The band at around 2030 cm$^{-1}$ is assigned to linear bound CO* (denoted as COL), the poison intermediate generated from the FA indirect pathway. The COL bands on Pt$_3$Pb-Pt(type B) NCs show a lower intensity compared to the ones generated from pure Pt, and no COL band is observed on both Pt$_3$Pb and Pt$_3$Pb-Pt(type A) NCs. The results suggest that FA oxidation occurs on Pt$_3$Pb or Pt$_3$Pb-Pt(type A) via the direct pathway and on Pt$_3$Pb-Pt(type B) or Pt black via the indirect pathway.

Apparent CO oxidation is observed neither in the polarization curves nor in the IRRAS spectra for both Pt$_3$Pb and Pt$_3$Pb-Pt(type A), because Pb alloying can relieve the CO-poisoning effect by weakening the adsorption strength of CO, as predicted in previous DFT calculations. As a result, the FA oxidation activity increases at low potential due to the reduced CO poisoning. On the other hand, the low activity of Pt$_3$Pb-Pt(type B) NCs (but still better than pure Pt) can be explained by the structural relaxation of the Pt atoms deposited on Pt$_3$Pb NCs. According to XRD results (Figure 4), the Pt$_3$Pb-Pt(type B) NCs have a lattice constant close to pure Pt, smaller than lattice constants for Pt$_3$Pb NCs and Pt$_3$Pb-Pt(type A) NCs. Excess Pt atoms in Pt$_3$Pb-Pt(type B) NCs form thick Pt layers and Pt cluster islands on the Pt$_3$Pb core. These Pt thick layers and islands have similar electrocatalytic properties to pure Pt, which generates CO* from FA dehydration and decreases the overall activity. However, this mechanism cannot explain the further increase of total activity for Pt$_3$Pb-Pt(type A) NCs relative to Pt$_3$Pb NCs, since both of them have little CO-poisoning effect; thus there must be other factors causing the increase of the activity besides the avoidance of CO poisoning originated from Pb alloying.

In order to understand physical mechanisms of activity enhancements on these Pt$_3$Pb NCs, we performed a series of DFT calculations to obtain the reaction energetics in different possible reaction paths on several model surfaces. The (111) surface is the most stable facet of the fcc lattice and contributes most of the area for the surface of bulk Pt and alloy, as well as most of the NCs. Here, pure Pt NCs are simulated by a Pt(111) surface; Pt$_3$Pb NCs are simulated by a (111) surface of Pt$_3$Pb crystal; Pt$_3$Pb-Pt(type A) NCs are simulated by the Pt$_3$Pb(111) surface with the top layer
as pure Pt, labeled as Pt3PbPt(111), as shown in Figure 7a. Lattice constants of Pt and Pt3Pb obtained from DFT calculations are 3.98 and 4.13 Å, respectively. Both the direct path and formate path are explored on these surfaces as follows: (i) direct pathway: HCOOH $\rightarrow$ HCOOH* $\rightarrow$ COOH* $\rightarrow$ CO2 $+$ 2H*; (ii) formate pathway: HCOOH $\rightarrow$ HCOOH* $\rightarrow$ HCOO* $\rightarrow$ CO2 $+$ 2H*. Here we use these surface reactions under ultrahigh-vacuum (UHV) conditions to simulate the corresponding electrochemical reactions, which is a general procedure to qualitatively describe the activities of electrocatalysts.44,45

The reaction and activation energies for all elementary steps in both pathways on these three types of model surfaces are listed in Figure 7b, c, and d, respectively. On the Pt (111) surface, the first dehydrogenation step in the formate pathway has almost the same activation barrier as the direct pathway (0.71 eV), indicating a significant proportion of HCOOH* may first lose the hydrogen atom connected to the oxygen atom; however, the formate pathway has a much higher activation barrier than the direct pathway for the second dehydrogenation step (1.23 vs 0.71 eV), thus, even without CO poisoning, the total reaction rate may be impeded by the stable formate intermediate on the top Pt layer: type 1 [without Pb as nearest neighbor (NNPb = 0)] and type 2 [with one Pb as nearest neighbor (NNPb = 1)], and type 1 has a stronger adsorption strength for reaction intermediates than type 2. The paths are found to have the lowest activation barriers when carbon-related intermediates (HCOOH*, COOH*, HCOO*) are adsorbed on a type 2 atom and H atoms are adsorbed on type 1 atoms. In these paths, the dehydrogenation steps for both direct and formate pathways have comparable activation barriers (0.58 vs 0.55 eV), much smaller than those on Pt(111), which means that the formate “poisoning” effect on the Pt3PbPt(111) surface is much smaller than on the Pt3Pb(111) surface. For the second dehydrogenation step in the direct pathway, the dehydrogenation barrier is also smaller than that on the Pt3Pb(111) surface (0.56 eV), so this path has the smallest maximum barrier on these investigated surfaces. In addition, as shown in Figure 7b–d, the adsorption strengths of HCOOH on Pt3PbPt(111) increase compared with Pt(111) and Pt3PbPt(111) surfaces. Because the adsorption energy of HCOOH is relatively weak compared with those of typical small molecules, such as H2 and O2 and is even comparable with H2O ($\approx$ $-$0.2 eV), a stronger adsorption strength may increase the coverage of HCOOH* on catalyst surfaces for the following reaction steps.

In summary, combined experimental and theoretical studies show that the increased activity for Pt3Pb NCs and Pt3Pb–Pt(type A) NCs relative to Pt NCs results from the elimination of CO poisoning and decreased barriers for dehydrogenation steps. The further increase of activity for Pt3Pb–Pt(type A) NCs relative to Pt3Pb NCs may result from continuous decreases of dehydrogenation barriers, strong adsorption of reactant molecules, and, most importantly, the suppression of the formate path and avoidance of stable formate intermediates. However, the overall activity decreases with further increase of the Pt ratio due to CO* poisoning caused by structural relaxation of the extra Pt atoms. Thus, both the existence and thickness of the Pt shell surrounding the Pt3Pb NCs are critical to achieve high reaction rate, reinforcing the notion that even materials with very similar chemical compositions can be manipulated by control of nanoscale structures to obtain high catalytic activities.

METHODS

Synthesis. Pt3Pb NCs: Under a nitrogen flow, 0.2 g of Pt-(acac)2 and 0.2 g of Pb(acac)2 are dissolved in 5 mL of benzyl ether, 18.4 mL of oleylamine, 3.2 mL of oleic acid, and 11.1 mL of 1-hexadecanethiol. The formed solution is dipped into an oil bath that is preheated to 180 °C. Once the temperature of the solution in the reaction flask reaches 180 °C, 0.46 mL of borane-triethylamine complex is injected into the reaction flask. The

Figure 6. In situ IRRAS spectra for formic acid oxidation on Pt–Pb nanostructures and Pt black.
Here the Reaction pathways of HCOOH $\rightarrow CO_2 + 2H^+$ with reaction/activation energies of elementary steps on different model surfaces. 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.

Characterizations. TEM images are taken on a JEOL100 TEM at 120 kV. The HRTEM images and EDX data are taken on a JEOL2010F TEM at 200 kV. Partial HRTEM images (insets of Figure 1) are taken using a Cs-corrected FEI Titan 80-300 at 300 kV, with the aberation corrector tuned to a flat phase region of $>20$ mrad ($<0.1$ nm information transfer), leaving a residual spherical aberation of $<1.5\,\mu m$. SEM images are taken on a JEOL JSM7600F. The HR scanning transmission electron microscope (STEM) images are taken using a Hitachi HD2700C dedicated 200 kV cold emission STEM. XRD patterns are obtained on a Rigaku Smartlab diffractometer with Cu Kα radiation ($\lambda = 1.5418\,\AA$). Quantitative elemental analyses for the composition of NCs are carried out with both EDX and inductively coupled plasma optical emission spectrometry on a SPECTRO GENESIS ICP spectrometer.

Electrochemical Measurements. Electrochemical measurements are performed on a potentiostat (Epsilon, Bioanalytical Systems Inc.). An Ag/AgCl electrode is used as a reference electrode, and a platinum coil is used as the counter electrode. All potentials are converted to values with reference to a normal hydrogen electrode (NHE). The electrolyte is 0.1 M sulfuric acid. All water used in the experiments is Millipore ultrapure water (18.2 MΩ). Working electrodes are prepared by dropping the NC solution (in hexane, the concentration has been determined by ICP-OES) onto glassy carbon. The electrodes covered with NC thin films are then treated by UV/ozone for 24 h before measurement. Pt/Pt/C catalysts are treated by plasma (O2, 100 W, 30 min) and thermal treatment (4% H2 argon balanced, 600 °C, 30 min) for the best performance. Pt/Pt/C catalysts are treated by thermal treatment (air, 210 °C, 30 min, temperature reduced in order to retain the core–shell morphologies; 4% H2 argon balanced, 210 °C, 30 min). All measurements are carried out at room temperature in 0.1 M H2SO4 + 0.5 M FA at a sweep rate of 20 mV/s. The third sweeps are recorded. For carbon-supported catalysts, the sweep with maximum activity is recorded. The rotating disk electrode (900 rpm) is used for carbon-supported catalysts to suppress the gas formation during reactions.

IRRAS Measurements. In situ IRRAS studies are carried out with a Nicolet Nexus 670 Fourier-transform infrared spectrometer equipped with a mercury cadmium telluride detector cooled with liquid nitrogen. An unpolarized light beam is used. The spectral resolution is set to 8 cm$^{-1}$, and 128 interferograms are together added to each spectrum. Spectra are given in absorbance units defined as $A = -\log(R/R_0)$, where $R$ and $R_0$ represent the reflected infrared intensities corresponding to the sample and reference single-beam spectrum, respectively. The reference spectrum is collected at 0.005 V. All spectra are collected in a solution of 0.1 M formic acid and 0.1 M sulfuric acid. The nanocrystals are placed on Au(111) surfaces to ensure a good contact with the electrode, and the nanocrystals are vertically aligned by thermal treatment (air, 210 °C, 30 min).
current collection and reflectivity. A ZnSe hemisphere is used as the infrared window.

**DFT Calculation Procedures.** All DFT calculations are performed by using the Vienna ab initio simulation package (VASP). We used a planewave basis (PAW) potential with Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional in non-spin-polarized condition, because all the adsorbed intermediates are found to be at nonmagnetic states. All (111) surfaces are modeled by (4 × 2) supercells with four-layer slabs (8 atoms per layer), where the top two layers are fully relaxed and the vacuum size is larger than 15 Å. A Monkhorst–Pack k-point of 3 × 5 × 1 grids is applied for Brillouin-zone integration. Partial occupancies of eigenstates are determined by first-order Methfessel–Paxton smearing of $\sigma = 0.2$ eV. The cut-off energy for plane wave basis is 400 eV. The minimum energy path of each dehydrogenation step is searched by the climbing image nudged elastic band (CI-NEB) method integrated in VASP.

**Conflict of Interest:** The authors declare no competing financial interest.

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**Supporting Information Available:** This material is available free of charge via the Internet at http://pubs.acs.org.

**REFERENCES AND NOTES**